5344 *Chem. Rev.* **2006,** *106,* 5344–5386

Renaissance of Annulene Chemistry

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Received March 31, 2006

Contents

1. Introduction

Originally defined by Sondheimer in the early 1960s,[1] an [*n*]annulene is a monocyclic hydrocarbon comprised of

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10.1021/cr050541c CCC: $59.00

Eric L. Spitler was born in Columbus, OH, in 1980 and received his B.S. degree in Chemistry at Ohio State University in 2003. He is currently completing his Ph.D. studies as an NSF IGERT Fellow at the University of Oregon under the direction of Professor Haley, investigating donor/acceptor-functionalized arylacetylenes and dehydrobenzoannulenes.

Charles A. Johnson II was born in Ridgecrest, CA, in 1976. He received his B.S. degree in Chemistry with departmental honors in 1998 from the University of Oregon and was commissioned as an officer in the U.S. Army upon graduation. After five years of active-duty service he returned to UO, where he is currently completing his Ph.D. studies under the direction of Professor Haley. He served as an NSF IGERT Fellow from 2004 to 2006 as well as a Visiting Scientist with Professor Yoshito Tobe's group at Osaka University in 2005. His research interests include platinum acetylide and benzocyclyne chemistry and their materials applications.

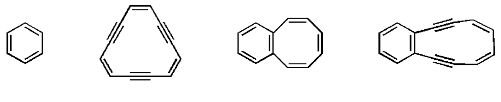
Michael M. Haley was born in 1965 in Lake Charles, LA. After growing up in Tulsa, OK, he studied cyclopropene and cycloproparene chemistry with Professor W. E. Billups at Rice University, where he received both his Bachelor's (1987) and Ph.D. degrees (1991). In 1991 he received a National Science Foundation Postdoctoral Fellowship to work with Professor K. P. C. Vollhardt on [*N*]phenylene chemistry at the University of California, Berkeley. In 1993 he joined the faculty at the University of Oregon, where he is currently a Professor of Chemistry and member of the Materials Science Institute. Among the awards he has received are a National Science Foundation CAREER Award (1995), a Camille Dreyfus Teacher–Scholar Award (1998), an Alexander von Humboldt Research Fellowship (2000), and a Herman Distinguished Teaching Award at UO (2002). His current research focuses on the chemistry of dehydro- and dehydrobenzoannulenes, metallabenzenes, and other novel aromatic systems.

alternating single and double bonds where the number in brackets denotes the number of contiguous sp^2 carbon centers. By definition, cyclobutadiene is therefore considered as [4]annulene, benzene as [6]annulene (**1**, Figure 1), etc. Replacement of one or more of the double bonds with an acetylene unit affords a dehydroannulene (e.g., **2**). An unfortunate side effect of installing triple bonds in the hydrocarbon skeleton often is compound instability. On the other hand, fusion of one or more benzene rings to furnish a benzoannulene (e.g., **3**) or dehydrobenzoannulene (e.g., **4**) heightens macrocycle stability in general.

Throughout the 1960s and 1970s, these four classes of closely related molecules were targets of intensive study. The research groups of Nakagawa,[2] Staab,[3] and Sondheimer,[4] the principal protagonists of this era, prepared an impressive array of annulenic structures and showed that these hydrocarbons possess a fascinating wealth of chemistry, such as Bergman cyclization of **4** to give anthracene.[5] The main factor driving annulene research was the dominating question of whether planar examples of such macrocycles were able to sustain induced ring currents, and if so, what was the strength of those ring currents. From the myriad of compounds produced, the main conclusion was that ring currents in these systems became progressively weaker upon benzannulation, by inclusion of triple bonds, and/or with increasing ring size. While these studies validated theoretical conclusions based on the Hückel rule for annulenes, it became apparent that there needed to be additional impetus for annulene research; thus, interest waned and the area languished in the 1980s.

The last decade of the 20th century heralded a rebirth of annulene chemistry. A number of synthetic discoveries, most notably Pd-mediated cross-coupling reactions between sp and sp^2 carbon centers,[6] were adopted from other areas of organic chemistry. These improvements made the previously laborious task of macrocycle assembly now a quick and efficient process. The ability to create new annulenes allowed chemists to easily functionalize the hydrocarbon backbone and thus tailor the chemical reactivity and physical properties of the macrocycles. Recognition of potential materials applications for these π-electron-rich systems has driven most of the annulene research conducted currently. Indeed, annulenes have been shown to exhibit nonlinear optical behavior, polymerize yielding tubular polymers, and even explode furnishing ordered carbon nanostructures (vide infra).

This review describes the numerous advances in the chemistry and reactivity of annulenes, dehydroannulenes, and their benzannelated analogues made over the last 20+ years.[7] For work prior to 1985, the reader is referred to the outstanding three-volume book series by Balaban, Banciu,



1 **2** **3** **4**

Figure 1.

and Ciorba.[8] To avoid creating an equally expansive document, a number of benzoannulenes and annulene-like structures, such as the smallest annulenes, cyclobutadiene and benzene, have not been included. Other structures not included are the cyclic phenylenes, of which there are myriad derivatives; biphenylenes,[9] triphenylenes,[10] and tetraphenylenes[11] all have been recently reviewed. Systems which are homoconjugated or meta- (1,3-) arene-fused have been excluded. Cross-conjugated annulenes,[12] Möbius annulenes,[13] and annulenes with belt-shaped topologies[14] (e.g., cyclocarbons, para- (1,4-) arene fusion) are covered by other authors in this special issue of *Chemical Reviews*.

2. Annulenes

2.1. [8]Annulenes

2.1.1. Aromaticity Probes

[8]Annulene (**5**, Figure 2), or cyclooctatetraene (COT), was first isolated in 1911[15] and caused a fair amount of confusion when it failed to display benzene-like properties.

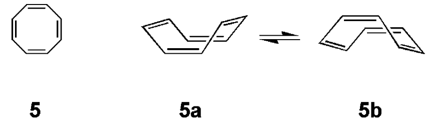
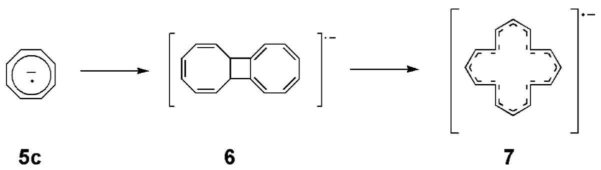


Figure 2.

This was prior to publication of Hückel's now-famous rule that only conjugated systems with $(4n + 2)$ π electrons would exhibit what is now called aromaticity.[16] The $(4n)$ π-electron [8]annulene, on the other hand, exhibits higher reactivity.[17] [8]Annulene exists in a tub conformation, which undergoes rapid interconversion, and thus is considered nonaromatic.[18]

Much of the recent work that has been done with [8]annulene involves the anion radical (**5c**) and dianion,[18b,19a−h] both of which are planar and much more stable. The majority of work by Stevenson involves [8]annulene anion radical, which has been shown to dimerize to **6**, followed by ring opening to [16]annulene anion radical (**7**, Scheme 1).[19a]

Scheme 1



Isotopic labeling experiments elucidated potential mechanisms for the dimerization. This reaction represents an improved route to the substituted [16]annulene anion radical, since direct synthesis is laborious and low-yielding.[20] Isotopic labeling and electron paramagnetic resonance (EPR) spectroscopy have also been used to explain sterically induced ring puckering as well as automerization of the anion.[18b] Intramolecular $\pi-\pi$ interaction results in transannular communication between the planar anion radicals of bis-COT systems (e.g., **8**, Figure 3),[19e] which is not seen with the tub-shaped neutral COT. Stevenson also recently prepared the highly strained, high-energy cycloprop[8]annulene (**9**),[19h] the second known cyclopropannulene (cyclopropabenzene being the first[19i]).

The cation radical of tetrakis(bicyclo[2.2.2]octene)-fused [8]annulene (**10**) was recently prepared by Komatsu et al.[19g] and shown to adopt the tub shape, while the cation radical of tetrakis(bicyclo[2.1.1]hexene)-fused [8]annulene (**11**) was planar. The planarity of the latter is attributed to the highly strained bicyclohexene units. Similarly, perfluorinated tetrakis(cyclobuta)COT synthesized by Soulen et al. (**12**)[21a] is planar, while perfluorinated tetrakis(cyclopenta)COT prepared by Gerson and Wirz[21b] (**13**) is tub-shaped. The former has shown powerful oxidizing properties, and its anion radical can be generated simply by contact with Hg metal.

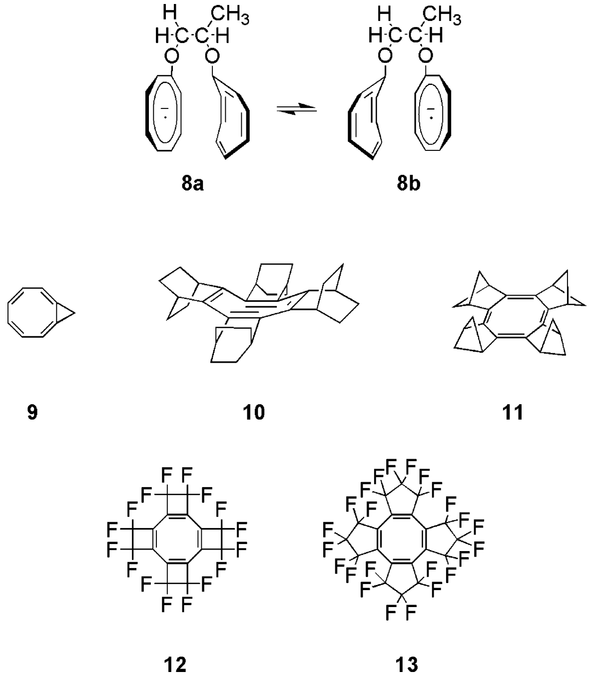


Figure 3.

Calculations by Baldridge and Siegel[21c] on neutral, fused COT derivatives **10**−**13** showed that enforced planarization could lead to "directing" of the positions of the double bonds, i.e., endo or exo to the fused ring systems. For example, as depicted in Figure 3, **10**, **12**, and **13** show the double bonds in the endo positions, while in **11** they are exo. Theoretical calculations also suggest that correct choice of annelating group can afford the desired form. Preparation of neutral **11** by Komatsu confirmed both its planarity and its preference for exocyclic double bonds crystallographically.[21d] Effects of annelation on the antiaromaticity of COT and other phenomena have been well examined,[21e] and it was recently found that paratropic ring current persists well into the transition from the planar to the tub-shaped geometry and that a minor distortion from the fully tub-shaped geometry is enough to restore it.[21f]

2.1.2. π-Stacking

Paquette and co-workers synthesized doubly stacked [8]-annulene cyclophane **14**,[22] which undergoes conformational equilibration involving bond-shift isomerization (Figure 4). The spectral data suggest that one isomer dominates, but no distinction between them is possible. The tetraanion **15** was prepared, requiring considerably strong reducing conditions at low temperatures. Interestingly, despite the strong Coulombic forces obviously present in the anion, homolytic cleavage of one of the enthano bridges does not occur. The authors observed bis-adducts from intramolecular cycloaddition upon heating, but the results were inconclusive.

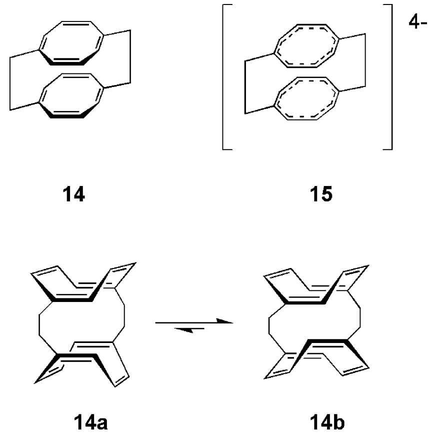


Figure 4.

2.2. [10]Annulenes

2.2.1. [10]Annulene

2.2.1.1. Aromaticity Probes. [10]Annulene (**16**, Figure 5), by the ($4n + 2$) rule, would be expected to be aromatic.

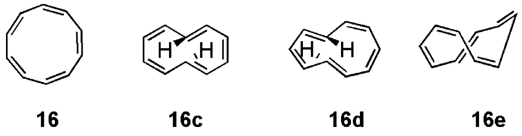
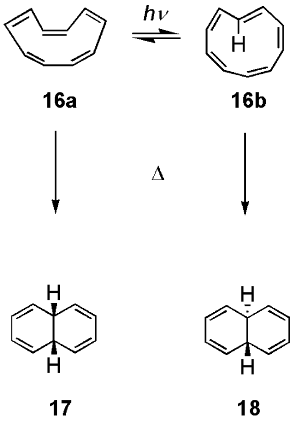


Figure 5.

However, such aromaticity requires a planar all-cis conformation, introducing significant bond angle distortion to 144°. [10]Annulene was first synthesized definitively in 1969 by Masamune and Seidner,[23] who demonstrated that it existed in two distinct yet rapidly interconverting forms **16a** and **16b** to which they assigned an all-cis "boatlike" conformation and a mono-trans "twist" conformation (Scheme 2). Both isomers were shown to undergo thermal cyclization to dihydronaphthalenes **17** and **18** while retaining their respective cis or trans character, as well as undergo hydrogenation to cyclodecane. The lack of planarity and hence aromatic stability in either of these conformations explains the relatively high reactivity of [10]annulene and implies significant bond localization rather than delocalization. The originally reported structures have been refined through computations over the years[24] using density functional theory and second-order perturbation theory. Comparison with experimental results has led to a reevaluation of the reliability of density functional theory (DFT) in predicting aromatic structures. Indeed, several other structures have been calculated as only slightly higher or even lower in energy (**16c**–**e**), revealing that further refinement of computational theories and methods involved may be required.[24e,f] The most recent computational investigations into the mechanisms of bond shifting and automerization of **16** support the original assignments of the two major isomers as **16a** and **16b**.[24g]

Scheme 2



2.2.1.2. Novel Topologies. Typically, planarization of an annulenic backbone is induced via introduction of linear triple bonds (a "dehydroannulene", see section 3). Schleyer and co-workers pointed out, however, that planarization can be accomplished through fusion of one or more cyclopropyl, cyclobutyl, or similar strained rings.[24d] This is computed by DFT to reduce the ring strain in the molecules and cause the planar geometry to occupy minima with D_{5h} symmetry. The geometries of three [10]annulenes (Figure 6) with two (**19**) and five (**20**) fused cyclopropyl rings and five cyclobutyl rings (**21**) were calculated at the B3LYP/DZd level of theory. All were found to satisfy various criteria for aromaticity and are predicted to be more stable than the parent [10]annulene. Synthesis of perfluorotetracyclobutaCOT (**7**),[21] mentioned in the previous section on [8]annulene, is pointed to as evidence for the synthetic accessibility of these cycloalkyl-fused annulene derivatives.

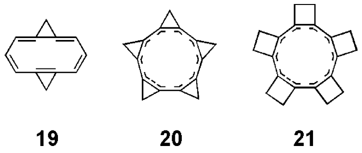


Figure 6.

2.2.2. Bridged [10]Annulenes

2.2.2.1. Aromaticity Probes. The potential aromaticity of [10]annulene is more readily illustrated by locking the π system into planarity, and thus, far more work has been done with 1,6-methano-bridged [10]annulenes[25] (**22**, first prepared by Vogel in 1964) and related isomers (Figure 7). These structures exhibit aromatic character with delocalized bond structures. The calculated relative stabilities of the localized and delocalized structures can vary depending on the method and basis sets used, and the determined preference is typically too small to be considered definitive. It has been shown that substitution anywhere in the system can disrupt the favorability of the "annulenic" form.[26a] For example, tetraiodination of 1,6-methano[10]annulene (**23a**) results in a disruption of the aromatic character, leading to bond localization and thermal instability. In addition, fusion of a cyclobutene unit onto 1,6-methano[10]annulene (**24**) has been shown to indicate a greater diatropic ring current than the

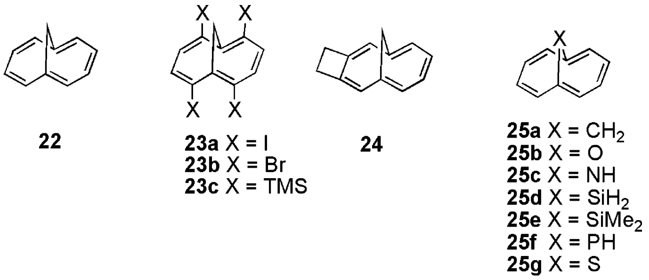
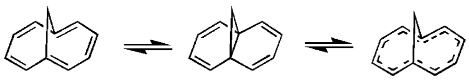


Figure 7.

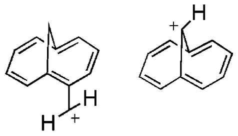
parent compound.[26f] It is believed that ring strain in **24** is relieved through enforced enlargement of the annulene ring by the cyclobutene unit. Hetero-bridged [10]annulenes **25** are particularly sensitive to bridging atom effects and can exhibit cyclic polyene, bisnorcaradiene (**26**), or delocalized aromatic (**27**) character (Figure 8).[27]



22a **26** **27**

Figure 8.

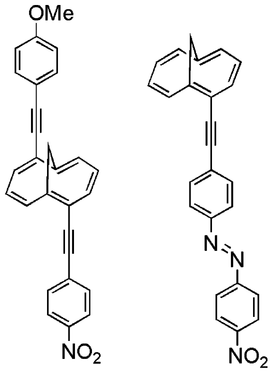
In addition to the neutral bridged annulene systems, their anion, cation, or radical analogues can serve as effective probes of bond theory.[28] Spin density, paratropism, and conformational measurements of cation radicals and anions of bridged π systems have proven especially useful in understanding the electronic effects of enforced planarity or nonplanarity. Studies of the ions of bridged [10]annulene as well as higher ring size ($4n + 2$) systems display pronounced paratropic character that is particularly sensitive to electronic and geometric effects. Cations from solvolysis of 1- or 2-chloromethyl-1,6-methano[10]annulene (**28**, Figure 9) exhibit particular stability upon formation, much greater than that of corresponding naphthyl groups. On the other hand, the 11-(1,6-methano[10]annulenyl) cation **29** is destabilized relative to cycloheptatrienyl cation with limited aromatic ring interaction.[28]



28 **29**

Figure 9.

2.2.2.2. Electron Donor−Acceptor Systems. As well as serving as interesting aromaticity probes, bridged [10]-annulene systems have demonstrated possible applications upon donor/acceptor functionalization. Pd-catalyzed coupling of phenylacetylene units to dihalo-1,6-methano[10]annulene and similar coupling of ethynyl-1,6-methano[10]annulene to bromo-substituted azobenzene has yielded novel donor/acceptor structures (e.g., **30** and **31**, respectively, Figure 10).[29]

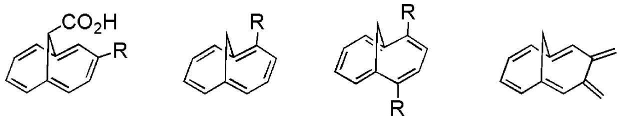


30 **31**

Figure 10.

Optical properties compare well with their benzene analogues, which have been shown to exhibit interesting nonlinear optical susceptibilities. The azobenzene derivatives also provide promising candidates for new azo dyes.

The aromaticity and stability data on bridged annulenes gained by computation and experiment allows more targeted application toward fused-ring syntheses. Gellman and coworkers[26b] developed a method using a semi-benzylic Favorskii rearrangement to provide 1,6-methano[10]annulene derivates **32** bearing substituents on both the bridge carbon and the aromatic ring, thus greatly increasing the availability of a wide variety of bridged annulenes. Another method affords enantiomerically pure 1,6-methano[10]annulene derivatives (**33**, Figure 11).[26c] Both of these techniques have demonstrated generality and efficiency. A more convenient but less general procedure allows synthesis of 2,5-disubstituted 1,6-methano[10]annulene **34** from 1,6-diacetylcyclohepta-1,3,5-triene.[26d] A reactive *o*-quinodimethane derivative, 1,6-methano[10]annulene-3,4-quinodimethane (**35**), has also been generated and trapped as various Diels−Alder adducts,[26e] providing a practical method for the preparation of six-membered ring-fused [10]annulenes and a variety of theoretically and synthetically interesting compounds. It should be noted that these highlights represent only a few examples of the synthetic, computational, and spectroscopic work that has been undertaken in recent years.[30]



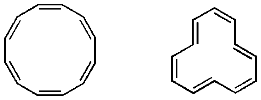
32 **33** **34** **35**

Figure 11.

2.3. [12]Annulene

2.3.1. Aromaticity Probes

Although there has been some controversy regarding the veracity of the preparation of the ($4n$) π-electron [12]-annulene (**36**, Figure 12),[31] it was first reported in 1970 by Oth and co-workers.[32] Low-temperature NMR spectroscopic analysis led the authors to conclude that **36** was significantly distorted from planarity due to steric crowding by the internal protons (**36a**) and that it readily underwent cis/trans isomerization through intermediate **37** (Figure 13).



36 **36a**

Figure 12.

The isolated electrocyclic ring-closure products **38** and **39** led the authors to hypothesize a very low (4.1−4.5 kcal mol^{-1}) automerization energy barrier. Since the original experimental work there have been numerous computational studies performed to determine what exactly is the most stable conformation of [12]annulene,[31,33] some of which yield starkly contradicting results. Early work on the automerization transition state suggested that the D_3-symmetric structure (**40**, Figure 14) might be possible, but very recent results support the original tri-*trans*-[12]annulene structure proposed by Oth[34a] and show that this automerization proceeds via a one-step, bond-alternating C_2-symmetric transition state with

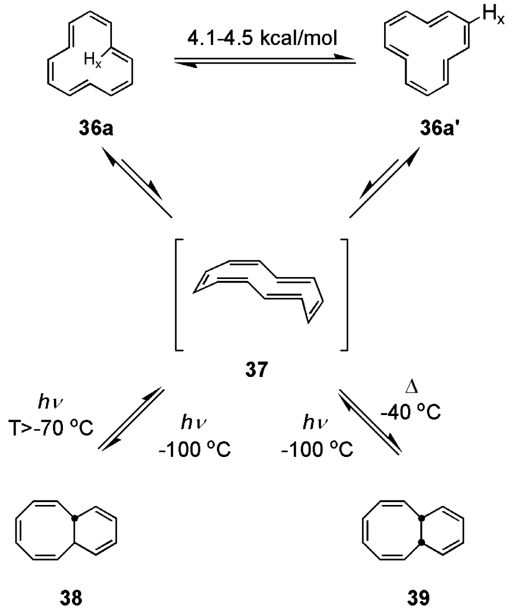


Figure 13.

nominal Möbius topology. Further computational work by Castro and Karney on tri-*trans*-[12]annulene revealed that its facile configuration change (i.e., **36a** → **37**) could be accounted for by bond shifting via a Möbius aromatic transition state (**41**), a mechanism referred to as "twist-coupled bond shifting".[34b] More complicated pericyclic reactions of [12]annulene (e.g., to **42**) have also been investigated computationally[35] and are believed to proceed through several transition states. For more on Möbius annulenes, the reader is referred to the contribution of Herges in this issue.[13]

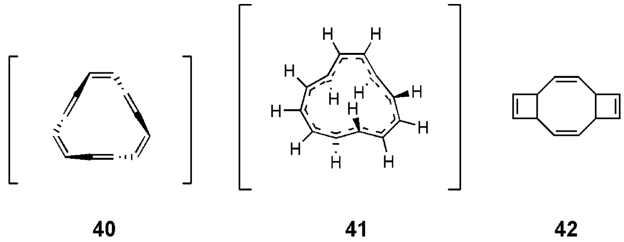


Figure 14.

The anion radical of [12]annulene (**43**, Figure 15) has been shown to be stable enough for spectroscopic characterization[36] and can be generated from either exposure of neutral [12]annulene to alkali metals or dehydrohalogenation of 1,2,5,6,9,10-hexabromocyclododecane **44**, a fire retardant.

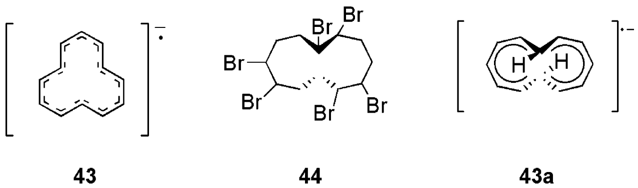
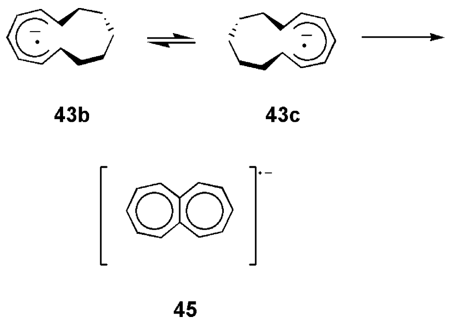


Figure 15.

The anion assumes a "half-planar" conformation (**43a**) wherein seven carbons lie in plane and consequently contain most of the spin density with the other five atoms twisted out of the plane with rapid ($k = 10^6 - 10^7$ s^{-1}) rearrangement between degenerate conformations (**43b** and **43c**). Thermal dehydrogenation collapses the anion into the heptalene anion radical **45** (Scheme 3).

Scheme 3



Bridged [12]annulene **46** (Figure 16), like bridged [10]-annulene, exhibits much greater stability than the parent annulene. 1,7-Methano[12]annulene was first prepared by Vogel in 1974[37] and found to be nonplanar with significant bond length alternation. Its relative stability combined with a weakened (but still significant) cyclic conjugation makes it a good candidate for electron delocalization studies.[38] For example, fusion of a benzene ring onto the 4*n* π-electron system to make **47** results in a reduction of the paramagnetic ring current.[39]

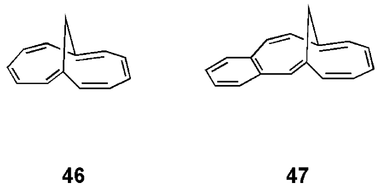


Figure 16.

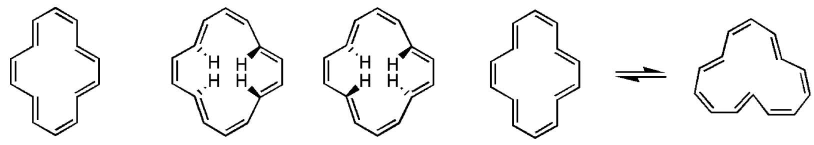
2.4. [14]Annulene

2.4.1. Aromaticity Probes

[14]Annulene (**48**, Figure 17) was first synthesized in 1960 by Sondheimer and Gaoni.[40] Computational and experimental studies performed since have consistently concluded that the molecule adopts a nonplanar conformation with a delocalized π-bond structure in the solid crystalline state.[41] The nonplanarity is ascribed primarily to nonbonding interactions between the internal protons. Nearly equalized bond lengths (~1.40 Å) have been confirmed by calculation as well as X-ray analysis and low-temperature UV−Vis studies.[41c] The photoelectron spectrum of [14]annulene[41e] reveals a vertical ionization energy consistent with an aromatic system. This study also concluded that of the three most-reported symmetry states for [14]annulene (C_{2h}, D_2, and C_s), the C_{2h}-symmetric state **48a** with π-bond delocalization is the most favored. In solution, [14]annulene exists in equilibrium between the C_{2h}-symmetric state and a minor (8%) tri-trans configuration **48b**,[41a] though some have asserted that localized structures of [14]annulene may not even exist.[41d]

Although planar *cis*-[14]annulene is theoretical, isomeric precursors such as the little studied "nonalternant hydrocarbons" (e.g., **49,** Figure 18) have been synthesized and correlated to calculated frontier molecular orbitals of the as-yet unknown annulene.[41f]

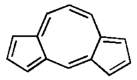
Octalene (**50**), another isomer, can be considered a perturbed [14]annulene with a zero-atom cross-link. That this structural variation does not preclude chemical similarity has been shown by reductive methylation of octalene (Scheme 4).[41g] Treatment of octalene with Li metal results in the dianion **51**, which reacts with dimethyl sulfate to yield the disubstituted annulene **52**. NMR spectroscopy of **52** indicates a pyrene-like structure with four internal protons. Temper-



48 **48a** **48b**

Figure 17.

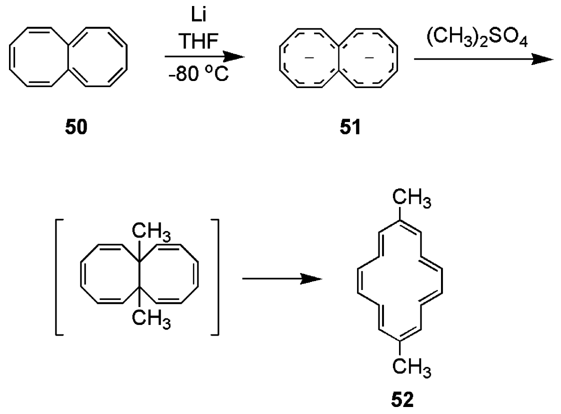
ature dependence of the NMR signals also indicates equilibration between three configurations (**52a**−**c**, Figure 19) that allows inner and outer protons to be exchanged. The X-ray structure shows a centrosymmetric crystalline configuration that precludes bond alternation. The bond delocalization is retained even with significant (up to 20° torsional angles) deviation from planarity. A promising application arises with this substitution method, since direct treatment of the parent [14]annulene with electrophilic reagents results in polymerization rather than substitution.



49

Figure 18.

Scheme 4



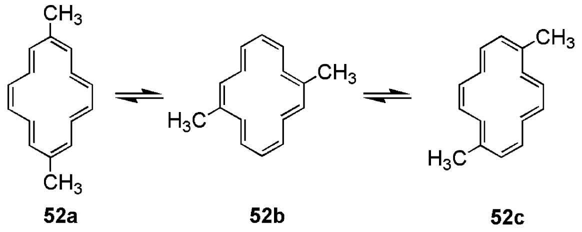
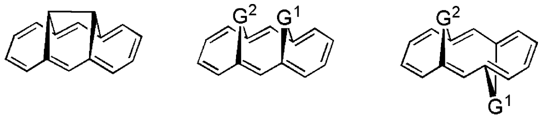


Figure 19.

2.4.2. Bridged [14]Annulenes

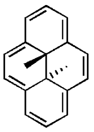
2.4.2.1. Aromaticity Probes. As in the case of bridged [10]annulenes, bridged [14]annulenes (**53**−**55**, Figure 20) show sensitivity to the bridging group.[42] Nonbonding interaction between bridging groups in multiply bridged annulenes (both syn and anti) can cause severe distortions of the annulene ring.[42a] Table 1 illustrates just two of the parameters that can be affected by several different substitutions in bridging pattern.



53 **54** **55**

Figure 20.

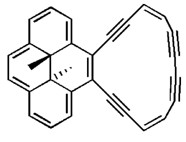
Dimethyldihydropyrene (DMDHP **56**, Figure 21) and its numerous derivatives have been one of the most studied classes of bridged [14]annulene systems known. The majority of work in this area over the last 20 years has been undertaken by Mitchell and co-workers.[43a−k] It is only the second annulene to have its enthalpy of formation (ca. 339 kJ/mol) measured.[43a] The planar, delocalized aromatic system[43b] is complemented by the internal methyl units that reside above and below the plane and thus present convenient handles for the probing of ring current effects from manipulation of the parent structure (most notably, from fusion of aromatic rings[43c] or organometallic complexes[43d] to the periphery, which can drastically and perhaps predictably attenuate the diatropicity of the annulene). Fusions of DMDHP units to each other[43e] and into a cyclophane structure[43f] have been accomplished.



56

Figure 21.

Fusion of a DMDHP to a dehydroannulene (e.g., **57**, Figure 22) has been shown to cause a reduction in diatropicity of both units.[43g] The attenuation is used to infer a weak diatropic ring current associated with the dehydroannulene, but the degree of change is too small for the relative differences in aromaticity of the two units to be reliably measured. Dehydroannulenes are discussed in more detail in later sections.

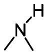
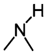
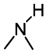
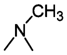
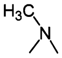
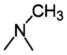
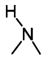
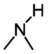
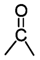
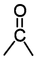
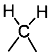
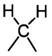
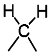
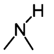
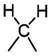
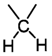
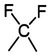
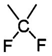


57

Figure 22.

2.4.2.2. Photochromic Switches. A DMDHP derivative has also found application as a photomeric switch.[43h] Exposure of the annulene-fused cyclopentadiene **58** to KH or $LiCH_2SiMe_3$ generates the [14]annulene-fused cyclopentadienide anion **59a** (Scheme 5), causing a reduction in diatropicity and significant deshielding of the internal methyl protons. The anion exhibits reversible photomeric opening of the bond between the methine bridges to generate **59b**, and it is concluded that the cyclopentadienide anion is acting

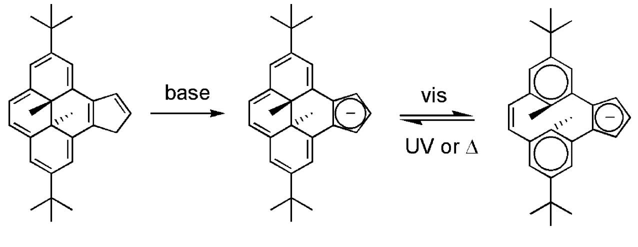
Table 1. [42a] **Effect of Bridging Substituents on Carbon−Carbon Bond Lengths of 54 and 55**

	G^2	G^1	G^2-bridged C-C distance, Å	G^1-bridged C-C distance, Å
a			2.294	2.294
b			2.290	2.274
c			2.279	2.274
d			2.325	2.356
e			2.259	2.249
f			2.470	2.472
g			2.359	2.360
h			2.340	2.326
i*			2.278	2.341
j*			2.502	2.440

*anti-bridged annulene **55**

in a manner chemically similar to benzene. Other derivatives of DMDHP have been prepared,[43i,j] and several photochemical studies have been performed.[43k]

Scheme 5



2.5. [16]Annulene

2.5.1. Aromaticity Probes

The (4*n*) π-system [16]annulene (**60**, Figure 23) was first synthesized in 1961 by Sondheimer and Gaoni.[44] Since then, a variety of conformations have been found to be stable, either through computation or X-ray crystallography.[33d,45] The annulene exists predominantly in the alternating cis/trans configuration with four internal protons that contribute to the considerable distortion from planarity (**60a**). A minor (12%) isomer **60b** with five internal protons is believed to exist in equilibrium with the major isomer (Figure 23).[41a] Recently, several new conformations, some with Möbius topography, have been predicted computationally.[33e] The geometry of the annulene shows significant temperature dependence in the NMR spectrum: as the temperature is decreased, the molecule becomes more planarized and antiaromatic character increases.[41a] Despite the classic hypothesis that (4*n*) π-electron systems are inherently destabilized relative to their acyclic analogues, recent work has advanced the possibility that larger (4*n*) systems such as [16]annulene are only slightly destabilized by π-electron interactions.[46]

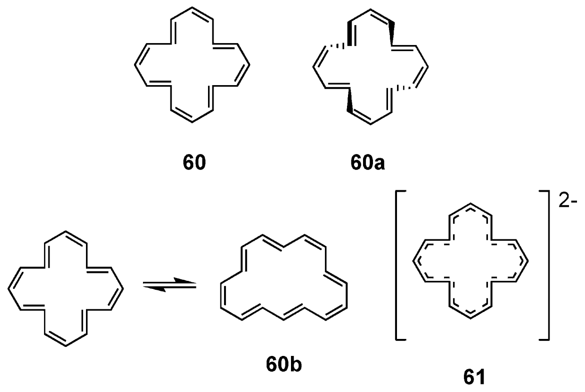


Figure 23.

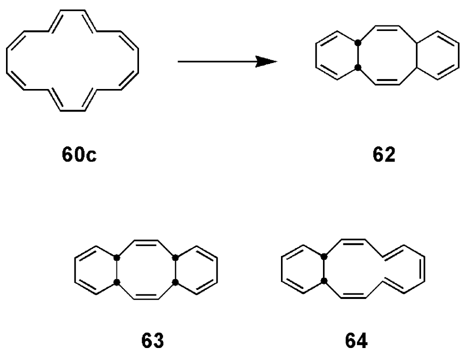
Stevenson and co-workers performed several isotopic perturbation studies on 95% deuterated [16]annulene illustrating the dramatic effects of ring planarity on ring tropicity.[47] The shorter length of the C−D bond relative to the C−H bond results in decreased steric interactions on the interior of the ring, allowing the system to relax into a more planarized state. This causes a marked increase in paratropicity, with the NMR resonance of the internal protons shifted downfield from 10.58 to 10.82 ppm upon deuteration.[47a] The external protons experience a similar upfield shift. Calculations predict decreased dihedral angles along the C−C bonds of nearly one-half the annulene.

As in the case of [8]annulene, the anion radical and dianion species of [16]annulene (**7** and **61**, respectively) have been easily made by reduction of the neutral molecules with alkali metals.[48a] Later, it was found that the anion can be generated by reduction of the [2 + 2] dimer of cyclooctatetraene (see Scheme 1) or equimolar reaction of COT anion radical with neutral COT.[48b] This last method shows the synthetic potential of anion radical−neutral molecule combination reactions. Formation of the dianion creates a $(4n + 2)$ π-electron system that displays even greater diatropicity than [18]annulene and is believed to be significantly more stable than neutral [16]annulene. Isotopic perturbation studies of the dianion of [16]annulene[47a] provide results directly opposite the neutral molecule: deuteration causes a pronounced increase in diatropicity, shifting the internal protons upfield from −8.03 to −8.11 ppm. The shifting of the external protons, however, is "not larger than experimental error".

2.5.2. Novel Topologies

The cyclization reaction of [16]annulene (Scheme 6) was investigated experimentally in 1967[49] and reported to proceed from the C_s-symmetric conformation (even though it is 31.4 kJ/mol less stable than the lowest energy conformation) to the tricyclic product with two bridgehead hydrogens pointing in one direction (**62**) and the other two in another. It was not known whether the cyclization occurred in a stepwise or concerted manner. The cyclized product with all four bridgehead hydrogens pointing in the same direction (**63**), however, was calculated to be thermodynamically more stable.[33d] The electrocyclic reactions of [16]annulene have recently been investigated computationally using ab initio and density functional theory calculations.[50] Several intermediates and transition states were determined, and it was found that cyclization to the more stable product was likely to be stepwise, with first one ring closure followed by the other from a bicyclic intermediate **64**. The overall energy barrier was calculated as 131.0 kJ/mol, which is the relative energy of the first transition state. A viable concerted transition state for the cyclization could not be found. The four computed stepwise mechanisms for cyclization to the less thermodynamically stable product were much more complex: there were four transition states and three intermediates, with the lowest overall energy barrier of about 131.0 kJ/mol determined by the third transition state. This was exactly the same energy barrier as the cyclization to the more stable product. On the basis of these barriers it was not possible to determine the dominant product of the reaction. A concerted transition state for this reaction also could not be determined.

Scheme 6



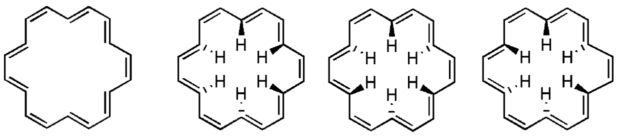
60c **62**

63 **64**

2.6. [18]Annulene

2.6.1. Aromaticity Probes

[18]Annulene (**65**, Figure 24) represents a unique target of study due to its status as not only a $(4n + 2)$ annulene but also a member of the aromatic subgroup $6(2p + 1)$ in which the D_{6h}-symmetric point group is allowed without severe nonbonded interactions.[51a] As annulene ring size increases, aromatic stabilization energies drop off and bond length alternation becomes more pronounced. An ongoing debate has centered on the ring size at which polyolefin-like, localized π-electron structures predominate over fully delocalized conjugation. Put simply, it is the question of the point at which drawing a closed circle inside the ring rather than alternating double and single bonds becomes inappropriate. Computational and theoretical estimates ranging from [30]annulene[51b] all the way down to [10]annulene[23] have been put forward. More and more, the front lines of this debate take root at or near [18]annulene.



65 **65a** **65b** **65c**

Figure 24.

Around the same time that Sondheimer and co-workers first synthesized **65**,[52a] Longuet-Higgins and Salem predicted the diminishing aromatic stabilization of large $(4n + 2)$ annulenes.[52b] Even earlier, Mislow predicted the unlikelihood of planar D_{6h} [18]annulene due to steric interactions between the internal protons.[52c] More recently, low-temperature NMR studies have yielded three conformations of nearly equal energy[53] with three internal protons above the plane and three below in three possible arrangements (**65a**−**c**). Furthermore, upon synthesis, chemical evidence revealed reactivity typical of localized π bonds (addition rather than substitution), behavior drastically different than benzene. It may be a bit surprising then that the X-ray crystal structure of **65**, first determined in 1965,[54a] showed a nearly centrosymmetric molecule distorted from planarity by 0.085 Å and a C_{3i} symmetry only slightly distorted from D_{6h} symmetry. The nonplanarity was explained by intermolecular nonbonded repulsions and crystal-packing forces. The crystal structure was reevaluated in 1995,[54b] and although an additional minor form with slightly different geometry was found, [18]annulene was confirmed by the authors as "having an essentially planar aromatic structure in the crystal". The 12 'inner' C−C bonds were determined to have lengths of 1.385 Å and the 6 'outer' bonds lengths of 1.405 Å, relatively close to the originally determined geometry. The authors also noted that the average C−C length in **65** is similar to benzene. The ring internal and reentrant angles are 124.0° and 127.9°, respectively.

Schleyer and co-workers recently challenged the essential symmetry and planarity of [18]annulene,[55] calling the experimental data into question. It has been pointed out by Shaik, Hiberty et al.[56] that adjacent overlapping π bonds prefer bond length alternation but that in small cyclic conjugated systems it is the σ framework that enforces a regular geometry. Cyclic conjugation is only weakened, not eliminated, by deviations from bond equalization. Thus, the

Table 2. Bond Alternation of [18]Annulene in Various Symmetry Point Groups[a]

point group	level of theory	Δr (Å)	δH_{inner}	δH_{outer}
D_{6h}	B3LYP	0.017	−10.9 to −11.0	11.5−11.6
D_{6h}	KMLYP	0.015	−11.3 to −11.5	11.2−11.4
D_{3h}	KMLYP	0.095	−4.9 to −5.0	9.3−9.8
D_3	KMLYP	0.095	−4.2 to −5.1	9.4−9.5
C_2	KMLYP	0.099	−2.3 to −2.6	8.9−9.0
D_{6h}	BHLYP	0.015	−11.2 to −11.4	11.2−11.5
D_{3h}	BHLYP	0.094	−4.9 to −5.1	9.6−9.8
D_3	BHLYP	0.095	−4.3 to −4.6	9.5−9.7
C_2	BHLYP	0.100	−2.7 to −2.9	9.0−9.4
	exp	0.042	−2.99	9.3

[a] 6-31+G** basis set used for optimization of all structures; Δr is the distance between the shortest and longest C−C bond lengths. δH_{inner} and δH_{outer} are the GIAO-B3LYP/6-311+G** ^{1}H NMR chemical shifts in ppm relative to TMS.

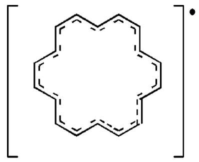
bonds in benzene are equalized by the σ skeleton, *not* the conjugated π system. Since this equalization tendency is a weaker force than the π preference for alternation, benzene is the exception to the norm rather than the prototype for aromatic systems. Schleyer points out that this π-induced distortion is in no way inconsistent with aromatic character, but it is important to determine the point at which the competing forces of "σ resistance and π distortivity" balance completely.[55a] To this end, Bühl and Schleyer used GIAO-B3LYP/6-311+G** methods to compute the ^{1}H NMR shifts of various boranes, carboranes, carbocations, and [*n*]annulenes and demonstrated that computed values matched experimental values only when geometries were correct. They then used this method to show that the shifts were in good agreement only when **65** did not have D_{6h} symmetry (Table 2) and that the shifts computed using the geometry derived from the X-ray data were in disagreement with the experimental shifts. Finally, they found that only a C_2 geometry gave acceptable results: at both the KMLYP and BHLYP levels, C_2 [18]annulene is lower in single-point energy.

Schleyer explains the contradictory crystal data in part by static disorder, in which superposition of a lower symmetry structure leads to an apparent higher symmetry. Although the authors of the 1995 investigation ruled this possibility out, they were using earlier geometry models that overestimated ring diameters[57] well beyond the computed deviations between the C_2, D_{3h}, and D_{6h} structures. Another issue with the crystal data is dynamic disorder: the rapid interconversion between two C_2 structures passes through D_{6h} as a transition state with a barrier of only ~3 kcal mol^{-1}, which would produce a time-averaged structure.

Ermer recently published a brief disputation of Schleyer and co-workers' assertions,[58] offering that it may in fact be possible to distinguish inversion disorder effects from true single structures at currently attainable resolutions. In addition, he noted that computation regards molecules as being in the gas phase and that the small barrier to symmetrization could be overcome by $\pi-\pi$ stacking and favorable crystal-packing forces, i.e., "driving the molecules in the crystal towards centrosymmetric forms with non-alternating character". If bond alternation does indeed exist in [18]annulene and then vanishes upon crystallization, it would be an extremely unusual phenomenon with important implications for solid-state NMR. Clearly, further computational efforts are in order.

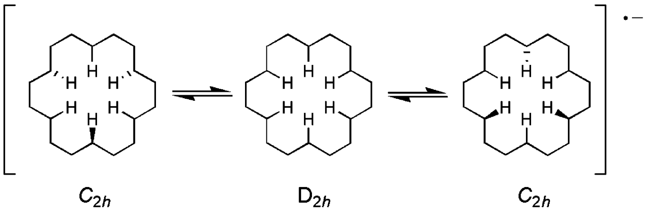
The same isotopic perturbation experiments undertaken by Stevenson and co-workers for [16]annulene were applied to [18]annulene.[53] Not surprisingly, the same effect, albeit opposite due to the aromaticity of **65** rather than antiaromaticity, is observed. Upon deuteration, the external proton NMR signals shift downfield from 9.17 to 9.20 ppm due to reduced steric crowding by the smaller deuterium and more effective π-orbital overlap, resulting in a more planarized structure with a larger ring current. Similarly, the internal protons experience an upfield shift from −2.96 to −3.08 ppm, again consistent with increased diatropicity.

The anion radical of [18]annulene (**66**, Figure 25) is obtained via reduction by K metal and has been shown to undergo Jahn−Teller distortion to two different structures when the odd electron occupies the degenerate antibonding molecular orbitals (D_{2h} and C_{2h} symmetries).[59a] The anion is not very stable but persists for nearly an hour at room temperature. In contrast to the C_{2v} anion radical of benzene, rapid pseudorotation of the system is prevented by the nonplanarity of the radical, as evidenced by the complex EPR spectrum. The anion is proposed to equilibrate between two degenerate C_{2h} conformations (**66a** and **66c**, Figure 26) in which three internal protons are in the plane of the ring, two are below and one is above, through a D_{2h} transition state **66b** in which all internal protons are in the plane. These results imply that the disruptive effect of the odd electron amplifies the π component to "overcome the symmetrizing force of the σ-framework". It has been suggested that [18]annulene anion radical has the potential to represent a superconducting material.[50,51]



66

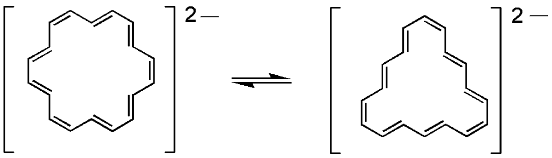
Figure 25.



66a **66b** **66c**

Figure 26.

The dianion **67** also adopts one of two equilibrating nonplanar conformations (**a** and **b,** Figure 27, 2.3:1 ratio) with antiaromatic character and bond alternation. The dianion is also unstable relative to the neutral molecule.[59b]



67a **67b**

Figure 27.

Scheme 7

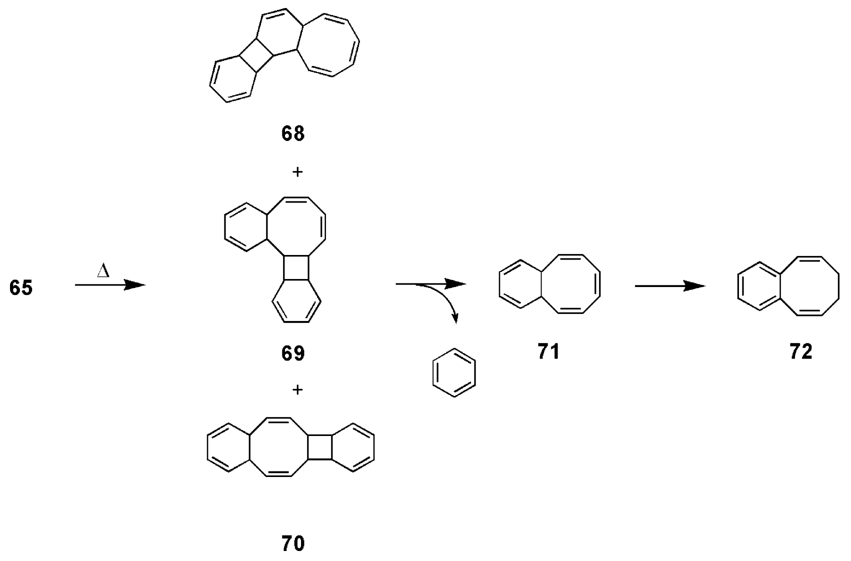


Table 3. Activation Parameters for Thermal Rearrangement of 65 to 72

reaction	$\Delta H^{\ddagger}$ (kcal mol^{-1})^{a}	$\Delta S^{\ddagger}$ (cal mol^{-1} K^{-1})	$\Delta G^{\ddagger}$ (kcal mol^{-1})
65 → **68**−**70**	36.03 ± 0.01	13.88 ± 0.08	31.89 ± 0.01
68−**70** → **71** + benzene	34.05 ± 0.2	14.20 ± 1.0	29.82 ± 0.2
71 → **72**	32.90 ± 0.21	14.22 ± 0.13	28.56 ± 0.21

[a] Values at 298.15K.

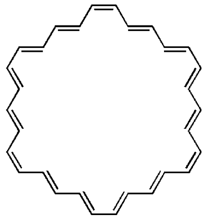
2.6.2. Novel Topologies

[18]Annulene has been shown to undergo thermal rearrangement (Scheme 7).[60] Although scanning calorimetry was able to determine the thermodynamic factors some years ago,[60a] elucidation of the mechanism was achieved through reinvestigation of the thermograms using an iterative method of integration of the kinetic equations established.[60b] The CALIT-3 program is able to simulate thermograms observed for successive first-order reactions: the three first-order reactions [18]annulene → **68**−**70** → **71** + benzene and **71** → **72**. Tetracyclic intermediates **68**−**70** believed to be generated in this reaction all play the same role in the mechanism and are therefore considered the same compounds from a kinetic standpoint. Using complex calorimetric methods in conjunction with the thermogram simulator program, a detailed mechanistic picture of the thermal rearrangement was deduced. The enthalpy of formation of [18]annulene (123.4 ± 3.7 kcal mol^{-1} at 298.2 K), stabilization energy (−37.6 ± 4.6 kcal mol^{-1}), and π-bond delocalization energy (ca. −120.5 kcal mol^{-1}) were determined. Activation enthalpy, entropy, and free energy for each step were also determined (summarized in Table 3). Interestingly, the last step in the mechanism is believed to include two suprafacial 1,5-hydrogen shifts. The kinetic parameters obtained are in good agreement with the thermograms, showing the utility of this method in analyzing complex reaction mechanisms.

2.7. Higher Annulenes

2.7.1. Aromaticity Probes

The higher annulenes (n > 18) present less synthetic interest, mostly due to their significant bond alternation, asymmetry, and conformational flexibility. All annulenes up to $n = 30$ (**73**, Figure 28) have been synthesized except $n =$ 26 and 28. Most of the recent work has been computational in nature and aims at understanding the complex interplay between geometric, energetic, and magnetic properties. Aromatic stabilization energies are greatly reduced in the larger systems, and it is believed that the mixing of low-lying excited states and ground states leads to pseudo-Jahn−Teller distortions.[61] The search for a discrete transition point between delocalized and localized structures, mentioned in the previous section, prompted a computational study by Choi and Kertesz that investigated bond length alternation in large annulenes up to $n = 66$.[62a] Various levels of theory and basis sets were sampled. While B3LYP/6-31G* acceptably predicted bond lengths of known ring sizes and oligoenes, Hartree−Fock methods consistently provided clearly incorrect (and at times impossible) values. Using experimental measurements as guides,[62b] DFT calculations accurately quantified the bond length alternation ($\delta = R_{\text{single}} - R_{\text{double}}$) of the minimized structures of both ($4n$) and ($4n + 2$) annulenes as a function of ring size (Table 4). In the progression of ($4n + 2$) annulenes, the data clearly show a sharp increase in δ for [30]annulene. Conversely, an enforced $\delta = 0$ produced a local maximum for [30]annulene−[66]-annulene in the energy profiles. δ values for the lower ($4n + 2$) annulenes ([14]-, [18]-, [22]-, and [26] annulenes) are essentially zero and thus not reported.



73

Figure 28.

Another value investigated was the nucleus-independent chemical shift (NICS) parameter, which has proven an effective criterion for aromaticity.[63] NICS is the negative of the absolute magnetic shielding at the center of a ring current.

Table 4. Calculated Bond Length Alternations in Various Annulenes[62A]

	n	C−C (Å)^a	C−C (Å)^a	d
(4n)	20	1.442	1.361	0.081
	24	1.432	1.363	0.069
(4n + 2)	14			
	18			
	22			
	26			
	30	1.417	1.382	0.035
	42	1.425	1.374	0.051
	54	0.427	1.371	0.056
	66	1.427	1.371	0.056

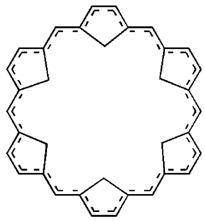
[a] Calculated at the B3LYP/6-31+G** level of theory.

A negative value denotes aromaticity and positive value antiaromaticity (e.g., benzene = −11.5; cyclobutadiene = 28.8). A sharp decrease in magnitude of the NICS value for [30]annulene was predicted, going from −15.9 in the case of [26]annulene to −12.4 for [30]annulene, with a further more gradual drop off at larger sizes. It is noted that this is still a large and negative value, implying that bond alternation is not necessarily correlated to antiaromaticity. The reasonable conclusion is that [30]annulene is the most likely candidate for the "transition point" to a localized, yet still aromatic, structure. Surprisingly, using these methods, the calculated aromatic stabilization energies do not decrease with increasing ring size but increase up to [18]annulene and then converge to a limiting value of about 23 kcal mol^{-1}. This provides further evidence that total delocalization is not required for aromaticity.

In the same work for which D_{6h} symmetry for [18]-annulene was discounted,[55a] Schleyer and co-workers also pointed to their computational comparison with experimental chemical shifts of [22]annulene for which the crystal structure is not known. The large disagreement between the two sets of shifts led them to reject the reported D_{2h} symmetry and assert bond alternation for [22]annulene which, by implication, "should be true of all the higher annulenes". On the other hand, Yoshizawa and co-workers performed vibrational analyses on both **65** and **73**[51a] and concluded that the B_{1u} and B_{2u} vibrational modes of [30]annulene lead to equivalent D_{3h} global minima with a D_{6h} transition state and an energetic barrier of 2.3 kcal mol^{-1} or less depending on the level of theory employed.

Yoshizawa and co-workers also computed the electronic structure,[64] vibrational frequencies, and linear vibronic coupling constants of [30]annulene as well as its normal and deuterated mono- and trianions to analyze the vibronic interactions and their effects on Jahn−Teller distortions. They found that the lowest E_{2g} mode (38 cm^{-1}) affords unusually large vibronic coupling constants and thus should play a significant role in Jahn−Teller distortions of **73**. This low-frequency mode is typical of nanosized molecular systems and in stark contrast to the cases of benzene, in which only the highest E_{2g} vibrational modes (1656 and 3184 cm^{-1}) play a significant role in Jahn−Teller distortions, and [18]-annulene, where the lowest E_{2g} modes at 116 and 405 cm^{-1} and the highest stretching frequency of 3201 cm^{-1} are most important. This implies that the low-frequency modes become more important in carbon ring distortions as the annulene size increases. In both the mono- and trianion the vibronic coupling constant of the 38 cm^{-1} mode is altered upon deuteration of the annulene and the vibronic coupling constant of the 1513 cm^{-1} mode is increased slightly.

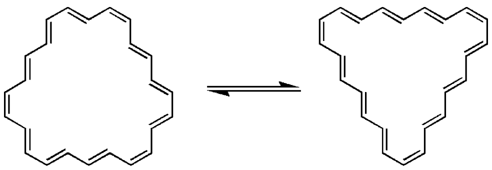
Kiran and Nguyen[65] calculated an enforced delocalization for [30]- and [42]annulene using symmetrically placed methylene bridges connecting adjacent internal carbons to create multiple cyclopentadiene units in the interior of the structures (e.g., **74**, Figure 29). The induced ring strain is enough in these cases to cause stabilization of the delocalized (D_{6h}) structure in preference to the localized (D_{3h}) structure. However, the same strategy fails in the cases of [54]- and [66]annulene, which still prefer localized structures. The higher annulenes experience less ring strain from the methylene bridging. The lower symmetry structures all experience less ring strain, with the higher annulenes experiencing much less. This shows that delocalization and aromaticity are adjustable in much the same way that, for example, the aromaticity of methano-bridged[10]annulene is enhanced (vide supra).



74

Figure 29.

Oth and de Zélicourt performed a detailed low-temperature ^{1}H NMR spectrum analysis of the (4n) [24]annulene (**75**)[66] and deduced its conformations. As expected, the annulene shows significant bond alternation and a paramagnetic ring current with a $\Delta\delta$ of 7.72 between the inner and outer protons. In solution, a rapid equilibrium exists between the major and minor conformers **75a** and **75b** (Figure 30, $K \leq 0.05$) with the resonance energy of the antiaromatic system estimated to be from −9 to −10 kcal mol^{-1}.



75a **75b**

Figure 30.

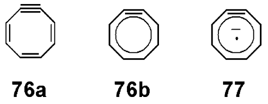
3. Dehydroannulenes

From a synthetic standpoint, replacement of one or more of the double bonds of an annulene with triple bonds is a fairly straightforward process. The resultant dehydroannulene often is considerably less stable than its annulene counterpart and thus prone to undergo deleterious side reaction, decomposition, etc.; nonetheless, the heightened reactivity also leads to some unusual observations (vide infra).

3.1. Dehydro[8]annulenes

3.1.1. Aromaticity Probes

Dehydro[8]annulene, or [8]annulyne (**76**, Figure 31), was first prepared by Krebs in 1965.[67a,b] Huang and Sondheimer published a thorough review of work up to 1980,[67c] and



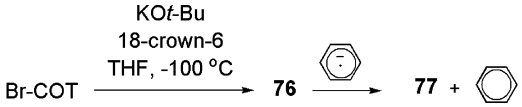
76a **76b** **77**

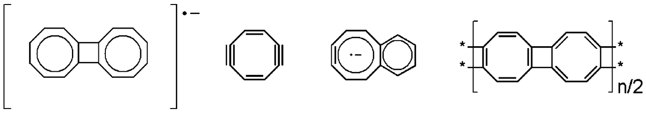
Figure 31.

recent work has focused mostly on the anion radical.[68] Wenthold and Lineberger measured the photoelectron spectrum of $C_8H_6^-$ [68a,b] and reported that it very closely resembled that of the COT anion ($C_8H_8^-$) with similar structures. The anion radical is obtained by reaction of O^- with COT in a liquid N_2-cooled flowing afterglow apparatus. There are two observed electronic states for [8]annulyne: the lowest described as a singlet 1,3,5-cyclooctatrien-7-yne (**76a**) and a higher triplet dehydrocyclooctatetraene state (**76b**). The electron affinity of neutral dehydro[8]annulene is 1.044 ± 0.008 eV, and the alkyne stretching frequency is 2185 cm^{-1}, which is expected for a strained triple bond in an eight-membered ring. Both the neutral molecule and ion are believed to be planar or pseudo planar, unlike the tub-shaped COT.

Stevenson and co-workers developed a one-step entrapment protocol for [8]annulyne anion radical **77**[68c] using dehydrohalogenation of Br−COT by *t*-BuOK in THF solution containing an equimolar amount of 18-crown-6 (Scheme 8). The resulting solutions are characterized by EPR spectroscopy. Neutral [8]annulyne is generated, and addition of benzene anion radical immediately forms the [8]annulyne anion radical, which is stable for several hours. Observation of the uncomplexed anion radical is allowed by the presence of the crown ether, which prevents spin delocalization into the K cation. [8]Annulyne also undergoes [2 + 2] dimerization when kept below 173 K without exposure to an electron source. Subsequent exposure also generates the corresponding dimeric anion radical **78** (Figure 32). Several other similar experiments were carried out involving fusion of cyclobutadiene units to [8]annulyne. The authors believe these methods to be generally applicable to the synthesis and storage of various annulyne, bisannulyne, and annulenoannulene anion radicals.

Scheme 8





78 **79** **80** **81**

Figure 32.

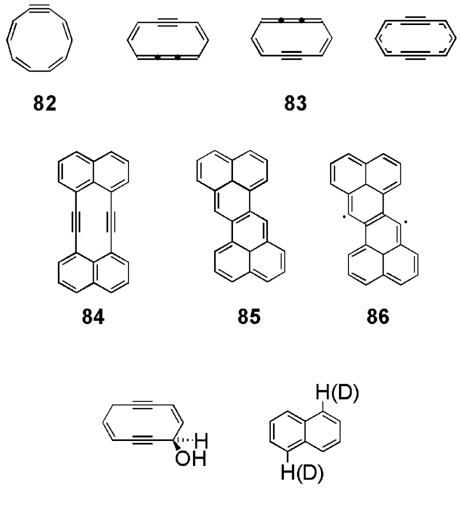
3.1.2. Polymerization

sym-[8]Annuldiyne **79** has also been prepared[68d] using the same dehydrohalogenation method. Exposure to K metal in the presence of 18-crown-6 again leads to capture of its anion radical, inhibiting rapid equilibration between alternating bond angle conformers induced by Jahn−Teller distortion. Fusion to a cyclobutadiene unit leads to the benzannelated anion radical **80**, but the EPR signal for this compound is weak. Under these conditions the annuldiyne preferentially undergoes polymerization via extended [2 + 2] cycloaddition to form a solid (**81**) that is insoluble in THF. Characterization revealed extensive cross-linking, with the MALDI analysis showing periodic peaks separated by 100 mass units up though $m/z = 10\,000$. The cross-linking is believed to take place via suprafacial [2 + 2] cycloadditions of the cyclobutadiene units.

3.2. Dehydro[10]annulenes

3.2.1. Aromaticity Probes

Didehydro[10]annulene (**82**, Figure 33) has yet to be isolated and structurally studied, but recent computational results[69] suggest that, with its $(4n + 2)$ π electrons, it should exhibit aromaticity in the planar geometry. The bond-localized configuration is expected to have C_2 symmetry with a tub shape similar to COT. This conformation is found to be more stable than the localized flat (C_{2v}) geometry, but the energetic differences between the two are smaller than for COT, apparently due to aromatic stabilization. The ease with which the bond angles are distorted reduces ring strain in the planar geometry.



82 **83** **84** **85** **86** **87** **88**

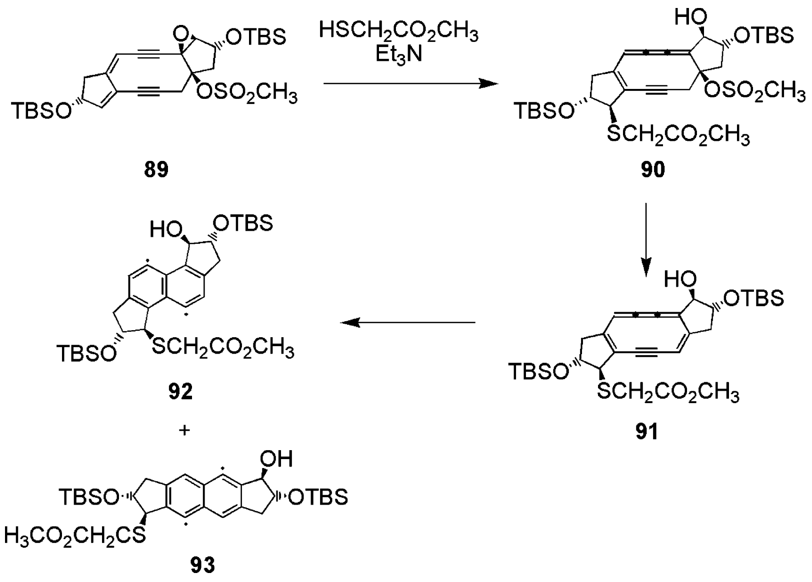
Figure 33.

3.2.2. Novel Topologies

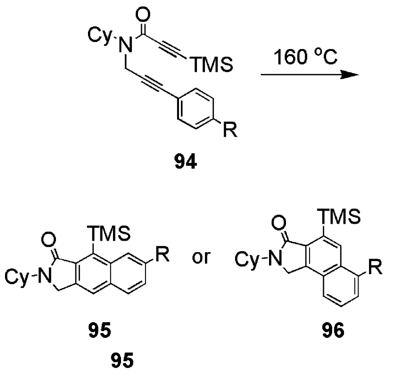
The first tetradehydro[10]annulene (**83,** Figure 33, various representations) was synthesized in 1992 by Myers and Finney.[70a] The authors were interested in its potential thermal rearrangement to the biradical 1,5-dehydronaphthalene and noted previous attempts by Sondheimer and Staab to prepare similar benzannelated hydrocarbon **84**, which instead lead to zethrene (**85**), presumably through a zethrene biradical **86**. Successful synthesis of tetradehydro[10]annulene proceeded from dehydration of the acetylenic alcohol **87**. The annulene had “no appreciable lifetime above −40 °C”, and any attempts to prepare it above this temperature led immediately to the biradical. At −90 °C, however, treatment of the alcohol with trifluoromethanesulfonic anhydride and triethylamine showed “clean and rapid conversion” to the desired product. Warming in deuterated solvents led to the corresponding 1,5-dideuteronaphthalene **88**. The kinetics for cyclization were measured at −51 °C and first order ($k = 4.6 \times 10^{-4}$ s^{-1}, $\Delta G^{\ddagger} = 16.3$ kcal mol^{-1}) with a cyclization half-life of ~25 min.

Indeed, soon after initial synthesis of the symmetric parent dehydroannulene, Myers and Dragovich reported the enan-

Scheme 9



Scheme 10



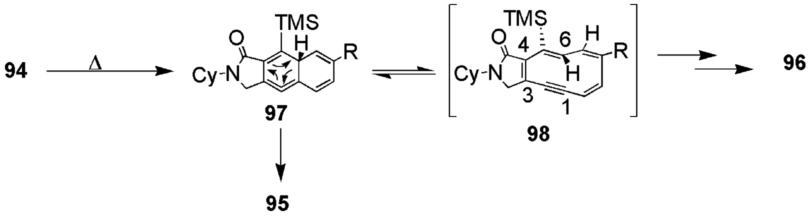
	R	solvent	product	%
a	H	Et_3N	**95**	89
b	OCH_3	Et_3N	**95**	76
c	NO_2	Et_3N	**95**	74
a	H	toluene	**96**	74
b	OCH_3	toluene	**96**	54
c	NO_2	toluene	**96**	70

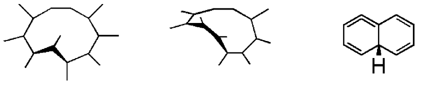
tioselective synthesis of epoxy dienediyne structure **89**.[70b] Ideally, **89** could undergo the same type of cyclization following attack by a thiol to make **90**, with subsequent elimination of the methanesulfonate to generate dehydroannulene **91** (Scheme 9). The reaction cascade is initiated by exposure to excess methyl thioglycolate and triethylamine in DMSO and THF at room temperature. The two expected isomeric naphthalene derivatives corresponding to biradicals **92** and **93** were isolated in 67% and 20% yield, respectively, showing the nondegeneracy of the cyclization pathways. These results represented the first step toward dehydronaphthalene biradical DNA cleavage agents.

Rearrangements of cyclic allenes (isonaphthalenes) have recently been observed in the intramolecular Diels−Alder cyclizations of silyl-protected acetylenes **94a**−**c** with phenylacetylenes to selectively form either **95** or **96** (Scheme 10).[71a−c] It is believed that cyclohexatriene intermediate **97** can undergo either isomerization to benzo[*f*]isoindol-1-one **95** (Scheme 11) or a six-electron electrocyclic ring-opening process through a more stable transition state, yielding the aromatic, bond-equalized dehydro[10]annulene **98**. Upon simultaneous rotation of two double bonds (between C5−C6 and C7−C8), the annulene can then further isomerize to a second cyclic allene, which affords benzo[*e*]isoindol-3-one product **96** upon rearomatization. The preference for each pathway can be manipulated by varying solvent conditions. Carrying out the reaction in triethylamine leads almost exclusively to the "linear" cyclized product, while reaction in toluene affords the "angular" product only. It is theorized that the base catalyzes the rearomatization of the initial cyclic allene by proton abstraction. Echavarren and co-workers proposed a similar dehydro[10]annulene intermediate[71d] with an all-cis configuration as well as a possible carbene analogue.

A thorough computational study of dehydro[10]annulene and various cyclization transition states was recently reported by Navarro-Vazquez and Schreiner in which the nearly planar C_1 "heart" geometry **99a** is calculated to be more stable than the potentially Möbius-like C_2-symmetric "twist" configuration **99b** (Figure 34).[72] This is ascribed to the release of strain energy caused by introduction of the alkyne moiety. Degenerate interchange of this form proceeds through a C_2 transition state with a barrier of 13.5−17.4 kcal mol^{-1} and conversion to its enantiomer through a planar C_s transition state with a barrier of only 4.3−4.8 kcal mol^{-1}. Cyclization

Scheme 11





99a C_1 "heart" **99b** C_2 "twist" **100**

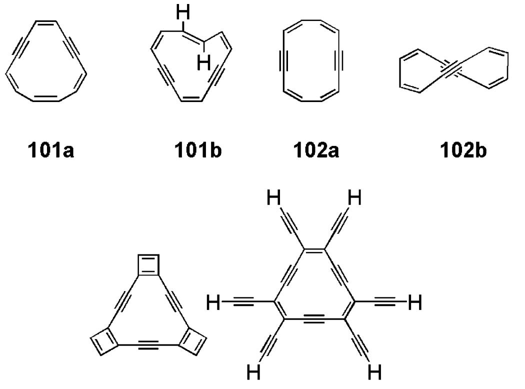
Figure 34.

of this form to a cyclic allene (**100**) takes place through a C_1 transition state (16.8 kcal mol^{-1}). [5,7]-Cyclization is possible but not likely from the most stable "heart" form due to a barrier of 23.3 kcal mol^{-1}. [5,7]-Cyclization is favored, however, from the "twist" form by 2.4 kcal mol^{-1}. Rearomatization affords the final naphthalene (23.9 kcal mol^{-1}). The authors conclude that this "should be taken as the working mechanism for the reported isomerizations during dehydro Diels−Alder reactions of phenylacetylenes".

3.3. Dehydro[12]annulenes

3.3.1. Aromaticity Probes

While the all-cis geometry of 1,2,5,6-tetradehydro[12]annulene **101a** has remained elusive, mono-trans structure **101b** has been known since the early 1960s (Figure 35).[73]



101a **101b** **102a** **102b**

103 **104**

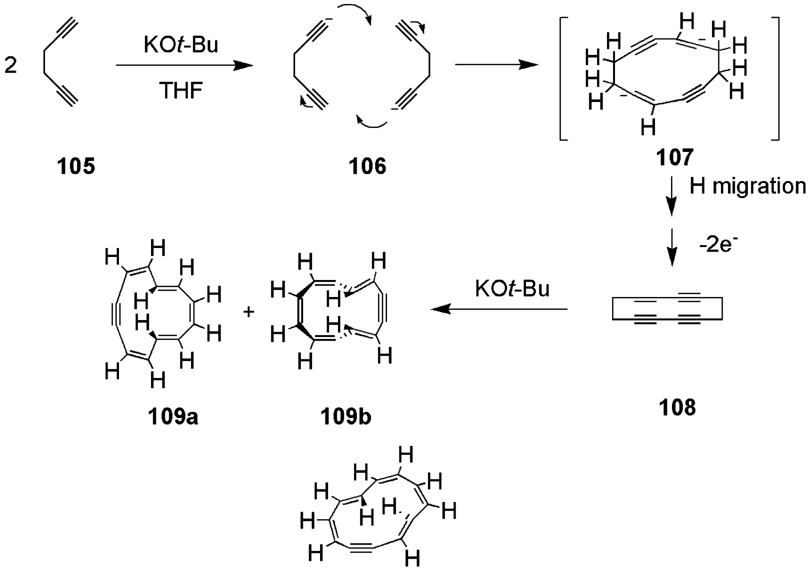
Figure 35.

1,2,7,8-Tetradehydro[12]annulene **102** is believed to adopt a D_2-symmetric twist boat conformation **102b** based on the NMR data. Compound **102** is calculated[69] to be 34.47 kcal mol^{-1} more stable than **101**, and their antiaromatic character causes the energy of the planarized structures to be relatively high. Additional calculations suggest that fusion of cyclobutadiene units onto hexadehydro[12]annulene (**103**) effectively destroys the antiaromaticity of the 12-membered ring,[74] in contrast to hexadehydrohexaethynyl[12]annulene (**104**), which has only slightly attenuated antiaromaticity.

Stevenson and co-workers adapted the original syntheses of **101**−**102** to prepare several isomers of didehydro[12]annulene (Scheme 12).[75] Exposure of commercially available 1,5-hexadiyne (**105**) to *t*-BuOK generates monoanion **106**, two of which cyclize to form dianion **107**. The dianion undergoes "transannular hydrogen migration and electron transfer" to cyclodecenetriyne **108**, which finally rearranges in the presence of *t*-BuOK to an isomer of didehydro[12]annulene **109a** or **109b**. The conformations were assigned based on a detailed analysis of the NMR signals. Exposure of the annulenes to K metal in a THF/18-crown-6 solution generates the anion radicals and eventually the dianions, which exhibit aromatic signatures in the ^{1}H NMR spectra: the internal protons resonate at −2.68 and −1.80 ppm, and the external protons appear as far downfield as 7.53 and 7.51 ppm. Interestingly, **109** does not appear to readily undergo self-condensation, persisting for weeks in solution without any evidence for cycloaddition product formation.

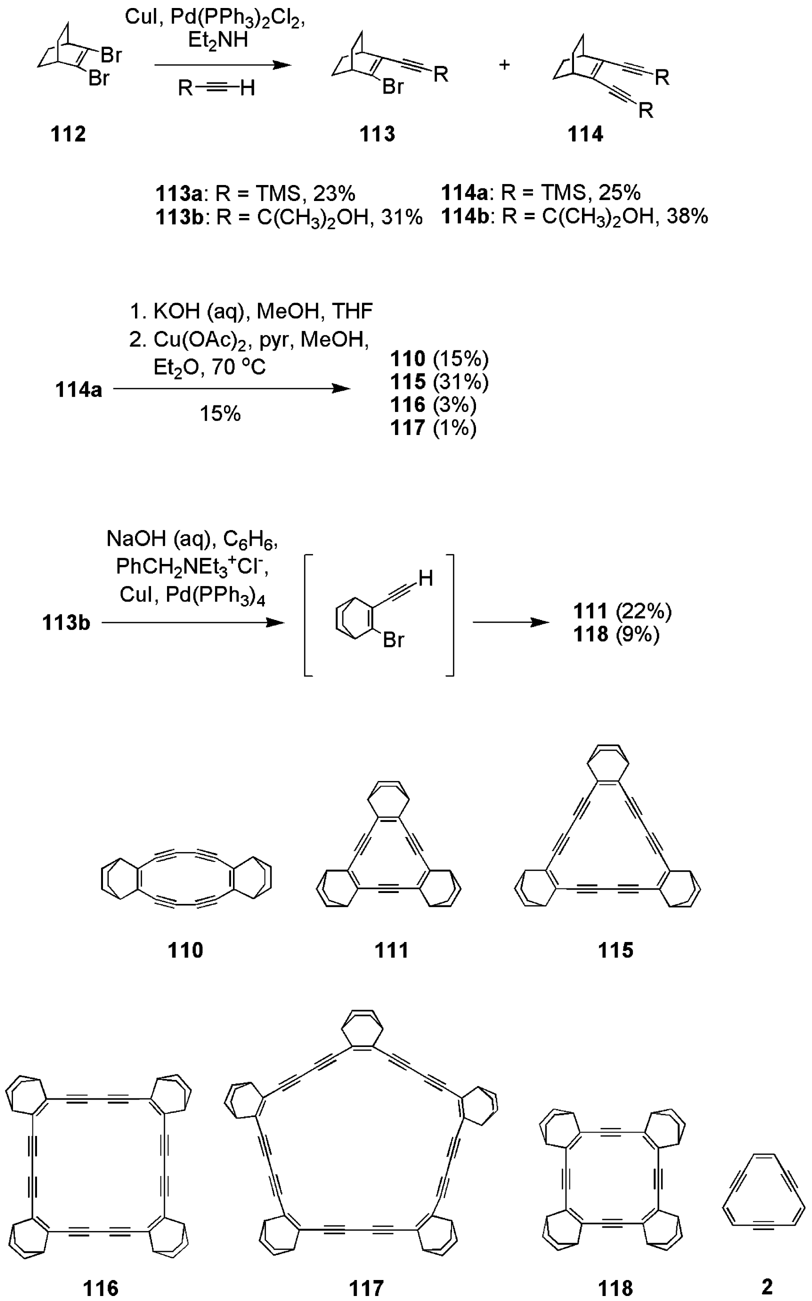
Annulene **109** was also prepared by serial dehydrohalogenation of hexabromocyclododecane **44**. The target molecule was not detected by NMR spectroscopy, but upon exposure of the solution to K metal, a strong, well-resolved EPR signal from the anion radical was observed. The signal was in good agreement with computation by DFT. Prolonged exposure led to the dianion, which was observed in the NMR spectrum. A new, less symmetric isomer **109c** was deduced, with internal protons appearing as a multiplet between −0.15 and −0.35 ppm, and a surprisingly far downfield external proton at +13.54 ppm. This is believed to be due to the additive effect of the diatropicity and deshielding from the K cation. The other dianions of **109** do not experience this effect, but there is not as much ring strain in their alkyne units, which in **109c** may be causing π-orbital overlap with σ bonds on adjacent protonated carbons.

Scheme 12



105 **106** **107** **108** **109a** **109b** **109c**

Scheme 13



Komatsu and co-workers prepared several dehydro[12]-, [18]-, [24]-, and [30]annulenes fused with bicyclo[2.2.2]-octene (BCO) frameworks to stabilize the corresponding cations for investigation of the redox behaviors of these compounds.[76] Synthesis of dehydro[12]annulenes **110** and **111** (Scheme 13) proceeded from BCO dibromide **112** through stepwise assemblies of the acetylene linker units **113** and **114** using Pd- and Cu-catalyzed chemistry. Unfortunately, **110** is unstable and decomposes upon concentration without deaeration, while **111** decomposes even in deaerated solution over several days at room temperature. Dehydro-[16]-, [18]-, [24]-, and [30]annulenes **115**−**118** were also synthesized in the same reactions. The ^{1}H and ^{13}C NMR spectra were taken (Table 5), and the BCO protons are shown to be sensitive to the ring current effect. The signals for the bridgehead protons on the dehydro[12]annulenes are shifted significantly upfield from their aromatic-fused counterparts (e.g., ^{1}H NMR 1.76 and 1.72 ppm for **110** and **111**, respectively, vs 3.41 ppm for the 18-electron system **115**).

Table 5. Bridgehead NMR Shifts and Redox Potentials of BCO-Fused Annulenes[76]

compound	electron count	δ^a (ppm)	E_{red}, V^b	E_{ox}, V^b
110	12π	1.76	−1.67	+0.93
111	12π	1.72	−1.93	+0.54
115	18π	3.41	−1.96	+1.21
116	24π	2.68	−1.53	
117	30π	2.75	−1.90	+1.07
118	16π	2.47	−1.96	+0.62
2	12π		−1.58	+1.17

[a] ^{1}H NMR shift of bridgehead proton. [b] Versus Ag/Ag$^+$.

Cyclic voltammetry was also performed on the BCO-fused annulenes. For reduction, all showed reversible waves between −1.5 and −2.0 V (Table 5) with the antiaromatic systems at slightly less negative reduction potentials. Interestingly, during the oxidation process, reversible waves were observed only for annulenes with BCO units that were connected through just one acetylene spacer (such as **111**).

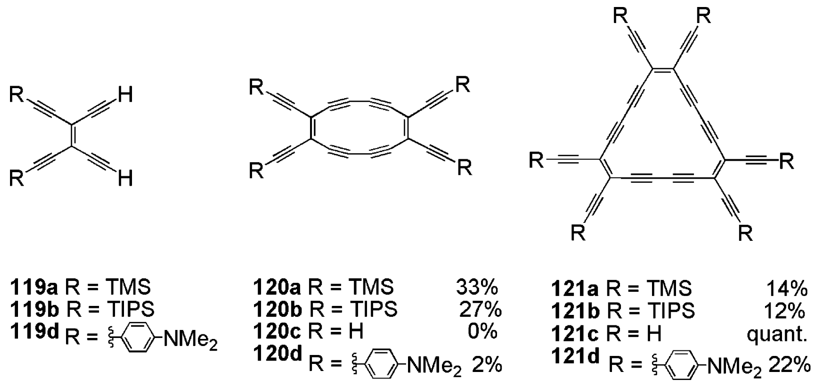


Figure 36.

Compound **111** is more easily oxidized than **110**, which is more easily oxidized than the non-BCO-fused system **2**, prepared for comparison. The authors assert that this may indicate stabilization of the cationic π systems by the BCO units, since such an effect might be attenuated by increasing the number of acetylenes per BCO unit. The authors also concluded that annelation with BCO units rigidly holds the σ framework and donates electron density via induction and $\sigma-\pi$ conjugation.[77] A plot of oxidation potential vs PM3-calculated HOMO energy shows a good linear correlation, but a plot of reduction potential vs calculated LUMO levels is scattered. This indicates that the rapid equilibration of conformers in solution may give rise to a variety of FMO levels, whereas the calculated LUMO levels are associated with the energy-minimized structure. This study effectively illustrates the electron-donating capability of the BCO group and its ability to stabilize some cationic π systems.

3.3.2. Substructures of Extended Networks

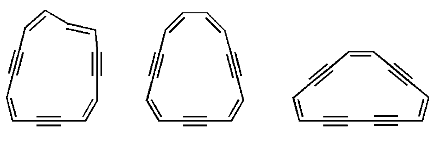
Diederich and co-workers synthesized and studied a variety of perethynylated dehydroannulenes (e.g., Figure 36) as precursors to extended carbon sheet networks.[78] Oxidative Hay coupling of key bisalkyne **119**[78a] provided dimeric dehydro[12]annulene **120**, trimeric dehydro[18]annulene **121**, as well as higher oligomers (yields from precursor shown). The TIPS-protected annulenes **120b** and **121b** are soluble, stable, and form deep red crystals and a yellow greasy solid, respectively. A crystal structure of **120b** revealed a planar carbon backbone, with a mean deviation from the plane of 0.089 Å. There is considerable strain in the molecule, with the butadiyne moieties having bond angles as low as 164.5° and the inner C−C═C angles compressed to ca. 118°. Although the crystal is stable, uncrystallized solutions of **120b** decomposed upon concentration. TMS derivative **120a** is much less stable, with solutions turning from purple to brown and to black insoluble material in the solid form, even under cold (−20 °C) and dark conditions. Attempted desilylation with mild borax caused rapid decomposition upon concentration of the product. Annulene **121a** decomposed slowly but nevertheless grew bright yellow crystals over a period of 9 months suitable for diffraction. The aromatic dehydro[18]annulene is perfectly planar, with the largest deviation from the plane of 0.074 Å. The acetylene segments adopt bond angles comparable to acyclic, strain-free analogues. Deprotection of **121a** afforded unstable **121c** in quantitative yield and thus provides a precursor to oxidative couplings for the preparation of extended carbon sheet networks. Not surprisingly, **120** undergoes stepwise one-electron reductions to the aromatic dianion more readily than **121** to the antiaromatic dianion. The electronic absorption spectra exhibit significant vibrational fine structure due to their rigid planarity. Annulene **120b** exhibits a UV cutoff around 480 nm, while the larger conjugated macrocycle **121b** has absorptions that extend out to 660 nm. The indicated HOMO−LUMO band gaps confirmed the essentially paratropic and diatropic natures of **120** and **121**, respectively.

Recently, donor-functionalized analogues **120d** and **121d** were reported.[78b,c] Donor functionalization causes a bathochromic shift in the electronic absorption spectrum, with strong, broad bands appearing in comparison to **120b** and **121b**, indicating intramolecular charge transfer from the electron-rich aniline moieties to the annulenic cores. The bands disappear upon acidification and are regenerated completely with addition of base. The $\lambda_{\max}$ of both charge-transfer bands is the same (518 nm), but surprisingly the extinction coefficient is much higher in the aromatic system (105200 vs 35100 M^{-1} cm^{-1}). While it could be expected that charge transfer in **120d** would be more efficient, since antiaromaticity is reduced upon electron absorption, the UV−Vis results seem to suggest that this is not the case. Recently, the electronic excitations in **120d** and **121d** have been calculated using density functional theory.[78d] In both cases the lowest excited states were found to correspond to a $\pi-\pi^*$ transition involving intense intramolecular charge transfer from the donor groups to the cores. In the aromatic **121d**, however, the transition proceeds from the ground state to a degenerate excited state of E′ symmetry. Since both of these E′ states contribute to the oscillator strength, the charge-transfer band is theorized to be more intense in the UV spectrum, which matches well with the experimental spectra for both annulenes.

3.4. Dehydro[14]annulenes

3.4.1. Aromaticity Probes

Although mono-*trans*-hexadehydro[14]annulene **122a** (Figure 37) was prepared in the mid-1960s,[79] the all-cis isomer **122b** is as yet unknown. Calculations suggest it adopts a tub-shaped conformation similar to didehydro[10]annulene



122a **122b** **123**

Figure 37.

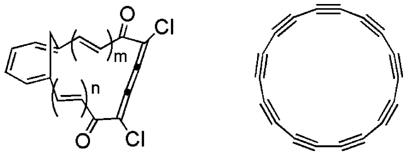
82.[69] Haley and Boydston synthesized the all-cis octadehydro[14]annulene **123** and used ^{1}H NMR shifts to infer its diatropicity.[80a] This parent compound was compared to various benzannelated analogues (see section 5.3.3), and it was found that fusion of benzene rings to the systems causes upfield shifts, implying a gradual reduction in diatropicity. This lends support to the computational results described in the previous section concerning fusion of cyclobutadiene units to dehydro[12]annulene reducing its antiaromaticity.[74]

3.5. Dehydro[16]annulenes

3.5.1. Aromaticity Probes

There has been surprisingly little new work involving dehydro[16]annulene, perhaps because dehydro[12]annulene has been much more extensively studied, and there is not believed to be a great deal of variation in structure and reactivity between these two (*4n*) annulenes. Furthermore, the macrocycle geometry required to provide the correct electron count does not lend itself well to the oxidative coupling reactions typically employed in synthesis (e.g., the low yield of tetramer **118** in Scheme 13). In most cases, synthesis of a dehydro[16]annulene represents one of a series of annulenes prepared either systematically[77,78a,c] or as one component of many in a one-pot intermolecular reaction.[76]

Ojima, Yamamoto, and co-workers[81] prepared several unique methanodehydro[16]-, [20]-, and [24]annulenedione structures (**124**−**126**, Figure 38) with an unusual 1,4-dichlorobutatriene moiety. A crystal structure of **124** revealed significant distortion from the expected C_s geometry, believed to be due to ring strain and transannular repulsion. The system is “fairly planar”, but the dihedral angle between the two ring systems separated by the methano bridge deviates from planarity by ca. 30°. The ^{1}H NMR spectrum shows that the inner protons of the annulenediones are shifted upfield relative to their respective acyclic precursors, while the outer protons are shifted downfield. The methylene protons are equivalent in the precursors but separate into upfield and downfield components upon cyclization. Interestingly, these compounds actually exhibit diatropicity in $CDCl_3$ due to polarization of the carbonyl groups. The dications of **124**−**126** show enhanced diatropicity and delocalization (formal 14, 18, and 22 π-electron systems, respectively) in D_2SO_4, which increases with ring size. This effect is so far unprecedented in true annulenes.



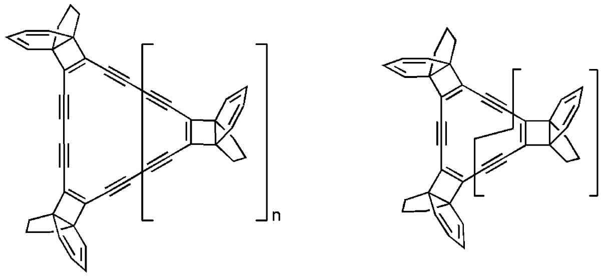
124 m = n = 1
125 m = n = 2
126 m = n = 3

127

Figure 38.

Small carbon clusters have been extensively investigated systems,[82] and there has been an impressive amount of work devoted to the smallest ($C_{n<10}$) clusters. With the ever-increasing interest in fullerene chemistry, this is also true of larger (C_{30-60}) carbon systems.[83] There has been comparatively little study involved with the intermediate size range, C_{10-24}, which are believed to exist as monocyclic rings. These monocyclic clusters, known as cyclo[*n*]carbons (e.g., **127**), exhibit a unique structure, composed of two sets of p orbitals which are orthogonal to each other, raising the intriguing question of whether they obey the ($4n + 2$) rule. Since cyclocarbons are belt-shaped compounds, the reader is referred in this issue to the contribution of Tobe and Tahara, which addresses this topic in detail.[14] Our focus here is primarily on the dehydroannulene precursors. Only salient cyclocarbon results will be discussed.

A very successful synthetic strategy toward accessing cyclo[*n*]carbons has been cycloreversion of ring-fused dehydroannulene precursors.[84] For example, Tobe and co-workers[84a,b] used laser ablation to induce [2 + 2] cycloreversion of [4.3.2]propella-1,3,11-triene-fused dehydroannulenes to generate various sizes of cyclocarbon structures. Dehydroannulenes **128**−**132** were synthesized (Figure 39, yields shown) and subjected to laser ablation[84a] and laser desorption-time-of-flight mass spectral analysis.[84b] Peaks corresponding to the C_{16}^- anion of the target cyclocarbon were detected. Alternatively, irradiation with a low-pressure Hg lamp was used to induce photochemical [2 + 2] cycloreversion (e.g., of **133** to **134** and **135**, Scheme 14)[84b] but yielded only indane and polymeric materials that could not be characterized. Attempted trapping of intermediates from the reaction using a furan matrix failed to afford the various [4 + 2] cycloaddition products.

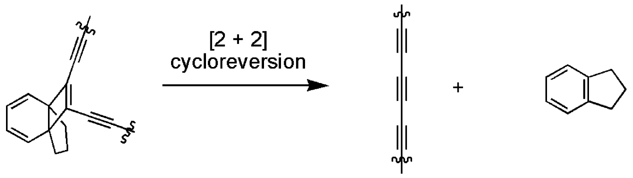


128 n = 1 28%
129 n = 2 28%

130 n = 1 1%
131 n = 2 11%
132 n = 3 1%

Figure 39.

Scheme 14

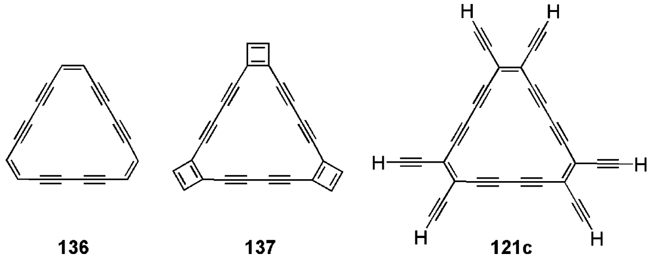


133 **134** **135**

3.6. Dehydro[18]annulenes

3.6.1. Aromaticity Probes

Although decidedly aromatic, unsubstituted dodecadehydro[18]annulene **136**[85] is unstable and potentially explosive. As in the case of hexadehydro[12]annulene **103**, fusion of cyclobutadiene rings (**137**, Figure 40) is calculated to interrupt the ring current, which destroys the aromaticity,[74] while fusion of ethynyl units (**121c**) only slightly reduces it. In the case of **137**, however, it was calculated that the bond lengths of the formal single bonds are significantly shortened to 1.34 Å, as opposed to 1.39−1.43 Å in the other molecules



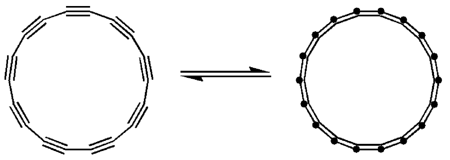
136 **137** **121c**

Figure 40.

studied, suggesting that the cyclobutadiene rings are "connected by cumulative double bonds yielding an allene structure". Since synthesis of these higher annulenes typically involves oxidative alkyne cyclooligomerization, several ring sizes are generated in one pot, and so many studies concerning dehydro[18]annulenes are also applied to those of lower macrocycles, some of which have been described previously (see sections 3.3−3.5).

The single crystal of the BCO-fused dodecadehydro[18]annulene **115** synthesized (Scheme 13) by Komatsu and co-workers[76] for their redox study was found to have an almost planar structure with a butadiyne bond angle of 177.4°. Spectroscopic data for **115** was the same in solution and in the solid state. Comparison of the ^{1}H NMR data among the annulenes synthesized (Table 5) shows the diatropicity of the macrocycle; the protons on the BCO units are the most downfield in each case. Similarly, the stability of **115** is shown by its resistance to both oxidation and reduction.

Indanyl-fused dehydro[18]annulene **128** was subjected to the same laser ablation conditions as dehydro[16]annulene **131** in an attempt to detect cyclo[18]carbon (**127**, Figure 41).[84a] Mass spectral analysis shows a peak corresponding to C_{18}^- as the highest peak. The vibrational frequency deduced from the data collected is much lower for neutral C_{18} than for other clusters. This is explained by a possibly cumulenic structure for the $(4n + 2)$ clusters rather than the localized single and triple bonds deduced for the $(4n)$ molecules (Figure 41).

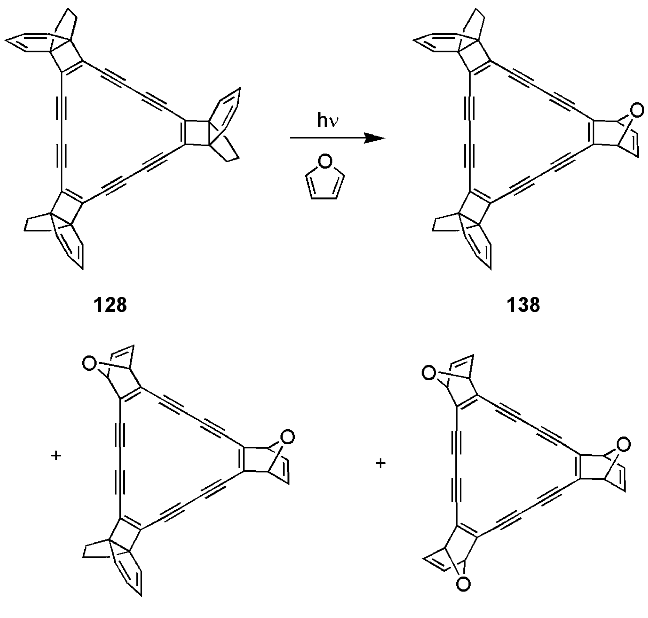


127a **127b**

Figure 41.

Unlike the case of **131**, [2 + 2]cycloreversion of [18]annulene **128** in the presence of furan succeeded in furnishing trapped species (**138**−**140**, Scheme 15). In the absence of furan only indane and uncharacterizable polymeric material were obtained. While these results do not prove conclusively formation of cyclo[*n*]carbons via this route, they do show that elimination of an indene unit does take place by cycloreversion to produce reactive dehydroannulene intermediates.

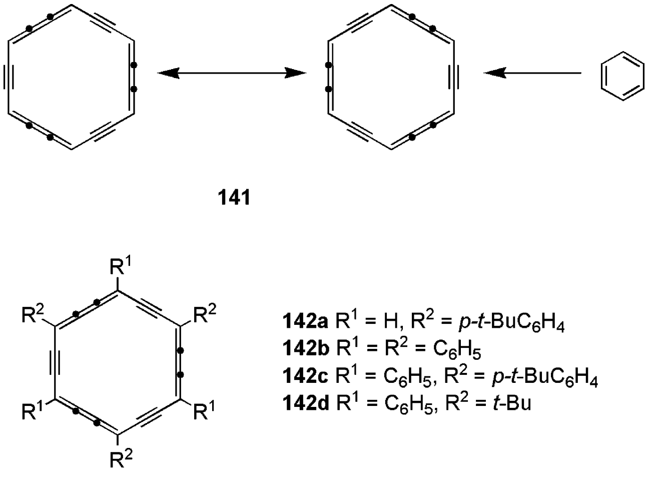
Scheme 15



128 **138** **139** **140**

Diederich et al. similarly reported generation of ions of C_{18} from flash vacuum pyrolysis-induced cycloreversion of anthracene-fused dehydro[18]annulenes.[84c] Ultraviolet irradiation under strong heating conditions followed immediately by time-of-flight mass spectrometry revealed a C_{18} fragment, while gentler heating conditions showed only anthracene fragments or the parent annulene, indicating that the retro-Diels−Alder reaction is the dominant fragmentation pathway. Bond-alternating acetylenic cyclo[18]carbon **127a** is also calculated to be more stable than the nonalternating allenic form **127b**.

Ueda and co-workers accomplished the synthesis of several dehydro[18]annulenes of the unusual type **141** (Figure 42) having D_{6h} symmetry.[86] This architecture is based on the Sworski concept of insertion of an unsaturated C_2 unit into each bond in benzene[87] and is expected to increase the size of the system while not affecting the conjugation, aromaticity, or symmetry. An interesting question is what effect this expansion might have on the physical and chemical properties. Thus, various permutations of hexasubstituted derivative of **142** were assembled. All compounds are described as "quite stable", with neither melting nor decomposition until 150−175 °C, at which point **142a** carbonizes, or 220−250 °C, around which **142b**−**d** decompose. In the crystal structure of **142b**, each "side" of the central ring has two "long" bonds, averaging 1.390 Å, and one "short" bond in between, averaging only 1.217 Å. This bonding pattern is not properly described by either the acetylenic or the



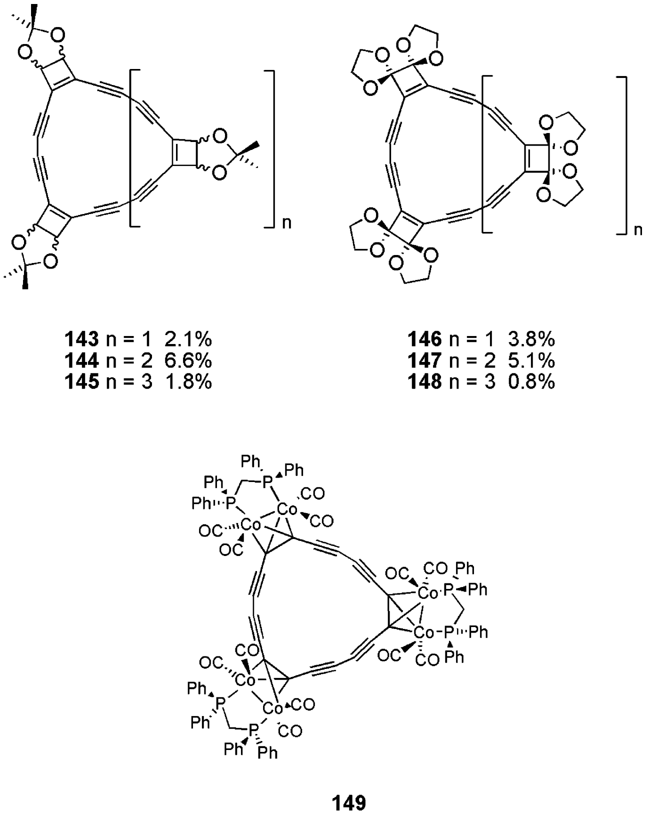
141

142a R^1 = H, R^2 = *p*-*t*-BuC_6H_4
142b R^1 = R^2 = C_6H_5
142c R^1 = C_6H_5, R^2 = *p*-*t*-BuC_6H_4
142d R^1 = C_6H_5, R^2 = *t*-Bu

Figure 42.

cumulenic model. The molecule does possess a planar π system with D_{6h} symmetry in the solid state. The electronic absorption spectra of **142** show a pattern typical of $(4n + 2)$ annulenes, with two principal absorptions between 400 and 550 nm, each separated by about 50 nm, with hexaaryl-substituted **142b** and **142c** possessing slight bathochromic shifts for these peaks.

Diederich and co-workers prepared several cyclobuteno-fused dehydro[18]annulenes, as well as higher oligomers, as potential precursors to cyclo[*n*]carbons.[88a] The targets molecules were the cyclodutenedione-fused dehydroannulenes as they could potentially undergo elimination of CO via radiation or flash vacuum pyrolysis to the corresponding cyclo[*n*]carbons. Since the cyclobutenediones were found to be unstable, the molecules were initially prepared as ketals **143**−**145** and bisketals **146**−**148** by cyclooligomerization of the corresponding diynes (Figure 43, yields from diynes shown). The protected dehydroannulenes were then subjected to acid hydrolysis, and the dione products were observed in situ but not isolated. Low-temperature matrix isolation/laser desorption experiments provided circumstantial, but not direct, evidence of CO loss from the cyclobutenedione-fused annulenes upon irradiation via loss of the characteristic carbonyl peak at 1792 cm^{-1} and the appearance of a new band at 2115 cm^{-1}. Cyclocarbon **127** should have only weak IR absorptions due to the symmetry of the alkyne groups. The electronic absorption spectra showed only disappearance of the long-wavelength bands upon irradiation with no new bands generated. To date, all attempts to isolate **127** have been unsuccessful.



143 n = 1 2.1%
144 n = 2 6.6%
145 n = 3 1.8%

146 n = 1 3.8%
147 n = 2 5.1%
148 n = 3 0.8%

149

Figure 43.

3.6.2. Organometallic Systems

Diederich also synthesized a stable hexacobalt complex of cyclo[18]carbon (**149**, Figure 43).[88b] The crystal structure confirms that it is indeed a complex of **127**, with a nearly planar C_{18} ring, with the largest deviation from the plane of 0.19 Å. The corner bond angles are 131° and 134°, and the smallest diyne bond angle is 166°. While the next step to **127** would be demetalation under mild oxidation conditions, such attempts[88c] using ceric ammonium nitrate, 4-methylmorpholine-*N*-oxide, and I_2 have all proven unsuccessful, yielding only polymeric material. It is likely that the stability of the complex, as well as steric hindrance from the ligands, prevents decomplexation. Although unambiguous evidence for the transient generation of cyclocarbons and their ions have been collected by various groups over the last 15 years, it is clear that isolation and characterization of these synthetically intriguing structures from stable precursors is far from trivial and may yet require development of new techniques not currently available.

Table 6. Geometric and Spectroscopic Comparisons between Benzene and Carbomer 141[90]

parameter	benzene	**141**
C_{sp^2}–C_{sp^2}, Å	1.394	
C_{sp}−C_{sp}, Å		1.239
C_{sp}−C_{sp^2}, Å		1.369
$C_{sp}(2)$−C_{sp^2}-$C_{sp}(2)$, deg	120	122.6
C_{sp^2}-C_{sp}−C_{sp}, deg		178.7
NICS (B3LYP), ppm	−8.0	−17.9
δ^1H (B3LYP), ppm	7.3	11.4
δ^1H (expt), ppm	7.27	9.87[a]

[a] Value for **142a** taken in $CDCl_3$.

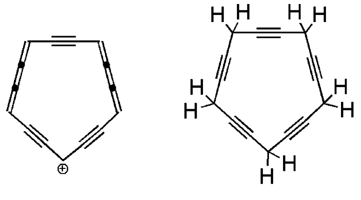
Dehydro[18]annulenes **121** prepared by Diederich and co-workers are described along with related structures **120** in the section concerning dehydro[12]annulenes, since they are synthesized at the same time. These systems are also discussed within the broader context of general acetylene chemistry in recent articles.[89]

3.6.3. Novel Topologies

Chauvin and co-workers[90] computationally investigated a variety of ring-expansion processes involving the unsaturated C_2 unit insertion mentioned above (Figure 42). These so-called "carbomers" have not been widely synthesized, but the nonderivatized **141** has been the subject of calculations aimed at finding out whether the physicochemical properties of benzene, of which **141** is the carbomer, are indeed preserved in the larger structure, as would be predicted. An important question is whether the orthogonal set of p orbitals has an effect on the total aromaticity of the system (in-plane homoaromaticity). Geometric parameters, magnetic shielding (including NICS values), and MO calculations have been employed in order to deduce these effects. Bond distances in the carbomer (Table 6) are calculated to be slightly shorter than in benzene due to the presence of the sp centers. The linear segments are slightly bowed outward, with corner bond angles of 122.6° vs 120°, and acetylenic (or allenic) bond angles of 178.7°. In comparison to the geometries of the dehydro[18]annulenes described above, the preservation of benzene-like character is remarkable. Calculation of the NICS at B3LYP/6-31+G* predicts values of −8.0 and −17.9 ppm for benzene and **141**, respectively, indicating that diatropicity is not only preserved but enhanced.

Predicted chemical shifts for the protons of each show a similar effect. The best experimental comparison comes from the triaryl derivative of **141**, **142a**, which shows a more moderate effect. The calculated resonance energy values of

[*n*]annulenes vary with their carbomers in agreement with the Hückel rule, indicating that the π_{xy} system in the carbomer ring has little effect on the π_z system. Comparison of certain carbomers with only weakly homoaromatic analogues (e.g., **150** and [5]pericyclyne **151**,[91] Figure 44) reveals that in-plane homoaromaticity exerts a weak influence at best and is "qualitatively bystanding". Thus, it is concluded that carbomerization of an annulenic structure does indeed preserve aromatic character. For more on carbomers, the reader should consult the review of Chauvin and Maraval in this issue.[92]



150 **151**

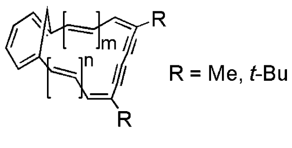
Figure 44.

3.7. Higher Dehydroannulenes

3.7.1. Aromaticity Probes

With each increase in ring size, the structural diversity attainable in the dehydro[*n*]annulenes grows exponentially. The oxidative cyclooligomerization route currently employed typically limits the isolability of higher annulenes from this route, however, where yields of higher macrocycles drop off quickly.[78,88,89] On the other hand, the geometry of the monomer unit can sometimes favor higher oligomers, as in the case of compounds **143**−**148**. The bond angles of the cyclobutene units cause ring strain upon formation of dehydro[18]annulene trimers **143** and **146** (the structures as drawn), which is alleviated in the dehydro[24]annulene tetramers **144** and **147**, thus affording a higher yield. The pentamers, however, are generated in smaller amounts. The opposite case is seen in the organometallic complex **149**, the tetramer of which is formed in very small amounts. It is worth noting that larger macrocycles also suffer from greater conformational freedom, which hinders planar, delocalized structures. The diatropicity of dehydro[30]annulene **148**, for example, is highly reduced relative to **147**. Fusion of sterically restrictive units, such as cyclobutenes, can help enforce planarity and increase stabilization to a great degree.

A very systematic effort was undertaken by Ojima and co-workers[93] to synthesize a series of 1,6-methanotetradehydro[*n*]annulenes (**152**−**162**, Figure 45), where $n = 18$, 20, 22, 24, 26, 28, 30, 32, 34, 36, and 38. Each system was studied in order to determine the upper limit of ring current as a function of size. As noted earlier, the cutoff point for diatropicity in annulenes has been postulated in one study to occur around [30]annulene. In the case of dehydroannulenes, the rigid acetylenic linkages, and in this case, 1,6-methano bridging, will serve to draw out that boundary still further. Indeed, hexadehydro[24]annulene had been one of the largest (4*n*) annulenes known to be paratropic.[94] Ojima and co-workers synthesized each annulene in the same manner and used the ^{1}H NMR shifts, as well as comparisons to their respective acyclic analogues, to assign the annulene's character as diatropic, paratropic, or atropic. It was found that diatropicity persists up to $n = 34$ but paratropicity only up to $n = 28$. The $n = 32$, 36, and 38 annulenes are found to be atropic, with the conformational freedom that comes with their size overcoming any aromatic stabilization or antiaromatic destabilization.



152	m = n = 1	[18]
153	m = 2, n = 1	[20]
154	m = n = 2	[22]
155	m = 3, n = 2	[24]
156	m = n = 3	[26]
157	m = 4, n = 3	[28]
158	m = n = 4	[30]
159	m = 5, n = 4	[32]
160	m = n = 5	[34]
161	m = 6, n = 5	[36]
162	m = n = 6	[38]

Figure 45.

4. Benzoannulenes

Interest in benzoannulenes originated in the latter half of the 20th century as a means to simplify syntheses and stabilize annulene cores; however, incorporation of arene moieties into the cyclic structure enhanced bond localization and decreased annulene ring tropicity.[4,7,8] Key pioneering contributors Staab, Sondheimer, Nakagawa, and Wittig produced a multitude of large benzannelated systems culminating in the late 1970s and early 1980s. Since then, ortho-fused benzoannulene production has been limited primarily to Mitchell's group with recent additions from Iyoda and Kuwatani.

4.1. Benzo[14]annulenes

4.1.1. Aromaticity Probes

Over the past 25 years, Mitchell and co-workers prepared a large library of benzannelated dimethyldihydropyrenes (DMDHP) and investigated their use as aromaticity probes.[95] Initial syntheses of the cycles focused on construction of a bis(bromomethyl)arene, conversion to a dithiacyclophane, and final elimination of Me_2S.[96] Although this method proved successful for isolating a multitude of new systems, the lengthy route required a different bromoarene starting material for each benzoannulene. Examples of the more highly fused systems produced via this method include **163**−**165** (Figure 46).[96] In 1990, a new multipurpose route using Diels−Alder addition of dihydropyrene cores containing a reactive aryne functionality (**166**) with furan-substituted arenes followed by deoxygenation with $Fe_2(CO)_9$ was introduced.[97] The alternate route enabled rapid production of several extensively annelated cycles (**167**−**171**) via common aryne **166**.[97,98] The Mitchell group's most recent work in this area has focused on synthesis and comparison of benzo-, naphtho-, and anthraceno-annelated systems (**172**−**174**), where judicious use of bulky alkyl substituents permitted preferential annelation in the [*e*] position.[99]

The internal methyl protons of the benzoannulenes were found to be especially sensitive to ring current shielding but almost invariant to external substitution of the annulene core due to distance (>5 Å). Dramatic chemical shift changes (up to 5 ppm) from DMDHP ($\delta = -4.25$), the direct result of bond fixation and aromaticity of the annelating species, have been observed for the group's benzoannulene deriva-

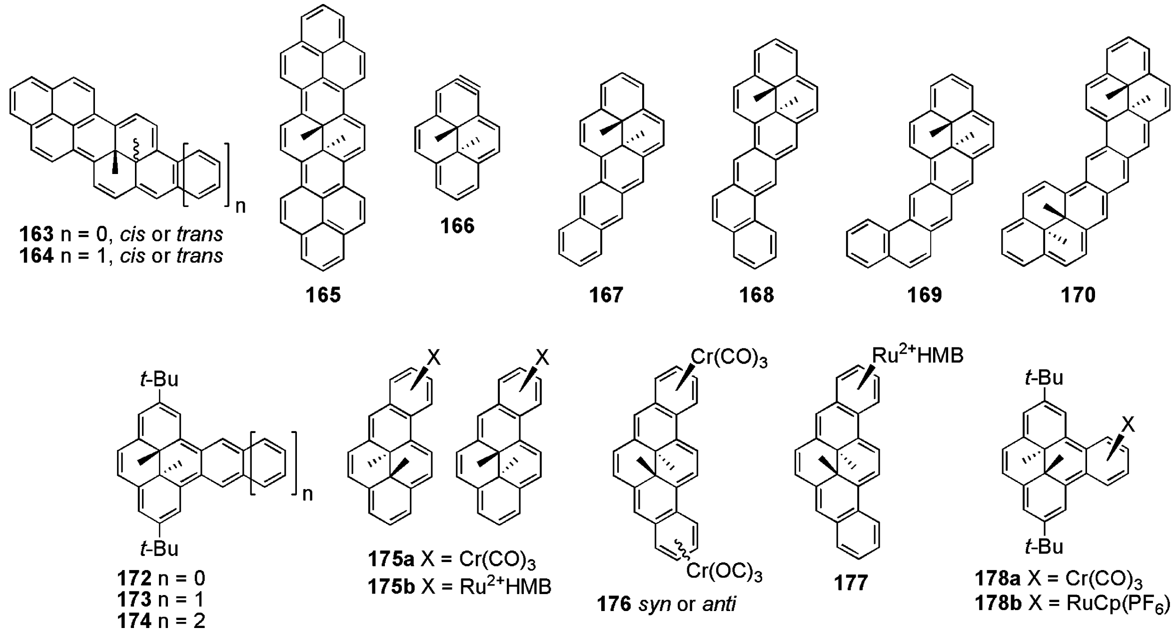


Figure 46.

Table 7. Internal Methyl Proton δ Values for Benzoannulenes 163−178

benzo-annulene	fusion site	δ (Me)	parent benzoannulene δ (Me)
163-*trans*		−4.24	N/A
164-*trans*		−1.38	N/A
165		−4.08	N/A
167	a	−0.44	N/A
168	a	−0.896, −0.899	N/A
169	a	−0.878, −0.882	N/A
170	a	−1.18, −1.19, −1.21, −1.22	N/A
171	a	−1.58, −1.62	N/A
172	e	−1.58	N/A
173	e	−0.54	N/A
174	e	0	N/A
175a[a]	a	−0.87, −0.98	−1.62
175b[b]	a	−0.52, −0.86	−1.62
176 *anti*	a	0.64	0.02
176 *syn*	a	0.42, 0.86	0.02
177[b]	a	0.29, 0.69	0.02
178a	e	−0.83, −1.22	−1.58
178b[c]	e	−0.31, −0.77	−1.58

[a] Major isomer. [b] Representative isomer. [c] Acetone-d_6.

tives. While higher annelation resulted in upfield shifts (less bond fixation) for [*a*]-fused cycles, downfield shifts (increased bond fixation) were observed for higher [*e*]-annelated systems (Table 7). The collected data has allowed the group to develop an empirical method to describe aromaticity of the new cycles as well as annelating species.

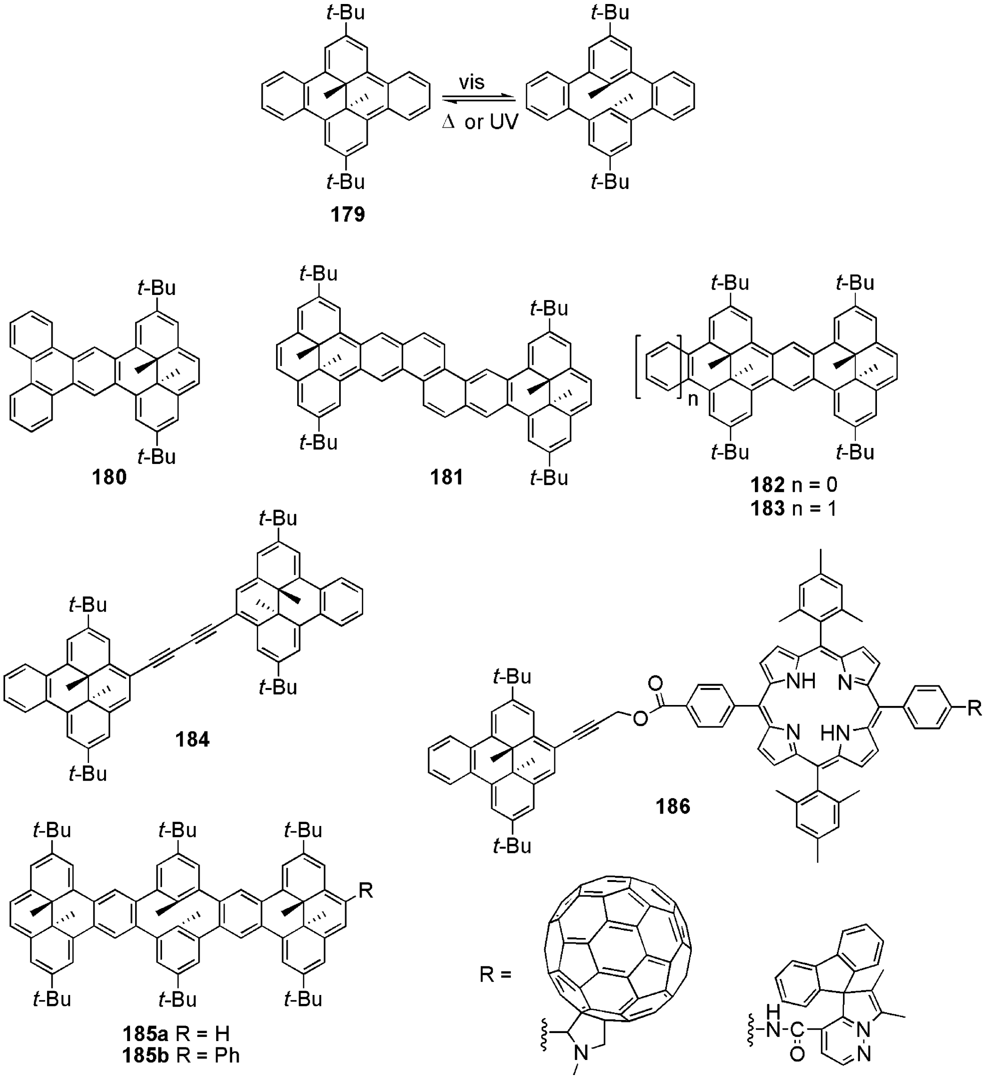
4.1.2. Organometallic Assemblies

Mitchell's group reported the first mono- (**175a**) and dinuclear benzoannulene complexes (**176**) in 1990[100] and 1996,[101] respectively, and has since prepared several additional Cr- and Ru-complexed organometallic analogues (**175b**, **177**, **178**) of previously reported benzannelated-DMDHPs (Figure 46).[43d,102] Organometallic complexes **175**−**178** were obtained from the parent annulene by THF-catalyzed ligand exchange reaction with (η^6-naphthalene)Cr(CO)$_3$, reflux with CpRu(CH$_3$CN)$_3$PF$_6$, or treatment with [RuCl$_2$(HMB)]$_2$ and AgBF$_4$. Isolation of the organometallic complexes occurred in moderate to good yields (50−80% for both isomers), but separation of isomeric analogues proved difficult in some cases (e.g., **175b**). Downfield shifts in δ values for the exotopic methyl groups upon metal complexation indicated more significant bond localization in the organometallic complexes than the parent benzo[14]-annulenes (Table 7). Ru complexes also possessed a slightly greater (<1 ppm) bond-fixing ability than analogous Cr(CO)$_3$ systems.

4.1.3. Photochromic Switches

In addition to service as an effective aromaticity probe, DMDHP is a photochrome that converts to a metacyclophanediene photoisomer upon irradiation with visible light and thermally reverts back to the bridged annulene by UV or heat (see **179**, Figure 47 for a representative benzannelated example).[103] The complete conjugation and orbital overlap of the annulene, which is disrupted by the stepped conformation of the metacyclophanediene, makes the annulene an ideal photochromic switch. Inability of the photoisomers to readily isomerize as well as lack of internal hydrogens, which can be abstracted to promote aromatization, are key advantages of the DMDHP systems over stilbene and dihydrophenanthrene photochromes. Experimental analysis has shown the DMDHP switches to be extraordinarily robust with no detectable decomposition after repeated conversion by flashing light. Comparison of cycles produced in the early 1980s showed that site-specific annelation of the DMDHP core at the [*a*] and [*e*] positions, respectively, increased and decreased the thermal return reaction to the benzoannulene, the latter being the favored shift in rate for a photochromic switch.

The Mitchell group's recent efforts in this area include production of highly annelated DMDHP switches (**172**−**174**, Figure 46; **179**, **180**, Figure 47)[104] as well as exploration of multistate π switches (**181**−**186**, Figure 47).[104b,105] Compound **183**, the group's first three-way photochromic switch, selectively differentiated the bispyrene (355 nm) and colorless biscyclophane (>598 nm) from the thermodynamically preferred monopyrene−monocyclophane isomer. Bispyrene **184** showed that two DMDHPs linked by a conjugated



179

180

181

182 n = 0
183 n = 1

184

186

185a R = H
185b R = Ph

R =

Figure 47.

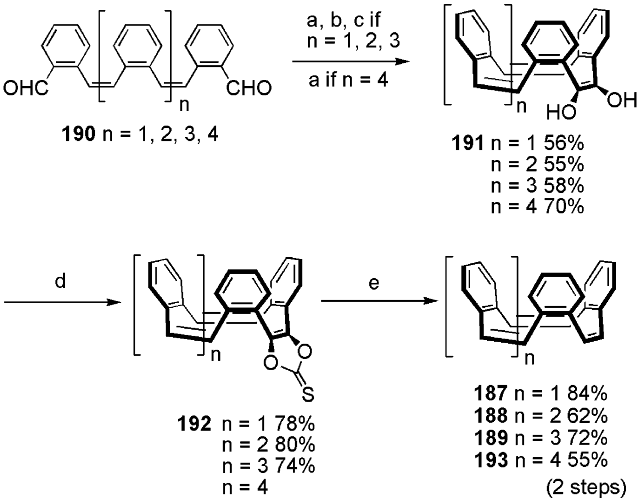
diethynyl spacer did not affect the photochromism, in contrast to previously reported dithienylethene photochrome systems. Trispyrene systems **185a** and **185b**, shown in the most thermodynamically favored closed−open−closed orientation, are the group's newest multistate π switches. Three of the five possible isomeric states of switch **185a** exhibited sufficient lifetimes to be observed by NMR spectroscopy and laser flash photolysis. Previously discussed organometallic analogues have also been examined for photochromic properties. Although the Cr-based systems did not exhibit photochromism, Ru-based **178b** exhibited electrochemic reversion to the pyrene in addition to photochromic and thermochromic methods.[102c] Mitchell and co-workers expanded their investigations of the DMDHP photochrome by incorporating it into larger porphyrin molecular triad systems (**186**) with either dihydroindolizine or fullerene photochromes to create molecular AND (produces an output of one when both inputs are one) and INHIBIT (an AND gate with an additional event) gates.[106]

4.2. Benzo[*n*]annulenes (*n* = 12, 16, 20, 24)

4.2.1. Substructures of Extended Systems

Iyoda, Kuwatani, and co-workers reported the production of several concave benzoannulene systems with alternating arene and alkene functionalities, of interest as precursors or mimics of larger conjugated systems (C_{60} and C_{70}) and cyclic belts (see review of aromatic belts by Tobe et al.[14]). The simplest system beyond dibenzocyclooctatetraene, benzo[12]annulene **187**, was obtained in 1988 from Ni-catalyzed trimerization of 1,2-dibromo-1,2-dihydrobenzocyclobutene followed by thermal ring opening.[107] The crown-like structure of cycle **187**, which results in an orthogonal relationship between benzene and ethylene linkages, prevents conjugation between arene rings. Due to interest in larger benzo[*n*]annulene systems ($n > 12$), the group explored alternate routes and developed a new versatile strategy that additionally afforded 16- (**188**) and 20-membered annulenes (**189**) in 2000.[108] V/Zn-mediated intramolecular pinacol coupling of bisaldehyde **190** resulted in a combination of threo and erythro diol isomers, of which the former was converted to the erythro conformer (**191**) via Swern oxidation and $NaBH_4$ reduction (Scheme 16). Treatment with thiocarbonyldiimidazole afforded the penultimate thiocarbonate **192**, which was subsequently placed under Corey−Winter reductive dehydroxylation conditions to afford cycles **187**−**189** in 62−84% yields. Most recently the group produced the benzo[24]annulene analogue (**193**) which displayed a unique benzene trimer substructure compared to the concave features of **187**−**189**.[109] Cycles **188** and **193** both displayed temperature dependence by NMR spectroscopy, while the frameworks of **187** and **189**, concluded to be, respectively, too

Scheme 16[a]



[a] Conditions: (a) $VCl_3(THF)_3$, Zn, DMF, CH_2Cl_2; (b) $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2; (c) $NaBH_4$, MeOH, CH_2Cl_2, 0 °C; (d) thiocarbonyldiimidazole, toluene, reflux; (e) 1,3-dimethyl-2-phenyl-1,3,2-diazaphospholidine, benzene, reflux.

rigid and too flexible, did not display significant structural change with temperature variance. Although organometallic complexes of **187**−**189** and **193** have been observed, only cycles **188** and **189** formed complexes with the transition-metal cavitated inside the annulene cage.

5. Dehydrobenzoannulenes

Dehydrobenzoannulenes (DBAs), also referred to as benzocyclynes, first appeared in the chemical record in the 1960s from the laboratories of Eglinton and Staab. Both groups continued their work into the late 1970s in conjunction with several other prominent chemists such as Nakagawa. Production of new cyclyne topologies in the early 1990s by Youngs and Vollhardt marked a resurgence in DBA synthesis that continues to this day. A key reason for this renaissance was isolation of the fullerenes[83b] as well as several theoretical studies that proposed unique thermal, optical, and electronic properties for highly unsaturated, nonnatural carbon allotropes such as graphyne (**194**, Figure 48) and graphdiyne (**195**), for which benzocyclynes could be envisaged as model substructures.[110]

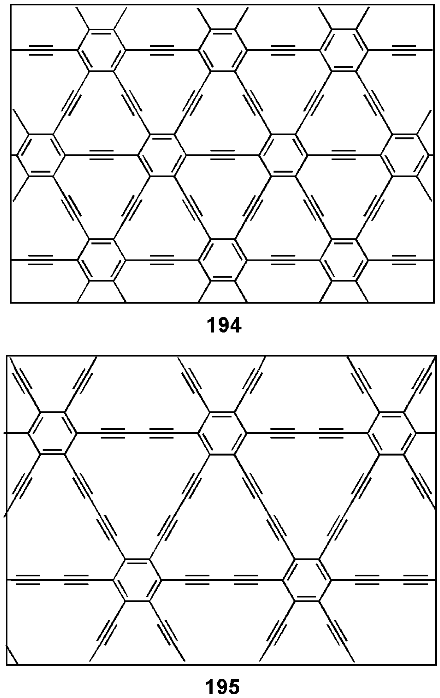


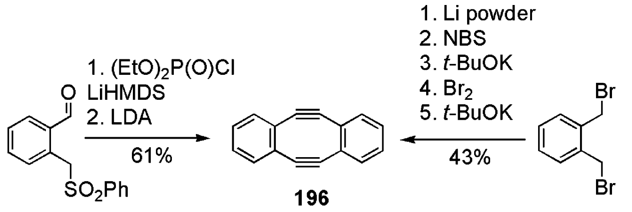
Figure 48.

5.1. Dehydrobenzo[8]annulenes

5.1.1. Substructures of Extended Systems

Cyclyne **196**, the simplest member of the DBA family, was first synthesized in 1974 by Sondheimer and co-workers in 27−36% yield via bromination of dibenzocyclooctatetraene and subsequent dehalogenation with *t*-BuOK.[111] Interest in this strained, anti-aromatic system continues due to the significant angle distortion of the alkyne moieties (∼155°)[112] and possibility as a precursor for extended carbon-rich systems.[113] Two different groups published superior alternate methods to the strained annulene in 2002 (Scheme 17). Otera and co-workers obtained the cycle in 61% yield via oxidative dimerization of *o*-(phenylsulfonylmethyl)benzaldehyde,[114] whereas Wudl et al. utilized two distinct multistep routes, the more efficient (43% overall yield) and cost-effective starting with α,α′-dibromo-*o*-xylene.[115]

Scheme 17



5.1.2. Organometallic Assemblies

Three organometallic complexes of **196** have been reported since the DBA renaissance (Figure 49). Bis-Pt complex **197**, isolated in 1997 by Tanaka et al. during investigation of silylation reactions of dehydro[8]annulenes, was obtained quantitatively by reaction of **196** with two equivalents of $Pt(PPh_3)_4$ or $Pt(CH_2{=}CH_2)(PPh_3)_2$.[116] Complexation of both

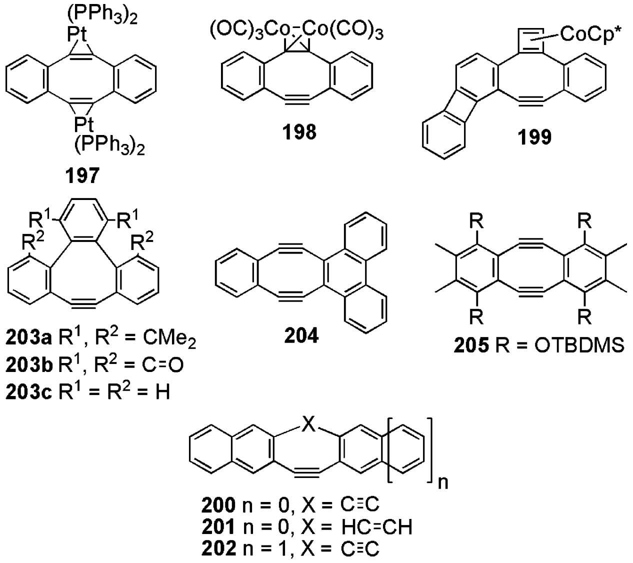


Figure 49.

alkyne moieties with Pt resulted in enhanced air and thermal stability with a decomposition temperature ~100 °C higher than that reported for **196** (~110 °C dec).[111] Both Otera and Vollhardt reported Co complexes of **196** 5 years later. Otera's laboratory produced dinuclear complex **198** by treatment of **196** with $Co_2(CO)_8$.[117] Although metal coordination to the single ethynyl group altered C−C bond length (0.16 Å) and angle (~8°), the remaining alkyne moiety in Co-complex **198** remained unchanged in angle and length. Alternatively, Vollhardt and co-workers obtained (cyclobutadieno)dibenzocyclooctatrienyne complex **199** from photochemical treatment of a mononuclear metallacyclopentadiene(alkyne) complex precursor designed for angular [4]phenylene.[118] The inherent strain in **199** resulted in a trapezoidal distortion of the cyclobutene moiety.

5.1.3. Novel Topologies

Wong's group prepared several analogues (**200**−**202**, **203a**, **203b**, **204**, Figure 49) of **196** in the early to mid-1990s. Benzo-fused cyclynes **200**−**202**, isolated as intermediates and characterized by high-resolution MS and/or NMR spectroscopy, were reacted with furan or isobenzofuran to construct benzo-fused tetraphenylenes.[113a] The group's interest in strained dehydroannulenes, such as cycloocta-1,5-diene-3,7-acetylene, led to production of annelated cycles **203a**, **203b**, and **204**.[119] Introduction of fluorene units provided enhanced stability and coplanar structures for **203a** and **203b**[119a,b] in contrast to the highly reactive, nonplanar parent tribenzocyclooctene **203c**, which exhibited a half-life of 30 min at −60 °C in solution.[120] The longevity of the fluorene derivatives, both crystalline solids that exhibited mp values >200 °C, was attributed to removal of the four eclipsed arene hydrogen atoms found in **203c**. Conversely, the improved stability (mp 183 °C) of **204**, obtained in two steps from benzo[*a*]phenanthro[9,10-*e*]cyclooctene, was based on kinetic protection of the alkyne groups from close proximity of phenanthrene hydrogen atoms as well as decreased ring strain of the central core from sp^2-C bond elongation.[119c] More recently, Youngs reported formation of tetrasilyloxy **205** from intermolecular Pd-catalyzed cross coupling in low yield (10%), the result of competitive formation of a more stable indenoindene byproduct (67% yield).[121]

5.2. Dehydrobenzo[12]annulenes

Prior to 2005, only two topologies existed for dehydrobenzo[12]annulene: the highly colored, dimeric dibenzoannulene **206**, also known as the Eglinton−Galbraith dimer, and tribenzocyclyne **207** (Figure 50). Eglinton and co-workers first isolated cycle **206** in 1960 via high-dilution oxidative coupling of *o*-diethynylbenzene.[122] Production of tribenzocyclyne **207** was subsequently reported in 1966 by Eglinton via trimerization of the cuprous salt of *o*-iodophenylacetylene in pyridine.[123] Staab and Graf simultaneously reported **207** through a halogenation/dehalogenation of a didehydrobenzoannulene obtained with Wittig chemistry.[124] Only with the Tobe group's report of highly strained dibenzocyclyne **208** almost 40 years later did a new triyne topology enter the chemical record.[125]

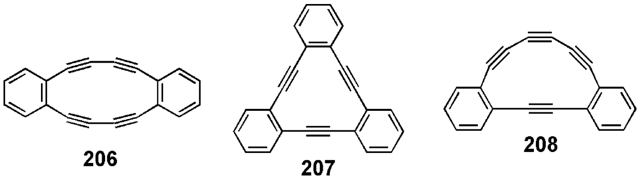
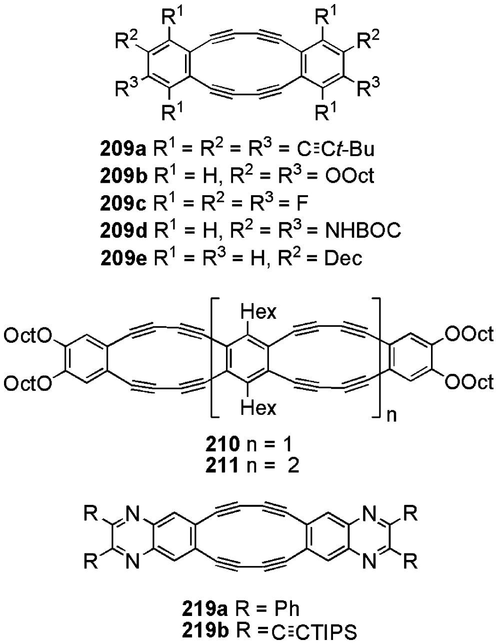

206 **207** **208**

Figure 50.

5.2.1. Octadehydrodibenzo[12]annulenes

5.2.1.1. Substructures of Extended Networks. Utilizing their new route for differentially protected hexaalkynylbenzenes via Diels−Alder cycloaddition of cyclopentadienones with alkynes, Rubin and co-workers investigated formation of larger graphyne substructures via Hay coupling in 1997.[126] The group successfully isolated **209a** in 25% yield from the final Cu-mediated homocoupling of 3,4,5,6-tetrakis(2-*tert*-butylethynyl)-1,2-diethynylbenzene (Figure 51). Although produced in the same reaction, trimeric and tetrameric analogues could not be separated and further characterized. Octasubstituted **209a** showed notable stability over the parent cyclyne, likely due to steric effects of the bulky alkyl groups and interspersed solvent molecules observed in the crystalline state.



209a $R^1 = R^2 = R^3 = C{\equiv}Ct\text{-Bu}$
209b $R^1 = H, R^2 = R^3 = OOct$
209c $R^1 = R^2 = R^3 = F$
209d $R^1 = H, R^2 = R^3 = NHBOC$
209e $R^1 = R^3 = H, R^2 = Dec$

210 n = 1
211 n = 2

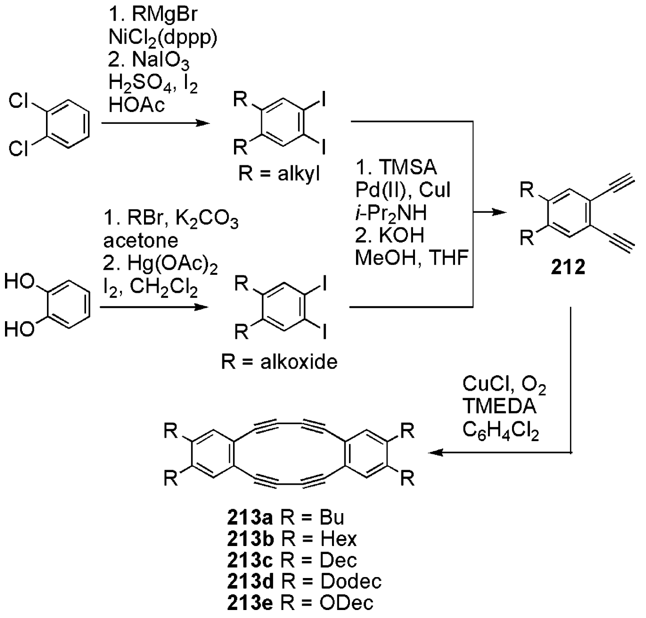
219a R = Ph
219b $R = C{\equiv}CTIPS$

Figure 51.

Gallagher and Anthony reported the production of linearly fused [12]annulene oligomers (**210** and **211**, Figure 51), referred to as acediynes, as well as tetraoctanoxy analogue **209b** in 2001.[127] Contrary to traditional intermolecular Hay cyclization techniques, they constructed the extended structures stepwise via Pd-catalyzed homocoupling of alkoxy-substituted benzene rings to a central dialkyl core followed by intramolecular Hay coupling. The electronic absorption spectra of the acediynes, which displayed increased bathochromic absorption with oligomer length, allowed calculation of a saturation wavelength (625 nm) similar to linear acetylene-based polymers. While both **210** and **209b** were found to be readily soluble and stable systems, oligomer **211** exhibited poor solubility in organic solvents and was found to decompose in nondeoxygenated solvents.

5.2.1.2. Precursors for Polymerization and Intermolecular Networks. The Swager group's interest in precursors for novel conjugated organic polymers led to the study of dimerization reactions of *o*-diethynylbenzene analogues in 1994.[128] The penultimate diethynylbenzene derivatives (**212**) were prepared in good yield from either *o*-dichlorobenzene or catechol with Pd- and Ni-catalyzed cross-coupling reactions, respectively (Scheme 18). Intermolecular Hay coupling of the diethynyl monomers in *o*-dichlorobenzene afforded a mixture of the dimer (**213**) with larger macrocycles and oligomeric/polymeric components. Cycles **213b**−**e** were isolated in 17−74% yields, while cycle **213a** and the larger macrocycles were analyzed as mixtures by ^{1}H NMR spectroscopy. Tetrasubstitution of the strained core enhanced stability of the [12]cyclyne to several days at room temperature, in contrast to the rapid and pronounced decomposition of concentrated samples of **206**. The solid-state structure of **213a** displayed a staggered conformation with alternating in and out of plane orientation for substituents, a structural feature that prevented intermolecular interactions from adjacent butadiyne linkages. Investigation of thermal behavior by DSC showed polymerization between 100 and 125 °C with very narrow transitions ($\omega^{1/2} \approx 1.5$ °C). X-ray powder diffraction, cross polarization/magic angle spinning NMR spectroscopy, ESR, and the intractable nature of the resultant polymeric materials all indicated that tetrasubstituted [12]-annulenes **213** did not exhibit a well-defined topochemical polymerization.

Scheme 18



Bunz and Enkelmann further investigated the Eglinton−Galbraith dimer (**206**) in 1999, specifically focusing on the solid-state behavior and crystal packing of the octadehydroannulene.[129] Cocrystallization with hexafluorobenzene and tetracyanoquinodimethane resulted in formation of 1:1 molecular complexes with guest molecules inserted between the stacked annulenic cores. Although concentrated samples would readily lose solvent and decompose, the solvent complexes were stable under ambient conditions if sealed in a capillary under partial pressure of solvent.

Komatsu and co-workers prepared octafluoro analogue **209c** in 2002 via Cu-mediated homocoupling of 1,2-diethynyl-3,4,5,6-tetrafluorobenzene (Figure 51).[130] Use of preparative GPC allowed facile isolation of **209c** in 48% yield as well as the trimer in lower yield. Although UV−Vis spectroscopy and DFT calculations indicated a comparable HOMO−LUMO with parent **206**, CV data indicated a more electron-deficient cyclyne core and lower LUMO by a less negative reduction peak. Investigation into polymerization characteristics showed that despite suitable solid-state orientation of the diyne bridges, cycle **209c** was stable to topochemical polymerization. The cycle also exhibited explosive decomposition at higher temperatures (120−135 °C) than **206**, a deactivating effect attributed to the electron-withdrawing octafluoro substitution.

5.2.1.3. Organometallic Assemblies.

A Ru-coordinated dehydrobenzo[12]annulene with exotopically fused diimine binding sites (**214**) was reported by Faust and Ott in 2004 (Figure 52).[131] The metallacycle was obtained in 21% yield by 4-fold Schiff-base condensation of BOC-protected tetraamino[12]annulene **209d** with [(bpy)$_2$Ru(phenanthroline-5,6-dione)]$^{2+}$(PF$_6^-$)$_2$ in TFA and CH$_3$CN. The electron-accepting nature of **214** was confirmed by CV experiments, which provided a similar reduction potential to that of the first reduction of the well-established electron acceptor C$_{60}$. Although responsible for a decreased excited-state lifetime by intramolecular quenching, the dehydroannulene core did provide electronic benefits of bathochromic absorption and emission spectra for **214** compared to acyclic Ru−polypyridyl model complexes.

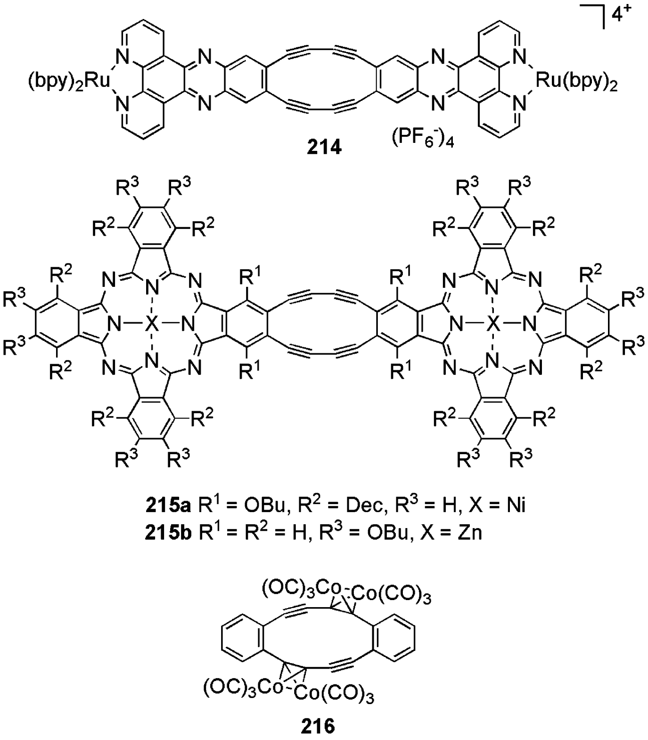


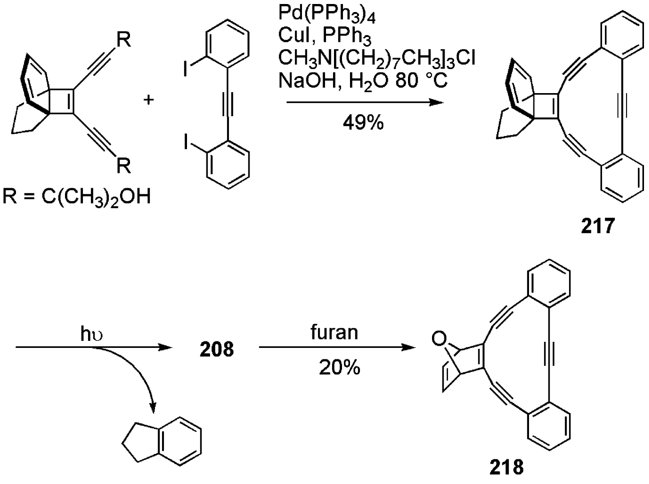
Figure 52.

Cook and Heeney[132] as well as Torres and co-workers[133] published reports in 2000 on phthalocyaninodehydroannulenes that differed only in arene substitution and transition-metal identity (Figure 52). Both groups used intermolecular Cu-mediated homocoupling reactions of diethynylphthalocyanino monomers with different results. Cook and Heeney obtained dimer **215a** in 24% yield as well as an additional 18% yield of dimer/trimer mixture with Eglinton conditions. Torres' group found that similar Eglinton coupling of the diethynyl precursor resulted only in an inseparable mixture of **215b** and trimer analogue while increased temperature (70 °C) and higher concentration afforded cycle **215b** as the sole macrocyclic product in 51% yield. Although absorption spectra were run in different solvent systems, both macrocycles **215a** and **215b** exhibited λ_{cutoff} values >800 nm with a distinctive broadening and splitting of the Q band, ascribed to intramolecular coupling of the phthalocyanine groups via the butadiyne linkages. Cook and Heeney further investigated the propensity for mesophase behavior, which showed that **215a** entered a mobile phase at 110 °C with an associated birefringence pattern. Heating of **215a** in toluene above 220 °C resulted in drastic changes in the absorption spectrum and the presence of higher molecular weight oligomers with interspaced molecular weights of **215a** by matrix-assisted laser desorption ionization time-of-flight MS.

The double-addition organometallic product **216**, which displayed enhanced stability to several days in solution under ambient conditions, was obtained by Adams and Bunz in 39% yield via reaction of **206** with $Co_2(CO)_8$ at room temperature (Figure 52).[134] Co-complex incorporation was found to occur on opposite sides of the carbon-rich skeleton to minimize unfavorable steric interactions between metal complexes.

5.2.1.4. Novel Topologies. In 2005, the Tobe group reported production of triyne **208** by photochemical [2 + 2] cycloreversion of [4.3.2]propellatriene-annelated **217** (Scheme 19).[125] The highly strained cyclyne could only be isolated as a Diels–Alder adduct (**218**) with furan in 20% yield or as an anti-dimeric adduct in THF in 18% yield. Spectroscopic characterization (UV–Vis and FT-IR) of the new triyne occurred only at low temperature in either a 2-methyltetrahydrofuran glass or Ar matrix. DFT geometry optimization of **208** exhibited C_{2v} symmetry with the most significant distortion of the triyne moiety unevenly manifested in the central ethynyl group (147.1°, 150.8°).

Scheme 19



Other novel substitutions of the benzo[12]cyclyne skeleton include a dialkyl analogue (**209e**) prepared by Haley's group in 2004[135] and two new quinoxalinodehydroannulenes (**219a,b**) reported by Ott and Faust (Figure 51).[136] Cycles **219a** and **219b** were obtained from a one-pot deprotection/condensation reaction of **209d** with 1,2-diphenylethane-1,2-dione or 1,6-bis-(triisopropylsilyl)hexa-1,5-diyne-3,4-dione in TFA and HOAc, respectively. Tetraethynyl-substituted **219b** exhibited bathochromic absorption and emission spectra (18 and 15 nm, respectively) compared to tetraphenyl **219a**, the result of limited *π* delocalization from sterically induced twisting of the phenyl substituents.

5.2.2. Hexadehydrotribenzo[12]annulenes

5.2.2.1. Substructures of Extended Networks. Several new routes, both inter- and intramolecular, have been reported for tribenzo[12]annulene **207** since the pioneering syntheses in 1966.[123,124] Table 8 provides a chronological display of penultimate structure, reaction conditions, and cyclization yield for reports issued in the last 25 years. In addition to increased efficiency for the parent cyclyne, the new routes specifically allow straightforward access and tailored production of substituted analogues (Table 9), an important facet for use of these carbon-rich cycles in materials systems.

Table 8. Synthetic Routes to Hexadehydrotribenzo[12]annulene (207)

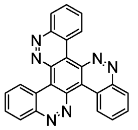
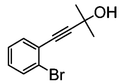
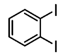
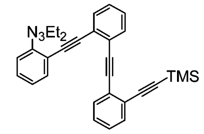
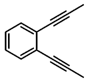
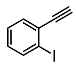
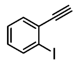
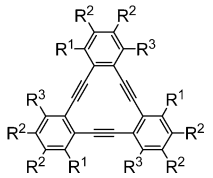
Entry	Cyclization Precursor	Conditions	Yield	Ref
1	 **221**	780 °C 0.005 Torr	8%	142
2	 **220**	Pd(PPh$_3$)$_4$, CuI, NaOH, BTEACl, benzene, 85 °C	36%	137
3		acetylene, CuI, PdCl$_2$(PPh$_3$)$_2$, DMF, piperidine, 60 °C	39%	138
4	 **222**	1. K$_2$CO$_3$, MeOH, THF 2. MeI, 120 °C 3. Pd(dba)$_2$, PPh$_3$ CuI, Et$_3$N	69%	143
5		(*t*-Bu$_3$O)WC(*t*-Bu)$_3$ toluene, 80 °C	54%	141
6		CuI, PPh$_3$, DMF K$_2$CO$_3$, 160-165 °C	55%	139
7		Pd(PPh$_3$)$_4$, CuI BMIMBF$_4$, Et$_3$N	37%	140

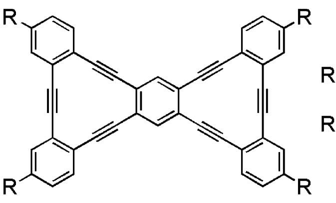
Table 9. Dehydrobenzo[12]annulenes 228a–n

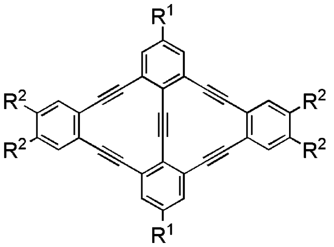


DBA	R^1	R^2	R^3	ref
228a	H	Dec	H	144
228b	H	ODodec	H	148
228c	H	OHexadec	H	148
228d	H	OOctadec	H	148
228e	H	ODec	H	149
228f	H	OTetradec	H	149
228g	OMe	H	OMe	155
228h	H	OHex	H	156
228i	H	F	H	138
228j	H	Br	H	141
228k	H	Me	H	138, 139, 141
228l	H	Bu	H	139
228m	H	OMe	H	139, 141
228n	H	OMe	OMe	140

The first significant intermolecular construction of **207** since Eglinton's initial Cu-mediated route was provided in 1988 by Linstrumelle and Huynh,[137] who obtained the benzocyclyne in 36% yield from an in situ alkyne deprotection/Pd-catalyzed cross-coupling of arene **220** (Table 8). Ten years later, Iyoda and co-workers reported an expedient route to cycle **207** via a one-step Pd-catalyzed reaction of *o*-diiodobenzene with acetylene (entry 3, Table 8).[138] Two recent reports have presented new cyclization conditions with *o*-ethynyliodobenzene as starting material (entries 6 and 7, Table 8): Iyoda and co-workers utilized a Pd-free, Cu-mediated route with PPh_3 and K_2CO_3 in DMF at high temperature,[139] while Li et al. used a Sonogashira coupling in ionic liquid, which afforded use of reduced amounts of CuI to minimize homocoupling side reactions.[140] In 2003, Vollhardt and co-workers reinvestigated *o*-DBA production with Schrock's W−alkylidyne catalyst and isolated **207** in 54% yield by 3-fold intermolecular metathesis of 1,2-dipropynylbenzene (entry 5, Table 8).[141] Two intramolecular cyclization routes have also been reported for **207**. Barton and Shepherd isolated the cycle in 8% yield from vacuum thermolysis of benzotricinnoline **221** in 1984,[142] and Haley and co-workers produced the cycle in 69% from Pd-catalyzed cross-coupling of triyne **222** after triazene decomposition and iodination with MeI.[143]

A key interest in cycle **207** arises from the theoretical and as yet unattainable carbon-rich network graphyne (**194**) of which **207** can be considered a subunit. Development of single-molecule systems based on the structural motif of **207** has been explored for insight into properties of the extended network. Cyclyne **223a**, composed of two 12-membered cycles fused to a central arene core, was first isolated by Haley and co-workers in 2000 in low overall yield (4%) via a lengthy intramolecular sequence (12 steps) concluded by 2-fold intramolecular Pd-catalyzed cross-coupling (Figure 53).[143] The electronic absorption spectra of **223a** displayed the characteristic three-peak pattern associated with the diphenylacetylene chromophore of **207** (280, 290, and 300 nm) with addition of a strong absorption at 325 nm and increase in λ_{cutoff} (>460 nm) by ~50 nm. The broad, exothermic decomposition of **223a** above 300 °C ($w^{1/2} \approx$ 30−40 °C) clearly indicated a marked difference in thermal properties associated with fusion of two tribenzo[12]cyclyne cores compared to **207**, which exhibited a distinct mp at 210 °C.


223a R = H
223b R = Bu


224a R^1 = *t*-Bu, R^2 = H
224b R^1 = R^2 = Dec
224c R^1 = R^2 = H

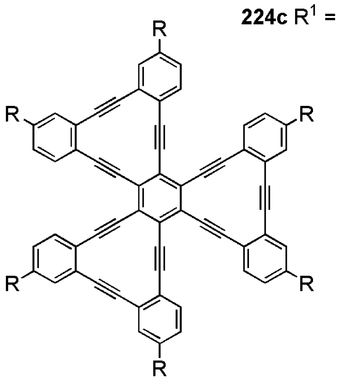

225 R = *t*-Bu

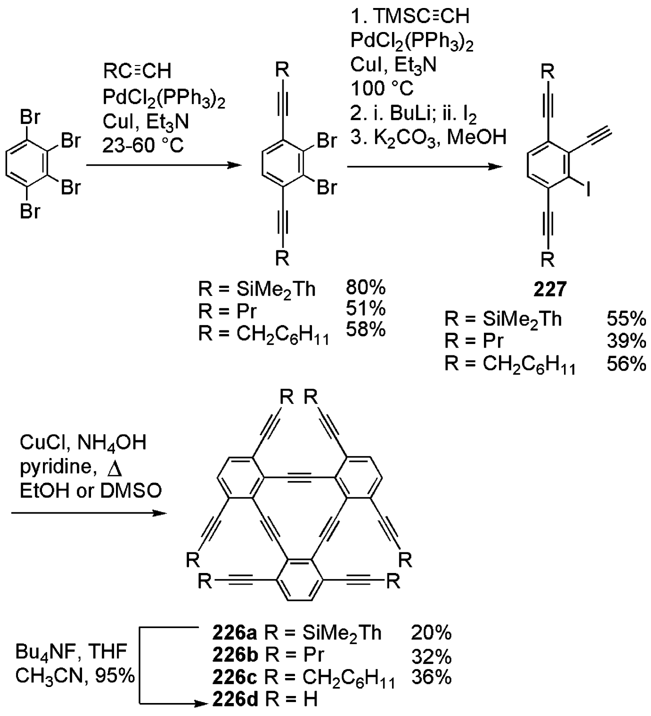
Figure 53.

In 2003, Vollhardt's group reported an identical overall yield for bowtie **223a** in only three steps. Six-fold intermolecular metathesis of a 4:1 mixture of 1,2-dipropynylbenzene and 1,2,4,5-tetrapropynylbenzene provided **223a** in an amazing 6% yield.[141] Although not reported due to solubility problems in 2000, Vollhardt obtained the ^1H NMR spectra of **223a** that confirmed a weak paratropic ring current of the anti-aromatic annulene core by a small upfield shift of the AA′BB′ multiplet. Iyoda and co-workers more recently reported octabutyl-substituted analogue **223b**, obtained from 2-fold Cu-mediated coupling of 1,2,4,5-tetraiodobenzene with an alkyl-substituted 2,2′-diethynyldiphenylacetylene in 1% yield.[139] The group was first to report the fluorescence quantum yield ($\Phi = 0.21$) and an associated 190 nm Stokes shift for the graphyne bowtie.

Additional single-molecule systems based on the graphyne network include diamond-shaped cyclyne **224** and trefoil **225** (Figure 53). Concurrent with **223a**, Haley and co-workers first reported cyclyne **224a**, containing solubilizing *tert*-butyl groups based on the poor solubility of **223a**, by an intramolecular stepwise route similar to that used for **207**.[143] In 2004, Tobe et al. reported **224b** by double cyclization of a didecyl-substituted 2,2′,6,6′-tetrabromodiphenylacetylene precursor with 4,5-didecyl-1,2-diethynylbenzene in 9% yield and noted a significant improvement in solubility with addition of six decyl groups.[144] Although the emission spectrum of **224b** exhibited resolved vibrational structure beyond **207**, the quantum yield ($\Phi = 0.06$) was inferior to **207** ($\Phi = 0.15$) and **223b**. Femtosecond Z scans of **224b** in $CHCl_3$ resulted in second-order hyperpolarizability values ($< 4 \times 10^{-35}$ esu) lower than those predicted for the non-alkyl-substituted parent of **224c** (5.49×10^{-35} esu).[145] The Tobe group most recently isolated the largest graphyne subunit, trefoil **225**, from 3-fold pinacol coupling with $Zn/VCl_3(THF)_3$ followed by chlorination/dehalogenation of the hexaethynyl precursor.[146]

In 1997, Vollhardt's group prepared several substituted hexaethynylbenzo[12]cyclyne systems (**226a**−**c**, Scheme 20) from Cu-mediated trimerization of triyne **227** in 20−36% yields.[147] Regioselective ethynylation of 1,2,3,4-tetrabromobenzene, which occurred at C1 and C4 with lower temperatures (30−60 °C) and C3 at increased temperature (100 °C), was used to construct the asymmetrically ethynylated skeleton of **227**. Lithium−halogen exchange followed by addition of I_2 afforded trialkynyliodobenzene **227** to facilitate a more successful 3-fold cross-coupling. Reaction of **226a** with Bu_4NF afforded the relatively stable hexaethynylbenzene **226d** in near quantitative yield. The crystal structure of **226d**, which exhibited a slightly twisted deformation from planarity of the arene moiety, displayed a columnar supramolecular structure with alternating THF disks resultant from chelating C−H--O H-bonding between adjacent molecules. Distortion of the cyclyne core was more apparent in the substituted analogues (**226a**−**c**) due to steric congestion. Absorption spectra of the hexaethynylbenzo[12]cyclynes exhibited lower intensity for $\pi-\pi^*$ transition than **207**, attributed to the decreased rigidity of the conjugated

Scheme 20



core. The group further explored the use of **226a**−**d** as precursors for radial phenylenes, such as antikekulene, via Co-mediated cyclotrimerization.[9]

5.2.2.2. Precursors for Polymerization and Intermolecular Networks. In collaboration with De Schryver and De Feyter, the Tobe laboratory observed self-assembly of several polysubstituted benzo[12]cyclyne derivatives into ordered two-dimensional networks at the liquid−solid interface via scanning tunneling microscopy (STM).[148] In addition to **224b** and **228a**,[144] the group focused on several new hexaalkoxy analogues (**228b**−**d**, Table 9) of **207**, produced in 22−33% yield from 3-fold coupling of 4,5-dialkoxy-1-ethynyl-2-iodobenzene precursors by Iyoda's method[139] as well as two hexaalkoxy-substituted cyclynes (**228e**,**f**) first reported by Youngs' group as potential liquid crystal precursors.[149] Analysis of cycle solutions in different solvents on HOPG showed that conjugated core shape, length of substituent chains, and solubility controlled identity, stability, and extent of monolayer formation. For example, in 1,2,4-trichlorobenzene, shorter chained **228a**,**b**,**e** predominately displayed a circular honeycomb pattern whereas longer alkoxy chained systems (**228c**,**d**,**f**) exhibited a linear arrangement of the triangular-shaped cyclyne cores. Increase in core size to diamond **224b** afforded kinetic formation of a linear monolayer that was replaced by a thermodynamically preferred Kagomé network.

5.2.2.3. Organometallic Assemblies. Several different organometallic complexes of cyclyne **207** have been reported by Youngs and co-workers since 1985 (Figure 54). Combination of the respective parent cyclynes with Ni(COD)$_2$ in benzene afforded Ni-complexes **229a**−**c**, all exhibiting internal cavitation of the metal and coordination to all three ethynyl moieties.[149,150] Mononuclear and trinuclear cofacial Cu-complexes **230**[151] and **231**[152] were obtained from diffusion of saturated and stoichiometric benzene solutions of Cu$_2$(OTf)$_2$(C$_6$H$_6$) and **207**, respectively. Sandwich complex **232** was obtained from a mixture of **207** with AgSO$_3$CF$_3$ in a 3:1 ratio in THF followed by precipitation with hexanes,[153] while 66-electron cluster **233** resulted from a mixture of the hexadecylcyclyne with Co$_2$(CO)$_8$ in Et$_2$O.[149,154] All of the transition-metal complexes were characterized by X-ray crystallography except **229c** and **233b**, which were based on FD-MS, IR spectroscopy, and/or elemental analysis. Of note, complexes **229a** and **232** were, respectively, the first transition-metal complex for the benzo[12]cyclyne and first observation of a macrocycle−metal sandwich complex. Iyoda et al. also reported a 2:1 Ag complex of octabutyl-substituted **223b**, which was characterized by time-of-flight MS and ^{1}H NMR spectroscopy.[139]

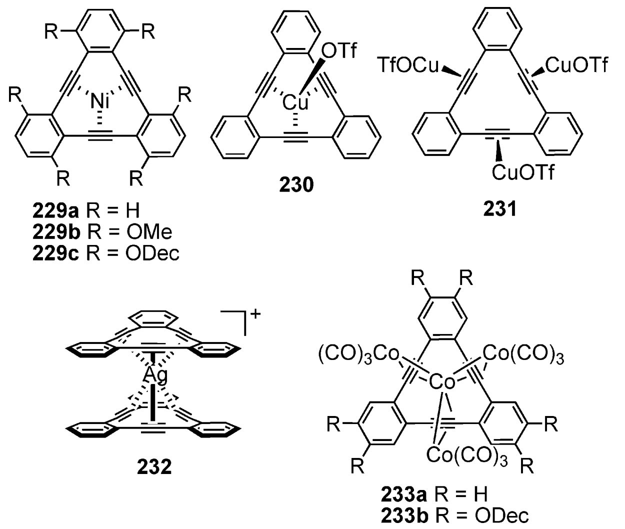


Figure 54.

5.2.2.4. Novel Topologies. Eight additional novel substitution patterns (**228g**−**n**, Table 9) have been reported for **207**. Youngs et al. produced *p*-dimethoxy-substituted tribenzocyclyne **228g** in 1993 by 3-fold Stephens−Castro coupling from a disubstituted *o*-ethynyliodoarene in excellent yield as well as in low yield from Pd-catalyzed cyclotrimerization.[155] To explore the metal binding capability of **228g**, the group then treated the cycle with (NH$_4$)$_2$Ce(NO$_3$)$_6$ and converted a single dimethoxyarene substituent to a quinone moiety. Cycle **228h** was prepared recently by Moore's group with a precipitation-driven Mo−amido metathesis catalyst in 86% yield.[156] The group confirmed reversible formation of **228h** by a scrambling experiment, which involved addition of a 1,3-dipropynylarene to the metathesis reaction and observation of two additional cycle products by MS. Polyalkyl- and polyalkoxycycles **228i**−**n** were prepared from substituted arene precursors by similar methods for **207** described in section 5.2.2.1 and will not be discussed further (see Table 9 for correlation to references).

Linstrumelle and Huynh simultaneously reported production of monobenzo- and dibenzo[12]annulenes **234** and **235** with the new route to **207** in 1988 (Figure 55).[137] The novel monobenzannelated **234** was isolated in 21% cyclization yield, while cycle **235** was obtained in comparable cycliza-

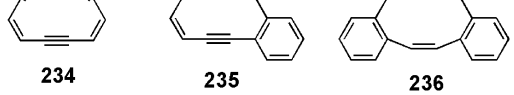
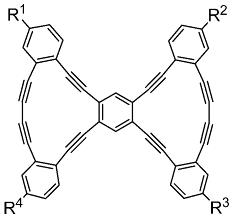


Figure 55.

Table 10. Bis[14]cyclyne Electron Donor−Acceptor Systems 239-242



DBA	R^1	R^2	R^3	R^4
239	Dec	Dec	Dec	Dec
240	NBu_2	NBu_2	NBu_2	NBu_2
241	NBu_2	NBu_2	NO_2	NO_2
242	NBu_2	NO_2	NO_2	NBu_2

tion yield (11%) with the first reported Cu-mediated route used by Staab (10%).[157]

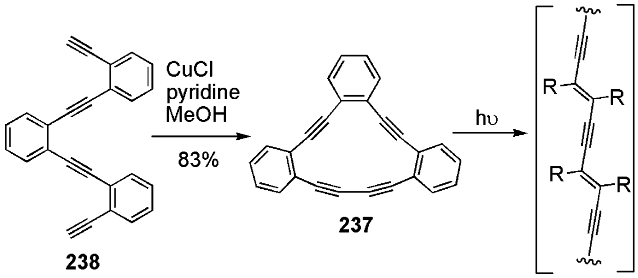
Iyoda and co-workers produced tetradehydrobenzo[12]-annulene **236** in 2000.[158] The crystal structure of **236** exhibited a warped central core with the *Z*-alkene above the plane of the diphenylacetylene moieties. Investigation of Bergman chemistry of enediyne **236** afforded only the *E* isomer upon irradiation but the desired annelated cyclooctatetraene product after thermal treatment at 250 °C for 4 days. Exploration of metal complexation of **236** resulted only in a mixture of several interesting polycyclic aromatic hydrocarbon products upon reaction with AuCl.

5.3. Dehydrobenzo[14]annulenes

5.3.1. Precursors for Polymerization and Intermolecular Networks

Vollhardt and Youngs reported the first synthesis of octadehydrotribenzo[14]annulene **237** in 1995[159] from Glaser coupling of tetrayne **238**, previously prepared by Youngs' group (Scheme 21).[160] X-ray crystallography provided packing diagrams which supported proper orientation for topochemical polymerization of the butadiyne linkages to form an ene−yne polymer.[161] Polymerization of the strained diphenyldiyne monomeric subunit was explored after observation that exposure of **237** to light rapidly changed the crystalline material to a surface with metallic, violet luster. The insoluble polymeric material, also available with application of direct pressure (20 000 psi) to crystals of **237**, was analyzed with high-energy laser desorption time-of-flight MS, which indicated the presence of oligomers up to $n = 9$.

Scheme 21



5.3.2. Electron Donor–Acceptor Systems

Haley's group investigated intramolecular charge transfer in 2005 with a series of novel bis[14]cyclyne bowties (**239**−**242**, Table 10) consisting of electron-donating (alkyl, NBu_2) and electron-accepting (NO_2) substituents.[162] During the macrocyclization of tetradonors **239** and **240**, the group discovered selective ring formation based on reactions conditions: Pd-catalyzed homocoupling favored formation of bis[14]annulenes **239**−**242**, whereas Cu-mediated macrocyclization selectively favored isomeric bis[15]annulenes from common octayne precursors.[162a] Analysis of the broad, low-energy charge-transfer absorption bands of the new bowties indicated that linear charge-transfer pathways, planarity, and large net dipoles were key factors for superior electronic properties. The new donor−acceptor systems displayed large Stokes shifts and exhibited a variety of emission colors, a direct result of a wide range of λ_{em} values (505−580 nm). Cycles **241** and **242** both displayed concentration dependence in ^1H NMR spectroscopy, attributed to self-association as a result of face-to-face stacking in solution. Analogous bis[15]annulene systems were also constructed but will not be discussed due to cross-conjugation of the central arene ring.

5.3.3. Aromaticity Probes

Haley's laboratory reported several variably benzannelated octadehydro[14]annulene analogues (**243**−**246**, Figure 56) in 2000 and 2001 and investigated the bond-fixing ability of benzene on the parent annulene (**123**) with spectroscopy and NICS calculations.[80,163] Incorporation of successive arene rings into **123** resulted in an upfield shift of alkene proton resonances by 0.67 and 0.38 ppm, respectively. Comparison of arene protons ortho to the diacetylene bridge between mono-, di-, and tribenzo[14]cyclynes also displayed upfield shifts (Δδ 0.19−0.25) upon higher benzannelation. The decreased aromaticity indicated by the continued upfield shift upon benzannelation was ascribed to competing ring currents. This consistent and rather sensitive effect on proton resonances for both alkene and arene protons of **243**−**246** provides further support for use of this methodology as a qualitative aromaticity probe.

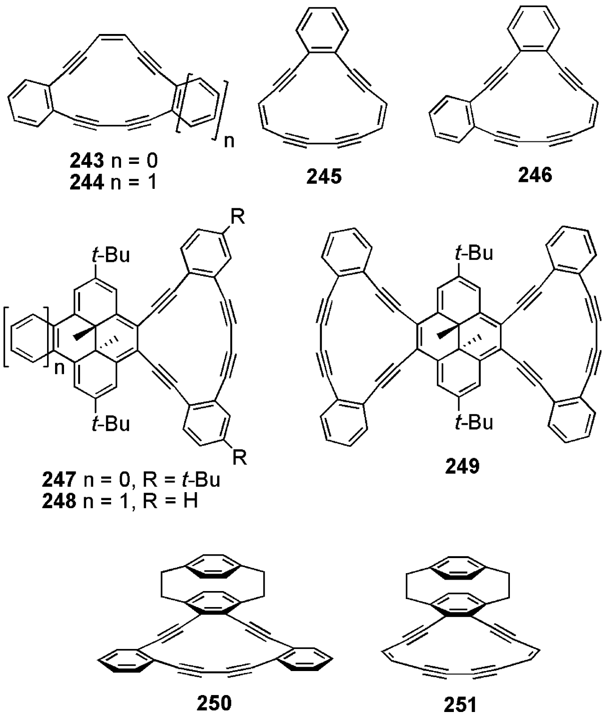


Figure 56.

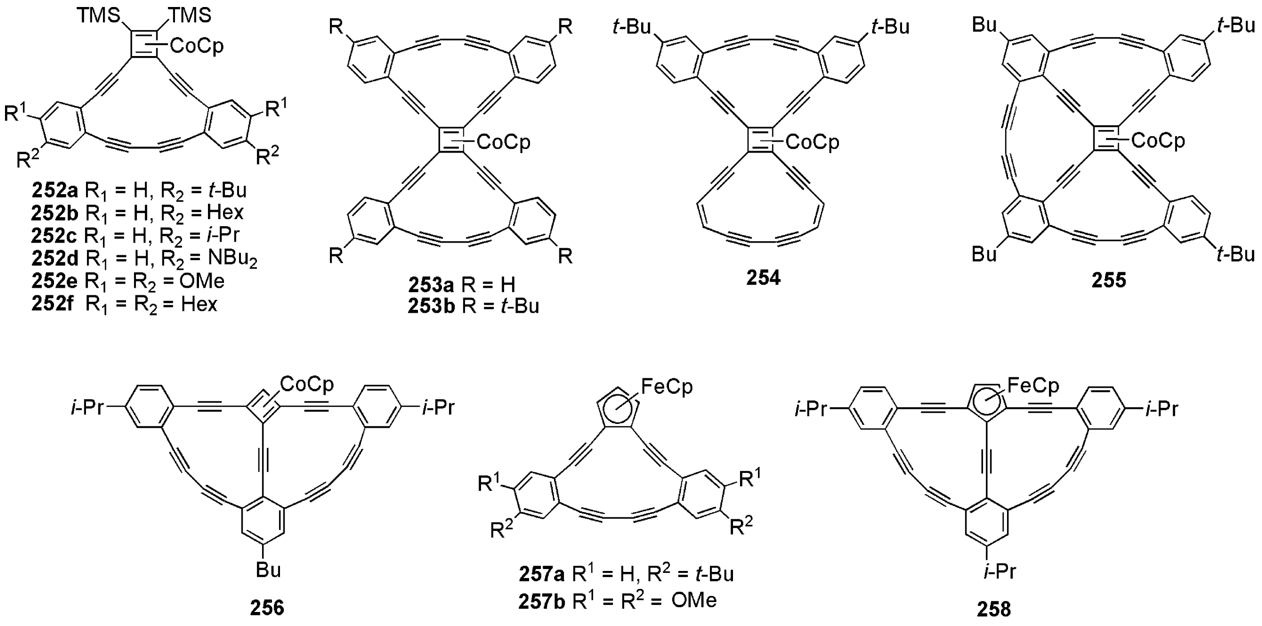


Figure 57.

The Haley group expanded on this aromaticity study by collaboration with Mitchell and Hopf in 2001 and 2005, respectively.[43g,164] Both mono- (**247**, **248**) and bis[14]-cyclynes (**249**) fused to a DMDHP core were initially produced, and subsequent investigation by ^{1}H NMR spectroscopy and NICS calculations confirmed the existence of weak diatropic ring currents for the ortho-fused systems. Cyclophane systems **250** and **251** were most recently prepared via cross-coupling of 4,5-diethynyl[2.2]paracyclophane with either 1-iodo-2-(trimethylsilylethynyl)benzene or (*Z*)−(4-chloro-3-buten-1-ynyl)trimethylsilane. The diatropic ring current of **250** and **251** was confirmed by changes in the chemical shift of cyclophane hydrogen atoms directly above the cycle core, with a larger effect observed for the more aromatic **251**.

5.3.4. Organometallic Assemblies

Through a series of articles initiated in 2001, Bunz reported a multitude of organometallic cycles with either a cyclobutadiene(cyclopentadienylcobalt) (**252**−**256**) or a cyclopentadienylferrocene complex (**257**−**258**) incorporated into the [14]annulene skeleton (Figure 57).[165] Pd-catalyzed cross coupling of iodoarenes to diethynyl-metalated cores followed by alkynylation and deprotection furnished the penultimate polyynes for monocycles **252** and **257**. Production of the larger asymmetric systems required a combination of acetal protecting groups and Ohira−Bestmann alkynylations to control substitution of the central organometallic cycle. Final macrocyclization by homocoupling under Vögtle conditions afforded the monocycles (19−93% yields) and fused systems (25−94% yields). The group conducted a detailed analysis of the solid-state structures of the new metallacyclynes. Although the majority of the CpCo-monocycles crystallized in different space groups, all lacked close proximity of butadiynyl moieties, a possible reason for observed melting transitions instead of solid-state polymerizations for **252b**−**f**. Seco-wheel **255** exhibited a distinct flattening of the hydrocarbon ligand beyond the nonlinear distortion of the less constrained butterfly **253b**, which suggested a full wheel analogue would be highly planar. Cycle **253b** also displayed an interesting grid-like supramolecular ordering that repeated the cyclobutadiene complex's tetragonal geometry, a phenomenon that suggested the potential for an extended network of covalently linked all-cyclobutadiene wheel substructures. A comparison of ^{1}H NMR spectroscopic δ values of the various substituted monocycle analogues indicated that both organometallic complexes were more aromatic than benzene by ring-current criteria, with cyclobutadiene(cyclopentadienylcobalt) superior to cyclopentadienylferrocene.

5.3.5. Novel Topologies

Two unique [14]annulene topologies, including either cumulene or triyne motifs, have been reported by Japanese research groups in the last 10 years (Figure 58). Kuwatani and Ueda produced a new Sworski-type octadehydro[14]-annulene (**259a**) as well as derivatized analogues **259b**−**d** in 1995.[166] The 14-membered ring was constructed with methodology used for the benzo[*n*]annulenes (section 4.2.1) prior to introduction of the cumulene functionalities by three

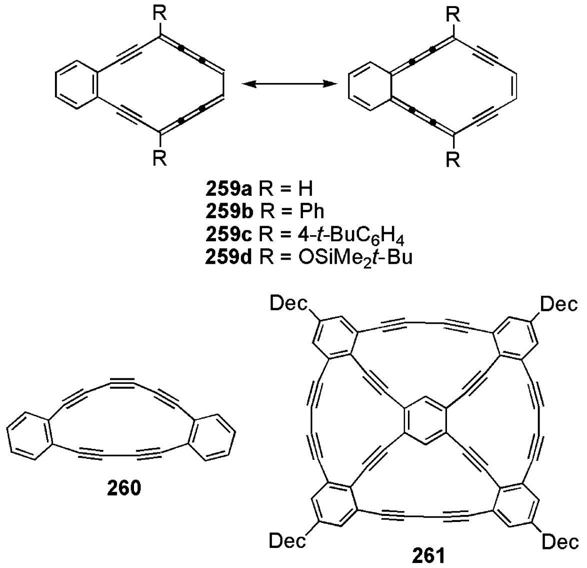


Figure 58.

different routes dependent on R group substitution. The aromatic enediynes showed limited stability, with only **259b** and **259c** stable upon concentration. The absence of ^{13}C NMR spectroscopy resonances in the characteristic region of alkyne or cumulenic sp-hybridized carbons suggested the significance of the two nonequivalent resonance contributors of **259**.

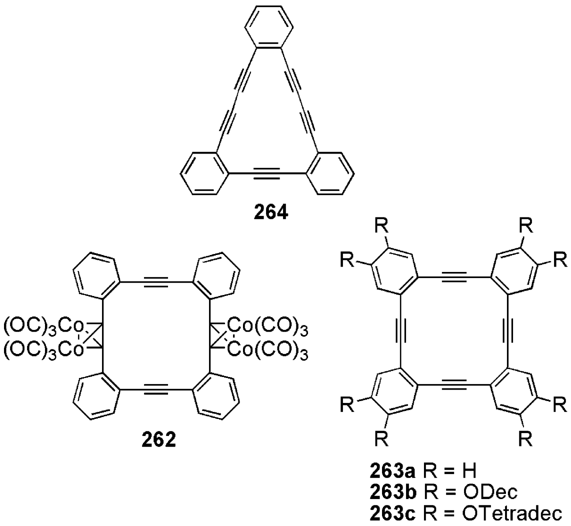
Tobe et al. synthesized dibenzo[14]cyclyne **260** via elimination of indane from a pentayne analogue of [4.3.2]-propellatriene **217**.[125] In contrast to highly reactive **208**, triyne **260** was sufficiently stable in solution for spectroscopic characterization. The presence of two new resonances downfield from the propellatriene precursor were in agreement with calculated values as well as the diatropic current of [14]cyclynes. The lower yields of the intramolecular and furan [4 + 2] adducts of **260** suggested decreased reactivity of the central alkyne group, a factor confirmed by decreased angle distortion from DFT calculations (157−165°).

Wheel-shaped fenestrane **261**, consisting of complete fusion of two 14- and two 15-membered benzocyclynes to a central arene core, was produced in 2004 by Marsden, O'Connor, and Haley (Figure 58).[135] Cycle **261**, calculated to possess a slightly concave distortion, displayed enhanced solubility beyond its planar bisannulene substructure **239** as well as a bathochromic λ_{cutoff} and broadened absorption patterns due to more complex conjugated circuits.

5.4. Dehydrobenzo[16]annulenes

5.4.1. Organometallic Assemblies

Tetracobalt complex **262** (Figure 59) was obtained in 70% yield[167] from reaction of the parent tetrabenzo[16]annulene (**263a**), first reported in 1966 by Eglinton and co-workers,[123] with two equivalents of $Co_2(CO)_8$ in THF at room temperature. Higher concentrations of $Co_2(CO)_8$ afforded only **262**, a steric factor due to close proximity of CO ligands to the uncomplexed alkyne groups. The tetranuclear−Co complex exhibited enhanced solubility beyond the bowl-shaped parent cyclyne.



264

262

263a R = H
263b R = ODec
263c R = OTetradec

Figure 59.

5.4.2. Novel Topologies

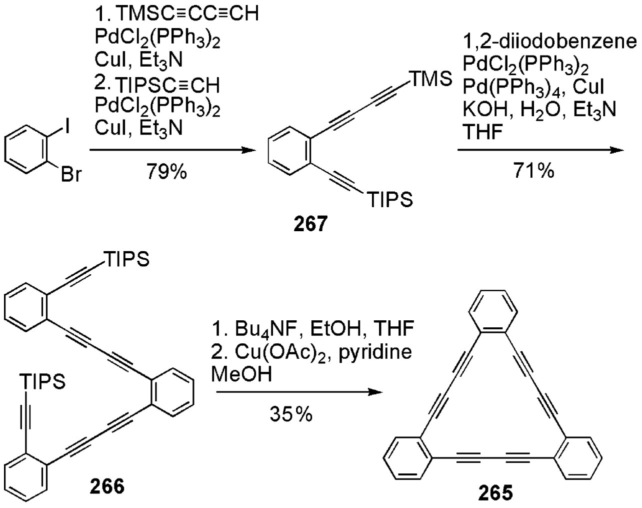
Haley and co-workers introduced a new tribenzo[16]-cyclyne topology in 1997 with the production of **264** via a multistep intramolecular route (Figure 59).[168] Tetrakis(4,5-dialkoxyphenyl)tetraynes **263b** and **263c** were produced by Youngs et al. in 12−16% cyclization yield as coproducts during the Cu-mediated intermolecular synthesis of triynes **228e** and **228f**.[149]

5.5. Dehydrobenzo[18]annulenes

5.5.1. Substructures of Extended Networks

Tribenzo[18]annulene **265**, first targeted by Eglinton and Galbraith in 1960 via intermolecular coupling of *o*-diethynylbenzene,[122] was not isolated until 40 years later by Haley's laboratory.[169] Cycle **265** was obtained in 35% yield via Cu-mediated intramolecular homocoupling of hexayne **266** following desilylation (Scheme 22). The key triethynyl arene intermediate **267**, produced from selective, successive alkynylations of 2-bromoiodobenzene, was reacted with 1,2-diiodobenzene under in situ deprotection/alkynkylation conditions, a procedure the group developed to overcome the inherent instability of terminal phenylbutadiyne moieties.[168] Incorporation of two decyl groups into **265** was found to improve the yield of the final step (56%) as well as cycle solubility. Diatropicity of the [18]cyclyne was confirmed by a small but distinct downfield shift ($\Delta\delta = 0.2{-}0.25$) of the arene protons upon cyclization. A slight hypsochromic shift in absorption (<19 nm) for the tribenzo derivative **265** compared to [18]annulene (**136**) indicated limited electronic effect from benzannelation.

Scheme 22



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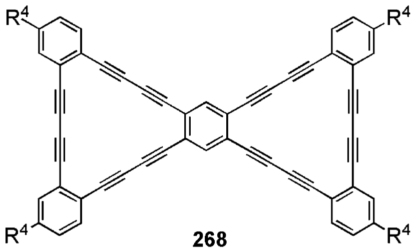
265

Due to lack of feasible synthetic routes to graphdiyne, substructures based on cycle **265**, which could be considered a core structure for the extended network, have been produced to gain insight into materials properties of the bulk nonnatural allotrope. The Haley group expanded their initial synthesis of **265** to produce several macrocyclic systems composed of two (**268**−**270**),[169] three (**271**−**273**),[169−171] and four (**274**−**276**)[171] fused dehydrobenzo[18]annulenes (Figure 60). Macrocyclization of the smaller systems (**268**−**272**, 6−88% yields) was accomplished with a combination of both Cu(I)- and Cu(II)-mediated homocoupling in pyridine and MeOH, while both Pd- and Cu-mediated homocoupling techniques were used for construction of **273**−**276** (1−49% yields). Comparison of the UV−Vis spectra of the allotropic substructures indicated that chromophore length instead of overall conjugation dominated electronic absorption. Specif-



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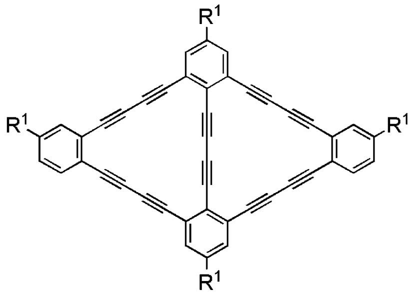

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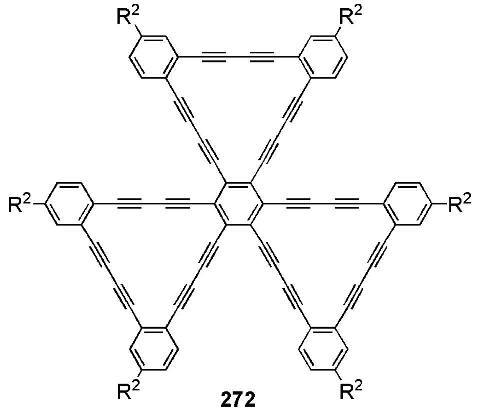

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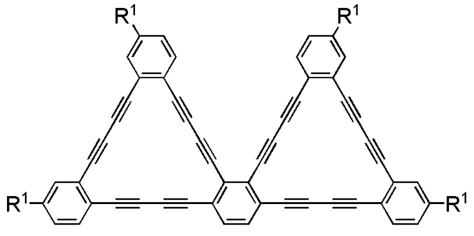

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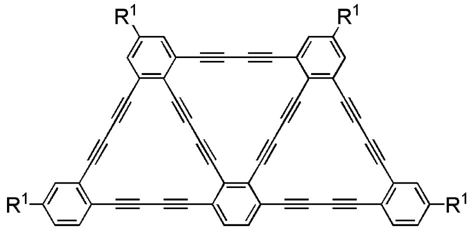

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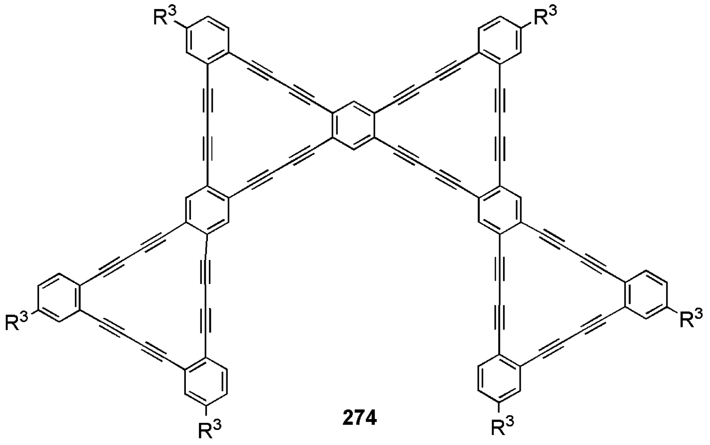

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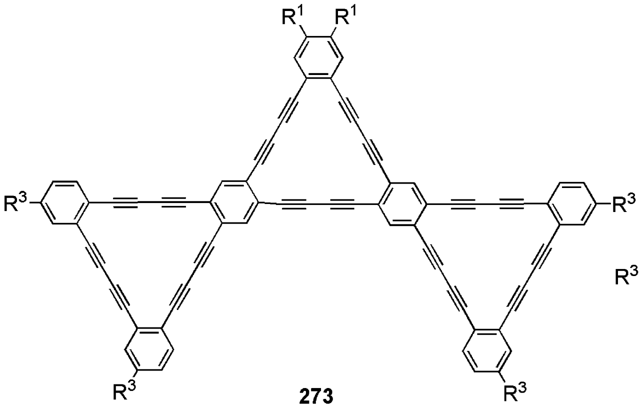

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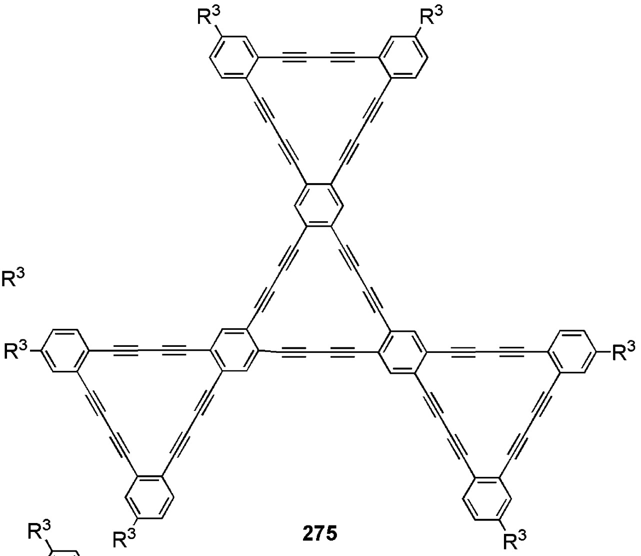

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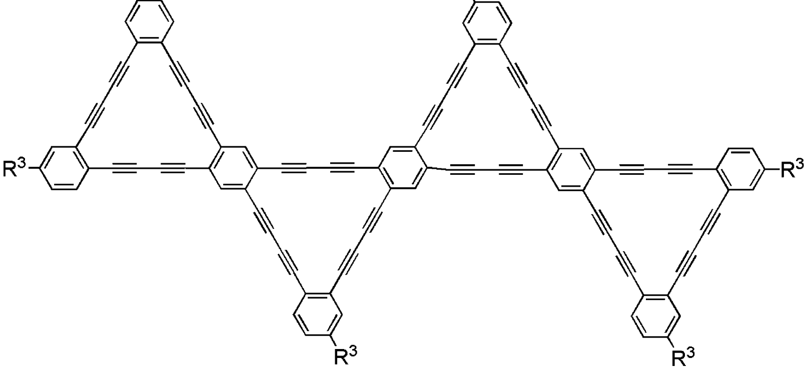
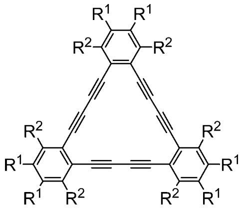


276

R^1 = Dec
R^2 = Dec or *t*-Bu
R^3 = 3,5-di(*t*-Bu)Ph
R^4 = Dec or *t*-Bu or 3,5-di(*t*-Bu)Ph

Figure 60.

Table 11. Dehydrobenzo[18]annulenes 277a−h



DBA	R^1	R^2	ref
277a	Dec	H	128,172,178
277b	ODec	H	128,172
277c	ODodec	H	172
277d	OTetradec	H	172
277e	OHexadec	H	172
277f	F	F	130
277g	Hex	H	128
277h	Bu	H	178

ically, bowtie **268** (λ_{max} = 413, 431 nm), which contains two linear diphenylbutadiyne chromophoric pathways, exhibited bathochromic absorption beyond the constitutional isomer **270** (λ_{max} = 404, 420 nm), which contains only one linear tetrayne pathway, and the more highly conjugated half-wheel **271** (λ_{max} = 411, 426 nm). Substructure **276**, the largest carbon-rich single molecule (~5 nm) based on the graphdiyne network, exhibited electronic absorption ($\log \epsilon = 5.59$; λ_{max} = 462 nm) that fell only 23 nm short of a calculated saturation wavelength for graphdiyne. The new substructures all exhibited exothermic decomposition above 200 °C with broader or more disordered transitions associated with the larger systems (**272**−**276**). Although several different solubilizing groups were explored, the largest substructures suffered from poor solubility predicted for the parent network; specifically, **275** and **276** could not be characterized by NMR spectroscopy.

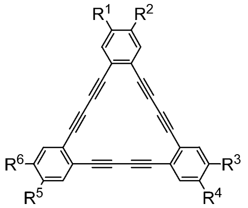
5.5.2. Precursors for Polymerization and Intermolecular Networks

A recent collaboration between the Haley and Tobe laboratories resulted in isolation of tribenzo[18]cyclynes **277a**−**e** (Table 11) and investigation of self-assembly of the derivatized molecules via STM.[172] The cyclynes, obtained by Hay coupling in CH_2Cl_2 in 8−15% yield, required recycling GPC purification to remove homocoupling byproducts. Although Swager reported **277a** and **277b** in 1994, the cycles were analyzed only as a mixture with tetrameric and oligomeric components by ^{1}H NMR spectroscopy.[128] Use of Pd-catalyzed homocoupling in *i*-Pr_2NH and THF surprisingly produced trimeric and tetrameric analogues without dimeric octadehydrodibenzoannulene byproducts. Initial STM studies elucidated formation of quadratic monolayers for shorter chained systems (**277b**) but linear monolayers for cyclynes with R ≥ ODodec (**277c**−**e**), a factor attributed to less efficient substituent chain interdigitation resultant from the lengthened butadiyne spacer.

5.5.3. Electron Donor–Acceptor Systems

On the basis of the group's successful approach to **265**, Pak and Haley reported a series of novel site-specific electron-donor- and/or -acceptor-functionalized [18]annulenes (**278a**−**p**, Table 12) in 1999.[173] A stepwise intramolecular synthesis starting with functionalized 1,2-dihaloarenes allowed access to previously inaccessible asymmetric C_{2v} and C_s topologies, a pronounced deficiency of intermolecular cyclotrimerization. UV−Vis spectroscopy, specifically the effects on the four characteristic $\pi-\pi^*$ absorption bands of the [18]cyclyne core, was used to investigate the structure−property relationships of the new donor−acceptor systems. The alkoxy systems (**278b**,**c**,**p**) exhibited a bathochromic shift and broadening of the low-energy absorption but retained the annulenic core pattern, suggestive of electron localization in the cyclyne core. Incorporation of stronger donor or acceptor functionalities (e.g., NBu_2, NO_2) resulted in broadened absorption pattern, increased molar absorptivity, and bathochromic λ_{cutoff} values. The greatest low-energy absorption (λ_{max} = 422 nm, ϵ = 57 300 M^{-1} cm^{-1}) was observed in cycle **278n**, composed of strong donors and acceptors as well as a linear conjugation pathway between the substituents. Further study of conjugation pathway between donor−acceptor substituents showed that linear relationships (**278n**) provided enhanced charge transfer compared to cross-conjugated isomers. Four of the systems (**278j**−**m**) and a new hexasubstituted analogue (**278q**) were further analyzed for second-order NLO susceptibility in 2001.[174] Cycle **278j**, which possessed a dipolar solid-state structure, exhibited the largest second-order NLO response as well as superior β values compared to 4-(dimethylamino)-4′-nitrostilbene. Systems **278r**−**w** were more recently produced to explore alternate donor (NHBu) and acceptor (CN, CO_2Me) groups.[175]

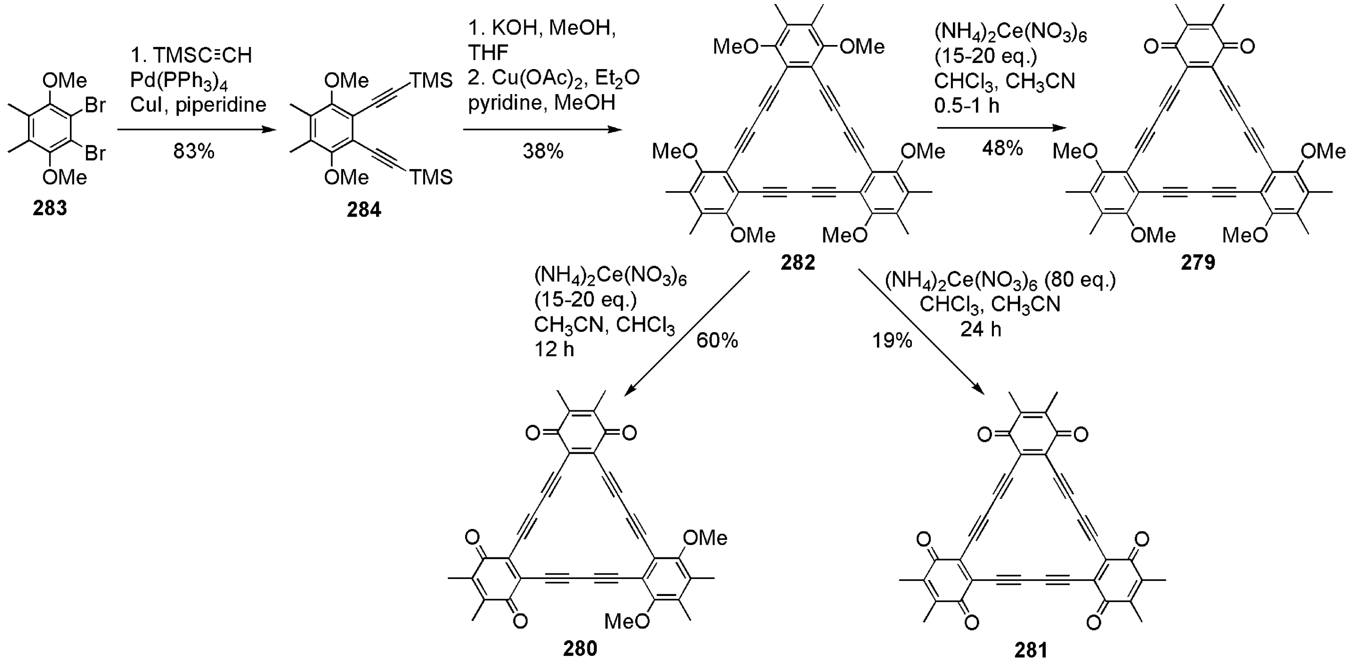
Table 12. Dehydrobenzo[18]annulene Electron Donor−Acceptor Systems 278a−w



DBA	R^1	R^2	R^3	R^4	R^5	R^6
278a	Dec	Dec	H	H	H	H
278b	OMe	OMe	H	H	H	H
278c	OOct	OOct	H	H	H	H
278d	H	H	H	NO_2	NO_2	H
278e	Dec	Dec	H	NO_2	NO_2	H
278f	OMe	OMe	H	NO_2	NO_2	H
278g	OOct	OOct	H	NO_2	NO_2	H
278h	NBu_2	H	H	H	H	H
278i	H	H	H	NBu_2	NBu_2	H
278j	NO_2	H	H	H	H	NBu_2
278k	NO_2	NBu_2	H	H	H	H
278l	NO_2	H	H	NBu_2	H	H
278m	NO_2	NBu_2	H	NO_2	NBu_2	H
278n	NO_2	NBu_2	H	NBu_2	NO_2	H
278o	OH	NO_2	H	NBu_2	NBu_2	H
278p	$-O(CH_2CH_2O)_4-$		H	H	H	H
278q	NO_2	NBu_2	NO_2	NBu_2	NO_2	NBu_2
278r	NO_2	NBu_2	NO_2	NBu_2	NBu_2	NO_2
278s	NHBu	NO_2	H	NO_2	NBu_2	H
278t	NHBu	NO_2	H	CN	NO_2	H
278u	CN	CN	H	NBu_2	NBu_2	H
278v	Dec	Dec	H	CN	CN	H
278w	CO_2Me	H	CO_2Me	H	CO_2Me	H

In 2004, Komatsu's group published a series of *p*-benzoquinone-fused hexadehydro[18]annulenes (**279**−**281**) as well as hexadonor **282**.[176] Synthesis began with Pd-catalyzed cross coupling of dihaloarene **283** and TMSA (Scheme 23). Desilylation of the resultant diyne (**284**) with KOH and use of oxidative Eglinton conditions afforded the [18]annulene **282** in 38% yield. Different electron-donor and/

Scheme 23



or -acceptor systems were obtained by sequential oxidative replacement of dimethoxyarene rings with electron-accepting *p*-benzoquinone moieties. Treatment of **282** with 15−20 equivalents of CAN over 1 h afforded **279**, while increased reaction time (12 h) produced **280**. Trisquinone system **281** required 24 h with 80 equivalents of CAN. The intramolecular charge transfer of **279** and **280**, which was confirmed with DFT calculations, resulted in superior absorption spectra ($\lambda_{\mathrm{cutoff}} \approx 600$ nm) and broadened low-energy bands compared to trisdonor **282** and trisacceptor **281**. The solvatochromism exhibited by **279** and **280** was very limited, a combination of poor solubility of the cyclynes and delocalization of the HOMO−LUMO over the entire cyclyne π system. Incorporation of *p*-benzoquinone moieties was also found to increase diatropicity of the [18]cyclyne core due to the enhanced double-bond character at the site of ring fusion.

5.5.4. Aromaticity Probes

Bowtie **285** represents the sole [18]annulene dimethyldihydropyrene probe produced in Haley and Mitchell's collaboration (Figure 61).[164a] The downfield shift of arene proton resonances upon cyclization was attributed to through-space deshielding caused by an interior annulene ring current. The larger changes in chemical shift for hybrid **285** compared to benzocyclyne analogue **268** agreed with previous assertions that DMDHP is less aromatic than benzene and hence less able to bond fix a fused arene.

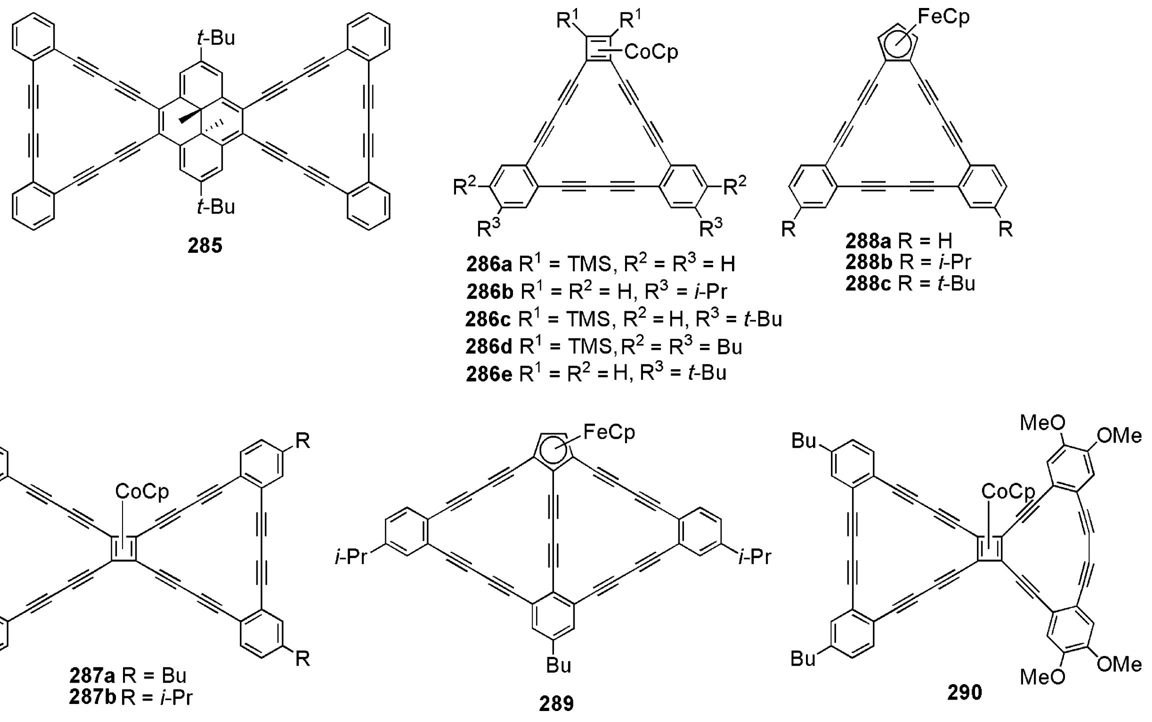


Figure 61.

5.5.5. Organometallic Assemblies

Concurrent with isolation of the [14]annulenes described in section 5.3.4, Bunz and co-workers prepared several organometallic [18]annulene analogues (**286**−**289**, Figure 61) as well as a hybrid bowtie system consisting of 14- and 18-membered cycles fused to a central cyclobutadiene−CoCp complex (**290**).[165c,d,177] Transmission electron microscopy of the HCl-treated soot from explosive decomposition of **288a** showed a variety of onion-shaped carbon nanostructures which became increasingly ordered upon annealing up to 900 °C. Preorganization of the butadiyne moieties was concluded as a key factor for explosive decomposition, which occurred only with crystalline samples instead of precipitated powders. Additionally, cycle **288a** exhibited a unique difference in solid-state structure from the other organometallic systems that possibly accounted for the propensity to form ordered carbon-rich structures: the diyne units of adjacent systems possessed several close contacts, i.e., the bonds were within the sum of the van der Waals radii (3.6 Å) for sp-C atoms.

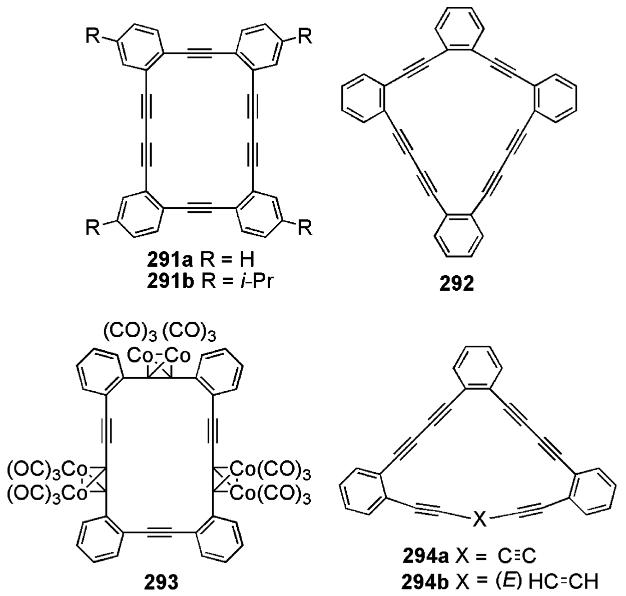
5.5.6. Novel Topologies

Komatsu's octafluoro-trimeric cyclyne **277f** and two hexaalkyl [18]cyclynes (**277g**,**h**) obtained independently by Swager and Baranovic's groups have also been reported (Table 11). Polyfluorinated **277f**, obtained as a coproduct with dimeric **209c** from homocoupling of 1,2-diethynyl-3,4,5,6-tetrafluorobenzene, underwent exothermic decomposition at 221 °C, almost 11 °C lower than the parent [18]annulene.[130] Although several different alkyl- (Bu, Dec, Dodec) and alkoxy-substituted (ODec) analogues were characterized as mixtures in NMR spectroscopy, cycle **277g** was effectively isolated from tetrameric and oligomeric components during Swager's investigation in 1994.[128] Baranovic and co-workers recently published a detailed vibrational spectroscopy study on **277a** and **277h** as well as several theoretical hexasubstituted analogues of **265**.[178]

5.6. Dehydrobenzo[20]annulenes

5.6.1. Precursors for Polymerization and Intermolecular Networks

Boese, Matzger, and Vollhardt produced the first tetrabenzo-[20]annulene (**291a**) in 1997 by Eglinton coupling of bis-(2-ethynylphenyl)ethyne in low yield (Figure 62).[179] The twisted D_2-symmetric confirmation of cycle **291a** as shown by X-ray crystallography was not susceptible to UV-light-induced topochemical polymerization like **237**; however, the system exploded violently under vacuum at 245 °C to afford ordered onion- and tube-type nanostructures. Cycle **291b** was subsequently produced to explore the possible enantiomerization of the chiral, twisted solid-state structure. Low-temperature NMR spectroscopy of **291b** ($\Delta G^{\ddagger} = 9$ kcal mol^{-1}) showed an enhanced interconversion rate not only beyond tetrabenzocyclooctatetraene ($\Delta G^{\ddagger} > 45$ kcal mol^{-1}) but cyclooctatetraene as well. Haley and co-workers simultaneously reported an isomeric [20]cyclyne topology (**292**) which displayed a saddle-like distortion and generated 50 kJ mol^{-1} more energy upon decomposition than **291a** as well as an alternate synthesis of **291a** via their in situ deprotection/alkynylation route.[168] The enhanced energy of decomposition of **292** was attributed to a combination of greater alkyne distortion and difference in solid-state packing.



291a R = H
291b R = *i*-Pr
292
293
294a X = C≡C
294b X = (*E*) HC=CH

Figure 62.

5.6.2. Organometallic Assemblies

Production and thermal decomposition of hexanuclear Co-complex **293** (Figure 62) was published 2 years after the report of cycle **291a**.[180] In contrast to the carbon-rich system, the organometallic analogue decomposed below 200 °C with the release of CO. Thermal treatment up to 800 °C resulted in formation of carbon onions and multiwalled nanotubes with metal composition concentrated amorphously or coating the tubes and onions.

5.6.3. Novel Topologies

A single tribenzo[20]heptayne (**294a**) and partially reduced analogue (**294b**) have also been prepared by Haley's group.[168b,181] In agreement with an anti-aromatic π system, the new [20]cyclynes exhibited either weakly paratropic or atropic behavior compared to *ortho*-diethynylbenzene in NMR spectroscopy. The unrestrained rotation of the isolated alkene bond was clearly demonstrated when the vinyl protons of **294b** did not resolve into discreet resonances in low-temperature NMR spectroscopy at −90 °C.

5.7. Higher Dehydrobenzo[*n*]annulene Systems ($n > 20$)

Four dehydrobenzo[22]annulenes (**295**, **296**, Figure 63) have been reported to date, all produced in 1997 and 1998 by Haley's group.[168,181] Cycle **296a**, of note as one the first two triacetylenic annulenes (see also **294a**, section 5.6.3), was obtained in a near identical fashion to **265** with a phenylhexatriyne synthon instead of butadiyne-substituted **267** (Scheme 22). Although cycles **296a**−**c** all exhibited diatropic shifts upon cyclization, the proximal ($\Delta\delta$ 0.05−0.08) and distal ($\Delta\delta$ 0.02−0.05) arene protons of the systems containing either one or two *E*-alkene bonds were paratropically shifted compared to benzocyclyne **296a**. The more constrained topologies of **296b** and **296c** resulted in larger interconversion rates ($\Delta G^{\ddagger} = 18.9-19.1$ kcal mol^{-1}) and temperatures ($T_c = 94-115$ °C) for alkene moieties compared to **294b** as well as [18]annulene.

Hexadecadehydrotetrabenzo[24]annulene **297a** was first reported in 1994 by Youngs and co-workers (Figure 63).[182] Similar to Sondheimer's route to [24]annulene in 1970,[183]

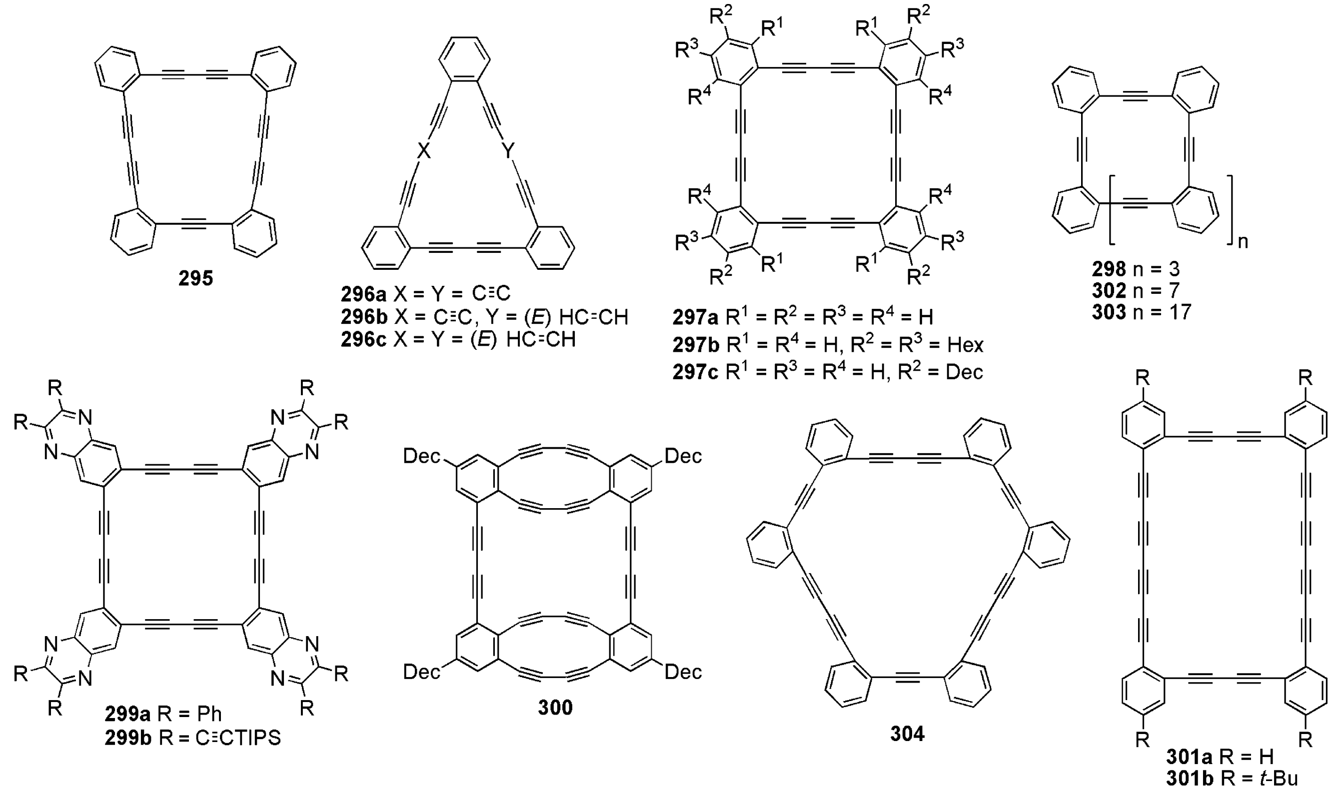


Figure 63.

intermolecular Glaser homocoupling of bis(2-diethynylphenyl)ethyne afforded the parent cyclyne in 50% yield. The crystal structure of **297a** displayed a characteristic saddle-like distortion, suggestive of localized π-electron density, and limited ethynyl distortion (0.6−6°). In the same year, Youngs' group introduced an additional hexabenzo[24]-cyclyne topology (**298**), which exhibited more significant ethynyl distortion (1.2−8.1°) as well as a distorted boat conformation with D_2 symmetry instead of the expected boat conformation.[167] An alternate intramolecular route to **297a** using triyne **267** was published in 1997 by Haley.[168] Several substituted analogues of **297a** have also been reported by Swager (**297b**),[128] Haley (**297c**),[135] and Faust (**299a**,**b**).[136]

Macrocycle **300**, an unusual topology containing a [24]-cyclyne and two [12]cyclyne cores, was isolated by Haley's group in 2004 from a key polyyne intermediate used for fenestrane **261** (Figure 63).[135] Treatment of (2,2′,6′6′-tetraethynyl)diphenyl-2,4-butadiyne with $Cu(OAc)_2$ and CuCl in pyridine at 50 °C resulted in initial intramolecular homocoupling, which formed the [12]cyclyne core, followed by intermolecular cyclization to afford the [24]cyclyne ring. The electronic absorption spectra of **300** exhibited a 75 nm red-shifted λ_{cutoff} and 35 nm greater $\lambda_{\max}$ than **297c** and **209e**, respectively.

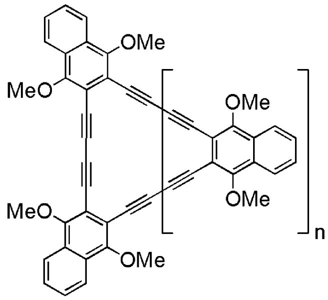
Tetrabenzo[32]cyclynes **301a** and **301b** (Figure 63), reported in 1997 by Haley et al. via Cu-catalyzed cyclization in 51−64% yield, were the first reported DBAs containing tetrayne linkages.[184] The tetrayne moiety was constructed by in situ desilylation and dimerization of butadiynyltrimethylsilane groups via addition of K_2CO_3 to Eglinton homocoupling conditions. In contrast to smaller cycles, cyclization of **301a** and **301b** exhibited very minimal (<2 nm) bathochromic absorption compared to the hexayne precursor, a factor attributed to the large size and nonplanar structure. The electronic absorption spectra of the remarkably stable dodecayne system, which exhibited no decomposition over several weeks in solution or the solid state, was only slightly red shifted (≤20 nm) beyond the characteristic pattern of 1,8-diphenyloctatetrayne.

Youngs and co-workers' interest in carbon-rich cycle precursors for rigid-rod polymers and fullerene tubules resulted in isolation of dehydrobenzo[40]annulene **302** in 1993.[160] The large DBA was produced by 2-fold intermolecular cross coupling of phenylacetylene oligomers. The crystal structure exhibited a highly distorted, compact structure, the result of $\pi-\pi$ interaction between two nonadjacent phenyl rings.[185] Further investigation of the cyclization reaction by time-of-flight secondary ion MS showed higher analogues (n = 17, 27, 37, and 47) from the intermolecular coupling; however, only **303** was isolated as a discreet product from the higher homologues. Vollhardt's group was also able to isolate large macrocyclic byproducts during production of **291a**, namely, [30]annulene **304** in 5% yield as well as trace amounts of a pentameric [50]annulene characterized by NMR spectroscopy and MS.[159]

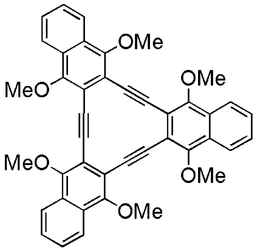
6. Other Arene-Fused Annulenes

6.1. Naphtho-Fused Systems

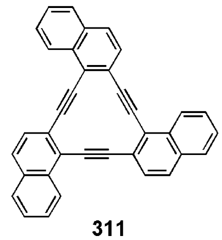
Komatsu et al. reported a series of 2,3-annelated 1,4-dimethoxynaphthalene cycles (**305**−**310**) in 1998 (Figure 64).[186] Alkynylation of 2,3-dibromo-1,4-dimethoxynaphthalene followed by desilylation with KF and Eglinton homocoupling conditions afforded cycles **305**−**309** in low yield with [18]annulene **306** as the prevalent species (31% yield). Pd-catalyzed cross coupling of 2-methyl-3-butyn-2-ol with 2,3-dibromo-1,4-dimethoxynaphthalene followed by in situ deprotection/3-fold cyclotrimerization produced trinaphtho-[12]cyclyne **310** in 25% yield. Comparison of ^{1}H NMR spectra showed very little difference between the new cycles, attributed to rapid conformational changes for the nonplanar



305 n = 0
306 n = 1
307 n = 2
308 n = 3
309 n = 4



310



311

Figure 64.

systems (**307**−**309**) and lack of ring current in the central annulene core. The atropicity of the naphtho−annulenes was confirmed with the crystal structure of **310**, which indicated increased bond length (∼0.03 Å) of the 2,3-naphtho fusion site. Minimal variance in redox potentials between antiaromatic (**305**) and aromatic systems (**306**) provided further evidence that the systems were better attributed as naphthalene moieties connected by alkyne bonds instead of DBAs. An additional trinaphthocyclyne (**311**) with fusion at the 1,2-positions was recently reported by She and Pan and co-workers.[140] While use of THF as solvent afforded only trace amounts of product, the group's previously discussed use of an ionic liquid as solvent afforded the cycle in 16−21% yield.

6.2. Azuleno-Fused Systems

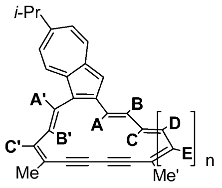
Ojima, Yasunami, and co-workers prepared both dehydro[14]- and [16]annulenes fused with azulene rings (**312** and **313**).[187] Their chemical shifts were then compared to benzo-fused annulenes **314** and **315** to determine effects on ring tropicity (Table 13).[188] The roughly analogous internal and external protons in **312** are consistently upfield and downfield from those in **314**, respectively. Between **313** and **315**, the trend is the opposite. Taking these shifts as an evaluation of aromaticity, it is clear that fusion to an azulene system causes much less attenuation of diatropic/paratropic character. This gives rise to the possibility of using the "strength" of a particular system, fused to an annulene, in suppressing tropicity to quantify that system's aromaticity itself.

7. Heterocycle-Fused Annulenes

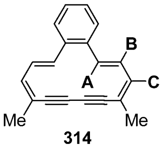
7.1. Pyrido-Annulenes

Baxter and Dali-Youcef recently synthesized the first all nitrogen heterocyclic *o*-fused dehydroannulenes (**316**, **317a**, Figure 65) as well as an additional hybrid cycle containing both pyridine and benzene rings (**317b**).[189] [20]Annulene systems **317a** and **317b** were constructed in a stepwise intramolecular fashion by selective alkynylation of 3-bromo-4-iodopyridine, whereas tripyrido[12]cyclyne **316** was obtained via intermolecular 3-fold coupling of 4-ethynyl-3-iodopyridine. Cycle **316** possessed a selective photoluminescent quenching sensory response for Pd(II) and also precipitated as a coordination polymer upon high Ag(I) concentrations.

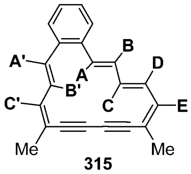
Table 13. Azuleno-Fused Systems 312 and 313, δ ppm



312 n = 0
313 n = 1



314



315

δ, ppm

^{1}H	312	314	313	315
A	3.81	4.99	9.89	1.70
A′	6.83		6.55	5.94
B	8.10	7.44	6.35	5.73
B′	4.70		10.00	6.07
C	7.36	7.08	8.75	9.42
C′	7.74		6.11	6.07
D			7.11	5.73
E			5.90	5.94
Me	2.55	2.36	1.66	1.70
Me′	2.48		1.65	

7.2. S-Based Heteroannulenes

7.2.1. Dehydrothieno[12]annulenes

Youngs reported the first thienocyclyne (**318**, Figure 65) in 1990 from cyclotrimerization of 3-ethynyl-2-iodothiophene via Stephens−Castro conditions in 20% yield.[190] The initial route for the 2,3-thieno-fused cycle from trimerization of isomeric 2-ethynyl-3-iodothiophene starting material produced only insoluble orange material. Interest in the cycle originated from successful metal complexation of **207** and a calculated larger internal cavity for **318**, anticipated to cavitate Pd or Pt atoms. An organometallic complex of **318** was isolated 4 years later; however, the tetranuclear Co complex exhibited significant distortion of the cyclyne core with Co complexation of only two alkyne groups.[190b]

Several additional 3,4-thienofused cyclyne analogues (**319a**−**d**, Figure 65) were published by Youngs' group in 1999 while investigating liquid crystallinity of substituted cyclynes.[149] The new systems were prepared from sequential, selective alkynylation of tetraiodothiophene and cyclized with Pd(0) in 1−25% yields. The cyclotriynes gradually decomposed under ambient conditions and did not display liquid crystallinity. The crystal structures showed that $\pi-\pi$ interactions between cyclyne cores were prevented by intermolecular attractions of substituent chains and conjugated cores, thus precluding columnar or slipped stacked arrangements exhibited by other known liquid crystalline systems.

Iyoda and co-workers produced the first parent thieno[12]annulene with fusion in the 3,4-positions (**319e**, Figure 65) in 2004 by Pd-catalyzed 6-fold coupling of 3,4-diiodothiophene with acetylene gas in 37%.[138] The group noted a significant increase in reaction rate for the diiodo-

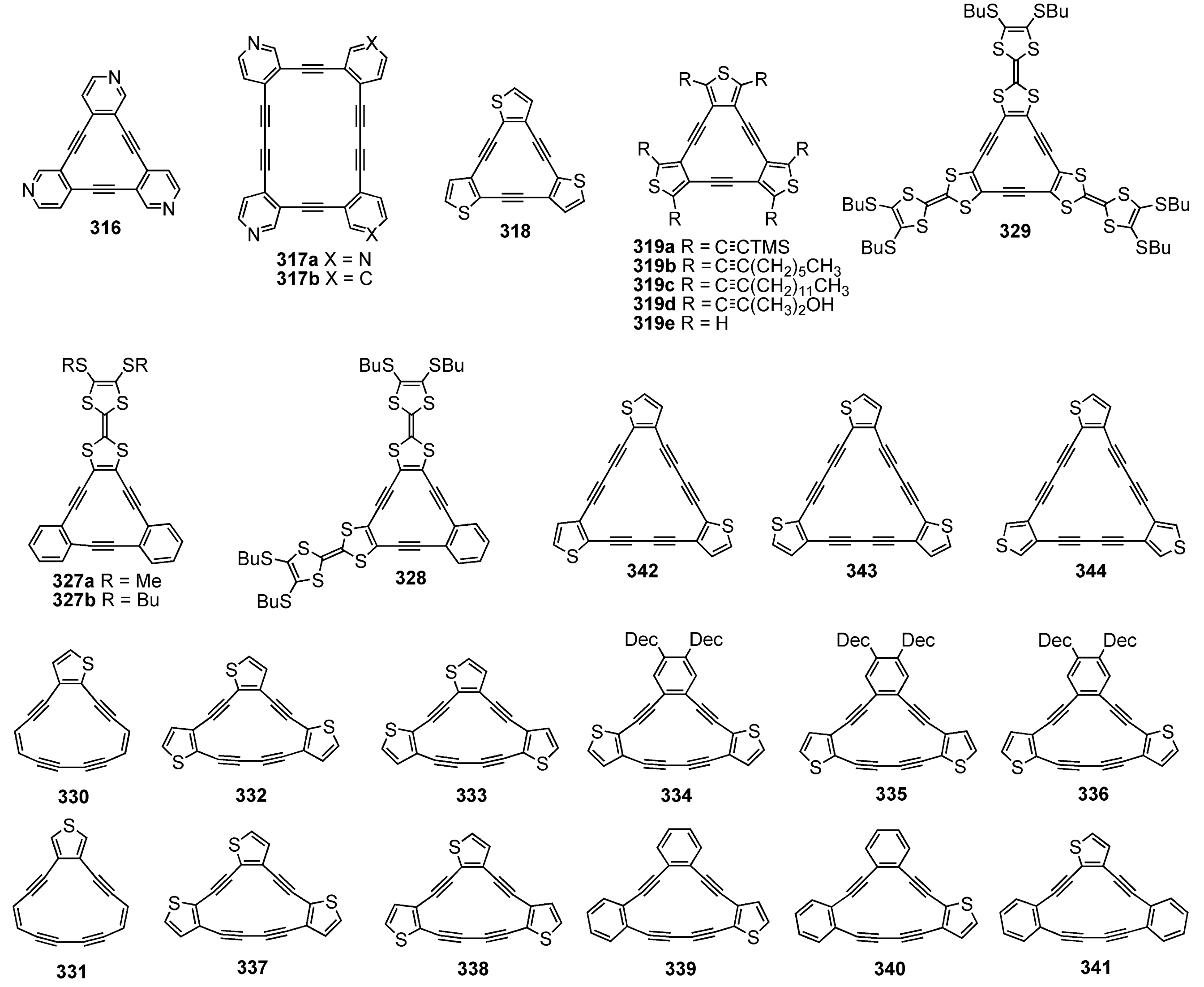


Figure 65.

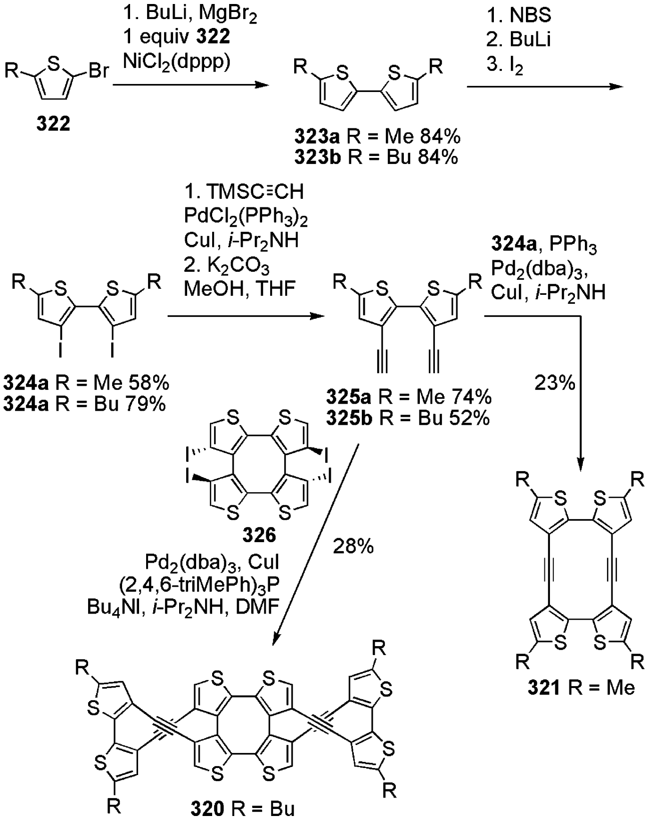
thiophene starting material compared to arene systems. A 2:1 sandwich complex of **319e** with Ag was proposed as a staggered conformation based on minimal changes in ^{1}H NMR spectra, a contrast with lack of shielding expected for an eclipsed conformation.

Investigation of single-molecule electromechanical actuators and molecular muscles by Marsella's group afforded additional octa- and tetrathiophene topologies **320** and **321** in 2000 and 2002, respectively.[191] Synthesis began with 5-alkyl-2-bromothiophene **322**, obtained from the corresponding alkylthiophene via bromination (Scheme 24). Conversion of **322** to a Grignard intermediate with BuLi and $MgBr_2$ and subsequent Ni-mediated homocoupling provided bithiophene **323** in 84% yield. Bromination of the 3,3′-positions followed by lithiation and iodination provided **324** in slightly lower yield. Cyclization precursor **325** was obtained in 52−74% yield by Pd-catalyzed cross coupling of TMSA followed by desilylation with weak base. Fourfold Pd-catalyzed cross coupling of **325b** with previously reported tetraiodotetrathienylene **326** afforded the octa-aryl double helix **320** in 28% yield. Key intermediate **325a** was more recently reacted with diiodobithiophene **324a** to produce the diyne macrocycle **321** in comparable cyclization yield. A large redox-induced conformational change between twisted and planar topologies, associated with an 18% change in distance, was predicted for the two-electron oxidation of **321** based on DFT calculations. The associated inversion barrier (9.7 kcal mol^{-1}) was calculated to be less than the parent tetra(2,3-thienylene), which bodes well for the group's target of actuating electromechanical stimuli through regiospecific homopolymers.

7.2.2. Tetrathiafulvaleno[12]annulenes

Mono- (**327**), bis- (**328**), and tristetrathiofulvalenylacetylene (**329**) macrocycles were reported by Iyoda et al. in 2004 (Figure 65).[192] The π-amphoteric systems, the result of tetrathiafulvalene (TTF) donor and [12]cyclyne acceptor moieties, were constructed with stoichiometric Pd and Cu catalysts under Krause's conditions in moderate to low yields (17−53%). The solid-state structure of **327a** displayed a slipped-stack dimeric association with a staggered cofacial array in addition to boat conformations for the TTF moieties. CV studies indicated a four-step redox process for the hybrid cycles **327** and **328** with oxidation potentials suitable for service as conducting radical salts. The hybrid cycles also formed sandwich complexes with Ag salts, both assigned as staggered conformations from upfield shifts in ^{1}H NMR spectroscopy.

Scheme 24



7.2.3. Dehydrothieno[14]annulenes

Over the past 5 years the Haley group has prepared a large collection of novel thioannelated octadehydro[14]annulenes (**330**−**341**, Figure 65). Monothiophene systems **330** and **331**, which readily polymerized upon concentration to afford an insoluble material, were found to survive for several weeks in dilute solutions at −20 °C, a sufficient time to characterize the systems with MS and NMR/UV−Vis spectroscopy.[80b] Asymmetric cyclyne **330** was found to be more aromatic by ring current criterion than **331** due to an increased double-bond character at the site of ring fusion. Cycles **332**−**341** have recently been prepared by the group, and electronic absorption and CV studies are currently underway.[193]

7.2.4. Dehydrothieno[18]annulenes

In an analogous route to **265**, Sarkar and Haley isolated regioisomeric dehydrothieno[18]annulenes **342**−**344** in 2000 via a thieno analogue of intermediate **267** (Figure 65).[194] Although longer than traditional 3-fold intermolecular trimerization routes for [18]cyclynes, the intramolecular route provides the only route to asymmetric C_{3h} and C_s isomers. Cycles **342** and **343** displayed enhanced electronic absorption spectra ($\lambda_{\max} = 428$ nm) compared to the 3,4-fused trithienocyclyne **344**, a factor attributed to the enhanced double-bond character of 2,3-fusion and more efficient overall conjugation. The three macrocycles were transformed to insoluble black material above 150 °C over a narrow temperature range in DSC measurements. Under TGA, a minimal weight loss (<5%) at the corresponding DSC exotherm suggested a solid-state polymerization reaction for cycle **342**.

8. Conclusions

This review illustrates the complex diversity of structures and wide variety of uses of annulenic molecules. No longer are these aesthetically pleasing compounds purely the realm of physical organic chemists. Besides traditional application as probes for ring currents, annulenes now have demonstrated potential as DNA cleaving agents, optoelectronic materials, molecular actuators, and sources for novel carbon allotropes. Such new uses, coupled with modern techniques for their synthesis, have truly heralded a renaissance in annulene chemistry, a renaissance that should continue for some considerable time.

9. Acknowledgments

The authors thank the University of Oregon graduate and undergraduate students and postdoctoral associates who made our work on annulene chemistry possible. The National Science Foundation, the Petroleum Research Fund, and the University of Oregon are gratefully acknowledged for support of this research. C.A.J. and E.L.S. acknowledge the NSF for IGERT fellowships.

10. Note Added after ASAP Publication

This paper was posted ASAP on September 19, 2006. Changes were made to the second paragraph of section 2.3.1, and ref 34b was added. The paper was reposted on October 23, 2006.

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CR050541C