Synthesis and Properties of Methano-Bridged Bisdehydro[17]-, -[19]-, -[21]annulenones and the Related Compounds

Hiroyuki Higuchi, Seiken Kiyoto, Chiaki Sakon, Naoki Hiraiwa, Kaori Asano, Shiro Kondo, Jūro Ojima,* and Gaku Yamamoto*,†

Department of Chemistry, Faculty of Science, Toyama University, Gofuku, Toyama 930

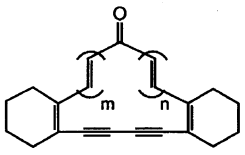
†Department of Chemistry, School of Science, Kitasato University, Kitasato, Sagamihara 228

(Received June 9, 1995)

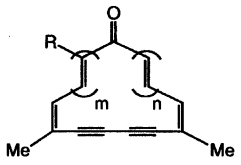
14-Methyl-10,12-bisdehydro-4,9-methano-1*H*-[17]annulen-1-one, 14-methyl-10,12-bisdehydro-4,9-methano-1*H*-[19]annulen-1-one, and 16-methyl-12,14-bisdehydro-6,11-methano-1*H*-[21]annulen-1-one, as well as their methylated and benzannelated derivatives, were synthesized and their tropic properties were studied by NMR and UV spectra under neutral and acidic conditions. The tropicity in these compounds was found to be lower than in their non-bridged monocyclic counterparts. Thus the methano-bridge works to decrease the planarity of the peripherally conjugated system.

In 1972, Sondheimer et al. reported the synthesis of a series of bis(cyclohexene)-annelated bisdehydroannulenones **1**—**3** (Chart 1) as well as the corresponding benzannelated derivatives.[1] After this work was carried out, it has been shown that monocyclic bisdehydroannulenes with methyl substituents at the propargylic positions are superior to the corresponding cyclohexene-fused compounds for the investigation of conformational mobility and ring current effects.[2] Therefore syntheses of dimethylbisdehydro[13]- **4**,[3] -[15]- **5**,[4] -[17]- **6**,[4] -[19]- **7**,[4] and -[21]annulenone **8**[4] (Chart 1) as well as their α-methyl-,[5] α-ethyl-substituted,[6] and benzannelated derivatives[7] were carried out. To elucidate the upper limit of the ring size showing the ring current effect, the higher analogues of these annulenones, the trimethylbisdehydro[23]- **9**[8] and -[25]-annulenone **10**,[8] could also be synthesized, but only with difficulty. Thus we have confirmed the presence of the tropic nature in $[4n+2]\pi$- and $[4n]\pi$-electron systems arising from polarization of the carbonyl group in dimethyl- or trimethylbisdehydroannulenones **4**—**10** with 13- to 25-membered rings (Chart 1). However, no one has reported annulenone derivatives larger than compound **10** with 25-membered ring.[9]

Also, from a study on a series of bisdehydromethanoannulenes **11** (Chart 1), we found that a

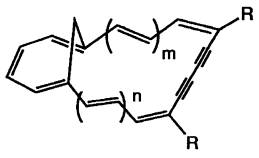


[13]- **1** m = n = 1
[15]- **2** m = 1, n = 2
[17]- **3** m = n = 2



R = H or Me

[13]- **4** m = n = 1
[15]- **5** m = 1, n = 2
[17]- **6** m = n = 2
[19]- **7** m = 2, n = 3
[21]- **8** m = n = 3
[23]- **9** m = 3, n = 4
[25]- **10** m = n = 4



R = Me or t-Bu

11 m = 1 ~ 6, n = 1 ~ 6

Chart 1.

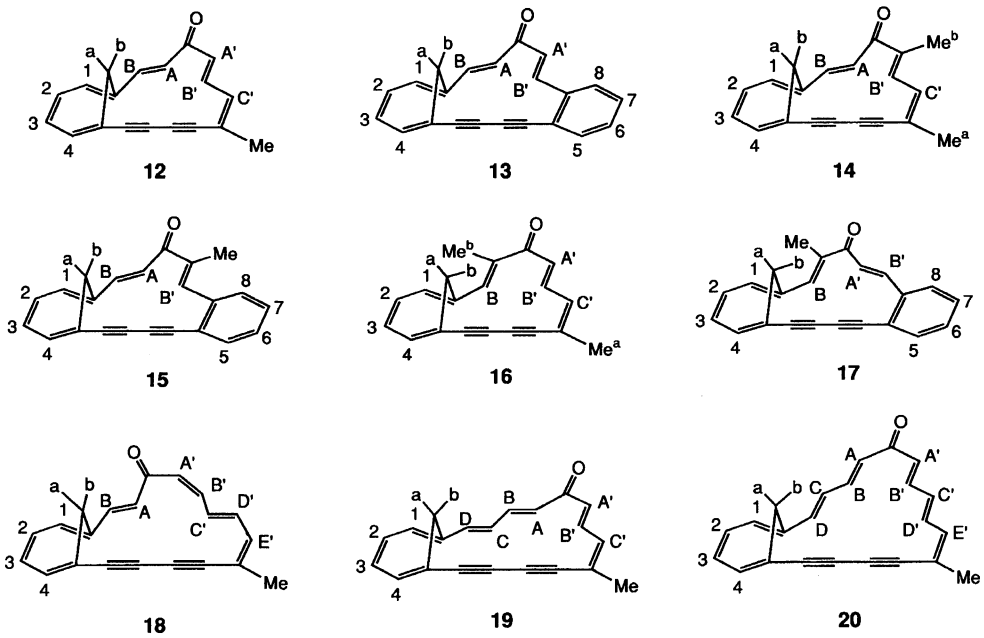


Chart 2.

methano-bridge does not disturb the π-electron distribution, but greatly contributes to keeping the annulene perimeter planar.[10]

Since a 1, 3, 5- cycloheptatriene ring has three conjugated double bonds, we considered that the monomethano- or bismethano-bridged annulenones, formally derived from **1**—**3** by replacement of one or both of cyclohexene rings by cycloheptatriene ring, would form large π-electron systems and that an annulenone with a larger ring size than 25-membered would be prepared. With these purposes in mind, we tested whether the monomethano-bridged annulenones, the title compounds, would show a similar degree of tropicity to those of the monocyclic bisdehydroannulenones with the same number of the π-electrons, e.g. the methano-bridged bisdehydro[17]annulenone **12** (Chart 2) vs. dimethylbisdehydro[17]annulenone **6**. In this paper we describe the synthesis of methano-bridged bisdehydro-[17]annulenone **12**, its α-methyl- **14**, α′-methyl- **16**, and their benzannelated derivatives **13**, **15**, **17**, and the methano-bridged [19]- **18**, **19**, and [21]annulenone **20**. We conducted ^{1}H NMR and UV spectral studies to examine their tropicity and the influence of introduction of an α- or α′-methyl substituent, and a fused benzene ring upon the structure and tropicity of the bisdehydro[17]-, -[19]-, and -[21]annulenone ring system.[11] However, contrary to our expectation, the tropicity of the methano-bridged annulenones was found to be lower than that of their non-bridged monocyclic counterparts.

Results and Discussion

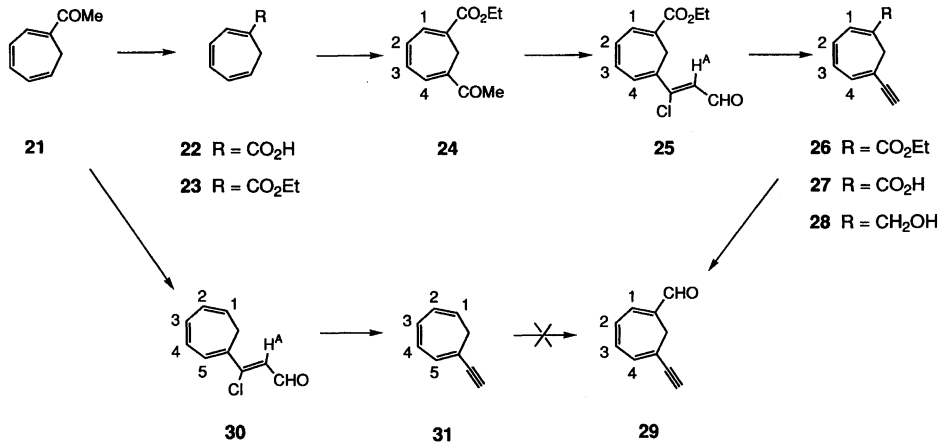
Synthesis. Sondheimer et al. have reported a simple general approach to bisdehydroannulenones **1**—**10**, in which the carbonyl group is flanked on both sides by ethylenic bonds.[1] The method employs construction of a ketone containing two terminal acetylene groups by aldol condensation of an appropriate aldehyde and a ketone, followed by cyclization of the resulting acyclic diethynyl ketone by intramolecular oxidative coupling. 2-Ethynylcyclohexene-1-carbaldehyde[12] and (*Z*)-3-methyl-2-penten-4-ynal (**44**)[3,13] (Scheme 3) were used as the key aldehydes for the preparation of compounds **1**—**3** and **4**—**10**, respectively.

We planned to apply this method to the synthesis of our target compounds, methano-bridged annulenones **12**—**20**, using 6-ethynyl-1,3,5-cycloheptatriene-1-carbaldehyde (**29**)# (Scheme 1) as the key aldehyde. This proved successful, as described in detail below.

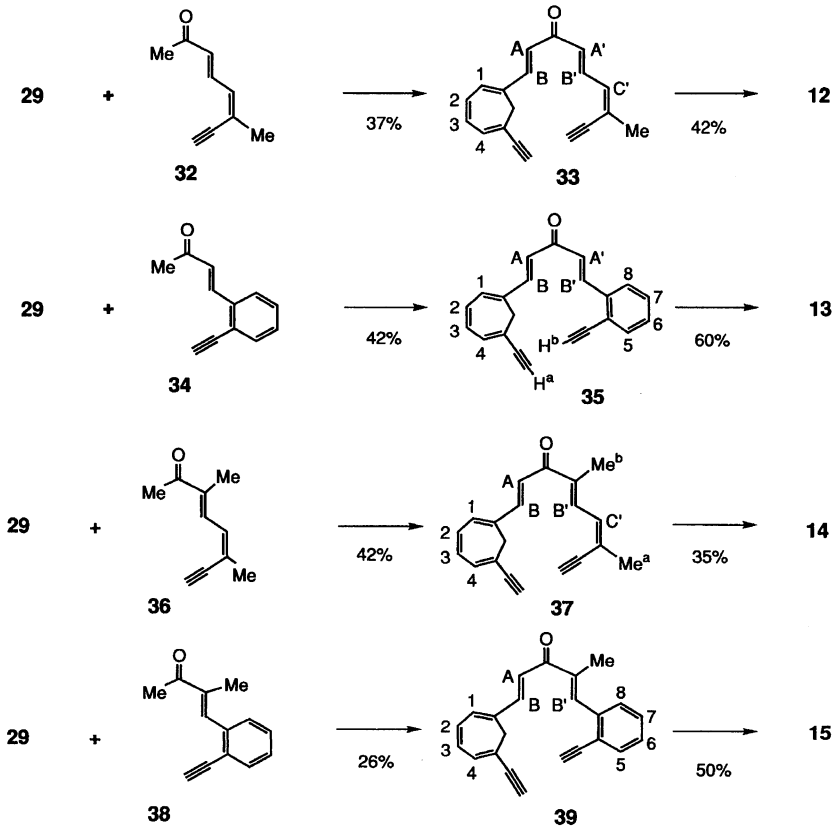
For the preparation of the key compound **29**, the known ester **23**[14] was chosen as the starting material. It was prepared from 1-acetyl-1,3,5-cycloheptatriene (**21**)[15] via compound **22** using three reactions (haloform reaction, conversion to the acid chloride, and then treatment with ethanol), as illustrated in Scheme 1.

The Friedel–Crafts acetylation of the ester **23** with $AcCl/AlCl_3$ gave compound **24** in 66% yield. Treatment of **24** under Vilsmeier conditions[16] gave the formyl derivative **25** in 57% yield. The (*Z*)-configuration of **25** was confirmed by NOE between the methylene protons and H^A.[17] Reaction of **25** with aqueous NaOH in *N*,*N*-dimethylformamide (DMF) caused dehydrochlorination, with concomitant loss of carbon monoxide, to afford the ethynyl ester **26** in 49% yield,[16] accompanied by formation of a small amount of the carboxylic acid **27**. Reduction of the ester **26** with DIBAH

#The marked numerals 1—8 are used in the structural formulae of compounds **12**—**54**. Their ^{1}H NMR locants are different from the locant numbering for their systematic nomenclature.



Scheme 1.



Scheme 2.

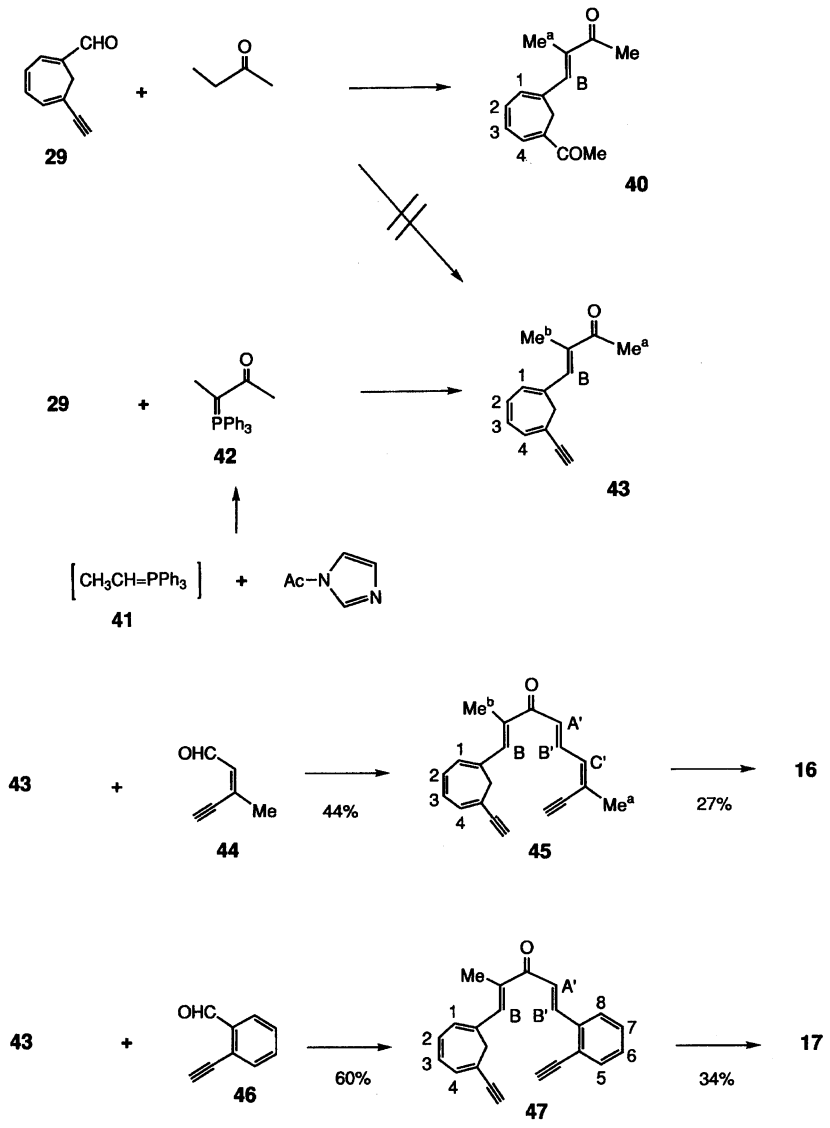
gave the alcohol **28** in 93% yield. The carboxylic acid **27** was also led to the alcohol **28** by reduction with $LiAlH_4$ (43%). Oxidation of the alcohol **28** with $Ba(MnO_4)_2$[18] gave the aldehyde **29** in 78% yield.

The overall yield of compound **29** from compound **21** by this route was rather poor, and only small amounts of **29** could be obtained conveniently in one run. An alternative preparation of compound **29** was therefore attempted. However, a Vilsmeier reaction of the compound **31**, which was prepared from compound **21** via the chloroformyl derivative **30**, did not afford the desired compound **29**, but regenerated compound **30**.

The syntheses of the annulenones **12**—**15** were carried out according to the reported procedure[1,3—5] as illustrated in Scheme 2. Aldol condensation of the aldehyde **29** with the ketones **32**,[3,13] **34**,[19] **36**,[3] and **38**,[5a] in the presence of ethanolic sodium ethoxide in diethyl ether gave the corresponding bisethynyl ketones **33**, **35**, **37**, and **39**, respectively. Oxidative coupling of compounds **33**, **35**, **37**, and **39** with anhydrous copper(II) acetate in pyridine–diethyl ether at 50 °C[3] afforded the annulenones **12**—**15**, respectively.

To obtain the α-methyl substituted [17]annulenones **16** and **17**, the preparation of the ketone **43** from the aldehyde **29** was attempted, as illustrated in Scheme 3.

Aldol condensation of the aldehyde **29** with 2-bu-



Scheme 3.

tanone in the presence of concd H_2SO_4 in acetic acid did not give the desired ketone **43**, but gave the ketone **40**. This presumably formed by hydration of the acetylenic bond of the desired ketone **43** under the attempted conditions. But the condensation of 2-butanone with both the (*Z*)-3-methyl-2-penten-4-ynal (**44**)[3,13] and *o*-ethynylbenzaldehyde (**46**)[19] readily gave the ketones **36**[3,13] and **38**[5a] (Scheme 2) respectively without hydration under similar conditions. Several attempts to obtain ketone **43** were therefore made by using a variety of condensation agents such as concd H_2SO_4 in the absence or presence of molecular sieves and gaseous HCl, but all attempts were unsuccessful.[20]

To avoid the hydration for acetylenic bond, condensation of 2-butanone with a cobalt complex of compound **29** was tried but without success.[21]

We finally succeeded in preparing ketone **43** using the Wittig reaction as follows, although the yield was low.

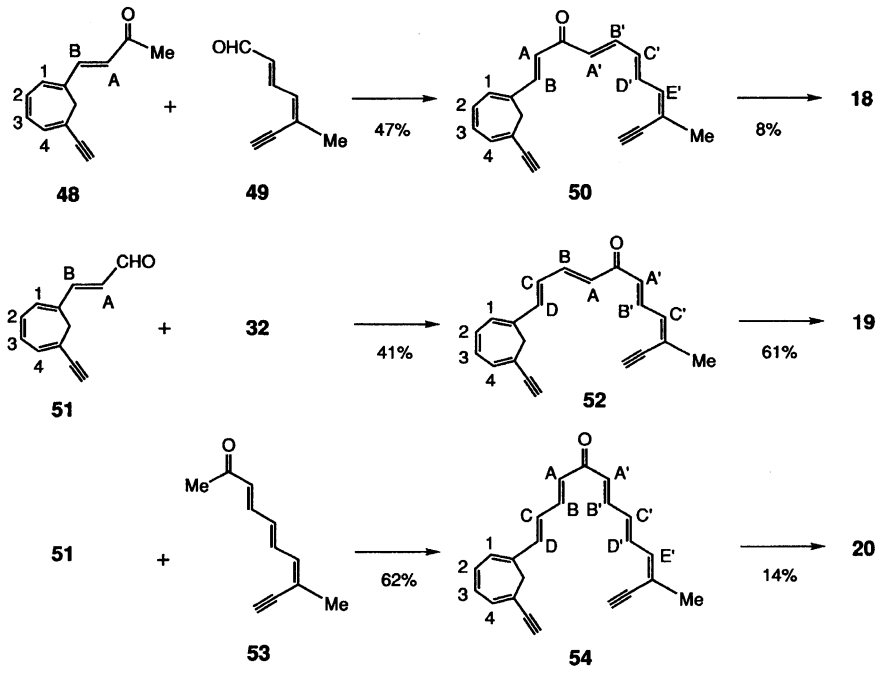
The acetylated phosphorane **42** was prepared from ethylidenetriphenylphosphorane (**41**)[22] and *N*-acetylimidazole.[23] The Wittig reaction of the aldehyde **29** with the phosphorane **42** gave the ketone **43** as a sole product in 12% yield; the (*E*)-configuration was confirmed by the absence of the NOE between the Me^b and H^B protons.

Aldol condensation of the ketone **43** with the aldehydes **44** and **46** gave the bisethynyl ketones **45** and **47**, respectively. Oxidative coupling of ketones **45** and **47** gave the α'-methyl-substituted annulenones **16** and **17**, respectively.

The syntheses of annulenones **18**—**20** are illustrated in Scheme 4.

Ketone **48**, prepared by aldol condensation of the aldehyde **29** with acetone, was condensed with aldehyde **49**[4,26] to afford ketone **50**. Oxidative coupling of **50** afforded the [19]annulenone **18**.

Aldehyde **51** was prepared from aldehyde **29** by Wittig condensation with 16 molar amounts excess of



Scheme 4.

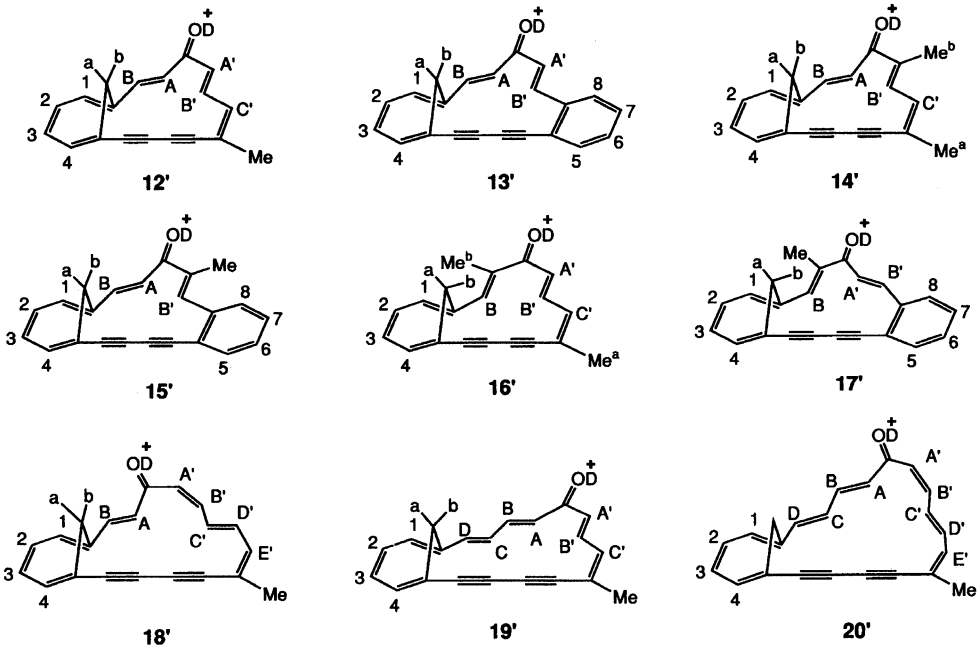


Chart 3.

[(1,3-dioxolan-2-yl)methyl]triphenylphosphonium bromide[27] and lithium ethoxide in *N*,*N*-dimethylformamide (DMF), followed by hydrolysis of the resulting acetal of the desired aldehyde **51** with dilute aqueous HCl.

Aldol condensation of aldehyde **51** with ketones **32**[3,13] and **53**[4] afforded the acyclic ketones **52** and **54**. Oxidative coupling of **52** and **54** yielded annulenones **19** and **20**, respectively.

Compounds **12**—**15**, **17**, and **18**—**20** thus obtained, formed thermally relatively stable crystals, but compound **16** was obtained as a liquid and was thermally very unstable, so satisfactory elemental analysis was not obtained.

Treatment of annulenones **12**—**20** with trifluoroacetic or trifluoroacetic acid-*d* gave the corresponding carbonyl-protonated or deuteronated species **12′**—**20′** (Chart 3) respectively: **12′** dark green, **13′** dark green, **14′** dark green, **15′** green brown, **16′** brown, **17′** dark brown, **18′** dark blue, **19′** dark blue violet, and **20′** green brown, respectively.

Quenching of **12′**—**15′** and **17′**—**19′** with aque-

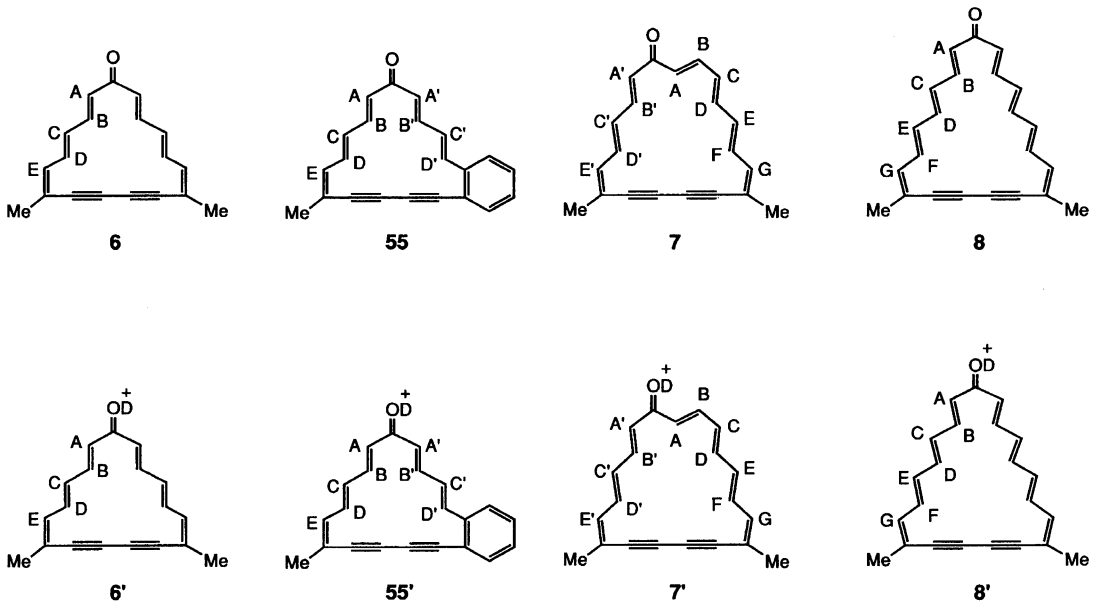


Chart 4.

ous $NaHCO_3$ resulted in regeneration of **12**—**15** and **17**—**19** respectively, revealing that these annulenones do not undergo irreversible changes in acidic conditions (in CF_3CO_2D), although such a change has been observed for compounds **5** (R=H and Me)[24] and **7** (R=H and Me).[25] Quenching of the species **16′** and **20′** resulted in decomposition, and compounds **16** and **20** could not be regenerated.

^{1}H NMR Spectra and Geometrical Determination. ^{1}H NMR spectral data of the annulenones **12**—**20** and their acyclic precursors **33**, **35**, **37**, **39**, **45**, **47**, **50**, **52**, and **54** are listed in Table 1 together with those of the related compounds **55** and **6**—**8** (Chart 4).[4,5c] Data for the deuteronated species **12′**—**20′** (Chart 3), **55′**, and **6′**—**8′** (Chart 4) obtained in CF_3CO_2D are also given in Table 1. Geometrical determination and chemical shift assignments were made on the basis of multiplicity and coupling constants (J) (see Experimental) and were assisted by decoupling, NOE and CH-COSY experiments where necessary.

For example, the geometry of compound **12** was assigned as given by the structural formula **12**. Another possible geometry **12a** (Chart 5) was also compatible with the observed coupling pattern, but this was excluded as follows. In α,β-unsaturated ketones, β-protons and β-carbons generally resonate at lower field than α-protons and α-carbons, respectively, because of the electron-density effect. In annulenones, ^{1}H chemical shifts are subject both to the electron-density effect and the tropicity effect, while ^{13}C chemical shifts are mainly governed by the former effect and are more reliable in assigning the relative positions to the carbonyl group. Among the signals assignable to the $CH^A{=}CH^B$ moiety, the protons at $\delta=6.95$ and 8.44 are related to the carbons at $\delta=141.52$ and 123.97, respectively, by the CH-COSY experiment. Thus the lower-field signal at $\delta_C=141.52$ is assigned to C^B and the higher-field signal at $\delta_H=6.95$ is assigned to H^B. On the other hand, NOE experiments revealed that H^A is close to $H^{B'}$ and H^B is close to H^1. Therefore the geometry of compound **12** is best represented by formula **12** rather than **12a**.

The geometries of compounds **13**—**20** were similarly determined as shown by the structural formulae. Especially for compounds **18**—**20**, the following NOE enhancements confirmed the structures: $Me\rightarrow H^{E'}$, $H^B\rightarrow H^1$, $H^b\rightarrow H^A$, and $H^A\rightarrow H^{C'}$ for compound **18**, $Me\rightarrow H^{C'}$, $H^b\rightarrow H^C$, $H^{B'}\rightarrow H^A$, and $H^B\rightarrow H^D$ for **19**, and $Me\rightarrow H^{E'}$, $H^C\rightarrow H^1$, $H^{B'}\rightarrow H^B$, and $H^B\rightarrow H^D$ for **20**.

The ^{1}H NMR spectra of these annulenones in CF_3CO_2D were similarly analyzed. For compounds **12**—**19**, the geometries under neutral conditions were retained in CF_3CO_2D, although **18** and **19** were rather unstable in CF_3CO_2D and gradual decomposition was observed. The ^{1}H NMR spectrum of compound **20** in CF_3CO_2D indicated that the compound exists as an equilibrium mixture of three isomers in a ratio of ca. 8:2:1, suggesting the occurrence of the isomerization of double bonds in compound **20**. The most populated isomer was shown to have the structure shown by the formula **20′** (Chart 3) with the (Z)-configuration for one of the CH=CH moieties, but no definite analysis could be made for the minor isomers.

Tropicity of the [17]Annulenones. We assume that tropicity of these annulenones can be judged from the chemical shift difference of protons between an annulenone and the corresponding acyclic reference compound. As for the [17]annulenones **12** and **14** in $CDCl_3$, the inner olefinic protons H^A and $H^{B'}$ resonate at considerably lower field by ca. 1.5 ppm than the corresponding protons of the acyclic counterparts. The averaged chemical shifts of the methylene proton signals also show downfield shifts relative to those of the acyclic

Table 1. ^{1}H NMR Chemical Shifts of Annulenones **12**—**20**, **6**—**8**, **55**, and the Reference Compounds at 26 °C (δ-Values)

Compd	Solv.	Inner protons H^A	Inner protons $H^{B'}$	CH_2	Outer protons H^B	Outer protons $H^{A'}$	$H^{C'}$	H^1—H^4	ArH	Me
33	$CDCl_3$	6.81	7.73	2.73	7.41	6.46	6.48	6.73—6.57		2.05
12	$CDCl_3$	8.44	9.27	2.38, 4.39	6.95	5.97	6.55	6.62—6.33		1.81
12′	CF_3CO_2D	10.10	11.71	3.14, 5.48	7.02	6.01	6.40	6.65—6.23		1.80
37	$CDCl_3$	7.19	7.61	2.73	7.43		6.74	6.74—6.56		2.09, 2.01
14	$CDCl_3$	8.52	9.17	2.37, 4.41	6.97		6.67	6.61—6.30		1.84, 1.82
14′	CF_3CO_2D	9.83	11.13	2.98, 5.26	6.98		6.62—6.20	6.62—6.20		1.84, 1.82
35	$CDCl_3$	6.91	8.20	2.77	7.49	7.07		6.75—6.60	7.72—7.35	
13	$CDCl_3$	8.07	9.02	2.18, 4.10	7.20	6.57		6.73—6.44	7.60—7.23	
13′	CF_3CO_2D	9.02	10.56	2.63, 4.70	7.44	6.78		6.81—6.42	7.62—7.17	
39	$CDCl_3$	7.24	7.87	2.76	7.48			6.74—6.58	7.58—7.32	2.09
15	$CDCl_3$	8.02	8.55	2.10, 4.03	7.30			6.75—6.42	7.54—7.25	2.10
15′	CF_3CO_2D	8.44	9.23	2.32, 4.29	7.43			6.82—6.39	7.56—7.23	2.17

Compd	Solv.	H^B	$H^{B'}$	CH_2	$H^{A'}$	$H^{C'}$	H^1—H^4	ArH	Me
45	$CDCl_3$	7.04	7.70	2.77	6.79	6.49	6.73—6.45		2.16, 2.04
16	$CDCl_3$	6.60	7.43	1.87, 3.52	6.47	6.61	6.81—6.41		1.92, 1.91
16′	CF_3CO_2D	6.69	7.87	1.98, 3.42	6.54	6.83	6.90—6.43		2.02, 1.95

Compd	Solv.	H^B	$H^{A'}$	CH_2	$H^{B'}$	H^1—H^4	ArH	Me
47	$CDCl_3$	7.16	7.43	2.80	8.09	6.72—6.49	7.69—7.34	2.22
17	$CDCl_3$	7.10	7.75	1.75, 3.65	7.60	6.89—6.45	7.51—7.26	2.09
17′	CF_3CO_2D	7.27	8.02	1.90, 3.70	7.75	6.93—6.47	7.64—7.30	2.15

Compd	Solv.	Inner protons H^B	Inner protons $H^{B'}$	H^D	$H^{D'}$	H^A	Outer protons $H^{A'}$	Outer protons H^C	$H^{C'}$	H^E	ArH	Me
6[a]	$CDCl_3$	8.60		8.63		5.80		6.02		6.33		1.77
6′[a]	CF_3CO_2D	11.68		11.75		5.71		5.64		5.91		1.58
55[b]	$CDCl_3$	8.21	8.21	8.08	8.05	6.10	6.00	6.27	6.60	6.48	7.2—7.6	1.92
55′[b]	CF_3CO_2D	9.71	9.67	9.65	9.75	6.17	6.14	6.30	6.51	6.25	7.2—7.6	1.85

Compd	Solv.	H^A	$H^{A'}$	H^B	$H^{B'}$	H^C	$H^{C'}$	H^D	$H^{D'}$	$H^{E'}$	H^1—H^4	CH_2	Me
50	$CDCl_3$	6.76	6.49	7.40	7.41		6.43		7.09	6.42	6.73—6.56	2.74	2.00
18	$CDCl_3$	5.86	6.20	7.91	6.68		6.33		6.53—6.47		7.08—6.99	1.19, 2.81	2.10
18′	CF_3CO_2D	2.04	7.65	9.86	8.67		2.56		8.35	7.82	8.17—7.98	−0.01, 0.34	2.85
52	$CDCl_3$	6.58	6.43	7.39	7.70	6.79—6.72	6.46	6.79—6.72			6.69—6.39	2.74	2.04
19	$CDCl_3$	6.46	6.23	7.01	7.19	6.42	6.81	6.65			6.91—6.47	1.43, 3.40	2.06
19′	CF_3CO_2D	4.70	7.64	8.20	5.10	4.81	7.69	7.24			7.45—7.13	0.84, 2.10	2.59
54	$CDCl_3$	6.56	6.44	7.43—7.33		6.79—6.71	6.41	6.79—6.71	7.09	6.41	6.69—6.38	2.74	2.00
20	$CDCl_3$	6.13	6.02	7.21	7.64	6.31	6.63	6.70	7.54	6.52	6.74—6.49	2.01, 3.62	1.89
20′	CF_3CO_2D	11.24	5.51	7.23	6.52	11.23	12.51	6.09—5.95	6.19	5.77	6.09—5.95	5.64	1.65

Compd	Solv.	H^A	$H^{A'}$	H^B	$H^{B'}$	H^C	$H^{C'}$	H^D	$H^{D'}$	H^E	$H^{E'}$	H^F	H^G	Me
7[a]	$CDCl_3$	6.20	6.48	7.1—6.8	5.90	6.67	7.1—6.8	6.02	5.85	7.1—6.8		5.65	7.1—6.8	2.21, 2.17
7′	CF_3CO_2D	1.6—0.9	8.8—8.2		1.6—0.9	8.8—8.2		1.6—0.9		8.8—8.2	1.6—0.9		8.8—8.2	3.04, 2.93
8[a]	$CDCl_3$	5.84	7.64		6.12		8.06		6.16		8.06	6.37		1.83
8′	CF_3CO_2D	5.7—5.2	11.62		5.7—5.2		12.22		5.7—5.2		12.10	5.7—5.2		1.48

a) See Ref. 4. b) See Ref. 5c.

compounds, although the outer olefinic and methyl proton signals show only small upfield shifts. These results suggest that these compounds are paratropic as might be expected for 16π-electron system due to polarization of the carbonyl group. From similar reasonings, we inferred that the benzannelated compounds **13** and **15** are at most weakly paratropic, and compounds **16** and **17** are atropic.

The tropicity of the deuteronated species observed in CF_3CO_2D can be evaluated by comparison of the chem-

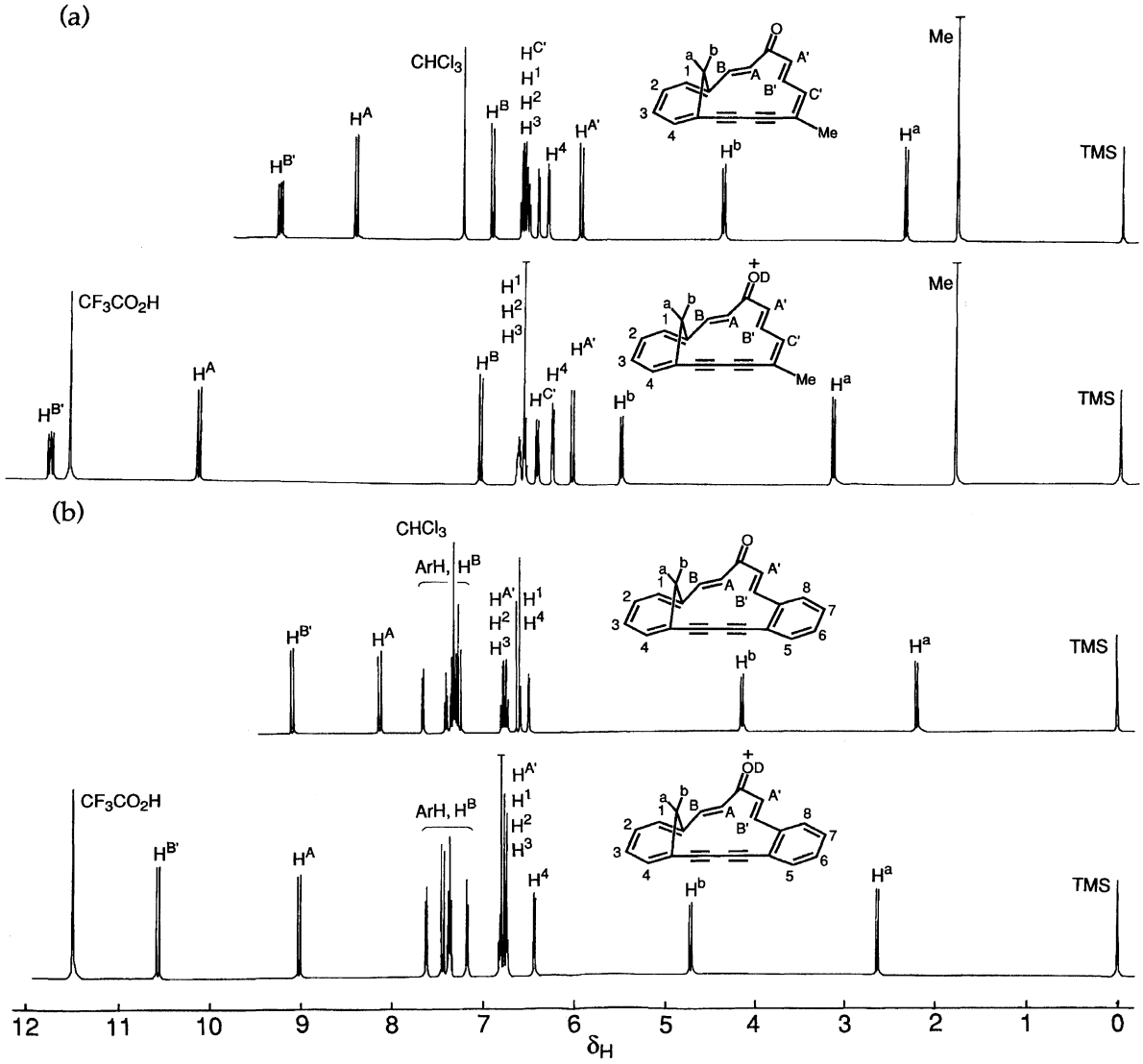
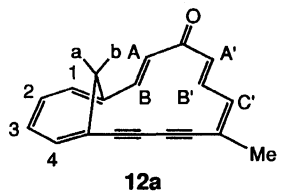


Fig. 1. 500 MHz ^{1}H NMR spectra of (a) Compound **12** and (b) Compound **13** in $CDCl_3$ and in CF_3CO_2D at 26 °C.



12a

Chart 5.

ical shifts with those of their neutral counterparts in $CDCl_3$. The chemical shifts of the deuteronated species are subject to the intrinsic deshielding effect due to the positive charge together with the tropicity effect. Therefore in the potentially paratropic [17]annulenones, inner protons suffer the cooperative deshielding effect, while the effects are antipodal for outer protons. Taking these into account, we can infer that for the species **12′**—**15′** (Chart 3) paratropicity is strengthened relative to the corresponding neutral species, while **16′** and **17′** (Chart 3) are still atropic (Table 1).

This is more readily seen from Fig. 1, which shows the 500 MHz ^{1}H NMR spectra of compounds **12** and **13** in $CDCl_3$ and in CF_3CO_2D at 26 °C, together with the signal assignments. In these spectra, compound **12** shows the inner proton signals at a low field, while the outer proton signals appear at a high field in both $CDCl_3$ and CF_3CO_2D. A similar observation was made for the spectra of compound **13**, although the extent of the shifts is smaller than that in compound **12**.

These results reveal the following. Introduction of a methyl group to the α'-position causes no significant change in the geometry and tropicity of the compounds, while such introduction to the α-position changes the geometry so that the molecules significantly deviate from planarity and show no tropicity. Benzannelation decreases tropicity, as have been proved in various cases.[5,7]

We can examine the extent of paratropicity of compounds **12**—**15** by comparison of the ^{1}H chemical shifts with those of the closely related compounds, dimethylbisdehydro[17]annulenone **6** and its benzannelated iso-

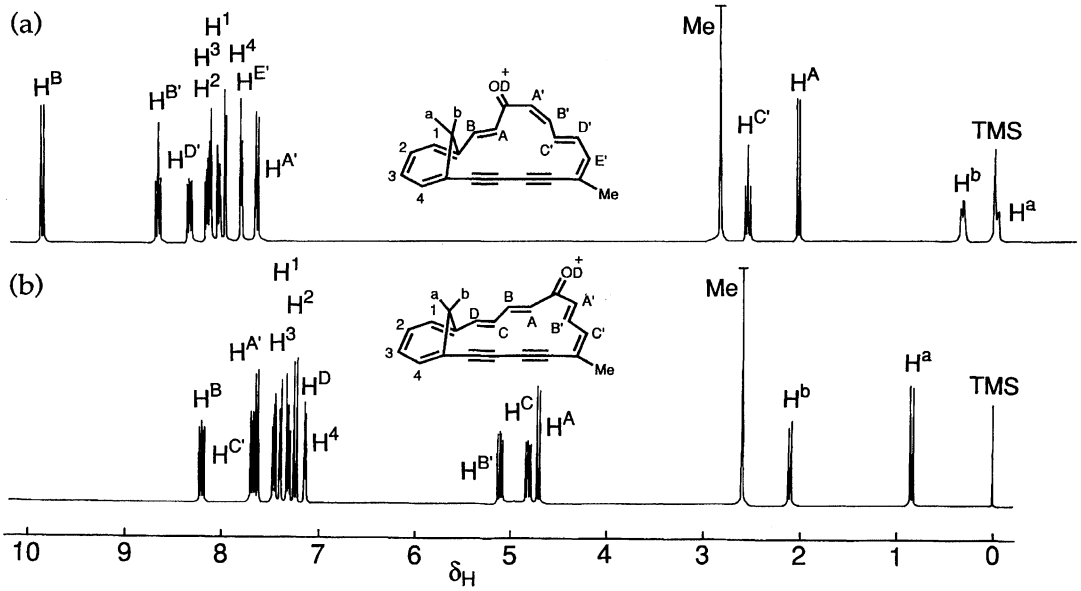


Fig. 2. 500 MHz ^{1}H NMR Spectra of (a) Compound **18** and (b) Compound **19** in CF_3CO_2D at 26 °C.

mer **55** (Chart 4). The annulenones **12** and **14** involve the peripherally conjugated 16π-electrons due to polarization of the carbonyl group. In the related monocyclic bisdehydroannulenones **4**—**10**, it has been confirmed that paratropicity decreases with increasing ring size.[4,8] Therefore, for comparison of the extent of paratropicity, we should compare among the compounds with the same ring size.

If we compare the extent of paratropicity between the annulenones **12** (or **14**) and **6**, and between **13** (or **15**) and **55** with the 16π-electron system, the dimethyl[17]-annulenone **6** and its benzannelated one **55** are seen to show a larger paratropicity than the methano-bridged [17]annulenone **12** (or **14**) and its benzannelated derivative **13** (or **15**). The former show the inner proton signals at a lower field than the latter, while the outer proton signals as well as those of the methyl protons are at a higher field under both neutral (in $CDCl_3$) and acidic conditions (in CF_3CO_2D), as can be seen from Table 1. This suggests that the skeleton of the bisdehydromethano[17]annulenone system of compound **12** (or **14**) is less planar than that of the dimethylbisdehydro-[17]annulenone **6**, because of a methano-bridge.

In the trimethyl[13]annulenone **4** (R=Me)[3] and its ethyl analogue **4** (R=Et),[6] significant dependence of the ^{1}H chemical shifts upon the temperature was observed because of the conformational flexibility of the monocyclic ring system. On the other hand in the present annulenones **12**—**15**, no essential temperature dependence of the chemical shifts or the line shapes of the signals of the olefinic, methyl, and methylene protons was observed in the range of −60 to +60 °C, indicating the conformational rigidity of the methano-bridged ring system.

Tropicity of the [19]- and [21]Annulenones. The [19]annulenones **18** and **19** are potentially diatropic because they form 18π-electron systems by polarization of the carbonyl group. The signals of the olefinic protons located inside of the macrocycle and those of the methylene protons are expected to shift upfield relative to those of the corresponding protons of the respective reference compounds, while the signals of the outer olefinic and methyl protons will shift downfield. The signals of the methylene and methyl protons of **18** shift ca. 0.7 ppm upfield and 0.1 ppm downfield, respectively, relative to those of the corresponding protons in **50** and those of **19** shift ca. 0.3 ppm upfield and 0.02 ppm downfield, while the olefinic proton signals show no definite tendency in either compound (Table 1). Thus we conclude that **18** shows only small diatropicity and **19** is even less diatropic or almost atropic.

As for compound **18** the signals of the inner olefinic and methylene protons in CF_3CO_2D shift upfield by ca. 3.8 and 1.8 ppm, respectively, relative to those in $CDCl_3$, while the outer olefinic protons and the methyl protons resonate at fields lower by 1.4—2.0 and 0.7 ppm, respectively, than the corresponding protons in $CDCl_3$. The significant increase in diatropicity was actually observed in CF_3CO_2D. Similar but smaller effects were observed for compound **19**. This suggests that the diatropicity of **19′** is smaller than that of **18′**, which may reflect the lower planarity of the skeleton of **19**.

This is more readily seen from Fig. 2, which shows the 500 MHz ^{1}H NMR spectra of compounds **18** and **19** in CF_3CO_2D at 26 °C, together with the signal assignments. In these spectra, the species **18′** show the inner proton signals at a very high field, while the outer proton signals appear at a very low field. Similar behavior is seen for the spectrum of species **19′**, although the extent of both the low-field shift and the high-field shift is smaller than those of **18′**. Thus, species **18′** and **19′** are seen to be strongly diatropic.

The [21]annulenone **20** is expected to be paratropic due to the potential 20π-electron system. Actually the signals of the methylene and the methyl protons shift 0.1 ppm downfield and 0.1 ppm upfield, respectively, relative to those of the corresponding protons in **54**, indicating that **20** is only slightly paratropic. The signals of the methylene and the methyl protons of the most populated isomer **20′** of the [21]annulenone **20** shift ca. 2.8 ppm downfield and 0.24 ppm upfield, respectively, upon changing the solvent from $CDCl_3$ to CF_3CO_2D, indicating a significant increase in paratropicity. The inner olefinic protons resonate at δ=6.7—7.6 in $CDCl_3$ and δ=11.2—12.5 in CF_3CO_2D, while the outer olefinic protons resonate at δ=6.0—6.6 in $CDCl_3$ and at δ=5.5—6.5 in CF_3CO_2D. Large deshielding of the inner protons and small shielding of the outer protons may be due to the addition and partial cancellation, respectively, of the deshielding electron-density effect of the cationic species and the tropicity effect.

Comparison of the extent of tropicity between the methano-bridged annulenones **18**—**20** and the monocyclic annulenones **7** and **8** (Chart 4) may be worthwhile. The methyl signals of **7** are at lower field than those of **18** and **19**, while that of **8** is at higher field than that of **20**. This suggests that the monocyclic annulenones show somewhat higher tropicity than the methano-bridged ones.

The enhancement of tropicity upon changing the solvent from $CDCl_3$ to CF_3CO_2D is also larger in the monocyclic compounds **7** and **8** than in the methano-bridged ones **18**, **19**, and **20**. Thus the methyl signals of **7** shift downfield by ca. 0.8 ppm upon the solvent change, while those in **18** and **19** shift by 0.75 and 0.53 ppm, respectively. Similarly, the upfield shifts of the methyl signal are 0.35 and 0.24 ppm for **8** and **20** (Table 1), respectively.

The methylene protons of **18** and **19** resonate as a pair of sharp doublets in both solvents, indicating that the flipping of the methano bridge through the average plane of the macrocycle is slow on the NMR time scale. The methylene protons of **20** resonate as a pair of slightly broadened doublets in $CDCl_3$ and as a broad singlet in CF_3CO_2D, reflecting the faster flipping because of the larger ring size.

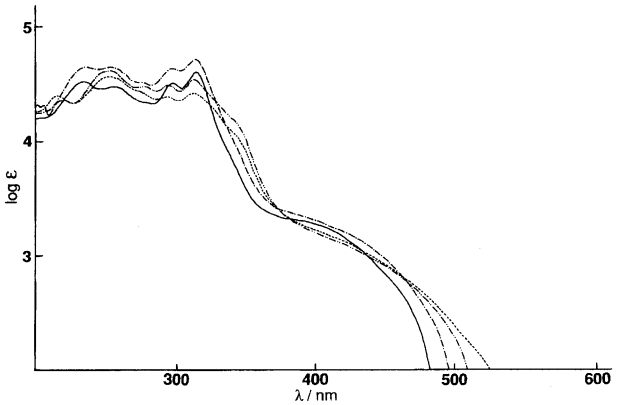


Fig. 3. Electronic Absorption Spectra of Compound **12** (---), **13** (-·-), **14** (-··-), and **15** (—) in THF.

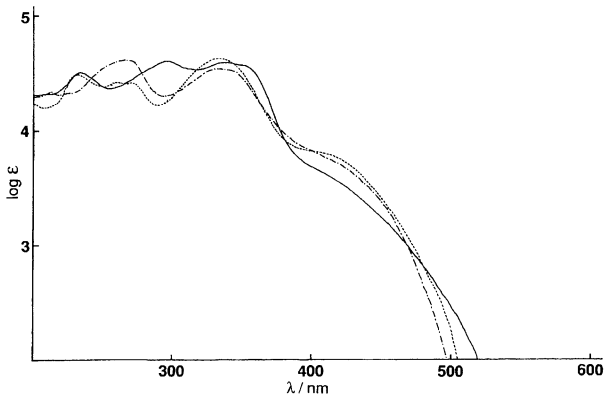


Fig. 4. Electronic Absorption Spectra of Bisdehydromethano[19]- **18** (---), -[19]- **19** (-·-), and -[21]-annulenone **20** (—) in THF.

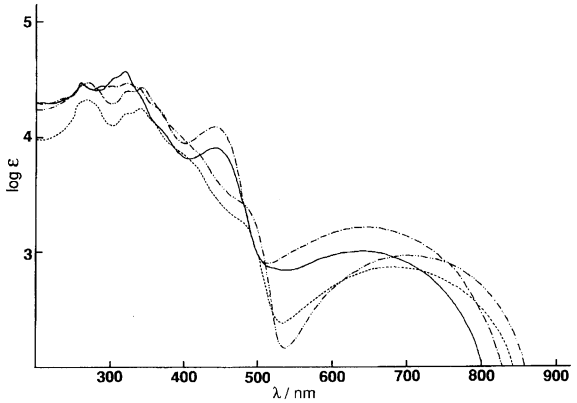


Fig. 5. Electronic Absorption Spectra of Compound **12** (---), **13** (-·-), **14** (-··-), and **15** (—) in CF_3CO_2H.

Electronic Spectra of Compounds 12—20. The electronic absorption maxima of the annulenones **12**—**20**, determined in tetrahydrofuran (THF) and CF_3CO_2H, are listed in Table 2. The absorption spectra of annulenones **12**—**15** and **18**—**20** in THF, and those of **12**—**15** in CF_3CO_2H, are shown in Figs. 3, 4, and 5, respectively.

The spectra of compounds **16** and **17** are very different from those of compounds **12**—**15** in both THF and CF_3CO_2H, reflecting the fact that the peripheral conjugation of π-electron systems is significantly hindered in compounds **16** and **17**, as is found from examination of the ^{1}H NMR spectra described above.

It is evident from Table 2 and Fig. 5 that all the bands of compounds **12**—**15** show an appreciable bathochromic shift upon changing the solvent from THF to CF_3CO_2H. The end absorption in CF_3CO_2H, appears toward longer wavelengths as compared with those in THF (Fig. 3), demonstrating the more extended conjugation of their π-electron systems compared to those in THF.

Table 2. Electronic Absorption Maxima of Annulenones **12**—**20** [a, in THF; b, in CF_3CO_2H; λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1})]

[17]- **12**	a	214 (25 200), 250.5 (36 600), 273sh (27 100), 291.5 (24 200), 310.5 (25 800), 342sh (11 000)
	b	257sh (19 800), 268 (21 700), 324.5 (15 900), 341 (17600), 413sh (5700), 483.5sh (1600), 680.5 (736)
[17]- **13**	a	234 (41 900), 254 (43 200), 276sh (31 800), 295 (42 600), 312 (51 500)
	b	257.5 (29 300), 287 (27 800), 299.5 (28 000), 321 (29 400), 340 (26 100), 364 (17 900), 440.5 (12 000), 648.5 (1660)
[17]- **14**	a	219.5 (22 800), 252 (40 700), 276.5 (29 500), 294 (30 200), 312 (33 600), 345sh (12 600)
	b	257 (29 200), 269 (30 200), 324 (24 800), 343 (26 300), 421sh (6600), 485sh (2300), 702.5 (940)
[17]- **15**	a	232 (32 600), 254 (29 600), 296 (31 300), 313 (39 700)
	b	256.5 (31 400), 301sh (31 800), 317.5 (37 400), 440 (7880), 646 (1050)
[17]- **16**[a)]	a	235 (18 000), 239sh (18 300), 246 (19 300), 252sh (18 600), 315 (11 200)
[17]- **17**	a	238 (40 700), 256 (43 600), 274 (39 500), 294sh (31 700), 310sh (28 500)
	b	256 (29 200), 262 (29 200), 274sh (27 500), 304 (25 400), 313sh (25 000), 424sh (3620)
[19]- **18**	a	232 (30700), 260 (26100), 271 (25800), 334 (41800), 394 (sh, 6800)
	b	278 (19900), 290 (19300), 396 (42900), 577 (19000), 627 (sh, 14700)
[19]- **19**	a	259 (sh, 39100), 267.5 (40700), 333 (33700), 414 (sh, 5500)
	b	277.5 (26900), 291.5 (25400), 383 (32500), 582 (18300), 630 (sh, 14000)
[21]- **20**	a	234 (32200), 295 (40000), 337 (39300), 355 (sh, 35500)
	b	299 (13600), 313.5 (13600), 386 (17800), 447.5 (10200), 580 (sh, 1500)

a) The spectrum in CF_3CO_2H could not be obtained because of instability of compound **16** in the solution.

As is seen from Figs. 3 and 5, the spectra of the annulenones **12** and **14**, and those of the benzannelated ones **13** and **15** are quite similar in shape both in THF and in CF_3CO_2H. However, the longest wavelength band of the annulenones **12** and **14** exhibits absorption toward longer wavelength than those of the benzannelated annulenones **13** and **15**, both in THF and in CF_3CO_2H, demonstrating that the fusion of benzene ring reduces the degree of extended conjugation of the π-electron system in the bisdehydromethano[17]annulenone ring. This is in accordance with the result from an examination of the ^{1}H NMR spectra of these annulenones (see above) and has been observed in a series of compounds **4**—**8**.[5)]

It is evident from Table 2 that all the bands of compounds **18**—**20** again show an appreciable bathochromic shift upon changing the solvent from THF to CF_3CO_2H. The conjugation of their π-electron systems is thus more extended in CF_3CO_2H than those in THF, as is revealed from ^{1}H NMR spectra described above and as observed for the compounds **12**—**15**.

As can be seen from Fig. 4 and as has been observed in carbocyclic annulene series,[28)] the spectra of [$4n-1$]-annulenones **18** and **19** are similar in shape, while the spectrum of the [$4n+1$]annulenone **20** is somewhat broader than those of **18** and **19**.

Thus, against our expectation, these results reveal that the molecular skeletons of the bisdehydromethano-[17]- **12** (or **14**), [19]- **18** (or **19**), and -[21]annulenone **20** are less planar and more strained than those of the monocyclic dimethylbisdehydro[17]- **6**, -[19]- **7**, and -[21]annulenone **8**, respectively, owing to the presence of a methano-bridge. This means that the molecular skeletons of monocyclic annulenones **6**—**8** are sufficiently rigid and planar so that the tropicity is fully manifested in these compounds.

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 spectra were measured in THF and in CF_3CO_2H solutions, and run with a Shimadzu 2200A spectrophotometer; results refer to THF solution unless otherwise specified. Mass spectra were recorded with a JEOL JMS-D 300 spectrometer operating at 75 eV using a direct-inlet system. Fast atom bombardment mass spectra (FAB MS) were obtained as a *m*-nitrobenzyl alcohol matrix on a JEOL JMS-

AX 505W high-resolution double-focusing mass spectrometer equipped with a D 5000 data system. ^{1}H NMR spectra at ambient temperature were recorded as $CDCl_3$ solutions, unless otherwise specified, with a JEOL FX-90Q (90 MHz), a JEOL GX-400 (400 MHz), or a Bruker AM-500 (500 MHz) spectrometer with TMS as an internal standard. The coupling constants (J) are given in Hz. ^{13}C NMR spectra were recorded as $CDCl_3$ solution, unless otherwise indicated, on GX-400 or AM-500 at 100.40 or 125.76 MHz with internal TMS as a reference. The letters, p, s, t, and q refer to primary, secondary, tertiary, and quaternary, respectively.

Freshly deoxygenated diethyl ether and acetone were used to minimize oxidation of the compounds employed for aldol condensation and were prepared by passing through a short column of basic alumina (ICN, activity I), followed by flushing with argon immediately before use. The 0.36 mol dm^{-3} ethanolic sodium ethoxide was used for the aldol condensations. It was prepared from sodium (250 mg) and dry ethanol (30 cm^3) immediately before use. Progress of all reactions was followed by TLC on Merck precoated silica gel. Alumina (Merck, activity II-III) or silica gel (Daiso gel 1001 W or Daiso gel 1002 W) was used for column chromatography. Preparative TLC (PLC) was carried out on 20×20 cm silica gel plates (Merck, 0.5 or 0.2 mm thick). Dry CH_2Cl_2 was prepared by distillation over calcium hydride before use. Dry *N,N*-dimethylformamide (DMF) was prepared by stirring with calcium hydride overnight and then by distillation before use. Solvents were evaporated under water-pump pressure. Ether refers to diethyl ether.

Ethyl 6-Acetyl-1,3,5-cycloheptatriene-1-carboxylate (24). To a stirred suspension of finely divided aluminium chloride (70.0 g, 0.46 mol) in dry CH_2Cl_2 (205 cm^3) was added dropwise acetyl chloride (36.0 g, 0.46 mol) during 50 min at room temperature. The mixture was then heated under reflex with stirring for 10 min. The ester **23**[14] (30.0 g, 0.18 mol) was added dropwise during 40 min at 40 °C. Then the mixture was heated for 4 h at 40 °C. After this was cooled to −20 °C, acetic acid (19 cm^3) was added dropwise during 30 min and water (91 cm^3) was then added to the mixture during 1.5 h at −20 °C. The mixture was poured onto ice-water and extracted with CH_2Cl_2. The combined extracts were washed successively with water, aqueous NH_3, and brine, and dried. The residue obtained after removal of the solvent was passed through a column of alumina (5.2×9.0 cm) and the fractions eluted with hexane–benzene (1 : 1) were collected. The residue after removal of the solvent was distilled to afford compound **24** (25.0 g, 66%) as a yellow liquid. Bp 135—140 °C/266 Pa (1 mmHg=133 Pa); Mass m/z 206 (M^+; 38%) and 177 (100); UV 229 (ε 23700) and 308 nm (5430); IR (neat) 1708, 1669 (C=O), 1612 and 1595 cm^{-1} (C=C); ^{1}H NMR (90 MHz) δ_H=7.24 (2H, d, J=10 Hz, H^1 and H^4), 6.95—6.91 (2H, m, H^2 and H^3), 4.25 (2H, q J=7 Hz, C$\underline{H}_2$CH$_3$), 3.01 (2H, s, CH_2), 2.41 (3H, s, COMe), and 1.33 (3H, t, J=7 Hz, CH$_2$C$\underline{H}_3$).

Found: C, 69.94; H, 7.03%. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84%.

Ethyl 6-[(*Z*)-1-Chloro-2-formylvinyl]-1,3,5-cycloheptatriene-1-carboxylate (25). To a stirred solution of compound **24** (21.0 g, 0.102 mol) in a mixture of dry DMF (210 cm^3) and dry benzene (100 cm^3) was added dropwise phosphoryl chloride (97.0 g, 0.633 mol) during 2 h at room temperature. Stirring was continued for 21 h at room temperature. The mixture was poured onto ice-water. The resultant dark solution was neutralized by addition of solid $NaHCO_3$ until the pH of the solution turned to 6—7 (litmus). The solution was passed through Hyflo Super-Cel and extracted with benzene. The combined extracts were washed with brine and dried. The residue obtained after removal of the solvent was chromatographed on silica gel (5.2×8.0 cm). The fractions eluted with hexane–benzene (2 : 3) afforded the aldehyde **25** (14.6 g, 57%) as yellow columns, mp 71—72 °C, from hexane–ether; Mass m/z 252 (M^+; 3%) and 115 (100); UV 219 (ε 11200), 223 (11200), 258 (sh, 30400), 264 (34000), and 343 nm (11700); IR 2873 (CHO), 1706, 1663 (C=O), and 1568 cm^{-1} (C=C); ^{1}H NMR (500 MHz) δ_H=10.232 (1H, d, J=6.6 Hz, CHO), 7.350 (1H, d, J=5.9 Hz, H^4), 7.232 (1H, d, J=6.3 Hz, H^1), 7.017 (1H, d, J=6.7 Hz, H^A), 6.974 (1H, dd, J=11.1 and 6.3 Hz, H^2), 6.894 (1H, dd, J=11.1 and 5.9 Hz, H^3), 4.266 (2H, q, J=7.1 Hz, C$\underline{H}_2$CH$_3$), 2.938 (2H, s, CH_2), and 1.342 (3H, t, J=7.1 Hz, CH$_2$C$\underline{H}_3$); ^{13}C NMR (125.76 MHz) δ_C=192.12 (t, CHO), 165.11 (q, $\underline{C}O_2$Et), 148.74 (q, ClC=), 133.94 (t), 133.44 (t), 132.98 (t), 130.16 (t), 129.67 (q), 125.18 (t), 124.61 (q), 61.45 (s, $\underline{C}H_2$CH$_3$), 28.37 (s, CH_2), and 14.23 (p, CH$_2\underline{C}H_3$).

Found: C, 61.94; H, 5.17%. Calcd for $C_{13}H_{13}ClO_3$: C, 61.79; H, 5.19%.

Ethyl 6-Ethynyl-1,3,5-cycloheptatriene-1-carboxylate (26) and 6-Ethynyl-1,3,5-cycloheptatriene-1-carboxylic Acid (27). To a stirred solution of the aldehyde **25** (2.00 g, 7.91 mmol) in DMF (14 cm^3) was added dropwise aqueous KOH (15 mol dm^{-3}; 2.2 cm^3, 33 mmol) during 1.5 h at room temperature. The mixture was poured onto water and extracted with benzene. The combined organic layers were washed with water and dried. The residue obtained after removal of the solvent was chromatographed on silica gel (3.2×6.5 cm). The fractions eluted with hexane–benzene (3 : 2) afforded the ester **26** (734 mg, 49%) as pale orange cubes, mp 34—35 °C, from hexane–benzene; Mass m/z 188 (M^+; 100%); UV 223 (sh, ε 9900), 230 (sh, 28100), 235 (30700), and 323 nm (5870); IR 3243 (C≡CH), 2082 (C≡C), 1692 (C=O), and 1594 cm^{-1} (C=C); ^{1}H NMR (90 MHz) δ_H=7.26 (1H, m, H^1), 6.73—6.60 (3H, m, H^2, H^3, and H^4), 4.26 (2H, q, J=7 Hz, C$\underline{H}_2$CH$_3$), 2.91 (1H, s, C≡CH), 2.84 (2H, s, CH_2), and 1.32 (3H, t, J=7 Hz, CH$_2$C$\underline{H}_3$).

Found: C, 76.87; H, 6.51%. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43%.

To the aqueous layer was added concd HCl until it turned acidic to litmus. The resulting suspension was extracted with CH_2Cl_2. The combined extracts were washed with water and dried. The residue obtained after removal of the solvent was chromatographed on silica gel (3.2×6.1 cm). The fractions eluted with hexane–benzene (1 : 1) afforded the acid **27** (35 mg, 3%) as pale orange needles, mp 123—125 °C (decomp), from hexane–benzene; Mass m/z 160 (M^+; 26%) and 115 (100); UV 210 (sh, ε 9500), 227 (sh, 24100), 234 (27400), and 321.5 nm (5420); IR 3269 (C≡CH), 3002—2842 (CO_2H), 2084 (C≡C), 1668 (C=O), and 1610 cm^{-1} (C=C); ^{1}H NMR (90 MHz) δ_H=9.9 (1H, br, CO_2H), 7.39 (1H, m, H^1), 6.82—6.63 (3H, m, H^2, H^3, and H^4), 2.93 (1H, s, C≡CH), and 2.85 (2H, s, CH_2).

Found: C, 74.86; H, 5.08%. Calcd for $C_{10}H_8O_2$: C, 74.99; H, 5.03%.

(6-Ethynyl-1,3,5-cycloheptatrienyl)methanol (28). To a stirred solution of the ester **26** (700 mg, 3.72 mmol) in dry benzene (120 cm^3) was added dropwise DIBAH in toluene (1.5 mol dm^{-3}; 18 cm^3, 27.0 mmol) by a syringe during 15 min at −3 °C. After stirring for 15 min at 0 °C, methanol (2 cm^3) was cautiously added. Then the mixture was poured onto an ice-cooled 1 mol dm^{-3} aqueous HCl and was extracted with benzene. The extracts were washed with aqueous $NaHCO_3$ and dried. The residue obtained after removal of the solvent was chromatographed on alumina (3.2×4.0 cm). The fractions eluted with benzene–CH_2Cl_2 (9:1) afforded the alcohol **28** (504 mg, 93%) as a colorless liquid, Mass m/z 146 (M^+; 21%) and 115 (100); UV 229 (ε 9270) and 297 nm (5410); IR (neat) 3400—3300 (OH), 3288 (C≡CH), and 2087 cm^{-1} (C≡C); ^1H NMR (90 MHz) δ_H=6.52—6.23 (4H, m, H^1, H^2, H^3, and H^4), 4.28 (2H, s, $C\underline{H}_2OH$), 2.80 (1H, s, C≡CH), 2.51 (2H, s, CH_2), and 1.85 (1H, br, OH, disappeared by addition of D_2O).

Found: C, 82.24; H, 7.31%. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.90%.

Alcohol 28 from Acid 27. To a stirred solution of the acid **27** (785 mg, 4.90 mmol) in dry THF (41 cm^3) was added in one portion $LiAlH_4$ (124 mg, 3.27 mmol) at room temperature. The mixture was heated for 30 min at 43 °C. After being cooled, ethyl acetate (1.0 cm^3) was added. Then the mixture was poured onto water and extracted with CH_2Cl_2. The extracts were washed with water and dried. The residue obtained after removal of the solvent was chromatographed on silica gel (4.2×3.5 cm). The fractions eluted with benzene–CH_2Cl_2 (9:1) afforded the alcohol **28** (306 mg, 43%).

6-Ethynyl-1,3,5-cycloheptatriene-1-carbaldehyde (29). A mixture of the alcohol **28** (495 mg, 3.39 mmol) and $Ba(MnO_4)_2$[18] (5.00 g, 19.5 mmol) in dry CH_2Cl_2 (400 cm^3) was stirred for 2 h at room temperature. Then the mixture was filtered and the inorganic material was washed with CH_2Cl_2. The combined filtrate and washings were concentrated under reduced pressure. The residual yellow solid was chromatographed on silica gel (3.2×3.0 cm). The fractions eluted with 30—50% benzene in hexane afforded the aldehyde **29** (380 mg, 78%) as pale yellow needles, mp 56—57 °C (decomp), from hexane–benzene; Mass m/z 144 (M^+; 32%) and 115 (100); UV 240 (ε 23300) and 330 nm (4210); IR 3219 (C≡CH), 2824, 2734 (CHO), 2079 (C≡C), 1661 (C=O), and 1597 cm^{-1} (C=C); ^1H NMR (500 MHz) δ_H=9.561 (1H, s, CHO), 6.960 (1H, m, H^1), 6.84—6.78 (2H, m, H^2 and H^3), 6.614 (1H, m, H^4), 2.938 (1H, s, C≡CH), and 2.871 (2H, s, CH_2); ^{13}C NMR (125.76 MHz) δ_C=191.36 (t, CHO), 141.36 (t), 135.19 (t), 132.90 (q), 132.69 (t), 130.12 (t), 117.65 (q), 85.00 (q, −C≡), 76.36 (t, ≡CH), and 28.09 (s, CH_2).

Found: C, 83.03; H, 5.65%. Calcd for $C_{10}H_8O$: C, 83.31; H, 5.59%.

(*Z*)-3-Chloro-3-(1,3,5-cycloheptatrienyl)propenal (30). To a stirred solution of 1-acetyl-1,3,5-cycloheptatriene (**21**)[15] (50.0 g, 0.373 mmol) in a mixture of dry DMF (450 cm^3) and dry benzene (300 cm^3) was added dropwise phosphoryl chloride (200 g, 1.30 mol) during 3.5 h at room temperature and the mixture was stirred for 26 h at room temperature. Then the mixture was poured onto water and extracted with benzene. The combined extracts were washed with brine and dried. The residue obtained after removal of the solvent was chromatographed on silica gel (5.2×11.0 cm). The fractions eluted with 2—5% ether in hexane afforded the aldehyde **30** (22.2 g, 33%) as yellow plates, mp 35—36 °C, from hexane; Mass m/z 180 (M^+; 54%) and 115 (100); UV 210 (ε 6650), 251 (9760), and 335 nm (8120); IR 2922, 2852 (CHO), and 1669 cm^{-1} (C=O); ^1H NMR (500 MHz) δ_H=10.188 (1H, d, J=6.7 Hz, CHO), 7.104 (1H, d, J=6.1 Hz, H^5), 6.803 (1H, dd, J=11.2 and 5.5 Hz, H^3), 6.727 (1H, dd, J=11.2 and 6.1 Hz, H^4), 6.537 (1H, d, J=6.7 Hz, H^A), 6.317 (1H, dd, J=9.2 and 5.5 Hz, H^2), 5.566 (1H, dt, J=9.2 and 7.2 Hz, H^1), and 2.666 (2H, d, J=7.2 Hz, CH_2); ^{13}C NMR (125.76 MHz) δ_C=192.07 (t, CHO), 150.41 (q, =C–Cl), 134.85 (t), 130.29 (t), 129.77 (t), 127.96 (t), 127.12 (q), 124.02 (t), 123.73 (t), and 29.30 (s, CH_2).

Found: C, 66.60; H, 5.05%. Calcd for $C_{10}H_9ClO$: C, 66.49; H, 5.02%.

1-Ethynyl-1,3,5-cycloheptatriene (31). To a stirred solution of the aldehyde **30** (4.20 g, 23.2 mmol) in DMF (60 cm^3) was added dropwise aqueous KOH (15 mol dm^{-3}; 10 cm^3, 8.42 mol) during 1 h at room temperature. After addition of benzene, the mixture was poured onto water and extracted with benzene. The combined extracts were washed with brine and dried. The residue obtained after removal of the solvent was chromatographed on silica gel (4.2×3.0 cm). The fractions eluted with hexane afforded the compound **31** (1.28 g, 47%) as a green liquid, Mass m/z 116 (M^+; 10%) and 78 (100); UV 230 (ε 3750) and 294 nm (6330); IR 3301 (C≡CH) and 2090 cm^{-1} (C≡C); ^1H NMR (90 MHz) δ_H=6.77—6.15 (4H, m, H^2, H^3, H^4, and H^5), 5.51 (1H, dt, J=9 and 7 Hz, H^1), 2.79 (1H, s, C≡CH), and 2.49 (2H, d, J=7 Hz, CH_2).

Found: C, 92.77; H, 7.05%. Calcd for C_9H_8: C, 93.06; H, 6.94%.

Attempted Vilsmeier Reaction for Compound 31. To a stirred solution of compound **31** (673 mg, 5.79 mmol) in dry DMF (25 cm^3) was added dropwise phosphoryl chloride (2.10 g, 13.7 mmol) in dry DMF (20 cm^3) during 50 min at −5 °C. After stirring for 1 h at −5 °C, a further quantity of phosphoryl chloride (1.00 g, 6.52 mmol) in dry DMF (5 cm^3) was added dropwise during 30 min at −5 °C. After this was stirred overnight at room temperature, a further quantity of phosphoryl chloride (1.0 g) in dry DMF (5 cm^3) was added dropwise during 30 min and the mixture was heated for 6 h at 45 °C. Then the mixture was worked up as for the isolation of compound **25**. The product was chromatographed on silica gel (3.2×3.5 cm). The fractions eluted with hexane–benzene (4:1) afforded the aldehyde **30** (165 mg, 16%).

4-(6-Acetyl-1,3,5-cycloheptatrienyl)-3-methyl-3-buten-2-one (40). A solution of the aldehyde **29** (630 mg, 4.37 mmol) in acetic acid (2.8 cm^3) was added dropwise during 30 min to a stirred solution of 2-butanone (1.35 g, 18.8 mmol) and concd H_2SO_4 (0.34 cm^3) in acetic acid (17 cm^3) at room temperature. The resultant dark red solution was stirred for 16 h at room temperature and then was cautiously poured onto saturated aqueous K_2CO_3 with stirring. The mixture was extracted with benzene, and the combined extracts were washed with brine and dried. The residue obtained after removal of the solvent was chromatographed on alumina (3.2×4.5 cm). The fractions eluted with hexane–ether (4:1) afforded the ketone **40** (370 mg, 43%) as yellow needles, mp 34—35 °C, from hexane–ether; Mass m/z 216 (M^+; 72%) and 173 (100); UV 265 (ε 22700) and

338 nm (7490); IR 1649 (C=O), 1616 and 1592 cm^{-1} (C=C); ^1H NMR (500 MHz) δ_H=7.143 (1H, d, J=6.0 Hz, H^4), 7.050 (1H, s, H^B), 6.942 (1H, dd, J=11.1 and 6.2 Hz, H^2), 6.776 (1H, dd, J=11.0 and 6.0 Hz, H^3), 6.473 (1H, d, J=6.3 Hz, H^1), 2.813 (2H, s, CH_2), 2.398 (3H, s, COMe), 2.393 (3H, s, COMe), and 1.956 (3H, d, J=1.4 Hz, Me^a); ^{13}C NMR (125.76 MHz) δ_C=200.34 (q, C=O), 197.16 (q, C=O), 139.56 (t), 138.96 (q), 135.20 (t), 133.06 (t), 133.02 (q), 131.58 (q), 129.97 (t), 128.58 (t), 30.40 (s, CH_2), 26.02 (p, CH_3), 25.80 (p, CH_3), and 13.37 (p, CH_3).

Found: C, 78.01; H, 7.44%. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46%.

An attempt to obtain ketone **43** from aldehyde **29** and 2-butanone using gaseous HCl instead of a mixture of acetic acid and concd H_2SO_4 was made, but was also unsuccessful.

An Attempt to Obtain Compound 43 via a Cobalt Complex. A solution of aldehyde **29** (400 mg, 2.77 mmol) in dry benzene (3.0 cm^3) wad added dropwise during 25 min to a stirred solution of $Co_2(CO)_8$[21] (1.14 g, 3.33 mmol) in dry benzene (3.0 cm^3) at room temperature under argon. After this was stirred for 14 h at room temperature, acetic acid (3.0 cm^3) was added. Then a solution of 2-butanone (1.31 g, 18.1 mmol) and concd H_2SO_4 (0.45 cm^3) in acetic acid (10 cm^3) was added dropwise during 35 min and the solution was stirred at room temperature overnight. After addition of THF (5.0 cm^3), the mixture was chilled to −20 °C and $Ce(NH_4)_2(NO_3)_5 \cdot 4H_2O$[21] (3.5 g) was added in one portion. The mixture was stirred for a further 6 h at room temperature, then cautiously added to a stirred saturated aqueous K_2CO_3, and filtered. The filtrate was extracted with CH_2Cl_2 and the extracts were washed with brine and dried. The product after removal of the solvent was chromatographed on alumina. However, the desired compound **43** was not detected from any fraction.

3-(Triphenylphosphoranylidene)-2-butanone (42). To a stirred suspension of ethyltriphenylphosphonium bromide[29] (13.7 g, 36.9 mmol) in dry THF (50 cm^3) was added dropwise a solution of butyllithium in hexane (1.6 mol dm^{-3}; 25.0 cm^3, 40 mmol) by a syringe during 50 min at room temperature under argon. After stirring for 4 h, a solution of *N*-acetylimidazole (2.27 g, 20.6 mmol) in dry THF (70 cm^3) was added dropwise during 1 h and the mixture was stirred for 3 h at room temperature. Then the mixture was poured onto water and extracted with ether. The combined extracts were washed with water and dried. The residue obtained after removal of the solvent was recrystallized from ethyl acetate, affording the phosphorane **42** (2.40 g, 39%) as pale yellow needles, mp 186—188 °C (decomp); Mass m/z 332 (M^+; 100%); IR 1513 cm^{-1} (C=O); ^1H NMR (90 MHz) δ_H=7.71—7.37 (15H, m, C_6H_5×3), 2.13 (3H, s, COMe), and 1.65 (3H, d, J=15.3 Hz, −(Me)C=).

Found: C, 79.60; H, 6.47%. Calcd for $C_{22}H_{21}OP$: C, 79.50; H, 6.37%.

4-(6-Ethynyl-1,3,5-cycloheptatrienyl)-3-methyl-3-buten-2-one (43). To a stirred solution of the aldehyde **29** (500 mg, 3.47 mmol) in dry toluene (15 cm^3) was added dropwise during 10 min a solution of the phosphorane **42**[23] (1.725 g, 5.19 mmol) in dry toluene (65 cm^3) at room temperature under argon. Then the mixture was stirred for 6 h at 100 °C. After being cooled, the mixture was concentrated under reduced pressure and the residue was chromatographed on alumina (3.8×4.1 cm). The fractions eluted with 25% ether in hexane afforded the ketone **43** (85 mg, 12%) as brown needles, mp 49—50 °C (decomp), from hexane–ether; Mass m/z 198 (M^+; 60%) and 115 (100); UV 264 (ε 20100) and 342 nm (7600); IR 3287 (C≡CH), 2092 (C≡C), 1662 (C=O), and 1609 cm^{-1} (C=C); ^1H NMR (400 MHz) δ_H=7.078 (1H, s, H^B), 6.709—6.579 (3H, m, H^1, H^2, and H^3), 6.445 (1H, d, J=6.2 Hz, H^4), 2.896 (1H, s, C≡CH), 2.759 (2H, s, CH_2), 2.392 (3H, s, Me^a), and 2.079 (3H, d, J=1.2 Hz, Me^b); ^{13}C NMR (100.40 MHz) δ_C=200.26 (q, C=O), 140.16 (t), 137.90 (q), 133.09 (t), 131.66 (t), 130.92 (t), 130.60 (t), 129.78 (q), 113.47 (q), 85.49 (q, −C≡), 75.55 (t, ≡CH), 36.34 (s, CH_2), 29.69 (p, CH_3), and 13.33 (p, CH_3).

Found: C, 84.57; H, 7.20%. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12%.

(*E*)-4-(6-Ethynyl-1,3,5-cycloheptatrienyl)-3-buten-2-one (48). An ice-cooled solution of 5% aqueous NaOH (8.0 cm^3) and ethanol (4.0 cm^3) was added to a stirred solution of the aldehyde **29** (350 mg, 2.43 mmol) in acetone (10 cm^3) during 1 h at 2 °C. The solution was stirred for a further 30 min at 2 °C and 2 mol dm^{-3} aqueous H_2SO_4 (10 cm^3) was then added. The mixture was poured onto water and extracted with benzene. The combined extracts were washed with aqueous $NaHCO_3$ and dried. The residue obtained after removal of the solvent was chromatographed on alumina (3.2×3.5 cm). The fractions eluted with 10% ether in hexane afforded the ketone **48** (260 mg, 58%) as an orange liquid, Mass m/z 184 (M^+; 54%) and 141 (100); UV 247 (sh, ε 20600), 254 (sh, 27200), 259 (30820), 263 (sh, 29500), and 347 nm (9520); IR (neat) 3288, 3249 (C≡CH), 2087 (C≡C), 1683, 1667 (C=O), 1607, 1586 (C=C), 1008 and 972 cm^{-1} ((*E*)-HC=CH); ^1H NMR (500 MHz) δ_H=7.251 (1H, d, J=15.5 Hz, H^B), 6.719 (1H, dd, J=10.7 and 5.9 Hz, H^2), 6.669 (1H, dd, J=10.7 and 5.9 Hz, H^3), 6.609 (1H, d, J=5.9 Hz, H^4), 6.539 (1H, d, J=5.9 Hz, H^1), 6.490 (1H, d, J=15.9 Hz, H^A), 2.919 (1H, s, C≡CH), 2.702 (2H, s, CH_2), and 2.336 (3H, s, Me); ^{13}C NMR (125.76 MHz) δ_C=198.41 (q, C=O), 143.89 (t), 132.71 (t), 132.49 (t), 132.12 (t), 131.45 (t), 129.42 (q), 127.70 (t), 114.71 (q), 85.17 (q, −C≡), 75.64 (t, ≡CH), 32.76 (p, CH_3), and 27.65 (s, CH_2).

Found: C, 84.61; H, 6.84%. Calcd for $C_{13}H_{12}O$: C, 84.75; H, 6.57%.

(*E*)-3-(6-Ethynyl-1,3,5-cycloheptatrienyl)propenal (51). An ethanolic lithium ethoxide solution, prepared from lithium (578 mg, 83.2 mmol) in dry ethanol (82 cm^3), was added dropwise to a stirred solution of [(1,3-dioxolan-2-yl)methyl]triphenylphosphonium bromide[27] (35.5 g, 83.2 mmol) in DMF (75 cm^3) during 1 h at 70 °C under argon. After this mixture was stirred for a further 4 h at 70 °C, a solution of the aldehyde **29** (750 mg, 5.20 mmol) in DMF (20 cm^3) was added dropwise to it during 1 h at 52 °C. After being stirred for one more hour at 52 °C, the reaction mixture was poured onto water and extracted with benzene. Then the extracts were washed with brine and dried. The residue obtained after removal of the solvent was chromatographed on alumina (3.8×6.0 cm). The fractions eluted with 5% ether in hexane were collected and evaporated to afford the acetal of compound **51**. The residue was dissolved in ethanol (50 cm^3) and the solution was admixed with 0.5 mol dm^{-3} aqueous HCl (50 cm^3). The mixture was stirred for 15 min at room temperature and then was poured onto water, and extracted with benzene. The extracts were washed with

aqueous $NaHCO_3$ and dried. The residue obtained after removal of the solvent was chromatographed on silica gel (3.8×6.5 cm). The fractions eluted with hexane–benzene (9 : 1) afforded the aldehyde **51** (511 mg, 58%) as yellow needles, mp 91—93 °C (decomp), from hexane–benzene; Mass *m/z* 170 (M^+; 79%) and 141 (100); UV 261 (ε 38800) and 351 nm (10400); IR 3237 (C≡CH), 2079 (C≡C), 1661 (C=O), 1606 (C=C), and 966 cm^{-1} ((*E*)-HC=CH); ^1H NMR (500 MHz) δ_H=9.634 (1H, d, *J*=7.7 Hz, CHO), 7.213 (1H, d, *J*=15.5 Hz, H^B), 6.69—6.77 (2H, m, H^2 and H^3), 6.625 (1H, d, *J*=5.3 Hz, H^1 or H^4), 6.597 (1H, d, *J*=5.3 Hz, H^4 or H^1), 6.503 (1H, dd, *J*=15.6 and 7.7 Hz, H^A), 2.935 (1H, s, C≡CH), and 2.729 (2H, s, CH_2); ^{13}C NMR (125.76 MHz) δ_C=193.76 (t, CHO), 152.76 (t), 133.36 (t), 132.92 (t), 132.45 (t), 131.22 (t), 129.16 (t), 128.97 (q), 115.10 (q), 84.98 (q, –C≡), 76.12 (t, ≡CH), and 33.00 (s, CH_2).

Found: C, 84.96; H, 6.05%. Calcd for $C_{12}H_{10}O$: C, 84.68; H, 5.92%.

1-(6-Ethynyl-1,3,5-cycloheptatrienyl)-7-methyl-1,4,6-nonatrien-8-yn-3-one (33). A Typical Procedure for Preparation of Bisethynyl Ketones by Aldol Condensation. An ethanolic sodium ethoxide solution (6.0 cm^3) was added in small portions to a stirred solution of ketone **32**[3,13] (1.02 g, 7.59 mmol) and aldehyde **29** (680 mg, 4.72 mmol) in deoxygenated ether (50 cm^3) during 50 min at 10 °C, and the solution was stirred for 25 min at 10 °C. Then the reaction was terminated by addition of 2 mol dm^{-3} aqueous H_2SO_4 (10 cm^3). The mixture was poured onto water and extracted with benzene. The extracts were washed with aqueous $NaHCO_3$ and dried. The residue obtained after removal of the solvent was chromatographed on alumina (3.2×7.0 cm). The fractions eluted with hexane–ether (4 : 1) afforded the ketone **33** (454 mg, 37%) as pale yellow needles, mp 74—76 °C, from hexane–benzene; Mass *m/z* 260 (M^+; 75%) and 202 (100); UV 239.5 (ε 16000), 316.5 (11000), and 367 nm (11400); IR 3266, 3230 (C≡CH), 2085 (C≡C), 1657 (C=O), 1602 (C=C), and 983 cm^{-1} ((*E*)-HC=CH); ^1H NMR (500 MHz) δ_H=7.734 (1H, dd, *J*=15.4 and 11.3 Hz, $H^{B'}$), 7.411 (1H, d, *J*=15.5 Hz, H^B), 6.809 (1H, d, *J*=15.5 Hz, H^A), 6.732 (1H, dd, *J*=11.0 and 6.0 Hz, H^2), 6.671 (1H, dd, *J*=11.0 and 6.0 Hz, H^3), 6.615 (1H, d, *J*=6.0 Hz, H^4), 6.570 (1H, d, *J*=6.0 Hz, H^1), 6.482 (1H, d, *J*=11.3 Hz, $H^{C'}$), 6.460 (1H, d, *J*=15.3 Hz, $H^{A'}$), 3.491 (1H, s, C≡CH), 2.934 (1H, s, C≡CH), 2.731 (2H, s, CH_2), and 2.047 (3H, s, Me); ^{13}C NMR (125.76 MHz) δ_C=189.23 (q, C=O), 143.54 (t), 139.73 (t), 135.75 (t), 132.74 (t), 132.45 (t), 131.97 (t), 131.67 (t), 130.20 (t), 129.75 (q), 128.32 (q), 125.55 (t), 114.52 (q), 86.22 (t, ≡CH), 85.39 (q, –C≡), 82.08 (q, –C≡), 75.56 (t, ≡CH), 33.18 (s, CH_2), and 23.88 (p, CH_3).

Found: C, 87.89; H, 6.44%. Calcd for $C_{19}H_{16}O$: C, 87.66; H, 6.19%.

1-(6-Ethynyl-1,3,5-cycloheptatrienyl)-5-(2-ethynylphenyl)-1,4-pentadien-3-one (35). The aldol condensation of the ketone **34**[19] (672 mg, 3.95 mmol) and the aldehyde **29** (350 mg, 2.43 mmol) followed by chromatography on alumina (3.8×6.0 cm) with hexane–ether (1 : 1) as the eluent afforded the ketone **35** (303 mg, 42%) as yellow needles, mp 101—102 °C (decomp), from hexane–benzene; Mass *m/z* 296 (M^+; 50%) and 252 (100); UV 236 (ε 34800), 306 (18000), and 365 nm (16600); IR 3243 (C≡CH), 2102, 2082 (C≡C), 1666 (C=O), 1613, 1575 (C=C), and 982 cm^{-1} ((*E*)-HC=CH); ^1H NMR (500 MHz) δ_H=8.198 (1H, d, *J*=16.1 Hz, $H^{B'}$), 7.719 (1H, d, *J*=7.3 Hz, H^8), 7.567 (1H, dd, *J*=7.6 and 1.5 Hz, H^5), 7.490 (1H, d, *J*=15.5 Hz, H^B), 7.394 (1H, td, *J*=7.6 and 1.5 Hz, H^7), 7.351 (1H, td, *J*=7.4 and 1.4 Hz, H^6), 7.067 (1H, d, *J*=16.1 Hz, $H^{A'}$), 6.914 (1H, d, *J*=15.5 Hz, H^A), 6.745 (1H, dd, *J*=11.0 and 6.0 Hz, H^2), 6.685 (1H, dd, *J*=11.0 and 6.0 Hz, H^3), 6.631 (1H, d, *J*=6.0 Hz, H^4), 6.601 (1H, d, *J*=6.0 Hz, H^1), 3.454 (1H, s, C≡CH^b), 2.954 (1H, s, C≡CH^a), and 2.765 (2H, s, CH_2); ^{13}C NMR (125.76 MHz) δ_C=189.06 (q, C=O), 144.00 (t), 140.46 (t), 136.90 (q), 133.59 (t), 132.98 (t), 132.52 (t), 132.08 (t), 131.66 (t), 129.77 (t), 129.11 (t), 128.32 (q), 127.99 (t), 126.11 (t), 125.46 (t), 123.20 (q), 114.60 (q), 85.43 (q, –C≡), 83.52 (t, ≡CH), 81.24 (q, –C≡), 75.62 (t, ≡CH), and 33.15 (s, CH_2).

Found: C, 89.21; H, 5.55%. Calcd for $C_{22}H_{16}O$: C, 89.16; H, 5.44%.

1-(6-Ethynyl-1,3,5-cycloheptatrienyl)-4,7-dimethyl-1,4,6-nonatrien-8-yn-3-one (37). The aldol condensation of the ketone **36**[3] (658 mg, 4.44 mmol) and the aldehyde **29** (400 mg, 2.77 mmol) followed by chromatography on alumina (2.8×6 cm) with 10% ether in hexane as the eluent afforded the ketone **37** (320 mg, 42%) as yellow needles, mp 125—126 °C (decomp), from hexane–benzene; Mass *m/z* 274 (M^+; 37%) and 69 (100); UV 202 (ε 15600), 241 (26300), 314.5 (20000), and 373 nm (sh, 12100); IR 3280, 3236 (C≡CH), 2084 (C≡C), 1642 (C=O), 1615 (C=C), and 977 cm^{-1} ((*E*)-HC=CH); ^1H NMR (500 MHz) δ_H=7.610 (1H, d, *J*=11.3 Hz, $H^{B'}$), 7.425 (1H, d, *J*=15.2 Hz, H^B), 7.187 (1H, d, *J*=15.2 Hz, H^A), 6.741 (1H, d, *J*=11.1 Hz, $H^{C'}$), 6.735 (1H, dd, *J*=11.0 and 6.0 Hz, H^2), 6.660 (1H, dd, *J*=11.0 and 6.0 Hz, H^3), 6.612 (1H, d, *J*=6.0 Hz, H^4), 6.561 (1H, d, *J*=6.0 Hz, H^1), 3.518 (1H, s, C≡CH), 2.927 (1H, s, C≡CH), 2.732 (2H, s, CH_2), 2.086 (3H, s, Me^a), and 2.006 (3H, s, Me^b); ^{13}C NMR (125.76 MHz) δ_C=191.56 (q, C=O), 143.45 (t), 138.38 (q), 135.01 (t), 133.34 (t), 132.30 (t), 132.07 (t), 131.77 (t), 131.59 (t), 129.99 (q), 126.18 (q), 122.12 (t), 114.30 (q), 86.22 (t, ≡CH), 85.55 (q, –C≡), 82.52 (q, –C≡), 75.60 (t, ≡CH), 33.58 (s, CH_2). 24.01 (p, CH_3), and 12.43 (p, CH_3).

Found: C, 87.26; H, 6.55%. Calcd for $C_{20}H_{18}O$: C, 87.56; H, 6.61%.

5-(6-Ethynyl-1,3,5-cycloheptatrienyl)-1-(2-ethynylphenyl)-2-methyl-1,4-pentadien-3-one (39). The aldol condensation of the aldehyde **29** (400 mg, 2.77 mmol) and the ketone **38**[5a] (700 mg, 3.80 mmol) followed by chromatography on alumina (3.2×5.5 cm) with 30% ether in hexane as the eluent afforded the ketone **39** (219 mg, 26%) as yellow needles, mp 134—136 °C (decomp), from hexane–benzene; Mass *m/z* 311 [$(M+1)^+$; 13%] and 154 (100) (FAB MS); UV 242 (ε 32900), 291 (18600), and 359 nm (12200); IR 3260, 3231 (C≡CH), 2081 (C≡C), 1645 (C=O), and 975 cm^{-1} ((*E*)-HC=CH); ^1H NMR (500 MHz) δ_H=7.870 (1H, br s, $H^{B'}$), 7.584 (1H, dd, *J*=7.8 and 1.0 Hz, H^5), 7.483 (1H, dd, *J*=15.4 and 0.6 Hz, H^B), 7.457 (1H, d, *J*=7.8 Hz, H^8), 7.408 (1H, td, *J*=7.5 and 1.2 Hz, H^7), 7.316 (1H, td, *J*=7.6 and 1.4 Hz, H^6), 7.235 (1H, d, *J*=15.3 Hz, H^A), 6.744 (1H, dd, *J*=11.0 and 6.0 Hz, H^2), 6.672 (1H, dd, *J*=11.0 and 6.0 Hz, H^3), 6.622 (1H, d, *J*=6.0 Hz, H^4), 6.583 (1H, d, *J*=6.0 Hz, H^1), 3.407 (1H, s, C≡CH), 2.941 (1H, s, C≡CH), 2.763 (2H, s, CH_2), and 2.094 (3H, d, *J*=1.4 Hz, Me); ^{13}C NMR (125.76 MHz) δ_C=192.80 (q, C=O), 144.06 (t), 139.73 (q), 138.60 (q), 136.64 (t), 132.98 (t), 132.38

(t), 132.33 (t), 131.74 (t), 131.72 (t), 129.91 (q), 129.08 (t), 128.58 (t), 128.12 (t), 122.74 (t), 122.46 (q), 114.42 (q), 85.58 (q, –C≡), 83.00 (t, ≡CH), 81.87 (q, –C≡), 75.63 (t, ≡CH), 33.39 (s, CH_2), and 13.76 (p, CH_3).

Found: C, 89.05; H, 5.95%. Calcd for $C_{23}H_{18}O$: C, 89.00; H, 5.85%.

1-(6-Ethynyl-1,3,5-cycloheptatrienyl)-2,7-dimethyl-1,4,6-nonatrien-8-yn-3-one (45). The aldol condensation of the aldehyde **44**[3,13] (1.54 g, 16.4 mmol) and the ketone **43** (200 mg, 1.01 mmol) followed by chromatography on alumina (3.2×6.0 cm) with 10% ether in hexane as the eluent gave the ketone **45** (123 mg, 44%) as a liquid. The liquid was purified by PLC with CH_2Cl_2–hexane (2 : 1). The fast moving, second band afforded pure **45** as an unstable yellow liquid, Mass *m/z* 274 (M^+; 8%) and 28 (100); UV 242 (ε 16500) and 313 nm (12600); IR (neat) 3292 (C≡CH), 2088 (C≡C), 1643 (C=O), and 986 cm^{-1} ((*E*)-HC=CH); ^1H NMR (400 MHz) δ_H=7.701 (1H, dd, *J*=15.1 and 11.7 Hz, $H^{B'}$), 7.040 (1H, s, H^B), 6.794 (1H, d, *J*=15.1 Hz, $H^{A'}$), 6.73—6.57 (3H, m, H^1 or H^4, H^2, and H^3), 6.490 (1H, d, *J*=11.2 Hz, $H^{C'}$), 6.453 (1H, d, *J*=5.9 Hz, H^4 or H^1), 3.458 (1H, s, C≡CH), 2.893 (1H, s, C≡CH), 2.766 (2H, s, CH_2), 2.161 (3H, s, Me^b), and 2.035 (3H, s, Me^a); ^{13}C NMR (100.40 MHz) δ_C=192.88 (q, C=O), 140.13 (t), 139.08 (t), 138.81 (q), 135.73 (t), 133.11 (t), 131.72 (t), 130.86 (t), 130.53 (t), 129.87 (q), 127.75 (q), 125.88 (t), 113.43 (q), 85.96 (t, ≡CH), 85.55 (q, –C≡), 82.02 (q, –C≡), 75.51 (t, ≡CH), 36.42 (s, CH_2), 23.80 (p, CH_3), and 14.16 (p, CH_3).

Found: C, 86.66; H, 7.01%. Calcd for $C_{20}H_{18}O$: C, 87.56; H, 6.61%. Attempts to improve the elemental analysis failed.

The ketone **43** (42 mg) was recovered from the fast moving, third band.

1-(6-Ethynyl-1,3,5-cycloheptatrienyl)-5-(2-ethynylphenyl)-2-methyl-1,4-pentadien-3-one (47). The aldol condensation of the aldehyde **46**[19] (164 mg, 1.27 mmol) and the ketone **43** (125 mg, 0.63 mmol), followed by chromatography on alumina (3.2×6.5 cm) with 30% ether in hexane as the eluent, afforded the ketone **47** (118 mg, 60%) as yellow microcrystals, mp 85—87 °C (decomp), from hexane–benzene; Mass *m/z* 310 (M^+; 30%) and 267 (100); UV 234 (ε 35100), 244 (36100), 302 (17900), and 358 nm (15000); IR 3274, 3231 (C≡CH), 2106, 2080 (C≡C), 1641 (C=O), 1587 (C=C), and 978 cm^{-1} ((*E*)-HC=CH); ^1H NMR (400 MHz) δ_H=8.088 (1H, d, *J*=15.8 Hz, $H^{B'}$), 7.687 (1H, d, *J*=7.6 Hz, H^8), 7.561 (1H, dd, *J*=7.6 and 1.4 Hz, H^5), 7.428 (1H, d, *J*=15.8 Hz, $H^{A'}$), 7.389 (1H, td, *J*=7.6 and 1.4 Hz, H^7), 7.336 (1H, td, *J*=7.6 and 1.2 Hz, H^6), 7.161 (1H, br s, H^B), 6.716 (1H, dd, *J*=10.4 and 6.0 Hz, H^2), 6.65—6.58 (2H, m, H^3 and H^4), 6.489 (1H, d, *J*=6.2 Hz, H^1), 3.437 (1H, s, C≡CH), 2.905 (1H, s, C≡CH), 2.797 (2H, s, CH_2), and 2.217 (3H, d, *J*=0.9 Hz, Me); ^{13}C NMR (100.40 MHz) δ_C=192.88 (q, C=O), 140.83 (t), 139.69 (t), 138.77 (t), 137.23 (q), 133.66 (t), 133.16 (t), 131.71 (t), 130.94 (t), 130.66 (q), 129.87 (q), 129.43 (t), 129.02 (t), 126.48 (t), 124.28 (t), 122.88 (q), 113.50 (q), 85.59 (q, –C≡), 83.38 (t, ≡CH), 81.41 (q, –C≡), 75.62 (t, ≡CH), 36.39 (s, CH_2), and 14.22 (p, CH_3).

Found: C, 88.71; H, 5.77%. Calcd for $C_{23}H_{18}O$: C, 89.00; H, 5.85%.

The later fractions eluted with 40% ether in hexane afforded the unreacted ketone **43** (45 mg).

1-(6-Ethynyl-1,3,5-cycloheptatrienyl)-9-methyl-1,4,6,8-undecatetraen-10-yn-3-one (50). The aldol condensation of the ketone **48** (770 mg, 4.18 mmol) and the aldehyde **49**[4,26] (660 mg, 5.49 mmol), followed by chromatography on alumina (3.2×5.0 cm) with hexane–ether (5 : 1) as the eluent, afforded the ketone **50** (560 mg, 47%) as orange needles, mp 92—94 °C (decomp), from hexane–benzene; Mass *m/z* 286 (M^+; 40%) and 115 (100); UV 242 (ε 28300), 284 (19000), 286 (19000), and 383 nm (36800); IR 3295, 3246 (C≡CH), 2084 (C≡C), 1653 (C=O), 1604 (C=C), 1006 and 974 cm^{-1} ((*E*)-HC=CH); ^1H NMR (500 MHz) δ_H=7.407 (1H, dd, *J*=15.2 and 11.5 Hz, $H^{B'}$), 7.399 (1H, d, *J*=15.6 Hz, H^B), 7.087 (1H, dd, *J*=14.8 and 11.4 Hz, $H^{D'}$), 6.763 (1H, d, *J*=15.6 Hz, H^A), 6.726 (1H, dd, *J*=11.0 and 6.0 Hz, H^2), 6.663 (1H, dd, *J*=10.9 and 6.0 Hz, H^3), 6.617 (1H, d, *J*=6.0 Hz, H^4), 6.563 (1H, d, *J*=6.0 Hz, H^1), 6.488 (1H, d, *J*=15.2 Hz, $H^{A'}$), 6.429 (1H, dd, *J*=14.8 and 11.5 Hz, $H^{C'}$), 6.419 (1H, d, *J*=11.6 Hz, $H^{E'}$), 3.443 (1H, s, C≡CH), 2.937 (1H, s, C≡CH), 2.738 (2H, s, CH_2), and 2.002 (3H, s, Me); ^{13}C NMR (125.76 MHz) δ_C=188.81 (q, C=O), 143.38 (t), 142.98 (t), 138.99 (t), 136.74 (t), 132.76 (t), 132.58 (t), 131.94 (t), 131.68 (t), 131.45 (t), 129.86 (q), 129.70 (t), 126.11 (t), 123.55 (q), 114.54 (q), 85.45 (q, –C≡), 85.16 (t, ≡CH), 82.53 (q, –C≡), 75.40 (t, ≡CH), 33.02 (s, CH_2), and 23.47 (p, CH_3).

Found: C, 87.80; H, 6.53%. Calcd for $C_{21}H_{18}O$: C, 88.08; H, 6.34%.

1-(6-Ethynyl-1,3,5-cycloheptatrienyl)-9-methyl-1,3,6,8-undecatetraen-10-yn-5-one (52). The aldol condensation of the ketone **32**[3,13] (615 mg, 4.58 mmol) and the aldehyde **51** (600 mg, 3.53 mmol), followed by chromatography on alumina (3.2×4.5 cm) with hexane–ether (3 : 2) as the eluent, afforded the ketone **52** (416 mg, 41%) as brown plates, mp 75—80 °C (decomp), from hexane–benzene; Mass *m/z* 286 (M^+; 18%) and 69 (100); UV 257 (ε 28300), 321.5 (21000), and 395 nm (31000); IR 3263, 3243 (C≡CH), 2083 (C≡C), 1657 (C=O), 1604 (C=C), and 996 cm^{-1} ((*E*)-HC=CH); ^1H NMR (500 MHz) δ_H=7.696 (1H, dd, *J*=15.4 and 11.3 Hz, $H^{B'}$), 7.386 (1H, m, H^B), 6.79—6.72 (2H, m, H^C and H^D), 6.687 (1H, m, H^3), 6.62—6.56 (2H, m, H^1 and H^2), 6.583 (1H, d, *J*=15.3 Hz, H^A), 6.462 (1H, br d, *J*=11.3 Hz, $H^{C'}$), 6.426 (1H, d, *J*=15.4 Hz, $H^{A'}$), 6.386 (1H, d, *J*=6.2 Hz, H^4), 3.499 (1H, s, C≡CH), 2.898 (1H, s, C≡CH), 2.738 (2H, s, CH_2), and 2.041 (3H, s, Me); ^{13}C NMR (125.76 MHz) δ_C=189.10 (q, C=O), 143.10 (t), 142.21 (t), 139.51 (t), 135.73 (t), 132.77 (t), 131.86 (t), 131.00 (q), 130.83 (t), 129.94 (t), 129.77 (t), 128.84 (t), 128.42 (t), 128.21 (q), 113.83 (q), 86.22 (t, ≡CH), 85.54 (q, –C≡), 82.03 (q, –C≡), 75.03 (t, ≡CH), 32.74 (s, CH_2), and 23.86 (p, CH_3).

Found: C, 88.36; H, 6.43%. Calcd for $C_{21}H_{18}O$: C, 88.08; H, 6.34%.

1-(6-Ethynyl-1,3,5-cycloheptatrienyl)-11-methyl-1,3,6,8,10-tridecapentaen-12-yn-5-one (54). The aldol condensation of the ketone **53**[4] (610 mg, 3.81 mmol) and the aldehyde **51** (605 mg, 3.55 mmol), followed by chromatography on alumina (3.2×4.0 cm) with hexane–ether (1 : 4) as the eluent, afforded the ketone **54** (682 mg, 62%) as yellow leaflets, mp 129—134 °C (decomp), from hexane–CH_2Cl_2; Mass *m/z* 312 (M^+; 14%) and 69 (100); UV 260 (sh, ε 24800), 273 (26400), 351 (sh, 26700), and 402 nm (42500); IR 3286 (C≡CH), 2083, 2017, (C≡C), 1653, 1640

(C=O), 1604 (C=C), and 997 cm^{-1} ((*E*)-HC=CH); ^1H NMR (500 MHz) δ_H=7.43—7.33 (2H, m, H^B and $H^{B'}$), 7.085 (1H, dd, J=14.8 and 11.3 Hz, $H^{D'}$), 6.79—6.71 (2H, m, H^C and H^D), 6.688 (1H, m, H^2), 6.62—6.57 (2H, m, H^3 and H^4), 6.563 (1H, d, J=15.1 Hz, H^A or $H^{A'}$), 6.443 (1H, d, J=15.4 Hz, $H^{A'}$ or H^A), 6.414 (1H, dd, J=15.0 and 10.8 Hz, $H^{C'}$), 6.414 (1H, d, J=14.8 Hz, $H^{E'}$), 6.383 (1H, d, J=6.1 Hz, H^1), 3.436 (1H, s, C≡CH), 2.900 (1H, s, C≡CH), 2.735 (2H, s, CH_2), and 1.999 (3H, s, Me); ^{13}C NMR (125.76 MHz) δ_C=188.69 (q, C=O), 142.94 (t), 142.72 (t), 142.09 (t), 138.87 (t), 136.77 (t), 132.74 (t), 131.86 (t), 131.50 (t), 131.00 (q), 130.81 (t), 129.72 (t), 129.65 (t), 129.14 (t), 128.47 (t), 123.46 (q), 113.84 (q), 85.52 (q, –C≡), 85.14 (t, ≡CH), 82.52 (q, –C≡), 75.04 (t, ≡CH), 32.77 (s, CH_2), and 23.46 (p, CH_3).

Found: C, 88.71; H, 6.65%. Calcd for $C_{23}H_{20}O$: C, 88.43; H, 6.45%.

14-Methyl-10,12-bisdehydro-4,9-methano-1*H*-[17]-annulen-1-one (12). A Typical Procedure for the Intramolecular Oxidative Coupling of Bisethynyl Compounds. A solution of the ketone **33** (300 mg, 1.15 mmol) in pyridine–ether (3 : 1; 80 cm^3) was added dropwise during 1.5 h to a stirred solution of anhydrous copper(II) acetate (2.50 g) in pyridine–ether (3 : 1; 70 cm^3) at 50 °C. The solution was stirred for further 15 min at 50 °C and cooled. The mixture was poured onto water and extracted with benzene. The combined extracts were washed successively with 2 mol dm^{-3} aqueous HCl and aqueous $NaHCO_3$, and dried with Na_2SO_4. The residue obtained after removal of the solvent was chromatographed on alumina (3.2×3.5 cm). The fractions eluted with hexane–ether (1 : 1) afforded compound **12** (124 mg, 42%) as orange microcrystals, mp 161—163 °C (decomp), from hexane–benzene; Mass *m/z* 258 (M^+; 27%) and 215 (100); for UV data see Table 2, Figs. 3 and 5; IR 2162 (C≡C), 1650 (C=O), 1585 (C=C), and 977 cm^{-1} ((*E*)-HC=CH); ^1H NMR (500 MHz) δ_H=9.273 (1H, dd, δ=16.5 and 11.3 Hz, $H^{B'}$), 8.440 (1H, d, J=15.6 Hz, H^A), 6.947 (1H, d, J=15.6 Hz, H^B), 6.622 (1H, dd, J=11.0 and 5.7 Hz, H^2), 6.572 (1H, dd, J=11.0 and 5.7 Hz, H^3), 6.546 (1H, d, J=11.3 Hz, $H^{C'}$), 6.439 (1H, d, J=5.7 Hz, H^1), 6.332 (1H, d, J=5.7 Hz, H^4), 5.969 (1H, d, J=16.4 Hz, $H^{A'}$), 4.393 (1H, d, J=12.9 Hz, H^b), 2.379 (1H, d, J=12.9 Hz, H^a), and 1.809 (3H, d, J=1.1 Hz, Me) and see Fig. 1; ^{13}C NMR (125.76 MHz) δ_C=191.96 (q, C=O), 144.63 (t, $C^{B'}$), 140.22 (t, $C^{C'}$), 140.13 (t, C^B), 132.60 (t, C^2), 131.77 (t, C^3), 131.51 (t, C^1), 131.45 (q), 130.96 (t, $C^{A'}$), 129.70 (q), 128.96 (t, C^4), 124.53 (t, C^A), 114.07 (q), 96.05 (q, –C≡), 92.87 (q, –C≡), 88.00 (q, –C≡), 72.46 (q, –C≡), 36.32 (s, CH_2), and 19.94 (p, CH_3); ^1H NMR (500 MHz, CF_3CO_2D) δ_H=11.706 (1H, dd, J=16.0 and 11.5 Hz, $H^{B'}$), 10.104 (1H, d, J=15.4 Hz, H^A), 7.023 (1H, d, J=15.4 Hz, H^B), 6.65—6.50 (3H, m, H^1, H^2, and H^3), 6.400 (1H, d, J=11.5 Hz, $H^{C'}$), 6.229 (1H, d, J=5.9 Hz, H^4), 6.013 (1H, d, J=16.0 Hz, $H^{A'}$), 5.478 (1H, d, J=13.3 Hz, H^b), 3.136 (1H, d, J=13.3 Hz, H^a), and 1.799 (3H, s, Me) and see Fig. 1; ^{13}C NMR (125.76 MHz, CF_3CO_2D) δ_C=200.03 (q, C=O), 159.50 (t), 150.25 (t), 143.22 (q), 141.38 (t), 139.74 (t), 137.61 (t), 134.61 (t), 131.82 (t), 130.30 (q), 127.88 (t), 122.01 (t), 119.07 (q), 99.99 (q, –C≡), 94.39 (q, –C≡), 93.92 (q, –C≡), 74.52 (q, –C≡), 39.84 (s, CH_2), and 20.99 (p, CH_3).

Found: C, 88.47; H, 5.63%. Calcd for $C_{19}H_{14}O$: C, 88.43; H, 5.46%.

16,18-Bisdehydro-10,15-methano-7*H*-benzo[17]-annulen-7-one (13). The oxidative coupling of the ketone **35** gave compound **13** in 60% yield as orange microcrystals, mp 192—194 °C (decomp), from hexane–benzene; Mass *m/z* 294 (M^+; 66%) and 265 (100); for UV data see Table 2, Figs. 3 and 5; IR 2174 (C≡C), 1655 (C=O), 1583 (C=C), and 976 cm^{-1} ((*E*)-HC=CH); ^1H NMR (500 MHz) δ_H=9.022 (1H, d, J=17.0 Hz, $H^{B'}$), 8.070 (1H, d, J=15.5 Hz, H^A), 7.600 (1H, d, J=7.6 Hz, H^8), 7.347 (1H, td, J=7.6 and 1.3 Hz, H^7), 7.288 (1H, td, J=7.6 and 1.2 Hz, H^6), 7.225 (1H, dd, J=7.6 and 1.2 Hz, H^5), 7.200 (1H, d, J=15.6 Hz, H^B), 6.733 (1H, dd, J=11.1 and 5.8 Hz, H^2), 6.682 (1H, dd, J=11.1 and 5.8 Hz, H^3), 6.567 (1H, d, J=17.0 Hz, $H^{A'}$), 6.543 (1H, d, J=5.8 Hz, H^1), 6.442 (1H, d, J=5.8 Hz, H^4), 4.104 (1H, d, J=12.8 Hz, H^b), and 2.175 (1H, d, J=12.8 Hz, H^a) and see Fig. 1; ^{13}C NMR (125.76 MHz) δ_C=191.42 (q, C=O), 142.60 (t, $C^{B'}$), 141.52 (t, C^B), 140.65 (q), 132.48 (t, C^2), 131.84 (t, C^3), 131.52 (t, C^1), 130.19 (q), 130.16 (t, C^6), 129.93 (t, $C^{A'}$), 129.79 (t, C^7), 128.84 (t, C^4), 128.57 (t, C^5), 125.96 (t, C^8), 123.97 (t, C^A), 123.36 (q), 113.42 (q), 93.79 (q, –C≡), 89.65 (q, –C≡), 85.04 (q, –C≡), 73.00 (q, –C≡), and 36.29 (s, CH_2); ^1H NMR (500 MHz, CF_3CO_2D) δ_H=10.559 (1H, d, J=16.5 Hz, $H^{B'}$), 9.017 (1H, d, J=15.2 Hz, H^A), 7.621 (1H, m, H^8), 7.439 (1H, d, J=15.3 Hz, H^B), 7.40—7.33 (2H, m, H^7 and H^6), 7.173 (1H, m, H^5), 6.807 (1H, m, H^3), 6.776 (1H, d, J=16.5 Hz, $H^{A'}$), 6.77—6.71 (2H, m, H^1 and H^2), 6.423 (1H, d, J=5.9 Hz, H^4), 4.701 (1H, d, J=13.2 Hz, H^b), and 2.626 (1H, d, J=13.2 Hz, H^a) and see Fig. 1; ^{13}C NMR (125.76 MHz, CF_3CO_2D) δ_C=199.59 (q, C=O), 155.28 (t), 151.67 (t), 141.34 (q), 139.29 (t), 137.20 (t), 135.14 (t), 134.22 (t), 132.82 (q), 132.27 (t), 131.33 (t), 130.97 (t), 129.17 (t), 127.80 (q), 127.30 (t), 121.90 (t), 117.86 (q), 95.89 (q, –C≡), 91.53 (q, –C≡), 87.67 (q, –C≡), 75.30 (q, –C≡), and 38.72 (s, CH_2).

Found: C, 90.06; H, 4.75%. Calcd for $C_{22}H_{14}O$: C, 89.77; H, 4.79%.

2,5-Dimethyl-6,8-bisdehydro-10,15-methano-1*H*-[17]annulen-1-one (14). The oxidative coupling of the ketone **37** afforded compound **14** in 35% yield as orange needles, mp 165—166 °C (decomp), from hexane–benzene; Mass *m/z* 272 (M^+; 53%) and 228 (100); for UV data see Table 2, Figs. 3 and 5; IR 2164 (C≡C), 1644 (C=O), 1616 (C=C), and 972 cm^{-1} ((*E*)-HC=CH); ^1H NMR (500 MHz) δ_H=9.174 (1H, d, J=11.6 Hz, $H^{B'}$), 8.516 (1H, d, J=15.5 Hz, H^A), 6.971 (1H, d, J=15.5 Hz, H^B), 6.669 (1H, dq, J=11.5 and 1.6 Hz, $H^{C'}$), 6.608 (1H, dd, J=11.1 and 5.7 Hz, H^2), 6.562 (1H, dd, J=11.1 and 5.7 Hz, H^3), 6.434 (1H, d, J=5.6 Hz, H^1), 6.298 (1H, d, J=5.6 Hz, H^4), 4.409 (1H, d, J=12.8 Hz, H^b), 2.371 (1H, d, J=12.8 Hz, H^a), 1.843 (3H, s, Me^b), and 1.819 (3H, s, Me^a); ^{13}C NMR (125.76 MHz) δ_C=192.79 (q, C=O), 140.27 (t), 138.90 (t), 138.78 (t), 138.21 (q), 132.45 (t), 131.84 (q), 131.70 (t), 131.28 (t), 128.38 (t), 127.17 (q), 124.50 (t), 114.08 (q), 95.69 (q, –C≡), 93.06 (q, –C≡), 86.94 (q, –C≡), 73.04 (q, –C≡), 36.72 (s, CH_2), 20.12 (p, CH_3), and 11.65 (p, CH_3); ^1H NMR (500 MHz, CF_3CO_2D) δ_H=11.132 (1H, d, J=11.6 Hz, $H^{B'}$), 9.827 (1H, d, J=15.4 Hz, H^A), 6.978 (1H, d, J=15.4, H^B), 6.62—6.52 (4H, m, H^1 or H^4, H^2, H^3, and $H^{C'}$), 6.204 (1H, d, J=5.8 Hz, H^4 or H^1), 5.262 (1H, d, J=13.1 Hz, H^b), 2.982 (1H, d, J=13.1 Hz, H^a), 1.842 (3H, s, Me^a), and 1.818 (3H, s, Me^b); ^{13}C NMR (125.76 MHz, CF_3CO_2D) δ_C=152.04 (t), 148.22 (t), 139.87 (t), 138.59 (q), 138.54 (t), 138.03 (q), 136.70

(t), 135.08 (q), 134.34 (t), 130.93 (t), 123.22 (t), 118.32 (q), 99.17 (q, –C≡), 94.46 (q, –C≡), 91.75 (q, –C≡), 74.84 (q, –C≡), 39.50 (s, CH_2), 21.00 (p, CH_3), and 11.93 (p, CH_3). The signal of the carbonyl carbon was not detected, probably due to the extremely long T_1.

Found: C, 88.20; H, 6.09%. Calcd for $C_{20}H_{16}O$: C, 88.20; H, 5.92%.

6-Methyl-16,18-bisdehydro-10,15-methano-7*H*-benzo[17]annulen-7-one (15). The oxidative coupling of the ketone **39** gave compound **15** in 50% yield as orange needles, mp 138—141 °C (decomp), from hexane–CH_2Cl_2; Mass m/z 308 (M^+; 70%) and 265 (100); for UV data see Table 2, Figs. 3 and 5; IR 2177 (C≡C), 1644 (C=O), 1578 (C=C), and 970 cm^{-1} ((*E*)-HC=CH); ^{1}H NMR (500 MHz) δ_H=8.554 (1H, br s, $H^{B'}$), 8.018 (1H, d, J=15.3 Hz, H^A), 7.536 (1H, d, J=7.8 Hz, H^8), 7.366 (1H, td, J=7.4 and 1.8 Hz, H^7), 7.304 (1H, d, J=15.3 Hz, H^B), 7.281 (1H, d, J=7.8 Hz, H^5), 7.245 (1H, dt, J=7.6 and 1.1 Hz, H^6), 6.746 (1H, dd, J=11.0 and 5.7 Hz, H^2), 6.698 (1H, dd, J=11.0 and 5.7 Hz, H^3), 6.553 (1H, d, J=5.7 Hz, H^1), 6.417 (1H, d, J=5.7 Hz, H^4), 4.033 (1H, d, J=12.7 Hz, H^b), 2.104 (1H, d, J=12.7 Hz, H^a), and 2.103 (3H, d, J=1.3 Hz, Me); ^{13}C NMR (125.76 MHz) δ_C=193.49 (q, C=O), 142.51 (t), 141.96 (q), 139.95 (q), 135.80 (t), 132.30 (t), 131.80 (t), 131.11 (t), 129.85 (q), 129.26 (t), 129.20 (t), 128.92 (t), 128.47 (t), 127.95 (t), 123.79 (t), 123.14 (q), 113.26 (q), 93.11 (q, –C≡), 89.36 (q, –C≡), 83.45 (q, –C≡), 74.42 (q, –C≡), 37.29 (s, CH_2), and 13.22 (p, CH_3); ^{1}H NMR (500 MHz, CF_3CO_2D) δ_H=9.230 (1H, br s, $H^{B'}$), 8.436 (1H, d, J=15.3 Hz, H^A), 7.555 (1H, d, J=7.9 Hz, H^8), 7.433 (1H, d, J=15.3 Hz, H^B), 7.372 (1H, t, J=7.6 Hz, H^7), 7.276 (1H, t, J=7.6 Hz, H^6), 7.229 (1H, d, J=7.7 Hz, H^5), 6.82—6.74 (2H, m, H^2 and H^3), 6.662 (1H, d, J=5.2 Hz, H^1), 6.394 (1H, d, J=5.3 Hz, H^4), 4.286 (1H, d, J=12.9 Hz, H^b), 2.319 (1H, d, J=13.0 Hz, H^a), and 2.168 (3H, s, Me); ^{13}C NMR (125.76 MHz, CF_3CO_2D) δ_C=150.01 (t), 144.19 (t), 143.13 (q), 140.61 (q), 136.96 (t), 135.87 (t), 133.97 (t), 132.03 (t), 131.86 (q), 131.65 (t), 131.45 (t), 131.16 (t), 130.18 (t), 126.21 (q), 124.14 (t), 116.79 (q), 95.01 (q, –C≡), 91.27 (q, –C≡), 85.34 (q, –C≡), 76.52 (q, –C≡), 39.16 (s, CH_2), and 14.17 (p, CH_3). The signal of the carbonyl carbon was not detected.

Found: C, 89.62; H, 5.08%. Calcd for $C_{23}H_{16}O$: C, 89.58; H, 5.23%.

2,14-Dimethyl-10,12-bisdehydro-4,9-methano-1*H*-[17]annulen-1-one (16). The oxidative coupling of the ketone **45** afforded a liquid in 27% yield, which was purified by PLC with benzene. The fast moving, third band afforded pure **16** as an unstable yellow liquid, Mass m/z 272.1174; mol wt 272.1199 for $C_{20}H_{16}O$; for UV data see Table 2; IR (neat) 2165 (C≡C), 1646 (C=O), 1602 (C=C), and 988 cm^{-1} ((*E*)-HC=CH); ^{1}H NMR (400 MHz) δ_H=7.430 (1H, dd, J=16.1 and 10.5 Hz, $H^{B'}$), 6.811 (1H, dd, J=11.2 and 5.8 Hz, H^2 or H^3), 6.668 (1H, dd, J=11.2 and 5.9 Hz, H^3 or H^2), 6.61 (1H, br d, J=11 Hz, $H^{C'}$), 6.595 (1H, s, H^B), 6.466 (1H, d, J=16.1 Hz, $H^{A'}$), 6.407 (2H, d, J=5.6 Hz, H^1 and H^4), 3.518 (1H, d, J=11.7 Hz, H^b), 1.916 (3H, d, J=1.5 Hz, Me^a), 1.906 (3H, d, J=1.5 Hz, Me^b), and 1.873 (1H, d, J=11.7 Hz, H^a); ^{1}H NMR (400 MHz, CF_3CO_2D) δ_H=7.867 (1H, dd, J=15.6 and 11.2 Hz, $H^{B'}$), 6.902 (1H, dd, J=11.2 and 6.1 Hz, H^2), 6.826 (1H, d, J=11.2 Hz, $H^{C'}$), 6.782 (1H, dd, J=11.2 and 5.9 Hz, H^3), 6.689 (1H, s, H^B), 6.539 (1H, d, J=15.8 Hz, $H^{A'}$), 6.497 (1H, d, J=5.6 Hz, H^4), 6.433 (1H, d, J=5.9 Hz, H^1), 3.415 (1H, d, J=12.0 Hz, H^b), 2.018 (3H, s, Me^a), 1.980 (1H, d, J=12.2 Hz, H^a), and 1.947 (3H, d, J=1.2 Hz, Me^b).

8-Methyl-16,18-bisdehydro-10,15-methano-7*H*-benzo[17]annulen-7-one (17). The oxidative coupling of the ketone **47** gave compound **17** in 34% yield as orange needles, mp 119—123 °C (decomp), from hexane–benzene; Mass m/z 308 (M^+; 23%) and 265 (100); for UV data see Table 2; IR 2179 (C≡C), 1653 (C=O), 1602 (C=C), and 977 cm^{-1} ((*E*)-HC=CH); ^{1}H NMR (400 MHz) δ_H=7.754 (1H, d, J=16.4 Hz, $H^{A'}$), 7.602 (1H, d, J=16.4 Hz, $H^{B'}$), 7.512 (1H, d, J=7.9 Hz, H^5), 7.40—7.26 (3H, m, H^6, H^7, and H^8), 7.097 (1H, s, H^B), 6.890 (1H, dd, J=10.8 and 5.9 Hz, H^2), 6.746 (1H, dd, J=11.0 and 5.8 Hz, H^3), 6.578 (1H, d, J=5.9 Hz, H^1), 6.446 (1H, d, J=5.6 Hz, H^4), 3.653 (1H, d, J=11.7 Hz, H^b), 2.089 (3H, s, Me), and 1.746 (1H, d, J=11.4 Hz, H^a); ^{13}C NMR (100.40 MHz) δ_C=195.93 (q, C=O), 141.57 (t, $C^{B'}$), 140.05 (q), 139.33 (q), 136.87 (t, C^B), 132.61 (t, C^2), 130.98 (t, C^6, C^7, or C^8), 130.70 (t, C^5), 129.99 (t, C^3), 129.55 (t, C^7, C^8, or C^6), 129.34 (t, C^8, C^6, or C^7), 126.30 (t, $C^{A'}$), 126.16 (t, C^4), 125.53 (t, C^1), 124.99 (q), 120.74 (q), 108.96 (q), 92.86 (q, –C≡), 89.38 (q, –C≡), 80.95 (q, –C≡), 76.84 (q, –C≡), 42.52 (s, CH_2), and 14.75 (p, CH_3); ^{1}H NMR (400 MHz, CF_3CO_2D) δ_H=8.018 (1H, d, J=16.6 Hz, $H^{A'}$), 7.754 (1H, d, J=16.1 Hz, $H^{B'}$), 7.640 (1H, d, J=6.8 Hz, H^5), 7.45—7.30 (3H, m, H^6, H^7, and H^8), 7.272 (1H, s, H^B), 6.932 (1H, dd, J=11.2 and 5.8 Hz, H^2), 6.824 (1H, dd, J=10.7 and 5.9 Hz, H^3), 6.592 (1H, d, J=5.9 Hz, H^1), 6.471 (1H, d, J=5.4 Hz, H^4), 3.703 (1H, d, J=11.7 Hz, H^b), 2.147 (3H, s, Me), and 1.896 (1H, d, J=11.7 Hz, H^a).

Found: C, 89.83; H, 5.45%. Calcd for $C_{23}H_{16}O$: C, 89.58; H, 5.23%.

14-Methyl-10,12-bisdehydro-4,9-methano-1*H*-[19]-annulen-1-one (18). The oxidative coupling of the ketone **50** gave compound **18** in 8% yield as orange needles, mp 123—126 °C (decomp), from hexane–CH_2Cl_2; Mass m/z 284 (M^+; 20%) and 239 (100); for UV data see Table 2 and Fig. 4; IR 2173 (C≡C), 1644 (C=O), 1600 (C=C), 980 ((*E*)-HC=CH), and 700 cm^{-1} ((*Z*)-HC=CH); ^{1}H NMR (500 MHz) δ_H=7.908 (1H, dd, J=15.0 and 0.5 Hz, H^B), 7.08—6.99 (2H, m, H^2 and H^3), 6.854 (1H, d, J=5.7 Hz, H^1), 6.823 (1H, d, J=5.7 Hz, H^4), 6.677 (1H, t, J=12.2 Hz, $H^{B'}$), 6.53—6.47 (2H, m, $H^{D'}$ and $H^{E'}$), 6.331 (1H, m, $H^{C'}$), 6.199 (1H, d, J=12.6 Hz, $H^{A'}$), 5.861 (1H, d, J=15.0 Hz, H^A), 2.812 (1H, d, J=12.4 Hz, H^b), 2.100 (3H, s, Me), and 1.189 (1H, d, J=12.4 Hz, H^a); ^{13}C NMR (125.76 MHz) δ_C=191.94 (q, C=O), 145.74 (t), 137.32 (t), 134.81 (t), 134.42 (t), 132.82 (t), 132.07 (t), 131.87 (t), 129.46 (t), 129.42 (t), 126.00 (t), 125.76 (t), 125.00 (q), 119.72 (q), 111.05 (q), 90.01 (q, –C≡), 86.10 (q, –C≡), 82.86 (q, –C≡), 75.00 (q, –C≡), 34.19 (s, CH_2), and 23.58 (p, CH_3); ^{1}H NMR (CF_3CO_2D) δ_H=9.858 (1H, d, J=14.2 Hz, H^B), 8.674 (1H, t, J=12.5 Hz, $H^{B'}$), 8.349 (1H, dd, J=14.5 and 8.5 Hz, $H^{D'}$), 8.172 (1H, dd, J=10.8 and 6.9 Hz, H^3), 8.136 (1H, d, J=7.1 Hz, H^1), 8.046 (1H, dd, J=10.9 and 6.9 Hz, H^2), 7.980 (1H, d, J=6.9 Hz, H^4), 7.815 (1H, d, J=8.2 Hz, $H^{E'}$), 7.654 (1H, d, J=11.9 Hz, $H^{A'}$), 2.850 (3H, s, Me), 2.563 (1H, t, J=13.7 Hz, $H^{C'}$), 2.040 (1H, d, J=14.2 Hz, H^A), 0.335 (1H, d, J=12.8 Hz, H^b), and –0.008 (1H, d, J=12.8 Hz, H^a) and see Fig. 2. Reliable ^{13}C data could not be obtained because of rapid decomposition of the sample in CF_3CO_2D.

Found: C, 88.80; H, 5.88%. Calcd for $C_{21}H_{16}O$: C, 88.70; H, 5.67%.

16-Methyl-12,14-bisdehydro-6,11-methano-1*H*-[19]annulen-1-one (19). The oxidative coupling of the ketone **52** gave compound **19** in 61% yield as orange needles, mp 152—161 °C (decomp), from hexane–CH_2Cl_2; Mass *m/z* 284 (M^+; 22%) and 239 (100); for UV data see Table 2 and Fig. 4; IR 2159 (C≡C), 1642 (C=O), 1596 (C=C), and 989 cm^{-1} ((*E*)-HC=CH); ^1H NMR (500 MHz) δ_H=7.185 (1H, dd, *J*=16.4 and 11.6 Hz, $H^{B'}$), 7.009 (1H, dd, *J*=15.3 and 10.9 Hz, H^B), 6.907 (1H, m, H^3), 6.807 (1H, d, *J*=11.6 Hz, $H^{C'}$), 6.76—6.71 (2H, m, H^1 and H^2), 6.653 (1H, d, *J*=16.1 Hz, H^D), 6.467 (1H, d, *J*=5.1 Hz, H^4), 6.457 (1H, d, *J*=15.3 Hz, H^A), 6.422 (1H, dd, *J*=15.5 and 10.8 Hz, H^C), 6.228 (1H, d, *J*=16.4 Hz, $H^{A'}$), 3.404 (1H, d, *J*=12.5 Hz, H^b), 2.059 (3H, s, Me), and 1.430 (1H, d, *J*=12.6 Hz, H^a); ^{13}C NMR (125.76 MHz) δ_C=193.96 (q, C=O), 145.17 (t), 137.42 (t), 136.38 (t), 136.20 (t), 135.04 (t), 132.78 (t), 132.21 (t), 132.07 (t), 129.92 (t), 129.85 (q), 129.62 (q), 129.38 (t), 127.29 (t), 109.74 (q), 89.33 (q, –C≡), 84.86 (q, –C≡), 81.32 (q, –C≡), 71.04 (q, –C≡), 32.34 (s, CH_2), and 21.64 (p, CH_3); ^1H NMR (500 MHz, CF_3CO_2D) δ_H=8.202 (1H, dd, *J*=14.5 and 11.3 Hz, H^B), 7.686 (1H, d, *J*=12.2 Hz, $H^{C'}$), 7.636 (1H, d, *J*=15.2 Hz, $H^{A'}$), 7.454 (1H, dd, *J*=11.0 and 6.5 Hz, H^3), 7.390 (1H, d, *J*=6.5 Hz, H^1), 7.308 (1H, dd, *J*=11.0 and 6.5 Hz, H^2), 7.235 (1H, d, *J*=15.5 Hz, H^D), 7.134 (1H, d, *J*=6.6 Hz, H^4), 5.102 (1H, dd, *J*=15.4 and 12.2 Hz, $H^{B'}$), 4.807 (1H, dd, *J*=15.2 and 11.4 Hz, H^C), 4.698 (1H, d, *J*=14.6 Hz, H^A), 2.588 (3H, s, Me), 2.096 (1H, d, *J*=13.0 Hz, H^b), and 0.842 (1H, d, *J*=13.2 Hz, H^a) and see Fig. 2.

Found: C, 88.99; H, 5.80%. Calcd for $C_{21}H_{16}O$: C, 88.70; H, 5.67%.

16-Methyl-12,14-bisdehydro-6,11-methano-1*H*-[21]annulen-1-one (20). The oxidative coupling of the ketone **54** gave compound **20** in 14% yield as orange needles, mp 133—139 °C (decomp), from hexane–CH_2Cl_2; Mass *m/z* 310 (M^+; 18%) and 69 (100); for UV data see Table 2 and Fig. 4; IR 2176 (C≡CH), 1648, 1620 (C=O), 1591 (C=C), and 997 cm^{-1} ((*E*)-HC=CH); ^1H NMR (500 MHz) δ_H=7.643 (1H, dd, *J*=16.1 and 11.0 Hz, $H^{B'}$), 7.536 (1H, dd, *J*=14.9 and 11.4 Hz, $H^{D'}$), 7.206 (1H, dd, *J*=16.1 and 10.4 Hz, H^B), 6.741 (1H, dd, *J*=10.8 and 6.3 Hz, H^2), 6.703 (1H, d, *J*=15.3 Hz, H^D), 6.699 (1H, d, *J*=6.0 Hz, H^1), 6.642 (1H, dd, *J*=10.8 and 6.0 Hz, H^3), 6.628 (1H, dd, *J*=15.4 and 10.4 Hz, H^C), 6.517 (1H, d, *J*=11.3 Hz, $H^{E'}$), 6.493 (1H, d, *J*=6.2 Hz, H^4), 6.306 (1H, dd, *J*=14.9 and 11.1 Hz, $H^{C'}$), 6.127 (1H, d, *J*=16.0 Hz, H^A), 6.016 (1H, d, *J*=16.1 Hz, $H^{A'}$), 3.621 (1H, d, *J*=12.2 Hz, H^b), 2.012 (1H, d, *J*=12.2 Hz, H^a), and 1.890 (3H, s, Me); ^{13}C NMR (125.76 MHz) δ_C=196.48 (q, C=O), 151.44 (t), 144.23 (t), 142.65 (t), 138.64 (t), 138.57 (t), 132.68 (t), 130.90 (t), 130.55 (t), 130.22 (t), 128.99 (t), 128.76 (t), 128.29 (t), 127.87 (q), 125.62 (q), 121.80 (t), 110.54 (q), 88.75 (q, –C≡), 83.92 (q, –C≡), 83.20 (q, –C≡), 71.71 (q, –C≡), 40.28 (s, CH_2), and 21.06 (p, CH_3); The ^1H NMR spectrum of compound **20** in CF_3CO_2D showed that the resulting species consists of at least three isomers. The major isomer **20′**: ^1H NMR (500 MHz, CF_3CO_2D) δ_H=12.509 (1H, dd, *J*=15.2 and 12.0 Hz, $H^{C'}$), 11.243 (1H, d, *J*=14.0 Hz, H^A), 11.23 (1H, dd, H^C), 7.228 (1H, dd, *J*=13.9 and 12.0 Hz, H^B), 6.520 (1H, t, *J*=11.9 Hz, $H^{B'}$), 6.186 (1H, dd, *J*=15.3 and 7.3 Hz, $H^{D'}$), 6.09—5.95 (5H, m, H^1, H^2, H^3, H^4, and H^D), 5.767 (1H, d, *J*=7.5 Hz, $H^{E'}$), 5.641 (2H, br s, CH_2), 5.509 (1H, d, *J*=11.3 Hz, $H^{A'}$), and 1.648 (3H, s, Me).

Found: C, 89.18; H, 5.88%. Calcd for $C_{23}H_{18}O$: C, 89.00; H, 5.85%.

We thank Professor Shigeyasu Kuroda, Toyama University, for suggesting suitable reaction conditions for preparing compound **24**. Financial support by a Grant-in-Aid for Scientific Research No. 05453029 from the Ministry of Education, Science and Culture, is gratefully acknowledged.

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