Structures and Tropicity of Hydrogenation Products of a Bisdehydro[13]annulenone and a Bisdehydro[15]annulenone

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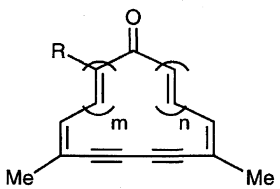
The catalytic partial hydrogenation of the 5,10-dimethyl-6,8-bisdehydro[13]annulenone using Pd–$BaSO_4$ afforded the 5,10-dimethyl[13]annulenone together with two isomeric 5,10-dimethyl-6-dehydro[13]annulenones. The dimethyl-[13]annulenone, which is the first example of a monocyclic non-dehydro annulenone derivative larger than tropone, was found to be atropic on the basis of ^{1}H NMR spectra. Molecular mechanics studies indicate the extensive deviation of the molecular skeleton from planarity and help to explain the lack of peripheral conjugation. Attempts to obtain the [15]-annulenone and the [17]annulenone from the bisdehydro[15]annulenone and the bisdehydro[17]annulenone, respectively, were unsuccessful.

The dimethyl- or trimethylbisdehydroannulenones **1** (Chart 1) with 13-membered to 25-membered rings as well as their benzannulated derivatives and methano-bridged ones have been synthesized and their tropic properties have been studied.[1] However until now, none of the non-dehydro annulenone derivatives solely containing double bonds have been reported in any monocyclic series except the small-membered ones, [3]-, [5]-, and [7]annulenones.[2] Thus the [7]annulenone, tropone, is still the largest non-dehydro annulenone known, although several attempts to prepare larger non-dehydro annulenones from the respective dehydroannulenones were made.[3] It has been theoretically predicted[4] that non-dehydro annulenones will show smaller tropicity than the respective one-carbon fewer annulenes, since the polarization of the carbonyl group is necessary for the appearance of tropicity in annulenones. However no direct experimental verification of this has been reported.

In this paper we describe the preparation of 5,10-dimethyl-[13]annulenone **5** from the corresponding bisdehydro derivative, 5,10-dimethyl-6,8-bisdehydro[13]annulenone **2**,[5] the lowest member of a series of compounds **1**[6] and the similar but failed attempts at the preparation of 2,5,10-trimethyl[13]-annulenone, 5,10-di-*t*-butyl[13]annulenone, 5,10-dimethyl-[15]annulenone, and 7,12-dimethyl[17]annulenone from 2, 5,10-trimethyl-6,8-bisdehydro[13]annulenone **6**,[5] 5,10-di-*t*-butyl-6,8-bisdehydro[13]annulenone **10**, 5,10-dimethyl-6, 8-bisdehydro[15]annulenone **13**,[7] and 7,12-dimethyl-8,10-bisdehydro[17]annulenone **15**,[7] respectively. It should be pointed out that the 5,10-dimethyl[13]annulenone **5** is the first example of a monocyclic non-dehydro annulenone to be obtained.[2]



R = H or Me

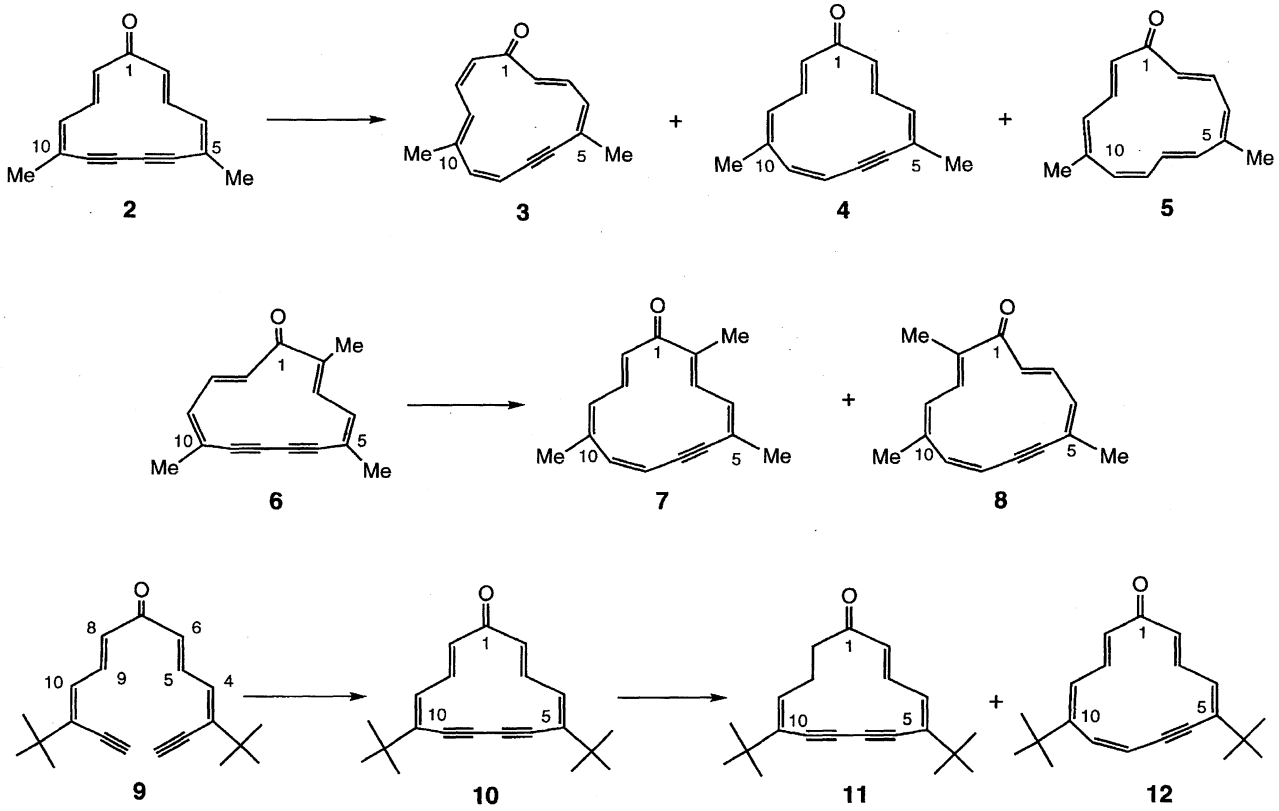
1 ; m = 1 ~ 4 , n = 1 ~ 4

Chart 1.

Results and Discussion

Synthesis. Several attempts to obtain the [13]annulenone from the corresponding bisdehydro[13]annulenone **2** were made by chemical reduction using diisobutylaluminum hydride in dry benzene[8] and 9-borabicyclo[3.3.1]nonane in THF,[9] and by catalytic hydrogenation using $NiBr_2$–Zn in *N*,*N*-dimethylformamide (DMF),[10] and Pd–C in benzene,[11] but all of them failed. A successful result was obtained only with hydrogenation using Pd–$BaSO_4$ in benzene.[12]

Catalytic partial hydrogenation of compound **2** over Pd–$BaSO_4$ under atmospheric pressure afforded two isomeric dehydro[13]annulenones **3** and **4** and the non-dehydro [13]annulenone **5** (Scheme 1). Careful chromatography of the hydrogenation products over alumina afforded the 'di-cis' isomer **3** (red needles, mp 64—65 °C) of the dehydro compound from the initial fractions. The second fractions afforded a mixture of the 'mono-cis' dehydro[13]annulenone and the non-dehydro [13]annulenone **5** in a ratio of ca. 7 : 1; this mixture could be separated by repeated thin-layer chro-



Scheme 1.

matography. The 'mono-cis' isomer **4** was obtained as orange plates, mp 95—96 °C. Compound **4** was found to be readily converted to **3** by allowing its benzene solution to stand without protection from daylight. This behavior of **4** made it easy to separate the mixture of **4** and **5**. Compound **5** was isolated as orange prisms, mp 85—87 °C.

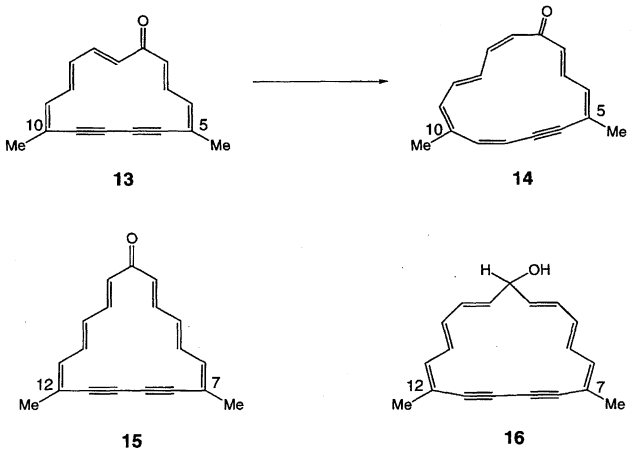
Catalytic hydrogenation of 2, 5, 10- trimethyl- 6, 8-bisdehydro[13]annulenone **6**[5] afforded two dehydro[13]-annulenones **7** and **8** in a ratio of 4 : 1, like the formation of the isomers **3** and **4** from **2**, but none of the corresponding non-dehydro trimethyl[13]annulenone could be obtained. The reason for the absence of the non-dehydro compound is not clear.

5,10-Di-*t*-butyl-6,8-bisdehydro[13]annulenone **10** was prepared by oxidative coupling of the corresponding acyclic diethynyl compound **9**[13] under the Eglinton conditions. Catalytic hydrogenation of **10** using Pd–$BaSO_4$ under the same conditions as above afforded the partly saturated ketone **11** and the dehydro[13]annulenone **12** in a ratio of 22 : 1, but the desired [13]annulenone was not obtained. The preferential formation of the partly saturated ketone **11** from compound **10** may be ascribed to the steric bulkiness of two *t*-butyl groups at propargylic 5- and 10-positions which might hinder the approach of hydrogen toward acetylenic bonds, as compared with the case of the dimethylbisdehydro[13]-annulenone **2**.

Upon catalytic hydrogenation of 5,10-dimethyl-6,8-bisdehydro[15]annulenone **13**[7] using Pd–$BaSO_4$ in toluene–ethanol (9 : 1), the dehydro[15]annulenone **14** was obtained as the only isolable product, but the desired [15]annulenone was not detected (Scheme 2).

Catalytic hydrogenation of 7,12-dimethyl-8,10-bisdehydro[17]annulenone **15**[7] using Pd–$BaSO_4$ in benzene afforded a complex mixture of hydrogenation products, some of which carried aliphatic hydrogens based on ^{1}H NMR, and no pure products could be isolated. We considered that the alcohol **16** obtained by $NaBH_4$ reduction of the ketone **15** might afford the hydrogenation products with eight double bonds. However hydrogenation of **16** with Pd–$BaSO_4$ in benzene afforded no detectable products.

^{1}H NMR Spectral Analysis and Structure Determination. ^{1}H NMR spectra of all the compounds obtained were measured in $CDCl_3$ and such spectra were also measured in



Scheme 2.

C_6D_6 for some compounds. These spectra were fully analyzed and unambiguously assigned with the aid of decoupling and NOE experiments. The spectral data of compounds **3**—**5** are complied in Table 1 together with those of compound **2**. Those of compounds **6**—**8**, **10**—**12**, and **13**—**14** are given in Tables 2, 3, and 4, respectively. The two-dimensional geometries of the compounds deduced from the NMR data are shown in Schemes 1 and 2.

While compound **4** retains the geometry of **2** except for the change of one triple bond to a *Z*-double bond, isomerization of the original *E,Z*-configuration of one diene moiety to *Z,E* had occurred in compound **3**, and a conformational change had also occurred: The C2=C3 moiety had flipped inside-out. In compound **5**, the new diene moiety has the *E,Z*-geometry, and both of the original diene moieties retains the *E,Z*-geometry. The nuclear Overhauser enhancement (NOE) is observed between 7-H and 12-H, indicating the proximity of these hydrogens. Also, irradiation of 7-H enhanced the 3-H signal rather than the 2-H one, although 3-H is located outside of the ring according to the two-dimensional representation. That the molecule is actually severely deviated from planarity and the two-dimensional representation is somewhat misleading, is shown by molecular mechanics studies mentioned later.

The trimethylbisdehydro[13]annulenone **6** is conformationally labile, as deduced before,[5] the conformer given in Scheme 1 being most populated. The hydrogenation products **7** and **8** retain the original configuration of the diene moieties of **6**, though they may be conformationally different depending on which of the triple bonds was hydrogenated. The di-*t*-butyldehydro[13]annulenone **12** was shown to have a similar skeletal geometry to that of the corresponding dimetyl compound **4**.

The dehydro[15]annulenone **14** (Scheme 2) was also shown to have a different skeletal geometry from the corresponding bisdehydro compound **13**. The NOE experiments showed the close proximity of 3-H and 13-H, suggesting the severe nonplanarity of the molecular skeleton.

A conformational change of the ring skeleton has also occurred upon conversion from the ketone **15** to the alcohol **16**: The C2=C3 (C16=C17) moiety had flipped inside-out (Scheme 2).

Tropicity. All of the 5,10-dimethyl[13]annulenone derivatives in this study, **2**—**5**, are expected to be paratropic because they would form a 12π-electron peripherally conjugated system by polarization of the carbonyl group. As previously reported,[5] the bisdehydro[13]annulenone **2** clearly shows paratropicity, judging from the large chemical shift difference (ca. 3.2 ppm) between the inner and outer olefinic protons. The dehydro[13]annulenones **3** and **4** are also paratropic. The chemical shift differences between the inner and outer olefinic protons are comparable to those in compound **2**, but the methyl proton signals appear at considerably lower field than that of compound **2**. This suggests that compounds **3** and **4** are less paratropic than **2**, although quantitative comparison is difficult because other factors than

Table 1. ^{1}H NMR Data of Compounds **2**—**5** in $CDCl_3$ at 24 °C[a)]

Compd	2[b)]	3	4	5
Proton				
2-H	6.092	8.536	5.868	5.928
	(d 16.7)	(d 15.7)	(d 16.7)	(dd 16.6, 1.7)
3-H	9.414	6.922	9.007	8.184
	(ddq 16.7, 9.4, 0.6)	(ddq 15.7, 5.5, 1.1)	(ddq 16.7, 8.9, 0.9)	(dd 16.6, 6.6)
4-H	6.287	5.997	6.330	5.996
	(ddq 9.4, 0.9, 1.6)	(dquin 5.5, 1.5)	(dquin 8.9, 1.4)	(dm 6.6)
6-H				5.771
				(d 16.4)
7-H				7.043
				(dd 16.3, 11.0)
8-H		5.508	5.703	6.032
		(d 11.8)	(d 13.2)	(dd 12.2, 11.0)
9-H		5.879	5.785	5.622
		(d 11.8)	(d 13.2)	(d 12.2)
11-H		9.428	5.910	6.018
		(d 12.2)	(d 11.8)	(d 11.5)
12-H		6.778	8.649	7.963
		(t 12.0)	(dd 15.8, 11.8)	(dd 15.9, 11.7)
13-H		5.751	5.725	5.913
		(d 11.8)	(d 15.8)	(d 15.9)
5-Me	1.752	1.911	1.904	1.845
	(dt 1.6, 0.6)	(t 1.1)	(br s)	(br s)
10-Me		1.856	1.883	1.925
		(d 1.1)	(br s)	(br s)

a) Chemical shifts are given in δ. In parentheses are the splitting pattern and coupling constants in Hz. b) Re-examined. See also Ref. 5.

Table 2. ^{1}H NMR Data of Compounds **6**—**8** in $CDCl_3$ at 24 °C[a]

Compd	**6**[b]	**7**	**8**
Proton			
2-H			6.194 (d 16.6)
3-H	9.584 (d 10.9)	8.968 (d 9.0)	8.208 (dd 16.6, 7.5)
4-H	6.556 (dq 10.7, 1.6)	6.359 (d 9.1)	6.321 (d 7.5)
8-H		5.688 (d 13.0)	5.730 (d 13.0)
9-H		5.780 (d 13.1)	5.822 (d 13.0)
11-H	6.208 (m)	5.888 (d 11.8)	6.212 (d 12.1)
12-H	7.72—7.60 (m)	8.530 (dd 15.8, 11.7)	8.333 (d 12.1)
13-H	7.72—7.60 (m)	5.729 (d 15.6)	
2-Me	1.816 (s)	1.805 (s)	
5-Me	1.777[c] (m)	1.894 (s)	1.89 (s)
10-Me	1.788[c] (m)	1.894 (s)	1.946 (s)
13-Me			1.89 (s)

a) Chemical shifts are given in δ. In parentheses are the splitting pattern and coupling constants in Hz. b) Re-examined. See also Ref. 5. c) Interchangeable.

Table 3. ^{1}H NMR Data of Compounds **10**—**12** in $CDCl_3$ at 24 °C[a]

Compd	**10**	**11**	**12**
Proton			
2-H	5.949 (d 16.8)	6.467 (d 16.4)	5.934 (d 16.8)
3-H	9.610 (dd 16.8, 9.5)	7.119 (dd 16.4, 10.2)	8.822 (dd 16.8, 9.0)
4-H	6.248 (dd 9.5, 0.7)	6.860 (d 10.3)	6.384 (dq 8.8, 1.0)
8-H			5.919 (d 13.2)
9-H			6.070 (d 13.2)
11-H		6.325 (t , 7.8)	6.050 (d 11.5)
12-H		2.44—2.35 (m)	8.181 (dd 15.9, 11.5)
13-H		2.35—2.23 (m)	5.814 (dq 15.9, 0.5)
5-*t*-Bu	1.084 (s)	1.218 (s)	1.150 (s)
10-*t*-Bu		1.153 (s)	1.157 (s)

a) Chemical shifts are given in δ. In parentheses are the splitting pattern and coupling constants in Hz.

Table 4. ^{1}H NMR Data of Compounds **13**—**14** in $CDCl_3$ at 24 °C[a]

Compd	**13**[b]	**14**
Proton		
2-H	6.629 (d 16.4)	5.937 (d 16.1)
3-H	5.825 (dd 16.4, 11.5)	8.150 (dd 16.1, 11.0)
4-H	7.202 (d 11.5)	6.315 (d 11.0)
8-H		5.671 (d 11.1)
9-H		6.268 (d 11.1)
11-H	7.214 (d 11.7)	6.056 (d 9.1)
12-H	5.463 (dd 15.4, 11.7)	6.390 (dd 15.8, 9.3)
13-H	6.812 (dd 15.4, 4.9)	6.271 (dd 15.8, 9.0)
14-H	7.534 (dd 15.6, 4.9)	6.703 (dd 12.3, 9.0)
15-H	5.632 (d 15.6)	5.780 (d 12.3)
5-Me	2.234 (s)	1.966 (d 1.0)
10-Me	2.174 (s)	1.888 (s)

a) Chemical shifts are given in δ. In parentheses are the splitting pattern and coupling constants in Hz. b) See Ref. 14b.

the ring current effect, such as the steric compression effect and the anisotropy effect of the acetylenic bonds, may affect the chemical shifts.

On the other hand, the [13]annulenone **5** is considered to be atropic. Although two signals assigned to 3-H and 12-H resonate at a low field of ca. $\delta = 8.0$, 3-H is formally located outside of the macrocycle according to the NMR spectral analysis (Table 1; see below). As these protons are located β to the carbonyl, the low field appearance of these protons can be ascribed to the electron-density and anisotropy effects of the carbonyl group rather than the ring current effect. In addition, the steric compression effect may partly be responsible for the low-field chemical shifts of 7-H and 12-H which are close to each other.

The 5,10-dimethyl[15]annulenone derivatives **13** and **14** are expected to be diatropic because they would form a 14π-electron conjugated system by polarization of the carbonyl group. As previously reported,[7] the bisdehydro[15]-annulenone **13** clearly shows diatropicity, judging from the chemical shift difference (ca. 1.4 ppm) between the inner and outer olefinic protons. However, the dehydro[15]annulenone **14** is not diatropic, but atropic, because inner and outer olefinic protons resonate in almost the same field, and the methyl protons resonate at a considerably higher field than that of compound **13** (Table 4).

Tropicity of annulenones is generally enhanced in acidic media such as trifluoroacetic acid (TFA) and sulfuric acid

because the polarization of the carbonyl is promoted by protonation on the carbonyl oxygen, as has been demonstrated for compounds **2**[5] and **13**.[7] ^{1}H NMR spectra of **2**—**5** were measured in trifluoroacetic acid-*d* (TFA-*d*) and the data are given in Table 5.

Dissolution of either **3** or **4** in TFA-*d* affords the same deuteronated species **3A** (Scheme 3). In annulenones, facile cis–trans isomerization of double bonds in acidic media has often been observed.[14] The ^{1}H NMR spectrum of **3A** exhibits signals due to the inner olefinic protons at very low field (2-H: δ=11.36; 11-H: δ=11.71) and those due to the outer olefinic protons at high field (δ=5.27—7.24), demonstrating that the deuteronated species **3A** is paratropic. On quenching with aqueous $NaHCO_3$, the species **3A** completely decomposed, irrespective of whether it was formed from **3** or **4**, and no neutral species could be recovered.

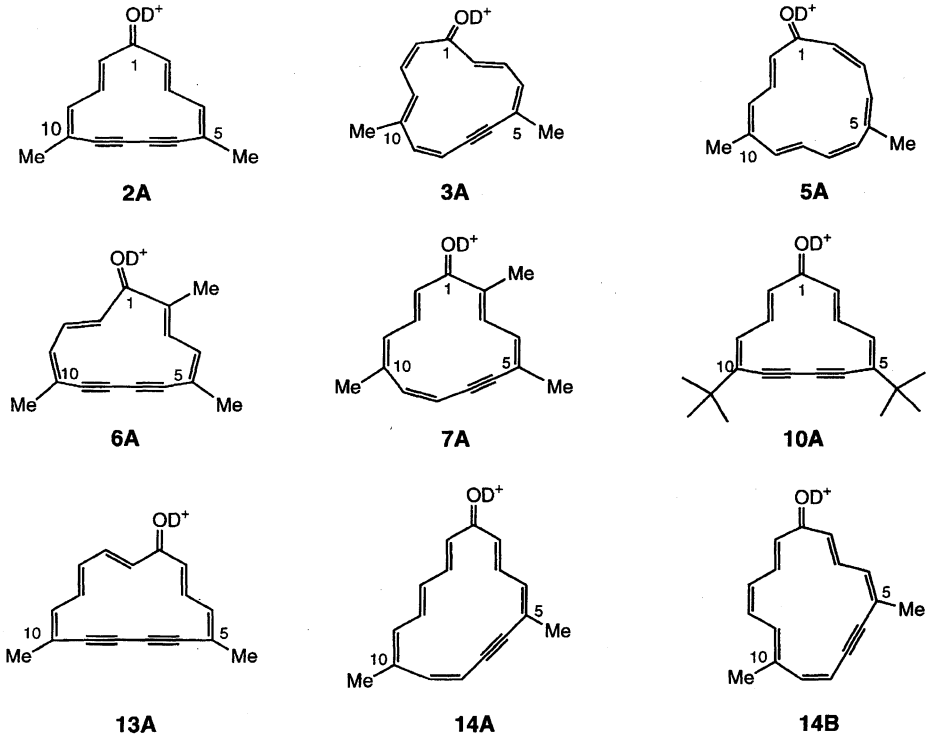
As compound **5** was also unstable in TFA-*d* at ambient temperature, the NMR spectrum was obtained at −10 °C, where the deuteronated species survived long enough to afford satisfactory spectra. Analysis of the ^{1}H NMR spectrum of **5** in TFA-*d* indicated that **5** existed in a conformation given as **5A** in Scheme 3 by two-dimensional representation, which was different from that in $CDCl_3$. This species showed no tropicity at all in this medium; the 'inner' protons 8-H and 12-H appeared at δ=4.95 and 6.36, respectively.

The ^{1}H NMR spectral data of dehydro compounds **7**, **8**, and **12** in $CDCl_3$ (Tables 2 and 3) indicate that paratropicity in these compounds is somewhat smaller than those in the respective bisdehydro counterparts **6** and **10**. The NMR spectral data of compounds **7** and **10** obtained in TFA-*d* are given in Table 6 together with the re-examined data of **6**.

Table 5. ^{1}H NMR Data of Compounds **2**, **3**, and **5** in CF_3CO_2D[a]

Species	2A[b,c]	3A[c]	5A[d]
Proton			
2-H	6.193 (d 16.4)	11.358 (d 15.6)	6.210 (d 10.9)
3-H	10.950 (dd 16.4, 9.7)	7.235 (dd 15.6, 6.1)	6.644 (dd 10.9, 8.3)
4-H	6.163 (dm 9.7)	5.801 (d 6.1)	6.254 (d 8.3)
6-H			7.152 (d 10.1)
7-H			6.980 (dd 11.8, 10.1)
8-H		5.271 (d 11.7)	4.946 (dd 13.7, 11.8)
9-H		5.665 (d11.7)	7.003 (d 13.7)
11-H		11.712 (d 12.1)	7.279 (d 11.3)
12-H		7.037 (t 11.7)	6.359 (dd 14.1, 11.3)
13-H		5.772 (d 11.3)	7.236 (d 14.1)
5-Me	1.717 (d 1.5)	1.879 (s)	2.581 (s)
10-Me		1.840 (s)	1.860 (s)

a) Chemical shifts are given in δ. In parentheses are the splitting pattern and coupling constants in Hz. b) Re-examined. See also Ref. 5. c) At 24 °C. d) At −10 °C.



Scheme 3.

Table 6. ^{1}H NMR Data of Compounds **6**, **7**, and **10** in CF_3CO_2D at 24 °C[a)]

Species	**6A**[b)]	**7A**	**10A**
Proton			
2-H			5.992
			(d 16.4)
3-H	10.723	11.056	11.440
	(d 10.5)	(d 9)	(dd 16.4, 9.5)
4-H	6.500	6.301	6.153
	(dp 10.5, 1.4)	(d 9)	(d 9.5)
8-H		5.623	
		(d 13)	
9-H		5.784	
		(d 13)	
11-H	6.157	5.959	
	(d 7.0)	(d 12)	
12-H	8.342	10.719	
	(dd 16.2, 7.0)	(dd 14, 12)	
13-H	8.010	5.974	
	(d 16.2)	(d 14)	
2-Me	1.846	2.043	
	(s)	(s)	
5-Me	1.786	1.973	1.104
(5-*t*-Bu)	(s)	(s)	(s)
10-Me	1.763	1.920	
	(s)	(s)	

a) Chemical shifts are given in δ. In parentheses are the splitting pattern and coupling constants in Hz. b) Re-examined. See also Ref. 5.

Table 7. ^{1}H NMR Data of Compounds **13** and **14** in CF_3CO_2D at 24 °C[a)]

Species	**13A**[b)]	**14A**[c)]	**14B**[d)]
Proton			
2-H	8.694	8.028	8.662
	(d 15.1)	(d 14.6)	(d 15.4)
3-H	0.287	1.561	0.063
	(dd 15.1, 12.3)	(dd 14.6, 11.8)	(dd 15.2, 11.9)
4-H	9.140	8.239	8.894
	(d 12.3)	(d 11.8)	(d 11.9)
8-H		7.577	8.352
		(d 13.7)	(d 12.1)
9-H		7.832	8.393
		(d 13.6)	(d 12.1)
11-H	9.140	7.660	−0.059
	(d 12.3)	(d 12.5)	(d 12.2)
12-H	−0.158	3.073	9.504
	(dd 15.1, 12.4)	(t 12.7)	(dd 13.3, 9.3)
13-H	8.761	8.233	8.764
	(dd 15.1, 6.3)	(dd 13.0, 11.8)	(dd 12.7, 9.6)
14-H	9.747	2.947	0.679
	(dd 14.8, 6.3)	(m)	(dd 14.8, 12.9)
15-H	−0.087	7.911	8.656
	(d 14.8)	(d 13.2)	(d 14.6)
5-Me	3.259	3.054	3.376
	(s)	(s)	(s)
10-Me	3.175	2.692	3.285
	(s)	(s)	(s)

a) Chemical shifts are given in δ. In parentheses are the splitting pattern and coupling constants in Hz. b) See Ref. 14b. c) Measured immediately after dissolution of **14** in TFA-*d*. d) Measured after left standing for one day in TFA-*d*.

The deuteronated species **6A**, **7A**, and **10A** are concluded to have stronger paratropicity than the respective neutral counterparts. Compound **10** was recovered on quenching the acid solution by aqueous $NaHCO_3$, similarly to the cases for bisdehydro[13]annulenones **2** and **6** as reported.[5)] NMR spectra of compounds **8** and **12** in TFA-*d* could not be obtained because of insufficient amounts of the samples.

Thus the present results indicate that paratropicity of the [13]annulenone derivatives decreases with the decreasing number of triple bonds; **2** > **3**, **4** > **5** ; **6** > **7**, **8** ; **10** > **12**.

Dissolution of **14** in TFA-*d* affords immediately a reddish purple solution containing the deuteronated species **14A**, but the species gradually underwent the cis–trans isomerization of double bond to afford finally the other species **14B** with purple color together with some decomposition products.

The ^{1}H NMR spectral data of these species are listed in Table 7 together with those of **13** in TFA-*d*, i.e. **13A**. As previously reported,[7)] **13A** shows diatropicity, judging from the chemical shifts of the inner and outer olefinic protons as well as the methyl protons. The data in Table 7 indicate that **14A** is less diatropic than **13A** and **14B** is as diatropic as or even more diatropic than **13A** if the methyl chemical shifts are considered. On quenching of the species **14A** or **14B** with aqueous $NaHCO_3$, the recovered neutral species was found to be different from the neutral species **13**, but the structure was not determined.

Electronic Spectra. The electronic absorption spectra of compounds **2**, **4**, and **5** in THF are shown in Fig. 1. All

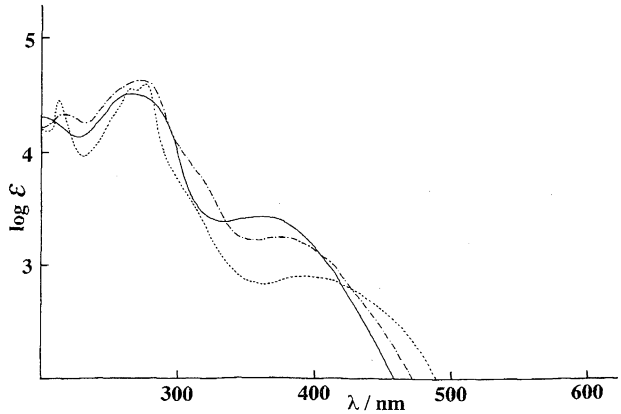


Fig. 1. Electronic absorption spectra of the annulenones **2** (- - -), **4** (— — —), and **5** (——) in THF.

the spectra are quite similar to each other, reflecting the fact that all of them are 12π-electron systems, but the longest wavelength band shifts toward shorter wavelength on going from **2** to **4** to **5**,[5)] indicating the decrease in the degree of extended conjugation in this order. This trend holds between compounds **6** and **7** (**8**), and between compounds **10** and **12** (see Experimental section).

These results are in agreement with those obtained from examination of the ^{1}H NMR spectral data described above.

Molecular Mechanics Studies. In order to get deeper

insight into the structures of the annulenones synthesized in this study, we planned to make X-ray crystallographic analyses of these compounds. Unfortunately, good single crystals suitable for the analysis were not obtained for any of compounds **3**, **4**, and **5**, nor for compound **2**. Therefore, molecular mechanics calculations (MM3) were performed for these compounds.[15] The optimized geometries of these compounds are shown in Fig. 2.

The molecular geometry of **2** is calculated to be considerably deviated from planarity because of the repulsion between the inner hydrogens 3-H and 12-H though retaining the C_2 symmetry (Fig. 2a). While the formal double bonds are almost planar (the average deviation from planarity is ca. 3°), the geometries around the formal single bonds (C1–C2 and C3–C4) are deviated from planarity by ca. 25°.

Among the isomeric dehydro[13]annulenones, **3** is calculated to be the most stable and **4** is calculated to be ca. 5.4 kcal mol^{-1} less stable than **3** (Figs. 2b and 2c). The energy difference mainly comes from the torsional energy term. In compound **3**, the intra-ring torsion angles around the formal double bonds are deviated from planarity by less than 3° and those around the formal single bonds are −178, −42, −36, −169, and 43° for the C1–C2, C3–C4, C9–C10, C11–C12, and C13–C1 bonds, respectively. In compound **4**, the intra-ring torsion angles around the formal double bonds are deviated from planarity by less than 8° and those around the formal single bonds are −21, −115, 49, 180, and −50° for the C1–C2, C3–C4, C9–C10, C11–C12, and C13–C1 bonds, respectively. These results may explain the thermal instability and the facile isomerization in the acidic medium of compound **4**. The distances between 2-H and 11-H in **3** and between 3-H and 12-H in **4** are calculated as 2.34 and 2.71 Å, respectively, supporting the presence of NOE between these protons.

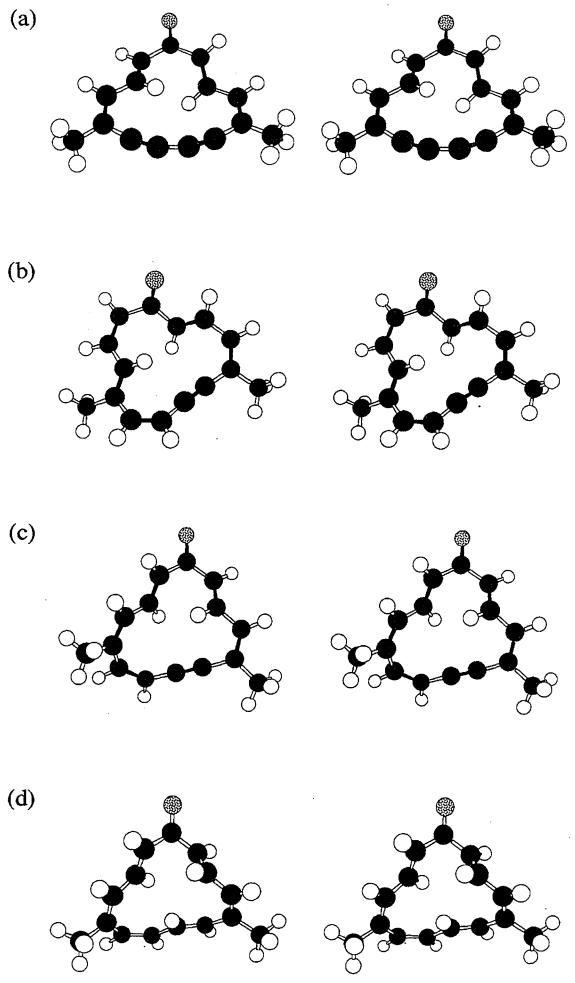


Fig. 2. Stereoviews of the MM3-optimized geometries of (a) **2**, (b) **3**, (c) **4**, and (d) **5**.

In compound **5**, nonplanarity is even severer than **4** (Fig. 2d). The intra-ring torsion angles are −49, −63, −42, −172, 49, −172, and −47° for the C1–C2, C3–C4, C5–C6, C7–C8, C9–C10, C11–C12, and C13–C1 bonds, respectively. The C3–C4 intra-ring dihedral angle of −63° suggests that this bond should be drawn as *s-cis* rather than *s-trans* in the two-dimensional representation. The distances between 3-H and 7-H and between 7-H and 12-H are 2.81 and 2.51 Å, respectively, being compatible with the NOE data.

In summary, we found that, in a series of [13]annulenones, the paratropicity decreases on going from the bisdehydro to the dehydro to the non-dehydro compounds, the planarity of the molecular skeleton and thus the peripheral conjugation being decreased in this order. This finding is clearly in line with the fact that the dehydroannulenes which incorporate acetylenic or cumulenic bonds have been shown to be more stable and of higher tropicity than the corresponding annulenes which lack such bonds.[16] This trend is much more pronounced in annulenones.

Experimental

The melting points were determined on a hot-stage apparatus and are uncorrected. IR spectra were taken with a JASCO-7300 spectrophotometer as KBr discs, unless otherwise specified; only significant maxima are described. Electronic (UV/visible) spectra were measured in THF or TFA solution with a Shimadzu 2200A spectrophotometer. Mass spectra were recorded with a JEOL JMS-D 300 spectrometer operating at 75 eV using a direct-inlet system. ^{1}H NMR spectra at ambient temperature were recorded on a Bruker ARX-300 spectrometer at 300.13 MHz with internal $SiMe_4$ (TMS) as the reference. ^{13}C NMR spectra were recorded on the ARX-300 at 75.48 MHz with $CDCl_3$ at $\delta = 77.0$ or CF_3CO_2D at $\delta = 116.6$ as the reference. The letters, p, s, t, and q, given with the ^{13}C NMR chemical shifts, refer to primary, secondary, tertiary, and quaternary, respectively.

Progress of all reactions was followed by TLC on Merck precoated silica gel. Alumina (Merck, activity II–III) and silica gel (Daiso gel 1001 W or Daiso gel 1002 W) were used for column chromatography. Compounds were preadsorbed from benzene solution onto the adsorbent before column chromatography. Preparative TLC (PLC) was carried out on 20×20 cm alumina plates (Merck, 0.5 or 0.2 mm thick). Organic extracts were washed with saturated aq. sodium chloride and dried over anhydrous sodium sulfate prior to removal of solvent. Solvents were evaporated under water-pump pressure. Ether refers to diethyl ether.

^{13}C NMR Spectral Data of Compound 2[5] in $CDCl_3$ and CF_3CO_2D. ^{13}C NMR ($CDCl_3$) $\delta_C = 194.93$ (q, C=O), 142.53 (t, 3-C and 12-C), 140.04 (t, 4-C and 11-C), 129.72 (t, 2-C and

13-C), 127.27 (q, 5-C and 10-C), 98.47 (q, –C≡), 85.92 (q, –C≡), and 20.06 (p, Me); (CF_3CO_2D) δ_C = 204.67 (q, C=O), 152.41 (t), 140.80 (t), 134.50 (t), 128.80 (q), 100.38 (q, –C≡), 88.87 (q, –C≡), and 20.57 (p, Me).

Isomeric 5,10-Dimethyl-6-dehydro[13]annulenones (3), (4), and 5,10-Dimethyl[13]annulenone (5). A suspension of 5% Pd–$BaSO_4$ (100 mg) in dry benzene (20 cm^3) was stirred under hydrogen atmosphere at room temperature until the uptake of hydrogen ceased. Then a solution of 5,10-dimethyl-6,8-bisdehydro-[13]annulenone **2**[5] (100 mg, 0.48 mmol) in dry benzene (10 cm^3) was added by a syringe and the mixture was stirred under atmospheric pressure while adsorbing 21 cm^3 (ca. 0.96 mmol) of gaseous hydrogen. The reaction mixture was filtered and the inorganic materials were washed with benzene. The filtrate and washings were combined and concentrated. The residue was chromatographed on silica gel (2.6×7.7 cm). The initial fractions eluted with benzene afforded the 'di-cis' 5,10-dimethyl-6-dehydro[13]annulenone **3** (36 mg, 36%) as red needles, mp 64.4—65.2 °C, from hexane–ether; Mass *m/z* 210 (M^+; 55%) and 165 (100); IR 2157 (C≡C), 1647 (C=O), 1604, 1585 (C=C), 980 [(*E*)-HC=CH], and 670 cm^{-1} [(*Z*)-HC=CH]; UV (THF) 296 (ε 34200), 280.5 (sh, 28400), and 341 nm (sh, 4600); (TFA) 291.5 (ε 30200) and 373 nm (6900); for ^{1}H NMR data in $CDCl_3$ and CF_3CO_2D, see Tables 1 and 5; ^{13}C NMR ($CDCl_3$) δ_C = 191.27 (q, C=O), 142.10 (t, 9-C), 140.45 (q), 138.00 (t, 3-C), 135.28 (t, 12-C), 133.49 (t, 4-C), 129.03 (t, 13-C), 127.76 (t, 2-C), 125.08 (t, 11-C), 124.05 (q), 109.14 (t, 8-C), 99.00 (q, –C≡), 95.12 (q, –C≡), 24.35 (p, 5-Me), and 17.91 (p, 10-Me). Found: C, 85.51; H, 6.73%. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71%.

The later fractions eluted with 5% dichloromethane in benzene afforded orange crystals (18.6 mg, 18.4%) which consisted of the 'mono-cis' 5,10-dimethyl-6-dehydro[13]annulenone **4** and the [13]-annulenone **5** in a ratio of 7 : 1 together with a small amount of the di-cis isomer **3**. The mixture was separated by repeated preparative TLC with hexane–ether (1 : 1). The first band afforded the [13]-annulenone **5** in 1.9% yield as orange prisms, mp 85.2—86.7 °C; Mass *m/z* 212 (M^+; 21%) and 18 (100): IR 1627 (C=O), 1615, 1581 (C=C), 995, 962 [(*E*)-HC=CH], 695, and 670 cm^{-1} [(*Z*-HC=CH]; UV (THF) 263.5 (ε 31800), 348.5 (2600), and 361 nm (sh, 2600) and see Fig. 1; (TFA) 255 (ε 10900), 274 (11600), 303.5 (8900), and 475 nm (6500); for ^{1}H NMR data in $CDCl_3$ and CF_3CO_2D, see Tables 1 and 5; ^{13}C NMR ($CDCl_3$) δ_C = 199.28 (q, C=O), 149.28 (t), 143.19 (q), 142.78 (t), 140.73 (q), 133.60 (t), 131.39 (t), 130.77 (t), 130.40 (t), 129.45 (t), 128.41 (t), 125.99 (t), 123.78 (t), 25.79 (p), and 24.07 (p). Found: C, 84.78; H, 7.75%. Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.60%.

The second band afforded **4** in 14.8% yield as orange plates, mp 95.2—96.4 °C, from hexane–ether; Mass *m/z* 210 (M^+; 40%) and 165 (100); IR 2159 (C≡C), 1625 (C=O), 1577, 1565 (C=C), 976 [(*E*)-HC=CH], and 685 cm^{-1} [(*Z*)-HC=CH]; UV (THF) 270 (ε 41100), 276 (sh, 40300), and 372 nm (1700), and see Fig. 1; (TFA) 291.5 (ε 43300), 345.5 (13000), 380.5 (sh, 11400), 398.5 (11500), 416 (sh, 10500), 504.5 (sh, 2400), and 688.5 nm (1200); for ^{1}H NMR data in $CDCl_3$, see Table 1; ^{13}C NMR ($CDCl_3$) δ_C = 198.12 (q, C=O), 150.64 (t, 3-C), 141.55 (t, 12-C), 141.31 (q, 10-C), 137.82 (t, 9-C), 132.72 (t, 4-C), 129.40 (q, 5-C), 128.11 (t, 13-C), 127.76 (t, 11-C), 126.35 (t, 2-C), 110.46 (t, 8-C), 99.32 (q, –C≡), 97.06 (q, –C≡), 26.22 (p, 10-CH_3), and 21.29 (p, 5-CH_3). Found: C, 85.83; H, 6.68%. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71%.

The ^{1}H and ^{13}C NMR Spectral Data of Compound 6.[5] For ^{1}H NMR data in $CDCl_3$ and CF_3CO_2D, see Tables 2 and 6; ^{13}C NMR ($CDCl_3$) δ_C = 195.60 (q, C=O), 139.75 (t), 139.58 (t), 138.17 (t), 137.40 (t), 136.83 (q), 129.12 (t), 127.13 (q), 123.40 (q), 97.51 (q, –C≡), 96.96 (q, –C≡), 88.19 (q, –C≡), 81.61 (q, –C≡), 21.24 (p, –CH_3), 20.01 (p, –CH_3), and 12.21 (p, –CH_3); (CF_3CO_2D) δ_C = 193.72 (q, C=O), 148.50 (t), 145.38 (t), 140.54 (t), 139.00 (t), 137.56 (q), 133.97 (q), 129.38 (q), 128.59 (t), 99.40 (q, –C≡), 98.80 (q, –C≡), 90.63 (q, –C≡), 84.50 (q, –C≡), 21.69 (p, –CH_3), 20.57 (p, –CH_3), and 12.79 (p, –CH_3).

2,5,10-Trimethyl-6-dehydro[13]annulenone (7) and 5,10,13-Trimethyl-6-dehydro[13]annulenone (8). A suspension of 5% Pd–$BaSO_4$ (100 mg) in dry benzene (20 cm^3) was stirred under hydrogen atmosphere at 6 °C until uptake of hydrogen ceased. Then a solution of 2,5,10-trimethyl-6,8-bisdehydro[13]annulenone **6**[5] (100 mg, 0.45 mmol) in dry benzene (10 cm^3) was added by a syringe and the mixture was stirred under atmospheric pressure while adsorbing 20 cm^3 (ca. 0.90 mmol) of gaseous hydrogen. The reaction mixture was filtered off and the inorganic materials were washed with benzene. The filtrate and washings were combined and concentrated. The residue was chromatographed on silica gel (1.9×13.5 cm). The second fractions eluted with benzene afforded the mixture which consisted of the isomers **7** and **8** in a ratio of 4 : 1.

The hydrogenation was repeated in the same scale as described above, and a total of 700 mg of the trimethylbisdehydro[13]-annulenone **6** was converted into the crude product, which was subjected to preparative TLC with hexane–ether (4 : 1). The fast moving, fourth band afforded the major isomer **7** (68 mg, 8.9%) as yellow needles, mp 50.5—51.5 °C, from hexane; Mass *m/z* 224 (M^+; 33%) and 165 (100); IR 2160 (C≡C), 1638 (C=O), 1620 (C=C), 986 [(*E*)-HC=CH], and 708 cm^{-1} [(*Z*)-HC=CH]; UV (THF) 215 (ε 20800), 254 (sh, 32000), 269 (40500), 310.5 (sh, 7600), and 365.5 nm (1900); (TFA) 256.5 (sh, ε 16000), 287 (21200), 300 (sh, 17500), 359.5 (sh, 7900), 456.5 (3700), and 505.5 nm (sh, 2700); for ^{1}H NMR data in $CDCl_3$ and CF_3CO_2D, see Tables 2 and 6; ^{1}H NMR (C_6D_6) δ_H = 9.027 (1H, dm, *J* = 9.1 Hz, 3-H), 8.574 (1H, dd, *J* = 15.9 and 11.7 Hz, 12-H), 5.945 (1H, d, *J* = 9.4 Hz, 4-H), 5.785 (1H, d, *J* = 16.0 Hz, 13-H), 5.504 (1H, d, *J* = 11.6 Hz, 11-H), 5.409 (1H, d, *J* = 13.1 Hz, 8-H), 5.238 (1H, d, *J* = 13.1 Hz, 9-H), 1.815 (3H, s, 2-Me), 1.531 (3H, s, 5-Me), and 1.416 (3H, s, 10-Me); ^{13}C NMR ($CDCl_3$) δ_C = 198.89 (q, C=O), 145.80 (t, 3-C), 140.82 (q), 140.69 (t, 12-C), 137.84 (t, 9-C), 133.45 (q), 132.11 (t, 4-C), 127.88 (q), 127.87 (t, 13-C), 127.82 (t, 11-C), 110.58 (t, 8-C), 98.50 (q, –C≡), 97.43 (q, –C≡), 26.00 (p, 5- or 10-CH_3), 21.45 (p, 10- or 5-CH_3), and 11.44 (p, 2-CH_3). Found: C, 85.58; H, 7.01%. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19%.

The minor isomer **8** (15 mg, 2.0%): For ^{1} NMR data in $CDCl_3$, see Table 2; ^{1}H NMR (C_6D_6) δ_H = 8.440 (1H, dm, *J* = 12.2 Hz, 12-H), 8.224 (1H, ddq, *J* = 16.6, 7.5, and 1.2 Hz, 3-H), 6.234 (1H, dd, *J* = 16.6 and 1.1 Hz, 2-H), 5.993 (1H, d, *J* = 12.3 Hz, 11-H), 5.727 (1H, dt, *J* = 7.5 and 1.6 Hz, 4-H), 5.477 (1H, d, *J* = 13.2 Hz, 8-H), 5.328 (1H, d, *J* = 13.1 Hz, 9-H), 1.887 (3H, s, 13-Me), 1.531 (3H, s, 10-Me), and 1.495 (3H, t, *J* = 1.4 Hz, 5-Me).

3,11-Di-*t*-butyltrideca-3,5,8,10-tetraene-1,12-diyn-7-one (9).[13] Yellow needles, mp 127.0—129.0 °C (decomp), from hexane–benzene; Mass *m/z* 294 (M^+; 9%) and 237 (100); IR 3295 (C≡CH), 2084 and 2058 (C≡C), 1659 (C=O), 1602, 1575 (C=C), and 989 cm^{-1} [(*E*)-HC=CH]; UV (THF) 247.5 (ε 15300) and 344.5 nm (35100); ^{1}H NMR ($CDCl_3$) δ_H = 7.777 (2 H, m, 5-H and 9-H), 6.525 (2H, d, *J* = 15.1 Hz, 6-H and 8-H), 6.519 (2 H, d, *J* = 11.4 Hz, 4-H and 10-H), 3.553 (2 H, s, C≡CH), and 1.203 (18 H, s, 3-*t*-Bu and 11-*t*-Bu); ^{13}C NMR ($CDCl_3$) δ_C = 189.56 (q, C=O), 143.15 (q), 140.62 (t), 131.22 (t) 129.99 (t), 88.04 (t, ≡CH), 80.37 (q, –C≡), 36.59 (q, –*C*Me_3), and 28.96 (p, -CH_3). Found: C, 85.97; H, 8.82%. Calcd for $C_{21}H_{26}O$: C, 85.67; H, 8.90%.

5,10-Di-*t*-butyl-6,8-bisdehydro[13]annulenone (10). A solu-

tion of the ketone **9**[13] (3.46 g, 11.7 mmol) in pyridine–ether (3 : 1; 264 cm^3) was added dropwise during 7 h to a stirred solution of anhydrous copper(II) acetate (14.3 g, 78.8 mmol) in pyridine–ether (3 : 1; 600 cm^3) at 45—50 °C. The solution was stirred for 30 min at 45—50 °C. The mixture was poured onto water and extracted with benzene. The combined extracts were washed successively with 5% aq HCl until they turned acidic, and then with aq $NaHCO_3$, and dried. The residue obtained after removal of the solvent was chromatographed on alumina (4.2×8.0 cm). The fractions eluted with 25% ether in hexane afforded the bisdehydro[13]annulenone **10** (3.10 g, 91%) as orange columns, mp 129.0—130.5 °C, from hexane–ether; Mass *m/z* 292 (M^+; 15%) and 57 (100); IR 2176 (C≡C), 1621 (C=O), 1607 (C=C), and 978 cm^{-1} [(*E*)-HC=CH]; UV (THF) 252 (sh, ε 15350), 264 (26650), 275 (29900), and 384 nm (650); (TFA) 249.5 (ε 12400), 272 (sh, 17000), 283 (21300), and 345 nm (sh, 3800); for ^{1}H NMR data in $CDCl_3$ and CF_3CO_2D, see Tables 3 and 6; ^{13}C NMR ($CDCl_3$) δ_C = 195.19 (q, C=O), 143.55 (t), 143.28 (q), 134.92 (t), 130.36 (t), 97.55 (q, –C≡), 88.80 (q, –C≡), 34.98 (q, –*C*Me_3), and 28.78 (p, –CH_3); (CF_3CO_2D) δ_C = 205.13 (q), 154.65 (t), 151.13 (t), 135.89 (t), 129.07 (q), 99.65 (q, –C≡), 92.34 (q, –C≡), 36.97 (q, –*C*Me_3), and 29.25 (p, –CH_3). Found: C, 86.38; H, 8.18%. Calcd for $C_{21}H_{24}O$: C, 86.25; H, 8.27%.

5,10-Di-*t*-butylcyclotrideca-2,4,10-triene-6,8-diyn-1-one (11) and 5,10-Di-*t*-butyl-6-dehydro[13]annulenone (12). A suspension of 5% Pd–$BaSO_4$ (100 mg) in dry benzene (20 cm^3) was stirred under hydrogen atmosphere at 10 °C until uptake of hydrogen ceased. Then a solution of 5,10-di-*t*-butyl-6,8-bisdehydro[13]-annulenone **10** (200 mg, 0.68 mmol) in dry benzene (20 cm^3) was added by a syringe and the mixture was stirred under atmospheric pressure while absorbing 15.3 cm^3 (ca. 0.68 mmol) of gaseous hydrogen. The reaction mixture was filtered and the inorganic materials were washed with benzene. The filtrate and washings were combined and concentrated. The residue after removal of the solvent was chromatographed on silica gel (2.7×6.8 cm). The initial fractions eluted with benzene afforded the unchanged **10** (20 mg). The following fractions eluted with benzene afforded compound **11** (16 mg, 7.9%) as pale yellow needles, mp 146.3—147.4 °C, from hexane–ether; Mass *m/z* 294 (M^+; 13%) and 57 (100); IR 2171 (C≡C), 1650 (C=O), 1610 (C=C), and 977 cm^{-1} [(*E*)-HC=CH]; UV (THF) 254 (sh, ε 14500), 262.5 (19200), 274.5 (19800), and 354 nm (5800); for ^{1}H NMR data in $CDCl_3$, see Table 3; ^{13}C NMR ($CDCl_3$) δ_C = 200.77 (q, C=O), 145.10 (q), 144.17 (t), 139.70 (t), 136.00 (q), 134.14 (t), 133.54 (t), 96.40 (q, –C≡), 94.92 (q, –C≡), 92.36 (q, –C≡), 80.86 (q, –C≡), 40.23 (s, –CH_2), 35.44 (q, –*C*Me_3), 34.95 (q, –*C*Me_3), 29.39 (p, –CH_3), 29.36 (p, –CH_3), and 28.82 (s, –CH_2). Found: C, 85.66; H, 8.82%. Calcd for $C_{21}H_{26}O$: C, 85.66; H, 8.90%.

The hydrogenation was repeated in the same scale as described above, and a total of 1.80 g of the di-*t*-butylbisdehydro[13]-annulenone **10** was converted into crude product. The crude product was purified by TLC with hexane–ether (3 : 1). The fast moving, second yellow band afforded compound **12** together with a small amount of impurity. Upon TLC with dichloromethane, the fast moving, second yellow band afforded compound **12** (6.5 mg, 0.36% from compound **10**) as yellow liquid; HRMS *m/z* 294.1979 (M, 294.1981); IR (neat) 2160 (C≡C), 1635 (C=O), 1579 (C=C), 983 [(*E*)-HC=CH], and 706 cm^{-1} [(*Z*)-HC=CH]; UV (THF) 271 (ε 29400) and 362 nm (sh, 1400); for ^{1}H NMR data in $CDCl_3$, see Table 3; ^{13}C NMR ($CDCl_3$) δ_C = 198.45 (q, C=O), 154.51 (q), 152.39 (t), 145.22 (q), 141.74 (t), 135.57 (t), 128.25 (t), 127.92 (t), 127.25 (t), 123.55 (t), 111.83 (t), 102.44 (q, –C≡), 95.54 (q, –C≡), 37.12 (q, –*C*Me_3), 35.86 (q, –*C*Me_3), 29.57 (p, –CH_3), and 29.00 (p, –CH_3).

5,10-Dimethyl-6-dehydro[15]annulenone (14). A suspension of 5% Pd–$BaSO_4$ (20 mg) in a mixture of dry toluene (13.5 cm^3) and dry ethanol (1.5 cm^3) was stirred under hydrogen atmosphere at room temperature until uptake of hydrogen ceased. Then a solution of 5,10-dimethyl-6,8-bisdehydro[15]annulenone **13**[7] (100 mg, 0.43 mmol) in a mixture of dry toluene (9.0 cm^3) and dry ethanol (1.0 cm^3) was added by a syringe and the mixture was stirred under atmospheric pressure while absorbing 19 cm^3 (ca. 0.86 mmol) of gaseous hydrogen. The reaction mixture was worked up as for the isolation of compound **12**. The product was chromatographed on silica gel (1.9×26 cm). The fractions eluted with 15% ether in hexane, were collected and concentrated.

The hydrogenation was repeated in the same scale as described above and a total of 700 mg of the dimethylbisdehydro[15]-annulenone **13** was converted into the crude product. The crude product was subjected to preparative TLC with dichloromethane. The fast moving, second band contained the compound **14**. Then the mixture was separated by preparative TLC with hexane–acetone (9 : 1) as eluent. The fast moving, third band afforded the compound **14** (12 mg, 1.7%) as yellow needles, mp 101.7—102.5 °C, from hexane–benzene; Mass *m/z* 236 (M^+; 72%) and 178 (100); IR 1619 (C=O), 1582 (C=C), 973 [(*E*)-HC=CH], 718 and 641 cm^{-1} [(*Z*)-HC=CH]; UV (THF)243 (ε 19600), 248.5 (19600), 276.5 (27600), and 316 nm (sh, 8600); (TFA) (red purple, **14A**) 260.5 (ε 13000), 354.5 (26800), 374.5 (22300), 402 (sh, 3300), 510.5 (sh, 9100), and 581 nm (sh, 3700); for ^{1}H NMR data in $CDCl_3$, see Table 4; ^{13}C NMR ($CDCl_3$) δ_C = 197.61 (q, C=O), 148.81 (t, 3-C), 142.02 (t, 13-C), 139.43 (q), 136.01 (t, 12-C), 135.81 (t, 14-C), 133.26 (t, 4-C), 130.90 (q), 129.96 (t, 2-C), 129.81 (t, 9-C), 127.04 (t, 11-C), 126.75 (t, 15-C), 96.19 (q, –C≡), 91.89 (q, –C≡), 24.12 (p, 5-CH_3), and 22.59 (p, 10-CH_3); for ^{1}H NMR data in CF_3CO_2D, see Table 7; (CF_3CO_2D, purple, **14B**) δ_C = 184.63 (q, C=O), 151.61 (t), 151.18 (q), 150.84 (t), 147.10 (t), 145.09 (q), 143.19 (t), 140.28 (t), 134.11 (t), 127.66 (t), 127.59 (t), 127.00 (t), 113.74 (t), 113.51 (q, –C≡), 110.83 (q, –C≡), 27.56 (p, –CH_3), and 22.28 (p, –CH_3). Found: C, 86.16; H, 6.86%. Calcd for $C_{17}H_{16}O$: C, 86.41; H, 6.83%.

7,12-Dimethylcycloheptadeca-2,4,6,12,14,16-hexaene-8,10-diyn-1-ol (16). $NaBH_4$ (80 mg, 2.1 mmol) was added in one portion to a solution of the 7,12-dimethyl-8,10-bisdehydro[17]-annulenone **15**[7] (30 mg, 0.12 mmol) in a mixture of dry benzene (5 cm^3) and dry ethanol (5 cm^3). Then the mixture was stirred for 3 h at 20 °C. This mixture was poured onto water and extracted with benzene. The extracts were washed with brine and dried. The residue obtained after removal of the solvent was chromatographed on silica gel (1.9×31 cm). The fractions eluted with hexane–ether (7 : 3) afforded the alcohol **16** (25 mg, 82%) as pale yellow needles, mp 153—154 °C, from hexane-benzene; Mass *m/z* 262 (M^+; 4%) and 229 (100); IR 3353 (OH), 2171 (C≡C), and 966 cm^{-1} [(*E*)-HC=CH]; UV (THF) 291 (ε 41000), 362 (sh, 5400), and 383.5 nm (5800); ^{1}H NMR ($CDCl_3$) δ_H = 6.738 (2H, d, *J* = 11.1 Hz, 6-H and 13-H), 6.469 (2H, dd, *J* = 15.0 and 5.9 Hz, 4-H and 15-H), 6.290 (2H, dd, *J* = 15.4 and 5.9 Hz, 3-H and 16-H) 6.190 (2H, dd, *J* = 15.0 and 11.3 Hz, 5-H and 14-H), 5.196 (2H, ddd, *J* = 15.4, 5.5, and 0.9 Hz, 2-H and 17-H), 4.899 (1H, t, *J* = 5.3 Hz, 1-H), 1.995 (6H, s, 7-Me and 12-Me), and 1.607 (1H, br s, OH, exchangeable with D_2O); ^{13}C NMR ($CDCl_3$) δ_C = 139.70 (t), 132.88 (t), 131.08 (t), 130.25 (t), 126.52 (t), 120.12 (q), 85.94 (q, –C≡), 81.38 (q, –C≡), 72.22 (t, CH–OH), and 21.21 (p, –CH_3). Found: C, 87.25; H, 6.93%. Calcd for $C_{19}H_{18}O$: C, 86.99; H, 6.92%.

Attempted Catalytic Hydrogenation of Compounds 15 and 16. Catalytic hydrogenations of compounds **15** and **16** were attempted with Pd–$BaSO_4$ in dry benzene under exactly the same

conditions as for those of compounds **2**, **6**, and **10**. However, no pure compound could be isolated from our products.

Molecular Mechanics Studies. Molecular mechanics calculations were performed employing the MM3 program[17] with the 1989 force field on a NEC EWS-4800/360 work station.

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