Synthesis, Structure, and Redox Behavior of the Dehydroannulenes Fused with Bicyclo[2.2.2]octene Frameworks

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Two series of dehydroannulenes fused with bicyclo[2.2.2]octene (BCO) units were synthesized either by an oxidative coupling with copper(I) under air or by a palladium−copper-catalyzed coupling. The first series of dehydroannulenes consisted of tetradehydro[12]annulene (**12**), hexadehydro[18]annulene (**13**), octadehydro[24]annulene (**14**), and decadehydro[30]annulene (**15**), which all have the BCO units connected by the butadiyne linkage. The second consisted of tridehydro[12]annulene (**16**) and tetradehydro[16]annulene (**17**), which have the BCO units connected by the acetylene bond. The molecular structures of the relatively stable annulenes **13** and **17** were determined by X-ray crystallography, which showed that **13** has a planar π-system, whereas **17** has a tub structure like cyclooctatetraene. The ^{1}H NMR signal for the bridgehead proton of the BCO units is a good measure for the ring current effect. This signal clearly indicated the presence of diatropicity in [18]annulene **13** and paratropicity in [12]annulenes **12** and **16**. The redox properties of these annulenes were examined by cyclic voltammetry. The antiaromatic [12]- and [16]annulenes **16** and **17** having only one acetylene bond between the BCO units were found to be more readily oxidized than the other annulenes as expected from the energy level of HOMOs calculated by the PM3 semiempirical MO method.

Introduction

In recent years, much attention has been paid to the chemistry of cyclic π-conjugated systems containing triple bond(s). For example, some compounds having an enediyne structure have come to be known as antitumors,[1] while macrocyclic planar π-systems composed of 1,3-diethynylbenzene units have been shown to exhibit intriguing properties as functionality materials.[2] In particular, dehydroannulenes fused with detachable cyclic units have been utilized as possible precursors of a new family of carbon allotropes, the cyclo[*n*]carbons.[3−5] Fundamental studies for all these cyclic conjugated hydrocarbons containing a triple bond originated in the first report on [18]annulene by Sondheimer in 1959.[6] Since then, a variety of dehydroannulenes have been prepared.[7] Among these, cyclic systems having butadiyne units have been synthesized by the oxidative coupling of the terminal enediyne precursors. These include the unsubstituted cyclic trimer, dehydro[18]annulene (**1**),[8] as well as several analogues with fused rings such as **2**[3a,e] and **3**.[3b,d,e] The more strained dimeric derivatives, dehydro[12]annulenes **4**,[9] **5**,[10] **6**,[11] have also been prepared by a similar method. The cyclic systems having an acetylene linkage such as **7**,[12,13] **8**,[14−16] and **9** (mixtures of diastereomers)[4b] have been synthesized using other methods, e.g., palladium−copper-catalyzed coupling for **9**.

In spite of these extensive studies of dehydroannulenes, systematic investigations of the redox behaviors of these compounds have been quite limited. This may be due to the relative instability of the cationic species of annulene compared with the anionic species. On the other hand, we have found that the annelation with a rigid bicyclic σ-framework such as bicyclo[2.2.2]octene (abbreviated as BCO) is effective for the stabilization of the cationic species of benzene **10**[17] or cyclooctatetraene **11**.[18] In particular, cyclooctatetraene derivative **11** can readily be oxidized with nitrosonium hexachloroantimonate to give the stable cation radical salt.[18a] In addition, the annelation with BCO units is expected to be quite advantageous in dehydroannulenes in rigidly

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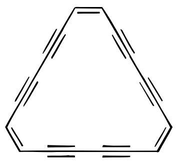
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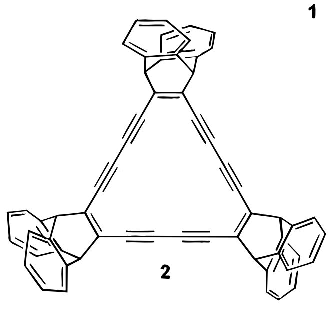
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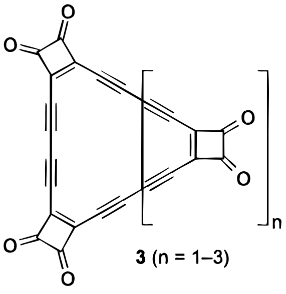
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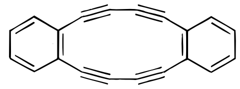
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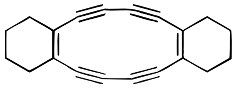
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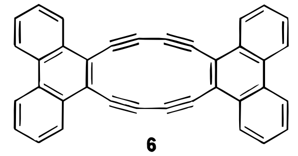
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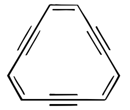
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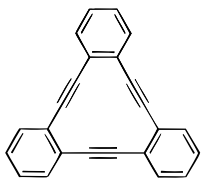
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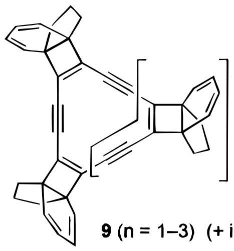
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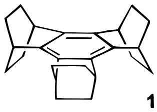
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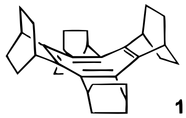
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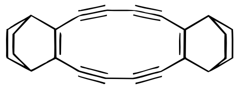
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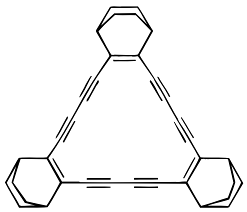
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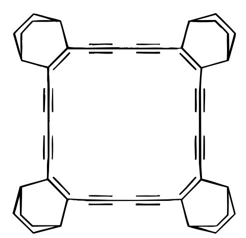
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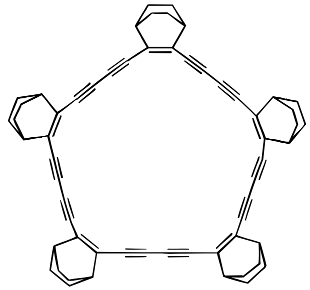
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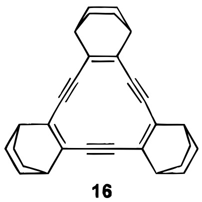
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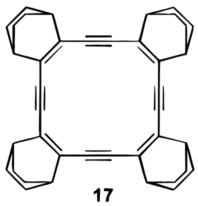
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holding the σ-framework of the π-systems in either a planar or bent geometry. Thus, we synthesized a series of dehydro[12]-, -[18]-, -[24]-, and -[30]annulenes **12**−**15** and dehydro[12]- and -[16]annulenes **16** and **17** fused with BCO units and investigated their structure and redox behavior.

Results and Discussion

Synthesis. For the synthesis of a series of annulenes having BCO units connected by a butadiyne moiety, the oxidative coupling of 2,3-diethynylbicyclo[2.2.2]octene (**20c**) under Eglinton conditions[19] appeared feasible. As shown in Scheme 1a, the reaction of BCO dibromide **18**[17] with either 2 or 3 equiv of (trimethylsilyl)acetylene under palladium−copper-catalyzed cross-coupling conditions[20] gave ethynylated products **19a** (23 or 7%) and **20a** (25 or 87%). The desilylation of **20a** by potassium hydroxide in methanol yielded the rather unstable enediyne **20c**, which was used for the oxidative coupling without rigorous purification. Previously, the oxidative coupling reaction of 1,2-diethynylbenzene (**23**) or 1,2-diethynylcyclohexene (**24**) has been reported to give dimer **4**[9] or **5**[10] as the only cyclized product. In the present work, however, a series of cyclic oligomers ranging from dimer **12** to pentamer **15** was formed when enediyne **20c** was reacted with cupric acetate in pyridine at 70 °C and then at room temperature, as shown in Scheme 1b: When the reaction was conducted at 50 °C, trimer **13** was the only cyclized product and its yield was 26%.

The yield of tetramer **14** was much lower than that of dimer **12** or trimer **13**. Its solubility was quite low (e.g., ~0.5 mg/mL in toluene), and its separation by preparative GPC was tedious. We therefore attempted to prepare tetramer **14** via another route. As shown in Scheme 1d, the diethynylation of dibromide **21** (see below) gave dodeca-3,9-dien-1,5,7,11-tetrayne **22a**. After desilylation, the oxidative coupling reaction afforded **14** in a modest yield (10%), but only as a cyclized product.

The notable difference in product distribution between the reaction of **20c** in the present study and that of **23** and **24** probably resulted from the wider angle between the ethylene and acetylene bonds in **20c** than in **23** and **24** (Figure 1). The oxidative coupling of the dibenzo analogue of **20c** has been reported to give only the cyclic trimer.[3a,e] On the other hand, four-membered enediyne **25**, which has a wider ethylene−acetylene angle (134.6°), affords the higher cyclic oligomers up to a cyclic pentamer.[3b,d,e,21]

In order to prepare the other series of dehydroannulenes, which has the BCO units connected by an acetylene moiety, we first attempted the palladium−copper-catalyzed coupling of 2-bromo-3-ethynyl-BCO (**19c**) in diethylamine. However, the reaction gave no cyclized product but afforded oxidatively coupled dimer **21** in 43%

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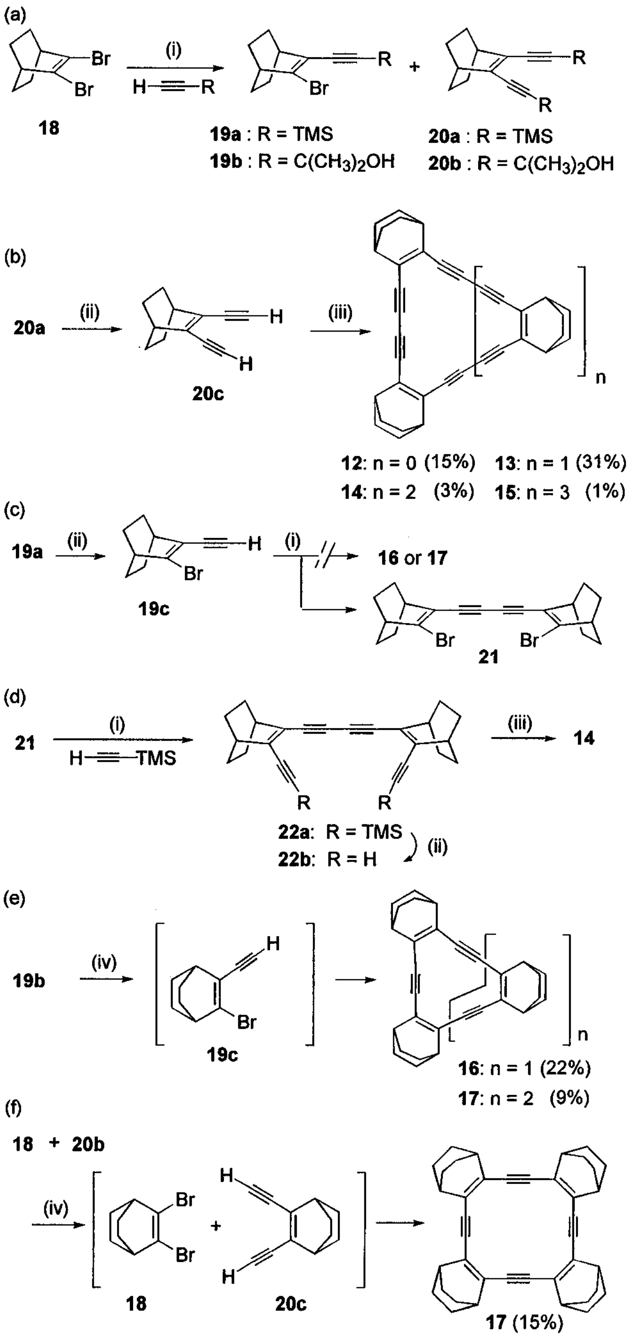
Scheme 1[a]



[a] Reagents: (i) CuI, $Pd(PPh_3)_2Cl_2$, Et_2NH; (ii) aqueous KOH, MeOH-THF; (iii) $Cu(OAc)_2$, pyridine−MeOH−Et_2O, air, 70 °C and then at rt; (iv) aqueous NaOH, C_6H_6, $PhCH_2NEt_3^+Cl^-$, CuI, $Pd(PPh_3)_4$.

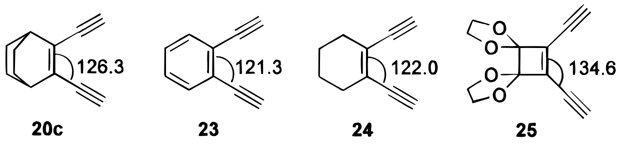


Figure 1. Internal angles of the enediyne systems obtained by PM3 calculations.

yield, as shown in Scheme 1c.[22] Recently, Tobe and coworkers successfully synthesized the annulenes fused with [4.3.2]propellatriene[4b] using the method of Huynh and Linstrumelle.[16] We therefore decided to apply this method to our system. As shown in Scheme 1a, the coupling reaction of dibromide **18** with 1.5 equiv of 3-hydroxy-3-methyl-1-butyne yielded monoethynyl derivative **19b** in 31% and diethynyl derivative **20b**in 38%. Treatment of 2-bromo-3-ethynyl-BCO (**19b**) in benzene at 80 °C with tetrakis(triphenylphosphine)palladium(0) and copper(I) iodide as coupling catalysts, aqueous sodium hydroxide, and benzyltriethylammonium chloride as the phase-transfer catalyst afforded cyclic trimer **16** (22%) and tetramer **17** (9%) in one pot, through the coupling of *in-situ* generated 2-bromo-3-ethynyl-BCO (**19c**) (Scheme 1e). Tetramer **17** was also obtained as the only cyclized product in 15% yield when dibromide **18** was reacted with **20b** under the same conditions (Scheme 1f).

Properties. Of the six BCO-annelated dehydroannulenes **12**−**17** that were synthesized in the present work, compounds **13** and **17** are quite stable, and their crystals can be kept for several months at room temperature under air without noticeable decomposition. The others, however, are less stable; dimer **12** decomposes during evaporation of the solvent unless the solution is deaerated by bubbling with nitrogen beforehand; the solids of tetramer **14** and pentamer **15** decompose at room temperature under air within several weeks; compound **16** decomposes in deaerated solution during several days at room temperature, although its crystals remain stable when kept at −15 °C under an inert atmosphere.

The single crystals of **13** and **17** were obtained by slow diffusion of acetonitrile into the benzene solution of **13** or the dichloromethane solution of **17**. X-ray crystallography was performed on these single crystals, and the obtained ORTEP views and the crystal packing diagrams are illustrated in Figures 2 and 3 for compounds **13** and **17**, respectively.

The crystal of annulene **13** also contains benzene molecules in a 1:1 ratio to **13**. As has been reported for the single crystal of the analogous derivative of dehydro[18]annulene (**2**),[3a,e] the central 18-membered ring π-system in **13** is almost planar. The butadiyne unit is bent slightly outward with, for example, an inner angle for C2−C3−C4 of 177.4(3)°. The crystal packing diagram shows that two molecules of **13** are facing each other in a staggered geometry with the distance between the mean planes of the two π-systems being 3.6 Å. This value is larger than the generally known distance between stacked π-systems (3.4 Å), and the electronic interaction between these π-system should be negligibly small if any. In fact, there was no difference observed between the electronic spectra of **13** in dilute solution and in the solid state. Furthermore, no significant lowering of the heat of formation was observed for the two molecules of **13** in the facing arrangement when the PM3 calculation was carried out using the coordinates obtained from X-ray crystallography, and the result was compared with the summation of the heat of formation independently determined for compound **13**.

On the other hand, the X-ray crystal structure of **17** is the first one determined for the tetradehydro[16]annulene derivative. As shown in Figure 3a, the central π-system of **17** has a tub-shaped structure, as has been reported for various cyclooctatetraene derivatives,[23,24] or like octadehydro[24]annulene, which has been reported to have a similar tub form based on the electronic spectros-

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[22] A homocoupling reaction of terminal acetylenes under palladium−copper-catalyzed condition were reported: Crisp, G. T.; Flynn, B. L. *J. Org. Chem.* **1993**, *58*, 6614.

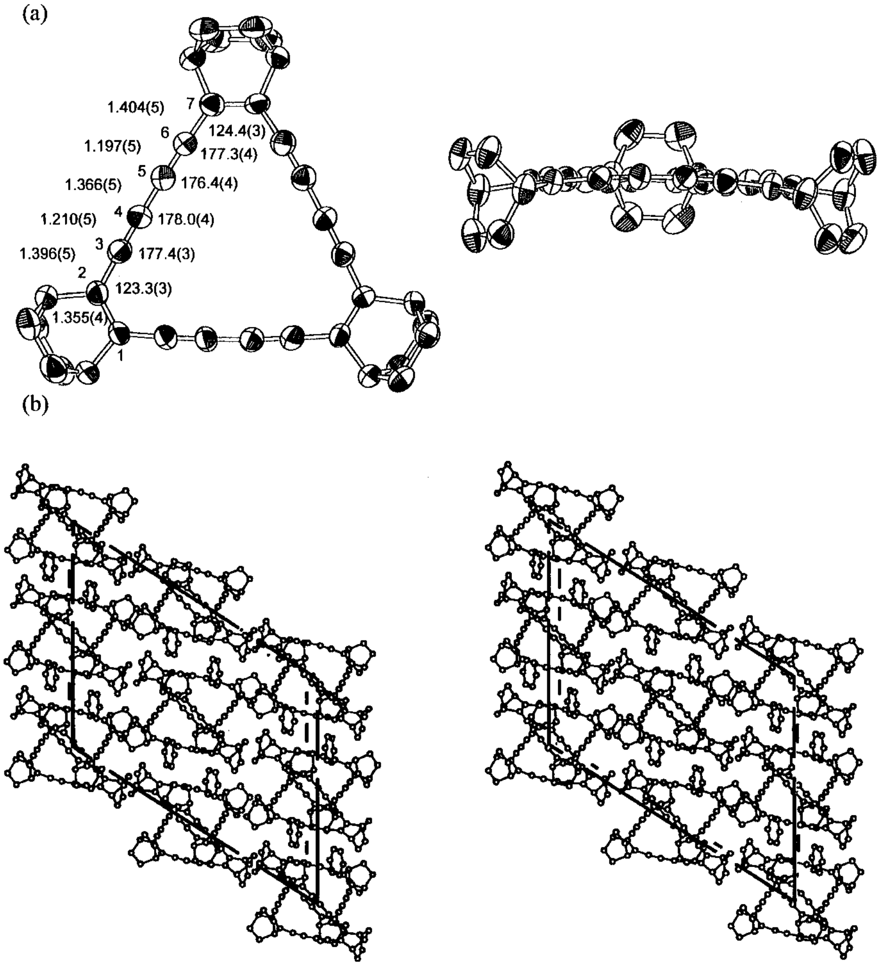

Figure 2. X-ray structure of **13**: (a) ORTEP (50% probability) drawings showing a top and side views and (b) a stereoview of the unit cell showing the crystal packing.

copy.[25] Although the angle strain of the cyclic π-system should be released by folding to a tub form, the acetylenic linkages of the molecule are not linear but are bent slightly inward with, for example, an inner angle for C2−C3−C4 of 185.0(3)°. This is in contrast to the optimized structure obtained by PM3 calculations (see Figure 4), in which no such bending is observed. In addition, the crystal structure of **17** is less folded within the tub structure, as indicated by the smaller value of the folding angle α than was predicted by the calculated structure (41°). These differences between the X-ray crystal structure and the calculated structure may have at least in part originated from the crystal packing effect. The crystal of **17** contained the solvent molecule, acetonitrile, in a 1:1 ratio. This acetonitrile is located at the position between the two BCO units oppositely placed in the molecule of **17** and is possibly exerting a steric effect that partially unfolds the [16]annulene π-system (Figure 3b).

The PM3 calculations were conducted for annulenes **12**−**17**, and the characteristic features of the compounds along with the values of the inner angles of the π-systems are shown in Figure 4. Among the planar π-systems, i.e., [12]annulenes **12** and **16** and [18]annulene **13**, the 12-membered ring of **12** is apparently the most strained. The considerable flexibility of the butadiyne linkage (C≡C−C angles, 166.0° and 163.0°) relaxes the molecule much more effectively than the narrowing of the C=C−C angle at the BCO junction.

The calculated structure by AM1 of [24]annulene **3** (n = 2) was reported to be planar owing to the much wider C=C−C angle (135.8°; PM3, 134.6°) caused by the fusion of the cyclobutene ring.[21] On the other hand, the structures of [24]annulene **14** as well as [16]annulene **17** were calculated to have a folded, "tublike" structure. Apparently, the tub form in the optimized structures of **17** and **14** results from the adoption of the optimum inner angles of C=C−C (126.3°) and C≡C−C (179.3°) of the diethynyl BCO (Figure 1) as indicated by the angles of a and b in **17** and **14**.

The structure of the decadehydro[30]annulene, i.e., cyclopentamer **15**, is quite intriguing. However, a single crystal could not be obtained in spite of various attempts, and we can only presume its structure based on theoretical calculations. As shown in Figure 4, the PM3-optimized structure places the three butadiyne edges nearly in the same plane, and other two edges are bent over this plane with a bent angle of 73°. Thus, the cyclic π-systems form an envelope-like structure with the three

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(23) For examples of the X-ray structure: (a) Pawley, G. S.; Lipscomb, W. N.; Freedman, H. H. *J. Am. Chem. Soc.* **1964**, *86*, 4725. (b) Bordner, J.; Parker, R. G.; Stanford, R. H., Jr. *Acta Crystallogr.* **1972**, *28B*, 1069. (c) Laird, B. B.; Davis, R. E. *Acta Crystallogr., Sect. B* **1982**, B38, 678.

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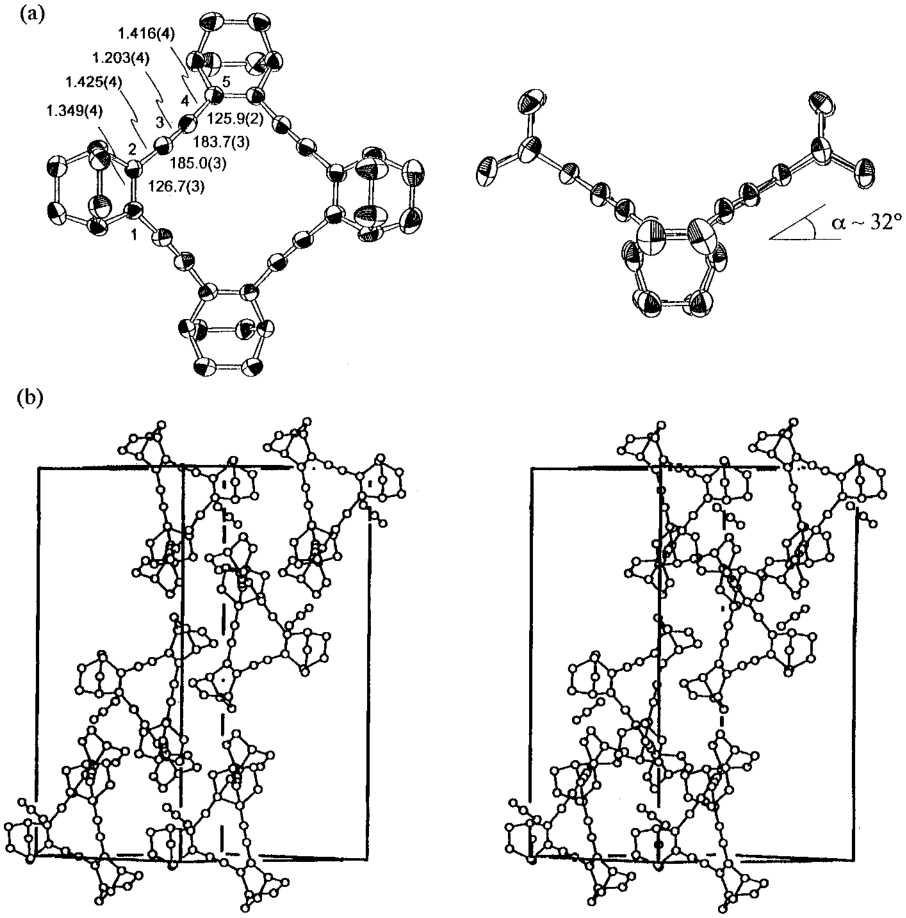

Figure 3. X-ray structure of **17**: (a) ORTEP (50% probability) drawings showing a top and side views and (b) a stereoview of the unit cell showing the crystal packing.

butadiyne moieties constituting a 16-π linear conjugated system.

The ^{1}H and ^{13}C NMR data for the dehydroannulenes **12**−**17** are summarized in Table 1, together with those of benzene **10** and enediyne **20c** for comparison. All of these dehydroannulenes exhibit simple NMR signals reflecting their highly symmetrical structures. The *exo*- and *endo*-methylene carbons in the BCO units of the compounds with nonplanar π-systems such as **14**, **15**, and **17** appear as an equivalent signal in the ^{13}C NMR spectra, suggesting that the conformational changes in these compounds are rapid in the NMR time scale. No spectral change was observed in the NMR of **14**, **15**, and **17** even when cooled to −90 °C. This appears quite reasonable because the differences in heat of formation between the tub form and the planar form (a possible transition-state structure for the ring inversion)[26] were calculated by PM3 to be only 2.2 and 3.3 kcal mol^{-1} for **14** and **17**, respectively.

In comparing the ^{1}H NMR data, it is clear that, due to the paramagnetic ring current, the signal for the bridgehead proton is shifted considerably upfield to δ 1.76 and 1.72 in the planar dehydro[12]annulenes **12** and **16**, irrespective of their structures exhibiting either D_{2h} or D_{3h} symmetries. On the contrary, the diatropicity in dehydro[18]annulene **13** causes a downfield shift for the bridgehead proton (δ 3.41) to an extent similar to that previously observed in benzene **10** (δ 3.29).[17] For the annulenes having nonplanar π-systems, not much shift is observed for this signal, as compared to the reference compound **20c**.

Redox Behavior. In order to investigate the redox behavior of the dehydroannulenes, cyclic voltammetry was performed in benzonitrile with tetrabutylammonium perchlorate as an electrolyte. The observable range under these conditions was from +1.2 V to −2.0 V vs Ag/Ag$^+$. For purposes of comparison, tridehydro[12]annulene **7** was synthesized according to the literature method.[13] Table 2 shows the observed redox potentials. As far as the reduction process is concerned, all of the annulenes except **15** exhibited reversible waves within a range from −1.5 to −2.0 V. The irreversibility of **15** is probably due to its highly bent structure, as has been discussed above. There appears to be a tendency for the antiaromatic planar systems such as **7** and **12**, as well as nonplanar **14**, to be reduced at relatively less negative potentials.

For the oxidation process, on the other hand, the reversible wave was observed only for the annulenes having BCO units connected by a single acetylene bond, i.e., **16** and **17**. This may indicate that annelation with BCO units stabilizes the cationic π-systems. Such an effect would be reduced upon increasing the number of triple bonds per BCO unit. This tendency becomes more apparent when we compare the redox potentials of **7**, **12**, and **16**. All of these compounds have planar conjugated systems with 12 π electrons, and the number of annelated BCO units is zero, two, and three for compounds **7**, **12**, and **16**, respectively. Although **12** has a considerably strained π-system, there is a qualitative tendency for

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[26] The transition state of ring inversion in cyclooctateraene was calculated to be a planar conformation: Paquette, L. A. *Pure Appl. Chem.* **1982**, *54*, 987.

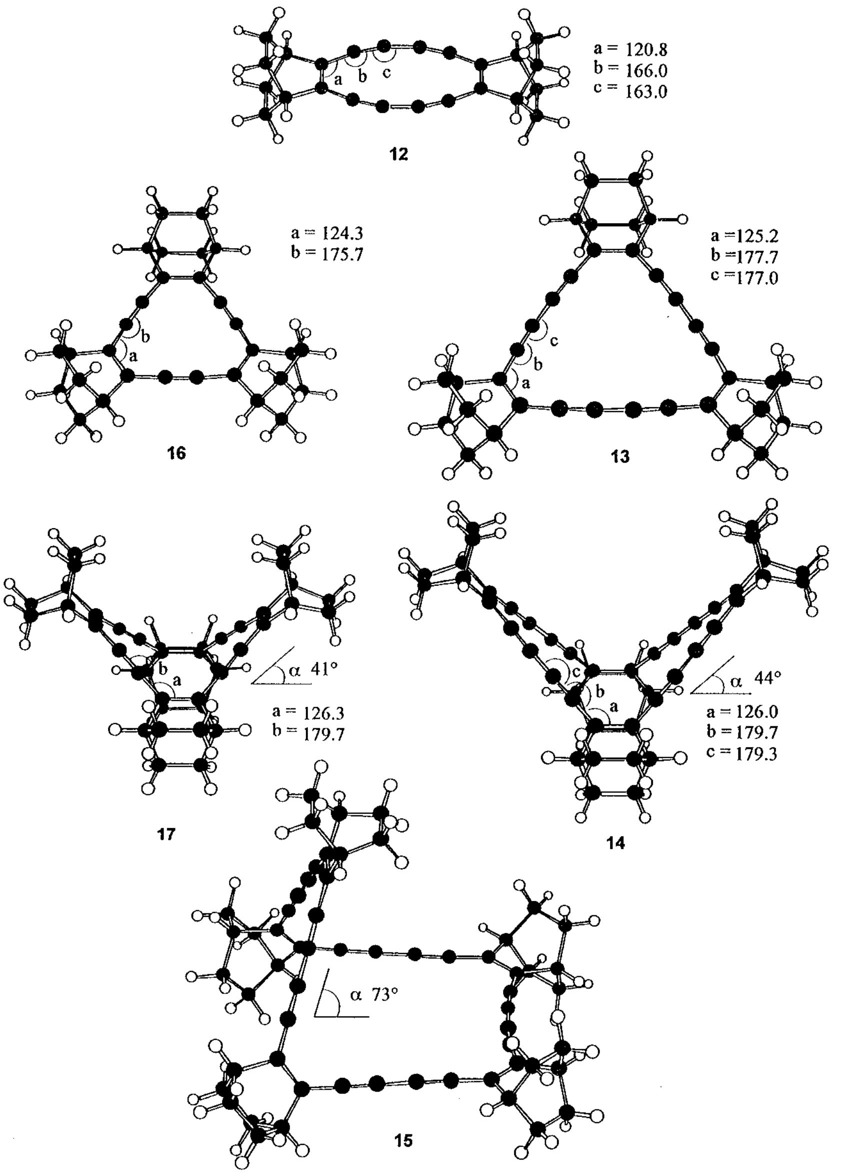

Figure 4. PM3-calculated structures of **12**−**17**. The inner angles of the π-systems of **12**−**14**, **16**, and **17** and the folding angle of the π-systems of **14**, **15**, and **17** are included. The folding angle (α) is a dihedral angle between the mean plane of the bottom part and the mean plane of the folded part.

Table 1. The NMR Chemical Shift (δ) of Benzene 10, Enediyne 20c, and Dehydroannulenes 12−17 in CDCl$_3$

		^{1}H NMR		^{13}C NMR			
compd		CH	CH$_2$	sp^2-C	sp-C	CH	CH$_2$
10	(6π)	3.29	1.75, 1.35	134.2		28.7	26.5
20c		2.72	1.57, 1.42	133.2	82.4, 81.7	35.8	25.1
12	(12π)	1.76	1.29	143.8	95.8, 87.4	32.1	24.6
13	(18π)	3.41	1.84, 1.56	135.6	84.2, 81.2	36.3	25.7
14	(24π)	2.68	1.59, 1.43	135.0	83.5, 81.0	36.6	25.2
15	(30π)	2.75	1.57, 1.42	134.3	83.4, 81.0	36.8	25.2
16	(12π)	1.72	1.26	136.8	96.4	33.7	24.6
17	(16π)	2.47	1.47	132.8	95.4	37.2	25.3

these 12-π electron systems to be more readily oxidized and less readily reduced as the number of BCO units increases. Thus, the annelation with BCO units has been shown to be effective both in rigidly holding the σ-framework and in donating electron by inductive and σ−π conjugative effects.[27]

The observed value of the oxidation peak potential for annulenes **7** and **12**−**17** changes from +0.5 to +1.20 V ranging over a nearly 0.7 V width. A plot of these values against the energy levels of the HOMO calculated by PM3 produces a fairly good linear correlation as shown in Figure 5a. On the other hand, the observed reduction

Table 2. Oxidation (E_{ox}) and Reduction Potentials (E_{red}) of Dehydroannulenes 7 and 12−17 in C$_6$H$_5$CN Measured by Cyclic Voltammetry[a]

compd		E_{ox}, V vs Ag/Ag$^+$	E_{red}, V vs Ag/Ag$^+$
7	(12π)	+1.17[b]	−1.58[c]
12	(12π)	+0.93[b]	−1.67
13	(18π)	+1.21[b]	−1.96
14[d]	(24π)		−1.53
15	(30π)	+1.07[b]	−1.90[b]
16	(12π)	+0.54	−1.93
17	(16π)	+0.62[e]	−1.96

[a] With 0.1 M Bu$_4$NClO$_4$; scan rate 0.1 V s^{-1}. Values are those for the half-wave potential ($E_{1/2}$) unless otherwise noted. [b] The peak potential for the irreversible wave. [c] The second reduction wave (irreversible) was observed with the peak potential at −2.16 V. [d] Because of the low solubility, the measurement was performed in C$_6$H$_5$CN−CH$_2$Cl$_2$ (4:3). The observable range in this solvent was from +1.0 V to −2.0 V. [e] The second oxidation wave (irreversible) was observed with the peak potential at +0.88 V.

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[27] Komatsu, K. *Pure Appl. Chem.* **1993**, *65*, 73.

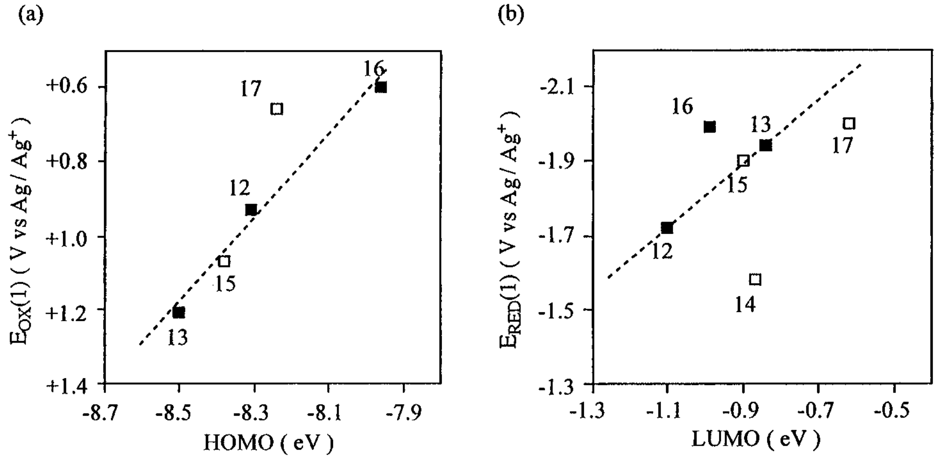

Figure 5. (a) Plot of the first oxidation peak potential, $E_{ox}(1)$, against the calculated HOMO level and (b) a plot of the first reduction peak potential, $E_{red}(1)$, against the calculated LUMO level for annulenes **12**–**17**. The closed squares correspond to the compounds with planar π-systems, while the open squares are for compounds with rather flexible, nonplanar π-systems.

peak potential ranges over a 0.4 V width. A plot of these potentials against the calculated LUMO levels is scattered as shown in Figure 5b. The calculated frontier MO levels are highly dependent on the structure. The MO levels used in these plots are associated with the energy-minimized structure in Figure 4. However, these molecules are presumably in rapid equilibrium with other conformers in solution. Such an effect might be a cause for the absence of linear correlation in Figure 5b.

In summary, when comparing the redox potentials of a series of dehydroannulenes having the butadiyne linkage, compounds **13** (18π system) and **15** (30π system) are shown to be more resistant against both oxidation and reduction than compounds **12** (12π system) and **14** (24π system). The observed readiness of **12** and **14** to release or gain electron is apparently due to the antiaromatic nature of these compounds. The higher potentials in both the oxidation and reduction of **13** would be due to the electronic stabilization resulting from the Hückel aromaticity, while those in **15** would be due to the greatly decreased conjugation caused by its highly bent structure. The other series, consisting of dehydroannulenes **16** (12π system) and **17** (16π system), are considered to be typical antiaromatic π-systems, which could readily undergo both oxidation and reduction in a similar way to **12** (and **7**). However, the presence of a relatively larger number of BCO units per triple bond has made these systems more readily oxidized and less readily reduced, both by 0.3–0.4 V, again demonstrating the considerable electron-donating character of the BCO group.

Experimental Section

General Procedures. Melting points are uncorrected. Elemental analyses were performed at the Microanalysis Division of Institute for Chemical Research, Kyoto University. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 300 and 75.4 MHz. FT-IR spectra were recorded as KBr pellets. Preparative GPC was conducted on a JAI LC-908 chromatograph equipped with two JAIGEL-2H columns connected in series. The PM3 calculations were conducted using the standard methods as implemented in the MOPAC 6.0 semiempirical molecular orbital package.

THF and ether were freshly distilled over sodium benzophenone ketyl before use. Diethylamine was distilled over calcium hydride, while pyridine was distilled over potassium hydroxide. Methanol was distilled over sodium methoxide. The other commercially available solvents and reagents were used without further purification. Bis(triphenylphosphine)palladium(II) chloride[28] and tetrakis(triphenylphosphine)palladium[29] were prepared according to the literature procedure. 2,3-Dibromobicyclo[2.2.2]oct-2-ene **18** was prepared as reported previously.[17]

2-Bromo-3-[(trimethylsilyl)ethynyl]bicyclo[2.2.2]oct-2-ene (19a) and 2,3-Bis[(trimethylsilyl)ethynyl]bicyclo-[2.2.2]oct-2-ene (20a). (Trimethylsilyl)acetylene (350 mL, 22.4 mmol, 3 equiv) was added dropwise to a stirred solution of **18** (1.99 g, 7.51 mmol), copper(I) iodide (0.0972 g, 0.510 mmol), and bis(triphenylphosphine)palladium(II) chloride (0.527 g, 0.750 mmol) in diethylamine (37 mL). Addition of each drop of (trimethylsilyl)acetylene caused a change in the color of the reaction mixture from orange to black-brown. After the mixture was stirred for 10 h at rt, the solvent was evaporated and the residue dried in vacuo. The crude product was extracted with hexane twice and separated by column chromatography over silica gel eluted with hexane into two fractions. The first fraction gave **19a** (0.154 g 7.2%) as a white solid: mp 75.5–77.0 °C; ^{1}H NMR δ 2.83 (br s, 2H), 1.4–1.6 (m, 8H), 0.22 (s, 9H); ^{13}C NMR δ 129.8, 127.2, 102.2, 99.0, 41.7, 38.7, 26.1, 25.4, 0.0; IR (KBr) 2151 ($C\equiv C$) cm^{-1}. Anal. Calcd for $C_{13}H_{19}SiBr$: C, 55.10; H 6.80. Found: C, 55.05; H, 6.75. From the second fraction was obtained **20a** (1.97 g, 87.4%) as a white solid: mp 63.5–64.0 °C dec; ^{1}H NMR δ 2.68 (br s, 2H), 1.55 (d, 4H), 1.41 (d, 4H), 0.22 (s, 18H); ^{13}C NMR δ 133.9, 103.1, 99.9, 35.7, 25.2, 0.1; IR (KBr) 2148 ($C\equiv C$) cm^{-1}; HRMS calcd for $C_{18}H_{28}Si_2$ 300.1730, found 300.1707. Anal. Calcd for $C_{18}H_{28}Si_2$: C, 71.92; H, 9.39. Found: C, 71.30; H, 9.44.

The same reaction conducted with a smaller amount (2 equiv) of (trimethylsilyl)acetylene afforded **19a** in 23.1% yield and **20a** in 25.1% yield, together with 33.1% of recovered **18**.

2-Bromo-3-(3-hydroxy-3-methyl-1-butynyl)-bicyclo[2.2.2]oct-2-ene (19b) and 2,3-Bis(3-hydroxy-3-methyl-1-butynyl)bicyclo[2.2.2]oct-2-ene (20b). Following the procedure described above, addition of 3-hydroxy-3-methyl-1-butyne (1.13 mL, 11.8 mmol, 1.6 equiv) to a solution of **18** (2.00 g, 7.53 mmol), copper(I) iodide (0.179 g, 0.938 mmol), and bis(triphenylphosphine)palladium(II) chloride (0.801 g, 1.14 mmol) in diethylamine (25 mL) gave the mixture of **19b**, **20b**, and **18**, which was separated by flash chromatography over silica gel. Elution with hexane gave 29.4% of recovered **18**, while elution with hexane–ether (1:1) gave 30.8% of **19b**, followed by 38.0% of **20b** as white solids. **19b**: mp 59.5–60.5 °C; ^{1}H NMR δ 2.83 (br s, 1H), 2.78 (br s, 1H), 2.46 (br s, 1H), 1.58 (s, 6H), 1.58–1.4 (m, 8H); ^{13}C NMR δ 128.9, 126.7, 98.2, 79.9, 65.8, 41.7, 38.6, 31.4, 26.1, 25.4; HRMS calcd for $C_{13}H_{17}OBr$ 270.0442, found 270.0464. Anal. Calcd for $C_{13}H_{17}OBr$: C, 58.00; H, 5.62. Found: C, 58.57; H, 6.43.

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(28) Goodall, D. C. *J. Chem. Soc. A* **1968**, 887.
(29) Malatesta, L.; Angoletta, M. *J. Chem. Soc.* **1957**, 1186.

20b: mp 128.6−130.2 °C; ^{1}H NMR δ 3.46 (br s, 2H), 2.63 (br s, 2H), 1.57 (s, 12H), 1.3−1.6 (m, 8H); ^{13}C NMR δ 132.1, 99.0, 80.4, 65.4, 35.3, 31.4, 25.1; IR (KBr) 2221 ($C\equiv C$) cm^{-1}; HRMS calcd for $C_{18}H_{24}O_2$ 272.1776, found 272.1793. Anal. Calcd for $C_{18}H_{24}O_2$: C, 79.37; H, 8.58. Found: C, 74.95; H, 8.59.

2,3-Diethynylbicyclo[2.2.2]oct-2-ene (20c). A 0.5 mL aqueous solution of one pellet (ca. 0.1 g) of potassium hydroxide was added at rt to a solution of **20a** (0.716 g, 2.38 mmol) in 3.5 mL of THF and 20 mL of methanol. After being stirred for 1 h, the reaction mixture was extracted with ether and dried over $MgSO_4$. After evaporation, the organic layer gave **20c** as the unstable white solid quantitatively, and this compound was used in the next step without further purification. **20c**: ^{1}H NMR δ 3.39 (s, 2H), 2.72 (br s, 2H), 1.58 (d, 4H),1.42 (d, 4H); ^{13}C NMR δ 133.2, 82.4, 81.7, 35.8, 25.1; IR (KBr) 2093 ($C\equiv C$) cm^{-1}; HRMS calcd for $C_{12}H_{12}$ 156.0939, found 156.0976.

Synthesis of Dimer 12, Trimer 13, Tetramer 14, and Pentamer 15. A solution of **20c** (0.219 g, 1.40 mmol) in dry pyridine (20 mL) and dry methanol (20 mL) was added dropwise over a 60-min period to a stirred solution of copper(II) acetate (1.27 g, 6.97 mmol) in dry pyridine (60 mL), dry methanol (60 mL), and dry ether (10 mL). The reaction mixture was heated at 70 °C for 30 min and then stirred for 15 h at rt. After being neutralized with aqueous sulfuric acid and extracted with ether, the reaction mixture was chromatographed in the same way as above to yield **12** (0.033 g, 15%) as an unstable red solid and a mixture of **13**−**15**. The mixture was subjected to preparative GPC eluted with toluene. Separation was effected by recycling the mixture twice to give **13** (0.066 g, 31%) as an orange solid, **14** (0.006 g, 3%) as a yellow solid, and **15** (0.003 g, 1%). A single crystal of **13**·C_6H_6 was grown by slow diffusion of acetonitrile into the benzene solution. **12**: mp >300 °C (the color turned to black at about 90 °C); ^{1}H NMR δ 1.76 (br s, 4H), 1.29 (br s, 16H); ^{13}C NMR δ 143.8, 95.8, 87.4, 32.1, 24.6; IR (KBr) 2159 ($C\equiv C$) cm^{-1}; UV−vis (benzene) λ_{max} 417, 446, 478, 527, 587 nm (no reliable ϵ data available due to the instability); HRMS calcd for $C_{24}H_{20}$ 308.1565, found 308.1590.

13: mp >300 °C (the color turned to black at about 170 °C); ^{1}H NMR δ 3.41 (br s, 6H), 1.84 (d, 12H), 1.56 (d, 12H); ^{13}C NMR δ 135.6, 84.2, 81.2, 36.3, 25.7; IR (KBr) 2175 ($C\equiv C$) cm^{-1}; UV−vis (cyclohexane) λ_{max}(log ϵ) 331(4.68), 347(4.90), 371(4.21), 394(4.26), 404(4.34), 424(3.20). Anal. Calcd for $C_{36}H_{30}\cdot C_6H_6$: C, 93.29; H, 6.71. Found: C, 92.92; H, 6.70.

14: mp >300 °C (the color turned to black at about 200 °C); ^{1}H NMR δ 2.68 (br s, 8H), 1.59 (d, 16H), 1.43 (d, 16H); ^{13}C NMR δ 135.0, 83.5, 81.0, 36.6, 25.2; IR (KBr) 2175 ($C\equiv C$) cm^{-1}; UV−vis (chlorobenzene) λ_{max} 286,324, 348, 373 nm, (no reliable ϵ data available due to the instability); DCI MS m/z 616 (M^-).

15: ^{1}H NMR δ 2.75 (br s, 10H), 1.57 (d, 20H), 1.42 (d, 20H); ^{13}C NMR δ 134.3, 83.4, 81.0, 36.8, 25.2; IR (KBr) 2187, 2173, 2154 ($C\equiv C$) cm^{-1}; UV−vis (cyclohexane) λ_{max} 257, 302, 323, 346, 373, 414, 442 nm (no reliable ϵ data available due to the instability); FAB MS m/z 770 (M^+).

Tetramer **14** was also synthesized as follows. Addition of (trimethylsilyl)acetylene (0.225 mL, 1.59 mmol, 4 equiv) to a stirred solution of **21** (see below) (0.168 g, 0.399 mmol), copper(I) iodide (0.011 g, 0.056 mmol), and bis(triphenylphosphine)palladium(II) chloride (0.042 g, 0.060 mmol) in diethylamine (10 mL) and dichloromethane (2 mL) and stirring the mixture for 24 h at 60 °C gave the crude product. This mixture was purified by flash column chromatography over silica gel eluted with dichloromethane−hexane (1:1) to give **22a** (66.7%): mp >99.5−101.5 °C; ^{1}H NMR δ 2.70 (br s, 4H), 1.57 (d, 8H), 1.42 (d, 8H), 0.23 (s, 18H); ^{13}C NMR δ 135.7, 132.5, 103.1, 101.3, 82.3, 79.7, 36.2, 36.1, 25.2, 0.1; IR (KBr) 2135 cm^{-1}; HRMS calcd for $C_{30}H_{38}Si_2$ 454.2512, found 454.2473. The same method for desilylation and the coupling under Eglinton conditions in the same way as that for synthesis of **12**−**15** yielded **14** (10%).

2-Bromo-3-ethynylbicyclo[2.2.2]oct-2-ene (19c). Silylethynyl compound **19a** was desilylated by the same procedure as described for **20c** above to give **19c** quantitatively. This compound was rather unstable under air and used in the following reaction without further purification. **19c**: ^{1}H NMR δ 3.33 (s, 1H), 2.85 (m, 2H), 1.6−1.4 (m, 8H); ^{13}C NMR δ 130.1, 126.3, 81.6, 81.5, 41.7, 38.7, 26.0, 25.3.

1,4-Bis(2-bromobicyclo[2.2.2]octen-1-yl)butadiyne (21). A solution of crude **19c** (0.386 g, 1.83 mmol), copper(I) iodide (0.027 g, 0.141 mmol), and bis(triphenylphosphine)palladium(II) chloride (0.124 mg, 0.176 mmol) in diethylamine (20 mL) was stirred at refluxing temperature for 4.5 h. Evaporation and separation of the crude mixture with flash column chromatography over silica gel gave **21** (0.167 g. 0.397 mmol 43.4%) as a white solid. **21**: mp 191.7−193.9 °C; ^{1}H NMR δ 2.86 (br s, 4H), 1.4−1.6 (m, 16H); ^{13}C NMR δ 133.2, 127.2, 81.5, 79.0, 42.9, 39.7, 26.9, 26.2; IR (KBr) 2139 ($C\equiv C$) cm^{-1}; HRMS calcd for $C_{20}H_{20}Br_2$ 417.9931, found 417.9943. Anal. Calcd for $C_{20}H_{20}Br_2$ C, 57.17; H, 4.80. Found: C, 57.88; H, 4.88.

Synthesis of Trimer 16 and Tetramer 17. An aqueous solution of sodium hydroxide (5 N, 1 mL) was added at 80 °C to a stirred mixture of **19b** (0.148 g, 0.549 mmol), tetrakis(triphenylphosphine)palladium(0) (0.026 g, 0.023 mmol), copper(I) iodide (0.015 g, 0.080 mmol), and benzyltriethylammonium chloride (0.012 g, 0.051 mmol) in benzene (2 mL). After the mixture was stirred at 85 °C for 24 h, the reaction was quenched by adding saturated aqueous ammonium chloride (4 mL) and the mixture extracted with benzene. Then the organic layer was dried ($MgSO_4$), evaporated, and separated by preparative GPC eluted with toluene to give **16** (0.016 g. 22%) and **17** (0.006 g. 9%). Compound **16** was recrystallized from dichloromethane−acetonitrile for elemental analysis, but the correct analytical data could not be obtained due to the instability. **16**: mp >300 °C (the color turned to black at about 180 °C); ^{1}H NMR δ 1.72 (br s, 6H), 1.26 (s, 24H); ^{13}C NMR δ 136.8, 96.4, 33.7, 24.6; IR (KBr) 2176 ($C\equiv C$) cm^{-1}; UV−vis (cyclohexane) λ_{max}(log ϵ) 252 (4.34), 261 (4.43), 498 (1.9) nm; HRMS calcd for $C_{30}H_{30}$ 390.2348, found 390.2347. Anal. Calcd for $C_{30}H_{30}\cdot CH_2Cl_2$: C, 78.31; H, 6.78. Found: C, 76.44; H, 6.84.

Compound **17** was recrystallized by slow diffusion of acetonitrile into the dichloromethane solution. **17**: mp >300 °C (the color turned to black at about 180 °C); ^{1}H NMR δ 2.47 (br s, 8H), 1.47 (q, 32H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 132.8, 95.4, 37.2, 25.3; UV−vis (cyclohexane) λ_{max}(log ϵ) 301 (5.04), 311 (5.06), 372 (3.29), 414 (3.10) nm; IR (KBr) 2251, 2173, 2156 ($C\equiv C$) cm^{-1}; HRMS calcd for $C_{40}H_{40}$ 520.3130, found 520.3145. Anal. Calcd for $C_{40}H_{40}\cdot CH_3CN$ C, 89.79; H, 7.71; N, 2.49. Found: C, 85.18; H, 7.47; N, 2.36.

Tetramer **17** was also obtained as an only cyclized product in 15% yield when dibromide **18** (0.207 g, 0.778 mmol) was reacted with **20b** (0.196 g, 0.720 mmol) under the same conditions and separated as described above.

X-ray Crystallography of 13·C_6H_6 and 17·CH_3CN.[30] Data for compounds **13**·C_6H_6 and **17**·CH_3CN were collected with graphite-monochromated Cu Kα radiation and a 12 kW rotating anode generator.

Crystal data for **13**·C_6H_6 are as follows: $C_{36}H_{30}\cdot C_6H_6$; space group $C_{2/c}$; $a = 27.196(5)$ Å, $b = 12.834(2)$ Å, $c = 21.280(3)$ Å, $\beta = 123.195(7)°$; $V = 6215(1)$ Å^3; $Z = 8$; $D_{calc} = 0.989$ g/cm^3; m(Cu Kα) = 4.19 cm^{-1}; total of 1825 reflections within $2\theta = 120.1°$ and $I > 3\sigma(I)$. The final R factor was 4.3% ($R_w = 4.1\%$).

Crystal data for **17**·CH_3CN are as follows: $C_{40}H_{40}\cdot CH_3CN$; space group $P2_{1/a}$; $a = 12.164(3)$ Å, $b = 24.412(4)$ Å, $c = 12.277(4)$ Å, $\beta = 116.92(2)°$; $V = 3250(1)$ Å^3; $Z = 4$; $D_{calc} = 1.064$ g/cm^3; m(Cu Kα) = 4.46 cm^{-1}; total of 2780 reflections within $2\theta = 120.1°$ and $I > 3\sigma(I)$. The final R factor was 4.7% ($R_w = 4.6\%$).

All of these structures were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were geometrically calculated and fixed.

Cyclic Voltammetry. The cyclic voltammetry was conducted using a three-electrode cell with a glassy carbon

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(30) The authors have deposited atomic coordinates for these structures with the Cambridge Crystallographic Data Centre. The coordinates, bond distances, and angles can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 4E2, U.K.

working electrode, a platinum counter electrode, and a Ag/0.01 M $AgNO_3$ reference electrode. The standard conditions for the measurement were as follows: concentration, 1 mM of the sample in benzonitrile containing 0.1 M tetrabutylammonium perchloarte; scan rate, 100 mV s^{-1}. Because of the instability of **12** and low solubility of **14** and **15**, the concentration of these compounds was about 0.5 mM. The potential was corrected against ferrocene used as an internal standard added immediately after each measurement.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of **12**−**17** and **19**−**22** and cyclic voltammograms of **7** and **12**−**17** (35 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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