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Strained Dehydrobenzoannulenes

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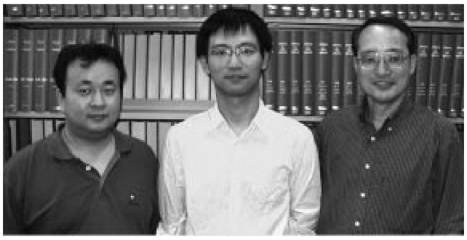
Dehydrobenzoannulenes (DBAs) have been attracting a great deal of interest as a result of their potential applications as optoelectronic materials, precursors of new forms of carbon materials, and as building blocks for hitherto-unknown 2D carbon networks consisting of sp and sp^2 carbon atoms. Among the DBAs, those with substantial strain due to bond-angle deformation at the triple bonds exhibit greater potential as electronic communication units and precursors of new polycyclic, conjugated ring systems owing to their high reactivity towards carbon–carbon bond-forming reactions. It is also of interest to see how the deformation of triple bonds affects the cyclic conjugation of π systems, that is, the aromaticity/antiaromaticity of DBAs. This article reviews these characteristic aspects of strained DBAs.

1. Introduction

Dehydrobenzoannulenes (DBAs), benzo-annelated dehydro[*n*]annulenes that are also called benzocyclynes, have been known for many years; they were investigated extensively during the late 1950s through to the mid-1970s in connection with the study on the aromaticity/antiaromaticity of annulene ring systems.[1] Because magnetic criterion is regarded as one of most critical measures of aromaticity/antiaromaticity in annulenes, the specific term "tropicity", which refers to the induction of either diamagnetic (diatropic) or paramagnetic ring current (paratropic) under an external magnetic field, has developed.[2] Incorporation of triple bonds into an annulene ring restricts the otherwise possible *cis–trans* isomerism of C=C double bonds and rotation around C(sp^2)–C(sp^2) single bonds, rendering the flexible annulene ring persistently planar and thereby en-



Ichiro Hisaki (middle) received his B.Sc. from the Faculty of Engineering Science, Osaka University, in 2000 and his Ph.D. from the Graduate School of Engineering Science, Osaka University, in 2005 under the direction of Professor Yoshito Tobe, conducting research on the synthesis and characterization of highly unsaturated, strained dehydroannulenes. He was a visiting scholar with Professor K. Peter C. Vollhardt at the University of California, Berkeley, in 2004. After JSPS postdoctoral research with Professor Atsuhiro Osuka at the Graduate School of Science, Kyoto University he was appointed as an Assistant Professor at the Graduate School of Engineering, Osaka University. His current research interests include the construction of new supramolecular systems.

Motohiro Sonoda (left) received his B.Sc. from the Faculty of Engineering, Osaka University, in 1993 and his Ph.D. from the Graduate School of Engineering, Osaka University, in 1998 under the direction of Professor Shinji Murai. His research was on the direct use of carbon–hydrogen bonds in organic synthesis with the aid of homogeneous transition-metal complexes. After spending ten months as a postdoctoral fellow with Professor Akira Hosomi at the University of Tsukuba, he was appointed as an Assistant Professor at the Graduate School of Engineering Science of Osaka University in 1999. His current research interests include the synthesis of novel conjugated π-electronic systems and their application as organometallic catalysts.

Yoshito Tobe (right) received his doctoral degree from the Graduate School of Engineering, Osaka University in 1979 under the direction of Professor Yoshinobu Odaira. After his doctoral degree, he was appointed as an Assistant Professor at the same institute and was promoted to an Associate Professor in 1984. From 1987–1988, he was a Visiting Professor with Professor Philip E. Eaton at the University of Chicago. In 1992, he moved to the Faculty of Engineering Science of Osaka University and was promoted to a Professor in 1998. As one of his administrative functions, he has been serving as a Member of University Council since 2003. His current research interests include the synthesis of strained organic molecules and novel conjugated π-electronic systems and the self-assembly of shape-persistent molecules. He was a recipient of the Chemical Society of Japan Award for Young Chemists in 1986.

MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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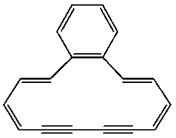
hancing its tropicity. Benzo-annelation to an annulene ring, on the other hand, not only suppresses this geometrical freedom but also bestows remarkable kinetic stability on the highly unsaturated system. Benzo-annelation, however, dramatically reduces the tropicity of the annulene ring because delocalization of the π bonds within the annulene ring competes unfavorably with that of the annelated benzene rings.[3] It also provides a practical index of the degree of aromaticity of the annulene ring annelated to the benzene ring – the Q values derived from the bond order of the specific bonds of the fused benzene ring, which can be correlated experimentally to the ^{1}H NMR coupling constants.[4] Compounds such as [14]DBA **1**,[5] [12]DBA **2**,[6] and [14]DBA **3**[7] represent classic DBAs, which were investigated by the three pioneers of this area of chemistry, Sondheimer, Staab, and Nakagawa, respectively.



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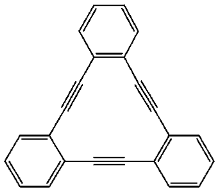

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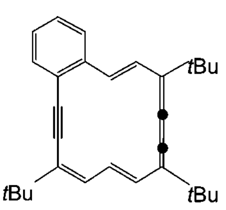

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In conjunction with the recent evolution of the field of carbon-rich molecules,[8] renewed interest in DBAs, owing to their potential applications as optoelectronic materials, as precursors of new forms of carbon materials, and as building blocks for hitherto-unknown 2D carbon networks consisting of sp and sp^2 carbon atoms, foe example, graphyne, has grown.[9] In addition to the above aspects of DBAs, those with substantial strain, mainly due to bond-angle deformation at the triple bonds, exhibit greater potential as electronic communication units and as precursors of new polycyclic, conjugated ring systems owing to their high reactivity towards C–C bond-forming reactions. Needless to say, such extraordinary molecules should provide fundamental information regarding the effect of strain on the physical and chemical properties of organic molecules. For DBAs in particular, it is of interest to see how the deformation of triple bonds affects the cyclic conjugation (i.e., the tropicity) of the π system of DBAs. As shown in Figure 1 for hexadehydrodibenzo[10]annulene (**4**) as an example, even though the overlap between the in-plane p orbitals (outlined lobes) would be considerably disturbed by deformation of the triple bonds, the overlap between the out-of-plane p orbitals (solid lobes) may also be perturbed relative to unstrained systems. In this article we review these characteristic aspects of strained DBAs focusing on those possessing all-carbon (ethynylene, butadiynylene, and hexatriynylene) units as the connecting linkages of aromatic rings, which are represented by the general formula **I** and **II** for dibenzo and tribenzo systems, respectively. In some instances, however, partially ethylene-bridged DBAs are also included for the purpose of comparison. To obtain deformed triple bonds, the sizes of the annulene rings are inevitably limited to 8–14 carbon atoms. Even though para- and metacyclophynes such as **5**,[10] **6**,[11] and **7**[12] possess extremely deformed all-carbon linkages, these are beyond the scope of this article because DBAs are regarded as orthocyclophynes.

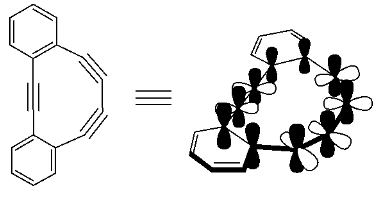

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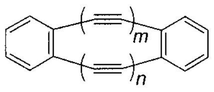
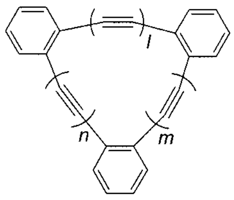
Figure 1. Hexadehydrodibenzo[10]annulene (**4**) and its in-plane (outlined lobes) and out-of-plane (solid lobes) p orbitals.



I



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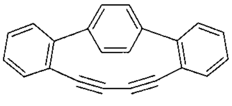

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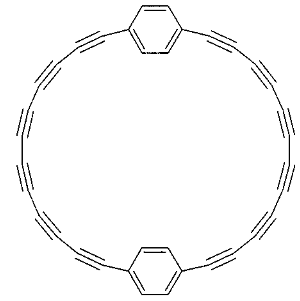

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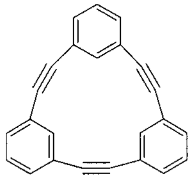

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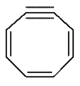
2. Disscusion

2.1 Strained Dehydrobenzo[8]annulenes ([8]DBAs)

Because two excellent reviews on [8]DBAs by Huang and Sondheimer[13a] and by Wong[13b] have already been published, the results obtained by the early 80s are only briefly described herein to allow us to focus more on the results obtained during the last two decades. Since didehydro[8]annulene (**8**)[14] was supposed to adopt a planar conformation, in contrast to [8]annulene (cyclooctatetraene), attempts were made to synthesize **8** to assess the antiaromaticity of a fully conjugated eight-membered carbocycle. However, it turned out that **8** was too reactive for isolation and spectroscopic characterization at ambient temperature; only the products resulting from nucleophilic addition of *tert*-butoxide, [4+2] addition of tetraphenylcyclopentadienone (cyclone), and [2+2] dimerization have been isolated, providing circumstantial evidence of its existence.[14,15] Recently, Stevenson reported that **8** could also be trapped by in situ generated reactive intermediates such as cyclobutadiene and benzyne to form the corresponding [2+2] adducts and that their subsequent in situ reduction produced the corresponding radical anions, which were characterized by ESR spectroscopy.[16] The radical anion of **8** itself was generated by the elimination of HBr from **9a** followed by in situ reduction and was characterized by ESR spectroscopy.[17] The radical anion was also produced in the gas phase by oxidation of cyclooctatetraene by O^- and was characterized by ultraviolet photoelectron spectroscopy (UPS).[18] These results indicated that the radical anion of **8** was indeed planar or pseudoplanar. Similarly to **8**, though tetradehydro[8]annulene (**10**) was not identified, its radical anion was generated from dibromide **9b** and was also characterized by ESR spectroscopy.[19] The radical anion was revealed to be a distorted symmetry-broken species as a result of its complexation with a potassium ion–18-crown-6 complex.



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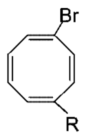
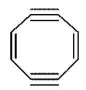


9a R = H
9b R = Br



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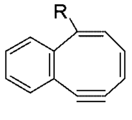
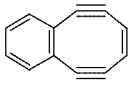


11a R = H
11b R = Me



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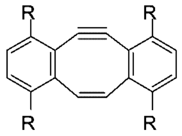
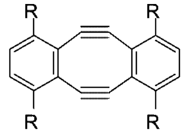
Single benzo-annelation gave rise to substantial kinetic stabilization of the dehydro[8]annulene system. Thus, even though didehydrobenzo[8]annulene derivative **11b** was shown to exist only as a reactive intermediate,[20] tetradehydrobenzo[8]annulene (**12**) was isolated as an unstable yellow oil which decomposed rapidly at 0 °C.[21] The chemical shift of the vinyl proton (δ = 4.97 ppm) of **12** indicated the presence of paratropicity in the eight-membered ring. The radical anions of **11a** and **12** were generated in solution through the corresponding neutral species prepared in situ and were characterized by ESR and ENDOR spectroscopy.[22]

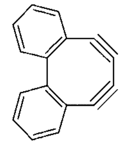
For doubly benzo-annelated systems, there are two possible modes of fusion; one is an *a*,*e*-fusion such as didehydroannulene **13a** and tetradehydroannulene **14a** (of D_{2h} point group) and the other is a C_{2v} symmetric *a*,*c*-fusion such as **15**. While initial attempts to prepare **15** gave no reasonable evidence for its existence,[23a] its formation was later supported by the interception of its [4+2] adduct with a diene in the synthesis of cyclic phenylenes.[23b] In contrast to **15**, its isomer **14a** turned out to be much more stable. It was first prepared more than 30 years ago by Wong and Sondeheimer from dibenzo[8]annulene [dibenzocyclooctatetraene (**16**)] by bromination followed by dehydrobromination.[24] Because **14a** has been employed as a useful building block in the synthesis of structurally novel polycyclic compounds, as described later, improvements to its synthesis have been reported. Namely, Wudl reported an improved synthesis of **16** by using reductive coupling of dibromoxylene as the key step.[25] The sulfinate–phosphate double elimination protocol of the triple-bond synthesis developed by Otera was applied to the synthesis of **14a** using *o*-tolunitrile as the starting material.[26] Transition-metal mediated cross-coupling reactions such as the Sonogashira- and Castro-type reactions, which are frequently used to prepare unstrained DBAs, gave strain-free, large macrocycles rather than strained eight-membered ring carbocycles.[1c–1e,1g] Exceptionally, however, a highly substituted [8]DBA derivative **14c** was obtained by the Sonogashira reaction as a minor product together with the tetracyclic product **17**, derived from the transannular cyclization of **14c**, as a major product. This indicates that strained eight-membered DBA **14c** was a major initial product of the cyclization reaction (Scheme 1).[27]



13a R = H
13b R = Me



14a R = H
14b R = Me



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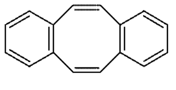

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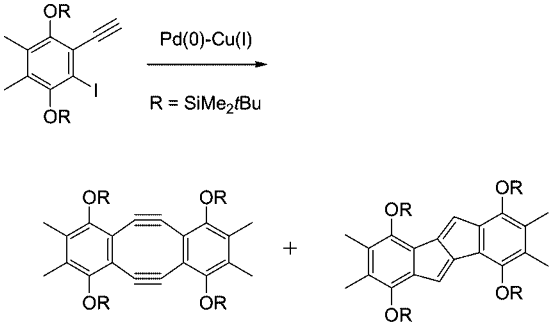
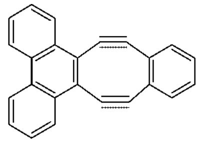


14c **17**

Scheme 1.

In the ^{1}H NMR spectrum, the aromatic protons in **14a** resonate at δ = 6.66 and 6.85 ppm with an AA′BB′ pattern, indicating its antiaromatic character.[28] The *Q* value (0.982), calculated from the coupling constants of the simulated spectrum, is consistent with this view. Similarly, theoretical calculations regarding the tropicity of **14a** indicate that its eight-membered ring should be weakly antiaromatic; the calculated magnetic susceptibility exaltation of **14a** relative to that of **16** (Λ = 14.5) suggests that it is less paratropic than **13a** (Λ = 21.5).[29] The small positive value of the nuclear independent chemical shift (NICS) of **14a**

[4.04 ppm (12.0 ppm when the local anisotropy of acetylene units is taken into account)] agrees with this view.[30] X-ray crystallographic analysis of **14a** showed that the annulene ring was planar as anticipated and that the triple bond was considerably deformed from linearity by 24.3°.[31] In contrast to **14a**, which decomposed slowly at room temperature, the tetramethyl derivative **14b**[32] and phenanthrene-fused analog **18**[33] were reported to be much more stable owing to kinetic protection of the reactive triple bonds. Their X-ray structure analyses showed that the distortion of their triple bonds was similar to that of parent **14a** [**14b**: 26.0°, **18**: 24.5° (average)]. Relative to tetradehydroannulene **14a**, didehydroannulene **13a**[24b] turned out to be much less stable, even though the latter was fully characterized. In spite of its lability, the structure of **13a** was analyzed by X-ray crystallography[34] as was the more stable tetramethyl derivative **13b**[32b,35] to reveal that their eight-membered rings were planar and the triple bonds distorted a bit more than those of **14a** and its derivatives (**13a**: 26.0°, **13b**: 27.1°). Note that both one-electron and two-electron reductions of **13a** by alkali metal or by cyclic voltammetry could be carried out to form its radical anion and dianion (a 10π-electron system), respectively, while only one-electron reduction of **14a** could be performed because irreversible polymerization took place upon further reduction.[24b,36] The radical anions of **13a**,[37] **13b**,[22] and **14a**[37] thus formed were characterized by ESR spectroscopy. Cp*Co–cyclobutadiene-fused derivative **19** was isolated by Vollhardt during an attempt to synthesize [4]phenylene and its X-ray analysis revealed that the eight-membered ring is planar and the triple bond slightly less deformed [23.0° (average)] than that of **13a**.[38]



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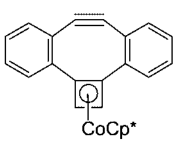

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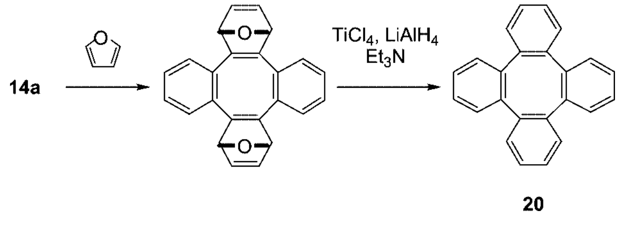
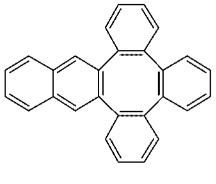
Because the triple bonds of **13a** and **14a** have such large deformation, they undergo facile cycloaddition reactions which were used for their characterization in the early studies on strained [8]DBAs.[24b] Since then, this characteristic has been utilized to construct new polycyclic ring systems. For example, Wong reported that the Diels–Alder reaction of **14a** with furan derivatives and subsequent deoxygenation gave tetraphenylene **20**, as shown in Scheme 2.[39] On the basis of the same methodology, a number of tetraphenylene derivatives **21**–**25** have been synthesized from **14a** and its homologs **26** and **27**.[39] Polycyclic hydrocarbon **28**, derived from [4+2] addition of **14a** with cyclone, was converted to graphitic hydrocarbon **29**, which has an eight-membered ring in the core of its structure.[40] [4+2] Cycloaddition of **14a** with a cyclopentadienone derivative possessing a fluoranthene unit gave **30** which may be transformed into a corranulene-tetraphenylene hybrid.[41]



Scheme 2.



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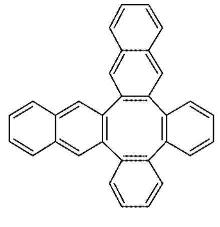

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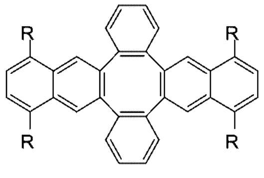
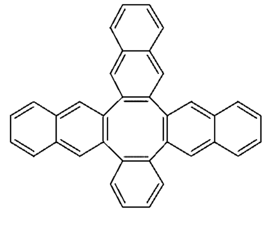


23a R = H
23b R = OMe



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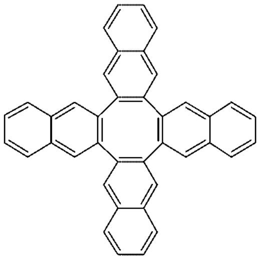

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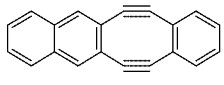

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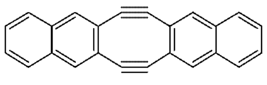

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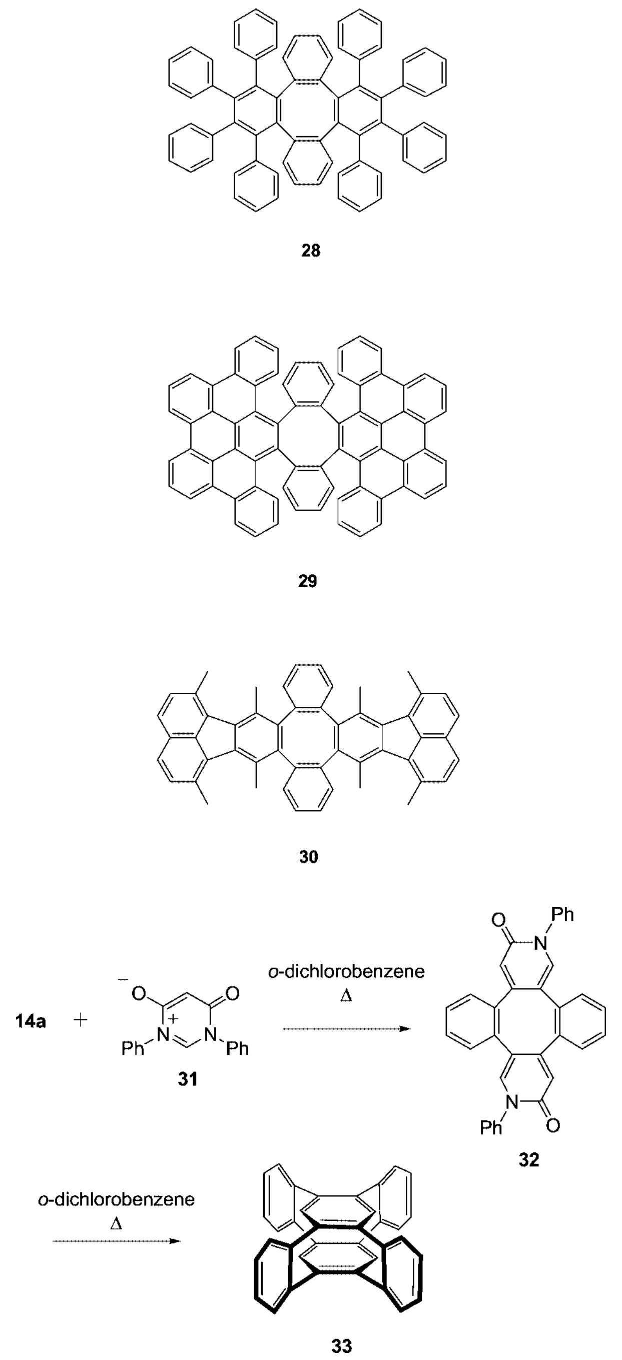
Wudl utilized reactive diene **31** in a [4+2] cycloaddition reaction with **14a** to give a new diene **32** through the subsequent thermal extrusion of phenyl isocyanate.[42] A second cycle of the same sequence of reactions, that is, with **14a** and **32**, furnished the tetrabenzo-fused [2.2.2.2](1,2,4,5)cyclophane derivative **33** (Scheme 3).

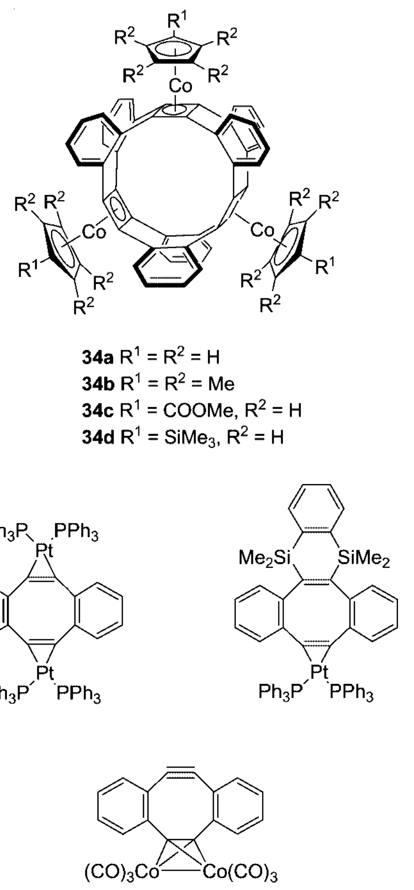
Recently, Gleiter reported a remarkable synthesis of belt-shaped molecules **34a**–**d**, so called beltenes, consisting of CpCo–cyclobutadiene and dibenzocyclooctatetraene units.[43] The synthesis of **34a**–**d** was achieved through sequential $Cp(CO)_5$-mediated [2+2] cyclodimerization reactions of three molecules of [8]DBA **14a**. Note that once the initial dimer was formed, subsequent reactions took place from the concave direction presumably because the dimer adopts a bent shape owing to the tub shape of the dibenzocyclooctatetraene units leading to the formation of the desired belt-shaped molecules.

[2+2] Cycloaddition of **14a** with dichloroketene gave **35** which was converted into cyclobutenedione **36**, which is re-



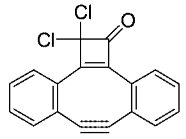
Scheme 3.

lated to the cobalt complex **19**.[24b,44] [3+2] Cycloaddition of diazoalkanes followed by extrusion of dinitrogen afforded cyclopropene derivatives **37a–d**.[45] A few transition-metal complexes of **14a**, shown in Figure 2, are also known.[46]



34a $R^1 = R^2 = H$
34b $R^1 = R^2 = Me$
34c $R^1 = COOMe$, $R^2 = H$
34d $R^1 = SiMe_3$, $R^2 = H$

Figure 2. Transition-metal complexes of tetradehydrodibenzo[8]annulene (**14a**).



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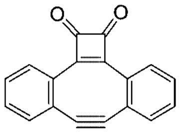

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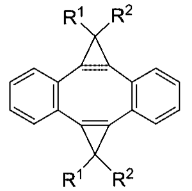
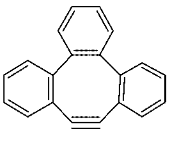


37a $R^1 = R^2 = Me$
37b $R^1 = R^2 = Ph$
37c $R^1\ R^2 = (o\text{-}C_6H_4)\text{-}(o\text{-}C_6H_4)$
37d $R^1\ R^2 = (o\text{-}C_6H_4)\text{-}CO\text{-}(o\text{-}C_6H_4)$

Attempts to isolate triply benzo-annelated dehydro[8]annulene **38** by Sondheimer were unsuccessful, merely giving the products derived from nucleophilic addition of the base employed in the elimination reaction or from [4+2] cycloaddition with 1,3-diphenylisobenzofuran (DPIBF), because of the substantial strain induced by overcrowding between the hydrogen atoms at the peri-position of the aromatic ring and that of the adjacent ring.[21b] Similarly, Meier reported the formation of **38** as a reactive intermediate by three different routes: double elimination of HBr, decomposition of a selenadiazole, and oxidative decomposition of a bishydrazone.[47] The half-life of **38** produced by the third method was reported to be approximately 30 min at –60 °C in solution. To suppress the nonbonding repulsion between the peri-hydrogen atoms thereby stabilizing this system, Wong designed and synthesized isopropylidene- and carbonyl-bridged tribenzo[8]DBA derivatives **39** and **40**, respectively.[48] [8]DBA derivative **39** turned out to be very stable. X-ray crystallographic analysis of **39** revealed that three independent molecules exist in the unit cell. The eight-membered rings of the two independent molecules are almost planar, while that of the third one deviates considerably from planarity. Similarly, while the distortion of the triple bonds of the two independent molecules is similar to that of **13a** (average 26.7°), the third molecule is considerably more deformed (33.5°).[48a] The results of CV as well as ESR and ENDOR analyses of the radical anion of **39** are consistent with a planar structure.[49] While stable, ketone **40** was not soluble preventing further study of its properties.



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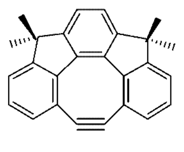

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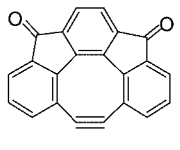
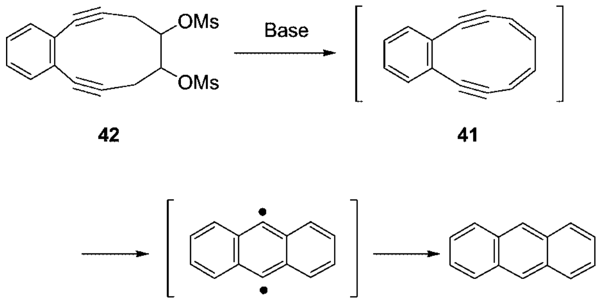


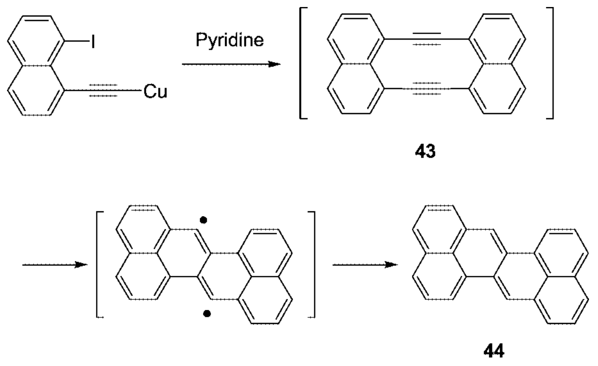
40

2.2 Strained Dehydrobenzo[10]annulenes ([10]DBAs)

Even though it was not isolated, the only monobenzo-fused [10]DBA attempted to be synthesized was tetradehydrobenzo[10]annulene (**41**); this compound was postulated as an intermediate in the elimination reaction of the dimesylate **42**, leading to the formation of anthracene through an intramolecular cyclization reaction (Scheme 4).[50] In connection with the Bergman-type cyclization, note that attempts to isolate tetradehydrodinaphtho[10]annulene (**43**) were unsuccessful, even though it is not strained, because of facile intramolecular cyclization to a diradical intermediate which abstracted hydrogen atoms to give an aromatic hydrocarbon zethrene (**44**) (Scheme 5).[51] This remarkable property was ascribed to the close proximity of the triple bonds. Theoretical predictions for hexadehydrodibenzo[10]-annulene (**4**: see Figure 1) suggest that it would be strongly diatropic (NICS = –8.59 ppm) if it were to exist.[30] However, in view of the large distortion of the triple bonds in **4**, it must be extremely reactive and should be produced under an inert atmosphere at a low temperature.



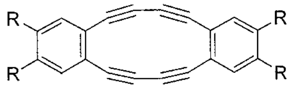
Scheme 4.



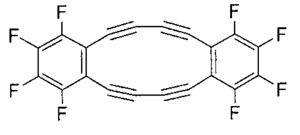
Scheme 5.

2.3 Strained Dehydrobenzo[12]annulenes ([12]DBAs)

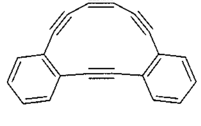
Like tetradehydrodibenzo[8]annulenes **14a** and **15**, there are two possible modes of double benzo-annelation to the octadehydro[12]annulene system, *a*,*g*-fusion (**45a** of D_{2h} symmetry) and *a*,*e*-fusion (**46** of C_{2v} symmetry). [12]DBA **45a** was first synthesized by Eglinton and Raphael by Cu^{II}-mediated oxidative coupling of 1,2-diethynylbenzene as a crystal which turned black and insoluble after a few days even in a dark vacuum.[52] It decomposed explosively when ground or when heated above 80 °C. In its ^1H NMR spectrum, the aromatic protons of **45a** resonate at 7.08–7.02 and 6.98–6.92 ppm, indicating a paratropic character. Theoretical calculations on **45a** are in agreement with this result [NICS = 5.75 ppm (8.08 ppm when the local anisotropy of the acetylene units is taken into account)].[30] X-ray crystallographic analysis of **45a** revealed that the annulene ring is planar and the triple bonds are moderately deformed from linearity by 13–15°.[53,54] In the crystal, the molecules of **45a** stacked parallel to form columns. Although the packing geometry is not ideal for topochemical polymerization, it may impart lability to **45a** in the solid state.[54]



45a R = H
45b R = *n*Bu
45c R = *n*Hex
45d R = *n*Dec
45e R = *n*Dodec
45f R = O*n*Dec



45g



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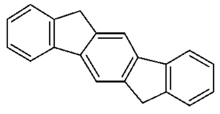
In connection with the topochemical polymerization of butadiynes to create single crystals of organic polymers with conjugated backbones, the preparation and crystal-structure analyses of a number of [12]DBA derivatives have been studied. Swager prepared alkyl- and alkoxy- substituted [12]DBA derivatives **45b–f** which were considerably more stable than the parent compound **45a**;[55] they underwent exothermic polymerization when heated at 100–125 °C, as observed by differential scanning calorimetry (DSC). X-ray analysis of tetrabutyl derivative **45b** showed that the butyl substituents occupy the space above and below the reactive [12]DBA cores thus separating them from each other. This packing geometry must be in part responsible for the stability of **45b** and related derivatives. The 1:1 cocrystallization of **45a** with hexafluorobenzene (C_6F_6) or tetracyanoquinodimethane (TCNQ) was investigated by Bunz with an expectation that the electron-deficient guests would stack with the benzene ring of **45a**.[54] However, although molecules of C_6F_6 and TCNQ are inserted between the disks of **45a**, the guests are located over the dehydroannulene. Nishinaga and Komatsu prepared perfluoro[12]DBA **45g**, whose reduction potential (–1.48 V vs. Fc/Fc$^+$) is substantially less negative than that of the parent hydrocarbon **45a** (–2.00 V) owing to the presence of electron-withdrawing fluoro groups.[56] In the two crystal forms of **45g**, one of which contains benzene as a solvate, the molecules are stacked in a slanted manner, while in the cocrystal of **45a** and **45g** (1:2), the molecules are stacked in a columnar arrangement forming a sandwich-like complex. In spite of packing geometries favorable for topochemical polymerization, none of the crystals underwent photochemical polymerization, presumably because of the high potential energy of the polymerization product.



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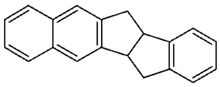

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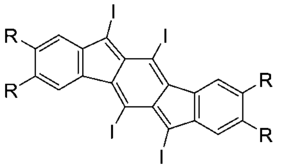
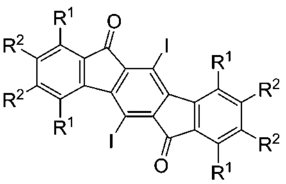
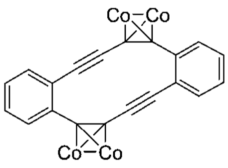


49a R = H
49b R = *n*Bu
49c R = *n*Dec



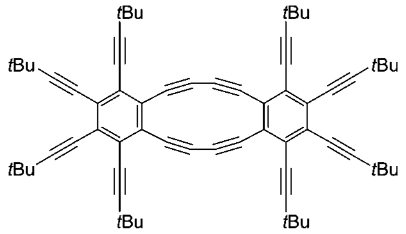
50a $R^1 = R^2$ = H
50b R^1 = H, R^2 = *n*Dec
50c R^1 = H, R^2 = *n*Dodec
50d $R^1 = R^2$ = F



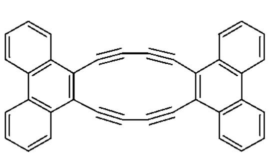
51

Intramolecular transannular C–C bond formation of the *a*,*g*-fused [12]DBA system has been known since the parent **45a** was first synthesized. Thus catalytic hydrogenation of **45a** resulted in the formation of not only the normal hydrogenation product, dibenzocyclododecane, but also the aromatic hydrocarbons **47** and **48**.[52b] Treatment of **45a**,**b**,**d** with iodine in benzene under argon afforded the corresponding tetraiodides **49a**–**c**.[55] The same reaction of **45b**,**c** when conducted under aerobic conditions gave diketones **50b**,**c**, respectively. The parent diketone **50a** and perfluoro derivative **50d** have also been reported recently.[57] The reaction of **45a** with $Co_2(CO)_8$ gave complex **51** containing two $Co_2(CO)_6$ units, X-ray crystallographic analysis of which revealed two cobalt atoms located on opposite tetrayne units.[58]

In contrast to the parent DBA **45a**, diphenanthreno[12]DBA **52**,[59] dimethoxynaphthalene derivative **53**,[60] and quinoxaline derivatives **54a**,**b**,[61] which were prepared by Nakagawa, Komatsu, and Faust, respectively, are reported to be stable. More elaborate derivatives of [12]DBA have also been prepared. For example, in connection with two-dimensional acetylenic carbon networks, Rubin prepared perethynyl[12]DBA **45h** by oxidative coupling of a differentially substituted hexaethynylbenzene derivative.[62] Haley recently reported the preparation of **55** in which two strained [12]DBA units share the central [24]annulene core.[63] Moreover, linearly fused [12]DBA systems, [*n*]acediynes **56** (*n* = 2) and **57** (*n* = 3), as well as the parent [12]DBA **45f** were prepared by Anthony by intramolecular oxidative coupling of the corresponding precursors **58a**–**c**, as shown in Scheme 6.[64] In contrast to **45f** and **56**, which are stable in both solution and the solid state, [3]acediyne **57** decomposes slowly in solution under aerobic conditions, while it is stable in the solid state. The absorptions of the acediynes extend to longer wavelengths with increasing numbers of [12]DBA units, like those of acenes.



45h



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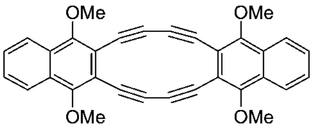
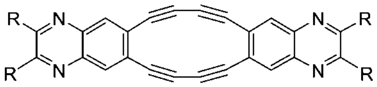
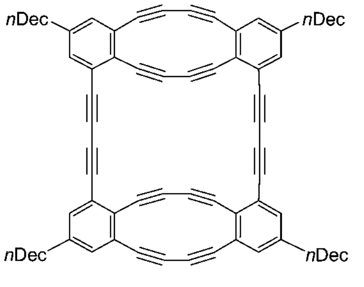


53



54a R = Ph
54b R = ≡—Si*i*Pr$_3$



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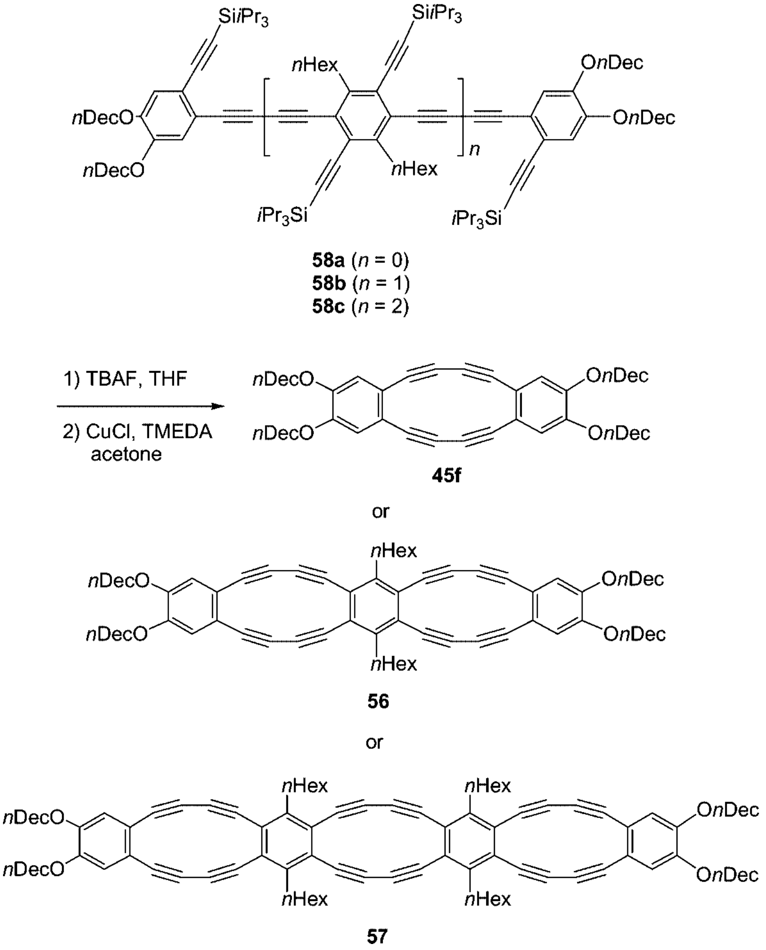
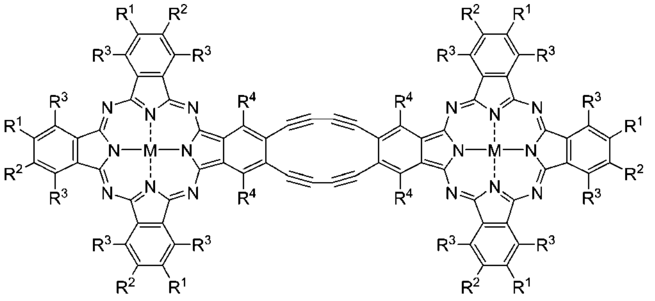
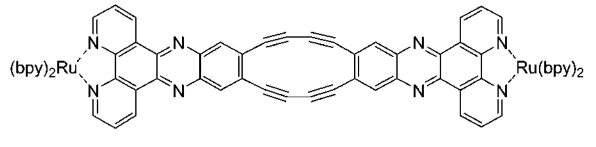
In view of the rigid, planar structure of [12]DBA possessing two butadiyne linkages, this unit is expected to serve as a linker for electronic communication between two chro-



Scheme 6.



59a $R^1 = R^2 = OnBu$, $R^3 = R^4 = H$, M = Zn
59b $R^1 = t\mathrm{Bu}$, $R^2 = R^3 = R^4 = H$, M = Zn
59c $R^1 = R^2 = H$, $R^3 = n\mathrm{Dec}$, $R^4 = OnBu$, M = Ni

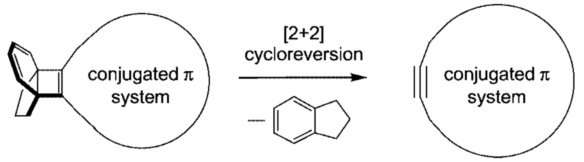


60

mophores or redox-active groups attached to both its ends. Thus Torres and Cook independently prepared phthalocyanine-annelated [12]DBAs **59a**,**b** and **59c**, respectively, which exhibit split Q-bands, indicating the presence of intramolecular electronic coupling between the phthalocyanine subunits.[65,66] Faust reported, however, that the redox potentials of the $\mathrm{Ru^{II}/Ru^{III}}$ couple and the reduction of the bpy ligands of $\mathrm{(bpy)_2Ru}$-coordinated [12]DBA **60** are similar to its acyclic model compounds, indicating little communication between the metal centers.[67]

In contrast to the strained DBAs possessing 8–12-membered rings described above, few DBAs containing highly strained hexatriyne (or even longer oligoyne) units are known because the stability of polyynes decreases dramatically with increasing numbers of conjugated acetylene units and also because longer alkyne units are much less easily synthesized.[8g,68] To generate cyclic compounds containing highly strained triple bonds such as cyclo[*n*]carbons,[8a,8b,69,70] we have developed a method based on the [2+2] fragmentation of [4.3.2]propellatriene derivatives.[71] Here the propellatriene unit, which is to be removed by photo- or laser irradiation to leave indane and an alkyne, serves as a masking group of a triple bond (Scheme 7).

We planned to generate highly strained octadehydrodibenzo[12]annulene (**46**) from the corresponding precursors **61** using the method mentioned above because it would give important information regarding the isolation/detection limit of cyclic polyynes like cyclo[*n*]carbons.[72] Even though the total strain in **46** should be smaller than that of cyclo[12]carbon, which was only detected by mass spectrome-



Scheme 7.

try,[71c,d,73] the distortion of the central triple bond of the triyne unit of **46**, estimated from the DFT calculations at the B3LYP/6-31G* level of theory and shown in Figure 3, is expected to be even larger than that of cyclo[12]carbon. Namely, in the energy-minimum structure of **46**, which is not symmetrical with respect to the plane bisecting the triyne unit, the bond angle of the most strained central triyne unit is predicted to be as small as 147.1°. The C_2 bridge of **46**, however, is predicted to be slightly deformed towards the inside of the annulene ring by 7.2–7.6° such that both the C_2 and C_6 bridges curve in the same direction. There is considerable bond-length alternation in the 12-membered rings of [12]DBAs **46** owing to benzo-annelation, as in its precursor **61**. The NICS value calculated at the center of the 12-membered ring is 6.14 ppm, indicating a paratropic nature.

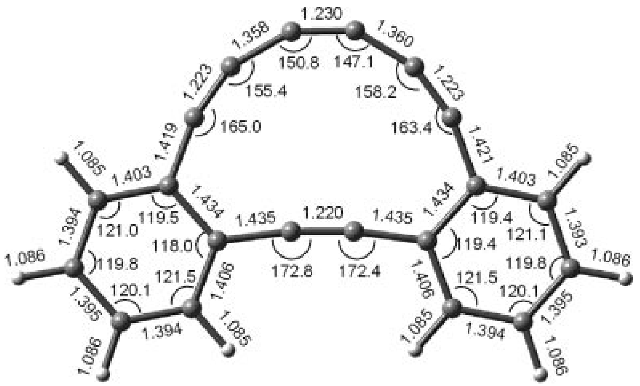
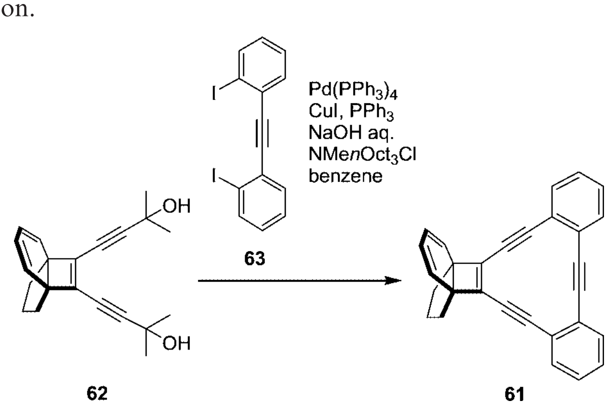
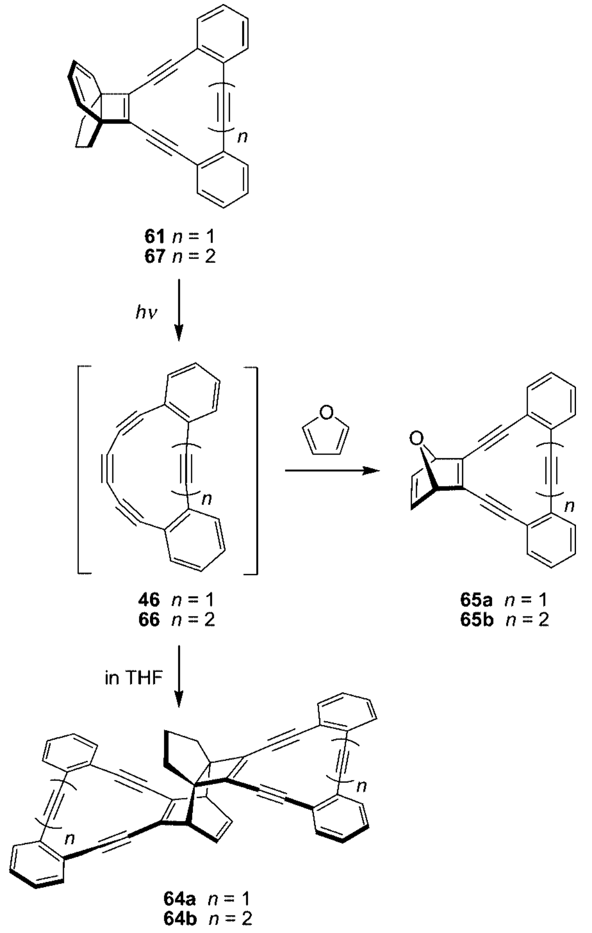


Figure 3. Theoretical geometry of octadehydrodibenzo[12]annulene (**46**) as calculated by the DFT method at the B3LYP/6-31G* level of theory. Bond lengths are given in angstroms and bond angles in degrees.

The precursor **61** was prepared as shown in Scheme 8. The key step of the synthesis was the cross-coupling reaction between diyne **62**, which was deprotected in situ, and diiodotolane **63** under phase-transfer conditions. Irradiation of **61** in [D_8]THF at room temperature with a low-pressure mercury lamp gave no NMR signals due to **46**; only signals due to indane and the [4+2] adduct **64a** formed between **46** and the cyclohexadiene unit of **61** were observed. By preparative-scale photolysis of **61** in THF, **64a** was isolated in 18% yield (Scheme 9). In addition, irradiation of **61** in furan gave the furan adduct **65a** in 20% yield. X-ray crystallographic analyses of **64a** and **65a** revealed that the propellatriene unit of **61** was replaced by another molecule of **61** and furan, respectively, indicating that the addition reaction takes place at the central, most-strained triple bond of the triyne unit of **46**. These results indicate that the photolysis of **61** leads to the generation of **46**, but that it is too reactive for spectroscopic characterization in solution.



Scheme 8.



Scheme 9.

On the basis of the above experiments, spectroscopic characterization of **46** was carried out in low-temperature matrices. First, for the UV/Vis characterization, a methyltetrahydrofuran (MTHF) glass matrix of **61** was irradiated at 77 K. As the absorption of **61** at 366 nm decreased, a new absorption band appeared at 361 nm which was assigned to **46**. The small hypsochromic shift, relative to the starting material **61**, is consistent with the slightly larger HOMO–LUMO gap of **46** (3.05 eV by the DFT method at the

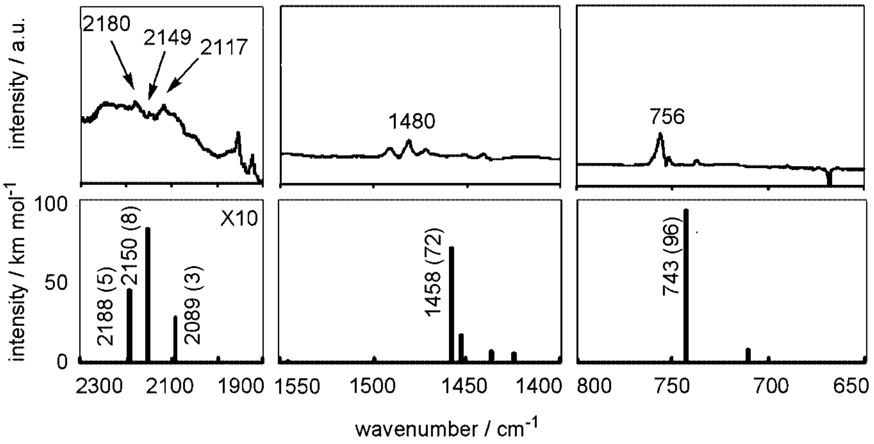


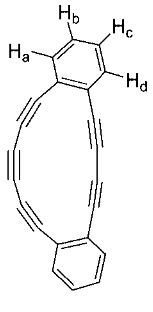
Figure 4. Upper panels: Selected differential FTIR spectrum obtained by subtracting the spectra of precursor **61** and indane from that of the photoproducts obtained after irradiation of **61** in an argon matrix at 20 K. Lower panels: Theoretical IR frequencies and intensities of decadehydrodibenzo[12]annulene (**46**) calculated by the DFT method at the B3LYP/6-31G* level of theory.

B3LYP/6-31G* level) relative to that of **61** (2.91 eV). When the matrix was thawed by warming to room temperature and then refrozen at 77 K, the new band at 361 nm was completely lost, indicating that the reactive intermediate **46** only exists in the matrix.

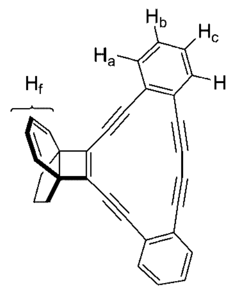
Next, in order to obtain more definite evidence for the formation of **46** by IR spectroscopy, **61** was irradiated in an argon matrix at 20 K; compound **46** was identified by comparing the observed FTIR spectrum with that theoretically calculated by the DFT method at the B3LYP/6-31G* level of theory. Since the conversion of the reaction was not high owing to the low efficiency of the photolysis, the IR spectrum of the photoproduct was obtained as a differential spectrum by subtracting the spectra of the starting material **61** and the byproduct (indane) from the observed spectrum (Figure 4). Figure 4 shows absorptions for C≡C stretching at 2180, 2149, and 2117 cm^{-1}, though the intensities of these bands are very weak. Similarly, C–H in-plane and out-of-plane bending absorptions appeared at 1480 and 756 cm^{-1}, respectively. The theoretical absorptions of **46**, which are predicted to appear at 2188, 2150, and 2089 cm^{-1} for C≡C stretching and at 1458 and 743 cm^{-1} for C–H in-plane and out-of-plane bending, respectively, are in good agreement with the observed spectrum. These results provide good evidence for the existence of the highly strained [12]DBA **46** and also suggest that it can only survive in matrices at low temperatures.

2.4 Strained Dehydrobenzo[14]annulenes ([14]DBAs)

For dehydrobenzo[14]annulenes, only decadehydrodibenzo and octadehydrotribenzo derivatives have been reported. In the former system **66**, the triyne unit of **66** is expected to be not as strained as structurally related [12]-DBA **46**, with bending angles of 22.4–15.6° for the optimized geometry obtained by DFT calculations.[72b,74] The diyne unit of **66** is much less distorted, with bending angles of 3.5–5.2°. The bond-length alternation of the annulene core of **66** is smaller than that of **46** as a result of its diatropic character. The NICS value calculated at the center of the 14-membered ring of **66** is –4.32 ppm, indicating that it is weakly aromatic.



66



67

We planned to generate **66** from the propellane precursor **67**, as in the case of **46**. In contrast to the latter, which was detected only in low-temperature matrices, however, both ^{1}H and ^{13}C NMR signals due to **66** could be observed in solution. The ^{1}H NMR spectrum obtained by irradiation of **67** in degassed [D$_8$]THF with a low-pressure mercury lamp at 220 K exhibits new multiplets at 7.93–7.91 and 7.63–7.57 ppm with a relative integration of 1:3 in addition to signals of **67** and indane (Figure 5). The conversion of **67** to **66**, however, remained low (ca. 19%) even after prolonged irradiation as a result of the absorption of the incident light by the photoproducts **66** and indane. These new signals are in good agreement with the theoretical chemical shifts of the aromatic protons of **66** estimated by GIAO-B3LYP/6-31G* calculations. Note that the signal due to H$_a$ of **66** appears at higher fields than that of the starting material **67**, while the signal due to H$_d$ of **66** appears at a lower field than that of the latter. This can be ascribed either to the difference between the local anisotropy of the triple bonds or to the tropicity of the annulene rings of **66** and **67**. In order to elucidate the reason, calculations were performed for appropriate model compounds of **66** and **67** at the GIAO-B3LYP/6-31G* level of theory. It turns out that the major reason for the downfield shift is the local anisotropy of the triple bonds of **66**, though it is also partly due to the larger diatropicity of **67** relative to that of the fully unsaturated **66**. This is consistent with (i) the smaller paratropicity estimated for [8]DBA **14a** compared with that of **13a** based on the calculated magnetic susceptibilities[29] and (ii) the smaller conjugation energy between the neighboring triple bonds (i.e., 1,3-butadiyne) relative to that of the double bonds (i.e., 1,3-butadiene), though there exists some controversy regarding this issue.[75]

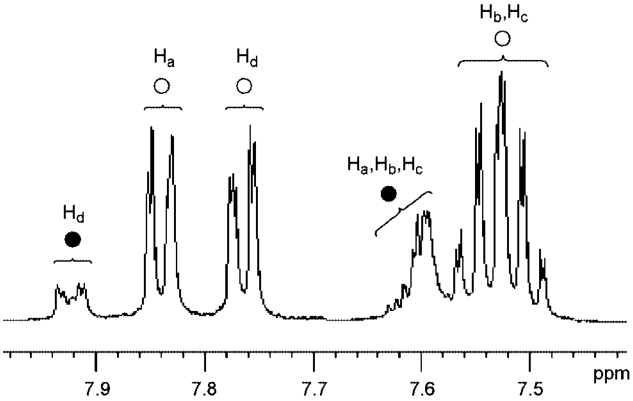


Figure 5. ^{1}H NMR spectrum obtained upon irradiation of **67** in [D$_8$]THF for 24 h at 220 K. Peaks due to starting material **67** are marked by open circles and those assigned to the photoproduct, decadehydrodibenzo[14]annulene (**66**), are marked by solid circles.

By standing the solution containing **66** for a few days at ambient temperature, its signals disappeared and instead two signals at 6.47–6.45 and 4.29–4.27 ppm appeared, albeit in low intensities. These signals have been attributed to the vinyl and bridgehead protons of the [4+2] adduct **64b** (Scheme 9). The [4+2] adduct **65b** was also isolated in low yield (ca. 2%) by irradiation of **67** in furan. The low yields of the [4+2] adducts **64b** and **65b** can be ascribed to the low reactivity of the central bond of the triyne unit that is a result of its small distortion.

The ^{13}C NMR spectrum obtained after irradiation of a solution of **67** in [D$_8$]THF at 213 K is shown in Figure 6. Besides the signals of the sp carbon atoms of unphotolyzed **67** at 94.0, 87.1, 83.6, and 79.4 ppm, five weak signals due to **66** at 101.4, 82.6, 81.6, 80.4, and 79.2 ppm are observed. Compared with the signals of **67**, one signal appears at a distinctly low field, while the other four seem to stay constant or move upfield. To assign the remarkably downfield-shifted carbon signal of **66**, theoretical chemical shifts were estimated by performing GIAO-B3LYP/6-31G* calculations. As a result, C1, C2, C3, C10, and C11 are predicted to resonate at 78.8, 79.9, 101.2, 80.0, and 79.1 ppm, respectively, indicating that the signal in question should be assigned to the C3 atom. This remarkable downfield shift in the ^{13}C NMR spectrum is discussed in the following section.

Thus, [14]DBA **66** was successfully characterized by ^{1}H and ^{13}C NMR spectroscopy in solution. However, it was not possible to isolate it because of its high reactivity and the low efficiency of its formation from its precursor **67**.

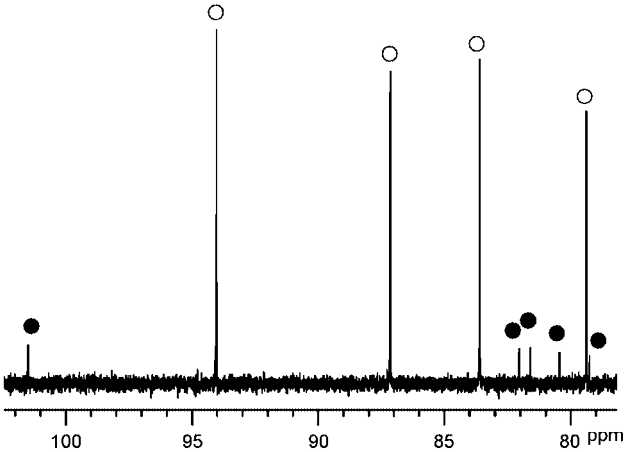
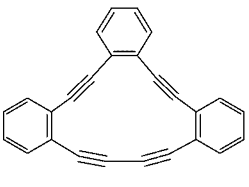


Figure 6. Partial ^{13}C NMR spectrum of **67** after irradiation in [D$_8$]-THF for 24 h at 213 K. Peaks due to starting material **67** are marked by open circles and those assigned to the photoproduct, decadehydrodibenzo[14]annulene (**66**), are marked by solid circles.

Octadehydrotribenzo[14]annulene (**68**) was synthesized by Vollhardt.[76] The ^{1}H NMR chemical shifts of **68** indicate a weak diatropic character. Even though the distortion of the triple bonds in **68** is not large, with bending angles of 8.6–11.2°, it underwent topochemical polymerization induced by photoirradiation or by applying pressure (2×10^4 psi). This remarkable reactivity has been ascribed to the packing of the crystal, as revealed by X-ray analysis, by which a *trans*/*trans* geometry of the resulting polymer chain was suggested. In addition to the parent hydrocarbon **68**, a number of its derivatives have been synthesized by the group led by Haley with a view to optoelectronic applications.[1g,77]



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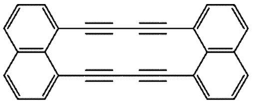
Just like the elusive [10]DBA **43**, which does not have distorted triple bonds, the corresponding [14]DBA **69** has also been reported to be highly reactive owing to the proximity of the butadiyne units which facilitates intramolecular cyclization leading to the formation of a diradical intermediate.[78] However, in the acenaphthene **70a** and fluoranthene derivatives **71**, the transannular distances between the triple bonds are estimated to be slightly longer than that of **69**. As a result, even though **70a** and **71** are not soluble enough for full characterization, the more soluble derivative **70b** was synthesized successfully by Anthony.[79] This compound turned out to be remarkably stable both thermally and photochemically.



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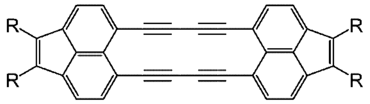
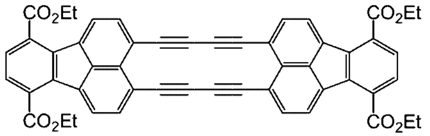


70a R = H
70b R = ≡—Si*i*Pr$_3$



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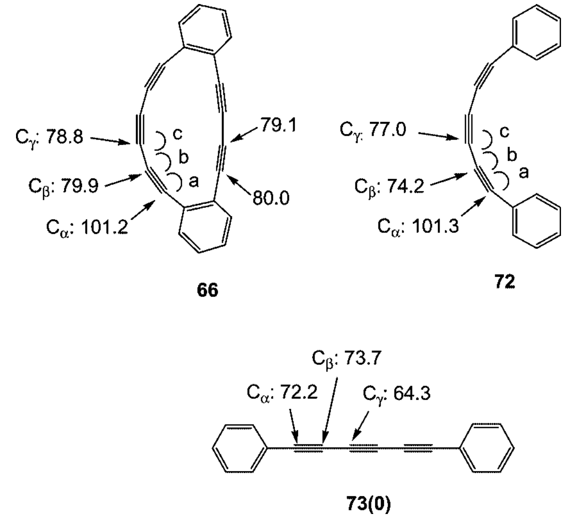


Figure 7. Theoretical ^{13}C NMR chemical shifts for [14]DBA **66**, bent hypothetical 1,6-diphenylhexatriyne (**72**), and linear 1,6-diphenylhexatriyne [**73(0)**] calculated by the GIAO-B3LYP/6-31G* method.

2.5 Relationship between the Deformation of Triple Bonds and ^{13}C NMR Chemical Shifts of Diphenylpolyynes

As described in the previous section, the ^{13}C NMR chemical shift of the C3 atom of [14]DBA **66** is shifted to a remarkably low field compared with that of the unstrained starting material **67**. It has been well documented that distortion of an sp carbon atom in nonconjugated aliphatic alkynes causes a downfield shift of the ^{13}C NMR chemical shift,[80] which can be understood in terms of rehybridization from pure sp to partial sp^2 hybridization.[80a] It has also been reported that highly strained cyclic *m*- and *p*-phenyleneethynylene oligomers exhibit downfield-shifted ^{13}C NMR chemical shifts of the sp carbon atoms.[12,81] However, the observed downfield shift of **66** seems to be peculiar since only the C3 atom exhibits such a remarkable shift, while the other similarly distorted carbon atoms do not. To clarify whether this unusual behavior is due to the deformed 1,6-diphenylhexatriyne unit, theoretical chemical shifts of hypothetical 1,6-diphenylhexatriyne (**72**) having the same bending angles (*a*, *b*, and *c* shown in Figure 7) as those of the hexatriyne part of **66** were estimated by performing GIAO-B3LYP/6-31G* calculations and the data compared with those of the unstrained hexatriyne **73(0)**.[82] As shown in Figure 7, the distortion of the triple bond causes a downfield shift of 14.5 ppm at the most distorted C$_\gamma$ atom (c = 161°), the degree of which is consistent with previously known data.[80] On the other hand, the chemical shift of the C$_\beta$ atom is unchanged in spite of the fact that the bond angle b is deformed to 167°. Moreover, C$_\alpha$ exhibits the largest downfield shift by approximately 30 ppm even though it is just as much deformed as C$_\gamma$ (a = 162°). The small shift of C$_\beta$ and the large downfield shift of C$_\alpha$ cannot be interpreted in terms of the rehybridization effect.

Next, to confirm the generality of the above unusual behavior, GIAO calculations were performed on systematically deformed 1,6-diphenylhexatriynes [**73(0)**, **73(5)**, **73(10)**, **73(15)**, and **73(20)**],[82] in which all of the sp carbon atoms (C$_\alpha$, C$_\beta$, and C$_\gamma$) are bent to the same degree (a), 5° for each step up to 20° (a = 0–20°). For the purpose of comparison,

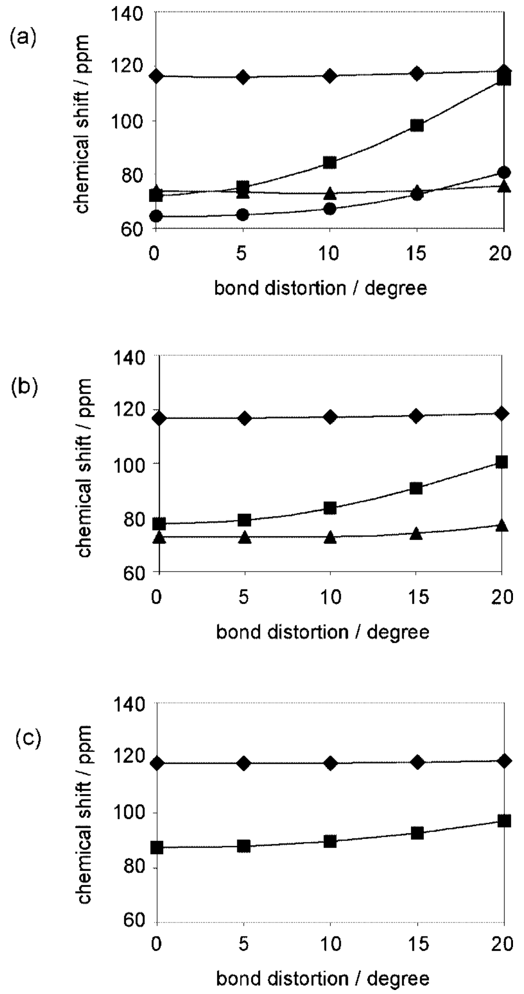
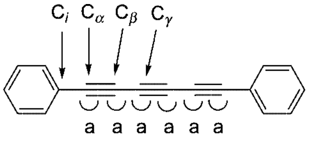
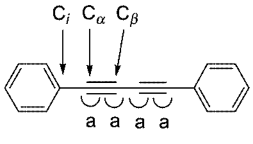


Figure 8. Theoretical ^{13}C NMR chemical shifts of (a) 1,6-diphenylhexatriynes [**73(0)**–**73(20)**], (b) 1,4-diphenylbutadiynes [**74(0)**–**74(20)**], and (c) diphenylacetylenes [**75(0)**–**75(20)**] as a function of angle of bending at the sp carbon atoms calculated by the GIAO-B3LYP/6-31G* method. ◆: C$_i$; ■: C$_\alpha$; ▲: C$_\beta$; ●: C$_\gamma$.

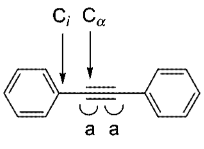
the same calculations were performed on hypothetical 1,4-diphenylbutadiynes [**74(0)**–**74(20)**][82] and diphenylacetylenes [**75(0)**–**75(20)**][82] having the same degree of distortion. Figure 8 (a–c) show the calculated chemical shifts of each sp carbon atom of **73(0)**–**73(20)**, **74(0)**–**74(20)**, and **75(0)**–**75(20)**, respectively, plotted against the bending angle. As shown in Figure 8 (c), the sp carbon atoms of the diphenylacetylenes [**75(0)**–**75(20)**] exhibit a gradual downfield shift as the bending angle increases, which is consistent with observed behavior.[12,80,81] In contrast, as shown in Figure 8 (b), the downfield shift of C_α of the diphenylbutadiyne series **74(0)**–**74(20)** is more prominent than that of diphenylacetylenes [**75(0)**–**75(20)**], while the shift of C_β is smaller than that of **75(0)**–**75(20)**. Moreover, in the case of 1,6-diphenylhexatriynes [**73(0)**–**73(20)**], the downfield shift of C_α is even more remarkable, whereas the magnitude of the shift of C_β is small (Figure 8, a). The behavior of C_γ is similar to that of **75(0)**–**75(20)**. These results suggest that, in general, as the bond-angle deformation of diphenylpolyynes increases, the ^{13}C NMR chemical shift of the α-carbon atom moves downfield much more sensitively than diphenylacetylene while the β-carbon atom does not move as much as the latter. Although the reason for this behavior is not certain at this moment, it is probably due to the polarization of the triple bond attached to the phenyl group since the ^{13}C NMR chemical shifts of the sp carbon atoms are known to be susceptible to the effect of charge.[83]



73(0)-73(20)



74(0)-74(20)



75(0)-75(20)

3. Conclusions

Recent advances in the chemistry of strained dehydrobenzoannulenes continue to enrich the knowledge of this fundamentally important class of molecules, such as the limit of their existence and the aromaticity in distorted π systems. Unexpectedly, it has been found that the ^{13}C NMR chemical shifts of unstrained α,ω-diphenylpolyynes are subject to the polarization effect and that distortion of the triple bonds causes changes in the chemical shifts as a result of both rehybridization and depolarization effects. Moreover, new compounds in this field have been synthesized as potentially useful materials for optoelectronic purposes and as precursors of new forms of carbon materials.

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