Syntheses and Properties of Trimethyltetradehydro[15]annulenones and the Benzannelated Derivatives

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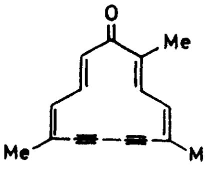
Syntheses of 5,10,15- (8) and 2,5,10-trimethyl-6,7,8,9-tetradehydrocyclopentadecenone (12), and 8,13- (9) and 6,13-dimethyl-14,15,16,17-tetradehydrobenzocyclopentadecen-7-one (13), 8,13- (10) and 10,13-dimethyl-14,15,16,17-tetradehydrobenzocyclopentadecen-9-one (14), and 8-methyl- (11) and 6-methyl-16,17,18,19-tetradehydrodibenzo[*a*,*g*]cyclopentadecen-7-one (15) are described. The influence of α-methyl substitution and benzannelation upon the structure and tropicity of the tetradehydro[15]annulenone ring system is discussed in view of the ^{1}H n.m.r. and u.v. spectra of these annulenones, as well as those of the α-methyl unsubstituted annulenones (4)—(7).

It has been found that the methyl substituent adjacent to the ketone group of the paratropic 2,5,10-trimethyl-6,7,8,9-tetradehydro[13]annulenone (1) causes a change of conformation due to a rotation of the opposite double bond so that the molecule exists essentially in the conformation (1a) at —60 °C.[1] In previous papers, we have reported the preparation of the benzannelated derivatives of (1), and showed that both α-methyl substitution and benzannelation exert a considerable influence on the development of the paratropicity in tetradehydro[13]-annulenones of type (1).[2] On the other hand, methyl substitution adjacent to the carbonyl group or benzannelation of (2) exert no significant influence upon the skeleton of tetradehydro[17]annulenone ring system,[3] in contrast to the [13]annulenone system.



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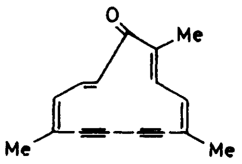

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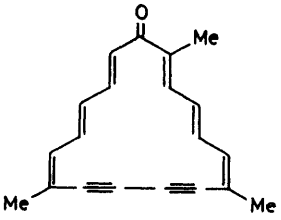

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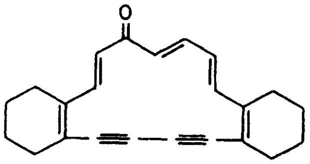

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The bis(cyclohexene)-annelated tetradehydro[15]annulenone (3), as well as the benzannelated analogues, have been synthesized by Weavers *et al.*, who discussed the effect of benzannelation on the ring current of the tetradehydro[15]annulenone system.[4a]

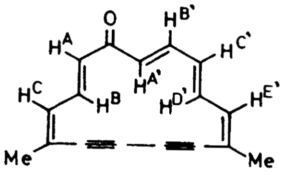
However, in view of the difference observed between the methylated tetradehydro-[13]- and -[17]-annulenone systems, we were interested in examining the properties of the title compounds, *i.e.* 5,10,15-trimethyl- (8), 2,5,10-trimethyl-6,7,8,9-tetradehydro[15]annulenone (12), and their benzannelated derivatives (9)—(11) and (13)—(15),[5] and with examining further the α-methyl unsubstituted annulenones (4)—(7), prepared previously.[6,7]

RESULTS AND DISCUSSION

The annulenone (4) was obtained according to the previously described method [7] except that (32), the precursor of (4), was prepared using ethanolic sodium ethoxide. The annulenones (5) and (6) were prepared by a modification of the reported method [6] using anhydrous copper(II) acetate instead of the monohydrate [8] in the oxidative coupling reaction. The yields were improved with these modifications and the annulenones (4)—(6) are relatively readily available substances, which made it desirable to utilize these compounds for the syntheses of fulvalene derivatives.[9] The yield of the annulenone (7) could not be improved by this modification, and thus (7) was prepared according to the reported method.[4]

The successful syntheses of the annulenones (4)—(7), together with a prediction from Dreiding molecular models, led us to expect that the annulenones possessing an α-methyl group inside the ring might form from the corresponding acyclic ketones [*e.g.* (8a) from (18)] by the same approach. Therefore, our original approach was to investigate the effect of different alkyl groups inside the ring on the molecular skeleton of tetradehydro-[15]annulenone ring system; thus we aimed at the preparation of α-methyl-α'-alkyl ketones corresponding to the ketone (16). However, the reaction of (2*E*,4*Z*)-methylhepta-2,4-dien-6-ynal (25) with methyl propyl ketone, isobutyl methyl ketone, and methyl neopentyl ketone was unsuccessful; thus it was impossible to obtain the annulenones possessing bulky α-alkyl groups, such as ethyl, isopropyl, and t-butyl.

The syntheses of the annulenones (8)—(15) were carried out by the same procedure as reported.[1-3] For (8)—(11) condensation of the ketone (16) [3] [prepared by the reaction of the dienyne aldehyde (25) [10] and butan-2-



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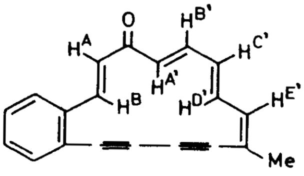

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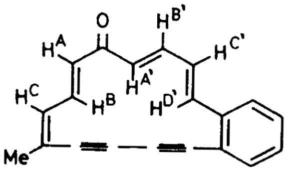

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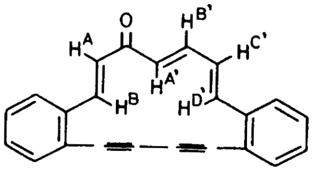

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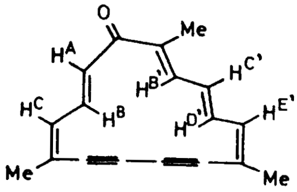

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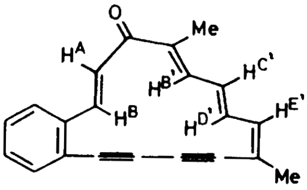

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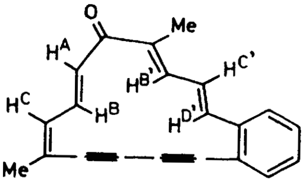

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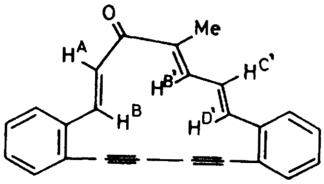

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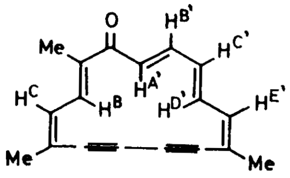

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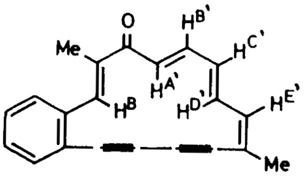

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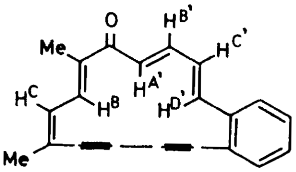

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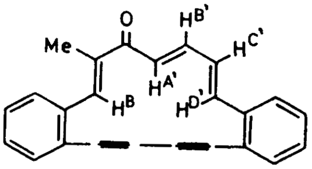

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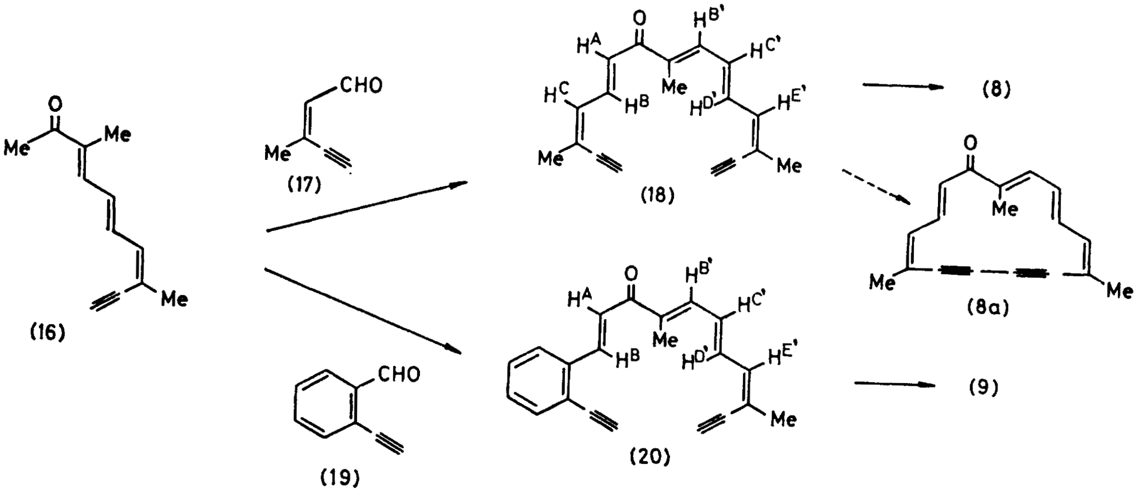


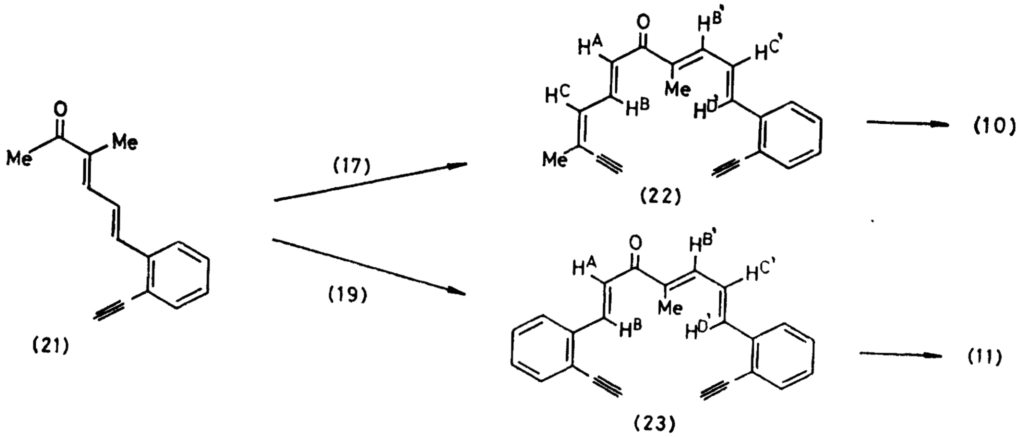
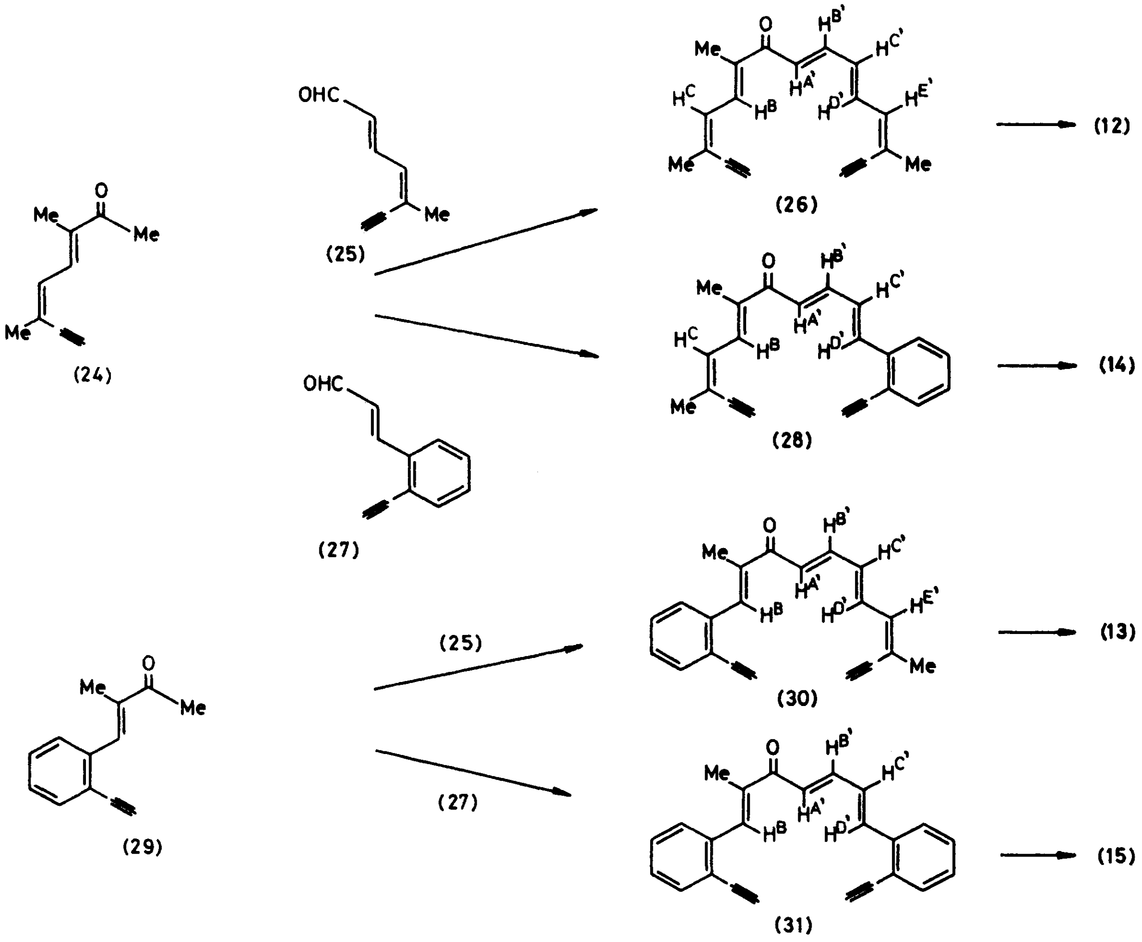


TABLE 1

Electronic absorption maxima of tetradehydro[15]annulenones in ether; $\lambda_{max.}$/nm ($\varepsilon_{max.}$)

(4)	(5)	(6)	(7)	(8)	(9)
215 (19 300)	223 (18 700)	228 (25 200)	218sh (39 400)	213 (21 300)	226 (33 400)
			224 (39 800)		
247sh (13 000)				247sh (12 500)	
258 (14 300)		256 (18 700)		257sh (14 200)	259sh (23 200)
	262sh (13 200)				
	278sh (18 200)	274sh (21 600)	287sh (38 300)		279sh (33 800)
301 (33 200)	299 (22 100)	302 (28 900)	300 (41 600)	298 (40 500)	293 (37 300)
382 (5 700)	379 (8 130)	372sh (8 210)	350sh (11 900)	366 (6 530)	366 (10 200)
(10)	(11)	(12)	(13)	(14)	(15)
221sh (31 900)	219sh (41 000)	211 (22 900)	220 (39 500)	223sh (40 900)	218sh (45 600)
228 (36 400)	229 (47 600)	232sh (13 400)		227 (42 600)	225 (47 100)
		246 (13 800)	245 (22 800)	252 (28 300)	
252sh (25 000)		258 (14 800)	251 (23 000)	262 (28 500)	
			258 (23 000)		
276sh (32 700)	287sh (43 400)		281sh (35 100)		275sh (31 400)
294 (37 500)	296 (44 400)	304 (42 600)	302 (47 200)	309 (52 700)	306 (50 900)
355 (11 300)		310sh (41 200)			
381sh (9 150)	352sh (13 300)	384 (7 880)	376 (11 400)	370sh (15 400)	353sh (15 500)
				390sh (12 200)	

one], with (*Z*)-3-methylpent-2-en-4-ynal (17)[11] in the presence of ethanolic sodium ethoxide in ether gave the acyclic ketone (18) (51%). Oxidative coupling of (18) with anhydrous copper(II) acetate in pyridine–ether at 50 °C[8] gave the annulenone (8) (44%). Similarly, condensation of *o*-ethynylbenzaldehyde (19)[12] with (16) gave the ketone (20) (69%) which was oxidized to afford the benzannulenone (9) (76%). Reaction of (21)[3] with (17), under the conditions described for that between (16) and (17), afforded the ketone (22) (36%). Oxidation of (22) as before afforded another benzannulenone (10) (48%). Similarly, condensation of (19) with (21) gave



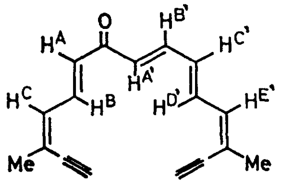
the acyclic ketone (23) (49%) which led to the dibenzannulenone (11) (68%). The annulenones (8)—(11) thus obtained proved to have the configuration with the α-methyl group outside the ring, by an analysis of their ^{1}H-n.m.r. spectra.

Table 2

Electronic absorption maxima of tetradehydro[15]annulenones in trifluoroactic acid; $\lambda_{max.}$/nm (relative extinction coefficients)

(4)	(5)	(6)	(7)	(8)	(9)
	272sh (0.51)	271 (0.26)			
292 (0.08)			287sh (0.90)		
			312 (1.00)		
	332sh (0.69)	346 (1.00)	337 (0.99)		322sh (0.80)
352sh (0.68)				350 (1.00)	355 (1.00)
367 (1.00)	367 (1.00)	368sh (0.89)	372sh (0.71)	366sh (0.72)	
	468sh (0.24)				488sh (0.30)
496sh (0.15)	498 (0.31)			502 (0.35)	
513 (0.19)		507sh (0.51)			512sh (0.35)
		539 (0.63)	526 (0.54)	536 (0.35)	
555 (0.34)	559sh (0.37)				555 (0.42)
	599 (0.49)		570sh (0.43)		
(10)	(11)	(12)	(13)	(14)	(15)
	283sh (0.84)			274 (0.49)	275sh (0.75)
		298sh (0.08)			289sh (0.83)
	305 (1.00)				315 (1.00)
332 (1.00)	320sh (0.97)		335 (1.00)		
348sh (0.93)	356sh (0.64)	356sh (0.72)	365 (0.99)	353 (1.00)	
		370 (1.00)	376sh (0.92)	375 (0.95)	370sh (0.54)
495 (0.45)	477 (0.37)	470sh (0.11)	471sh (0.24)		
		500sh (0.18)	506 (0.33)		
		524 (0.23)		516sh (0.47)	532 (0.32)
		562 (0.29)	545sh (0.26)		570sh (0.25)
			608 (0.45)	554 (0.62)	

The annulenones (12)—(15) were also easily synthesised. The aldol condensation of the ketone (24)[1] with the dienyne aldehyde (25) gave the acyclic ketone (26) (36%). Oxidative coupling of (26) with anhydrous copper(II) acetate in pyridine and ether at 50 °C gave the annulenone (12) (48%). Condensation of (24) with *o*-ethynylcinnamaldehyde (27)[13] gave the acyclic ketone (28) (53%). Oxidation of (28) as before gave the benzannulenone (14) (58%). Condensation of (29)[2] with (25) gave the ketone (30) (60%) which was oxidized to yield another benzannulenone (13) (43%). Condensation of (29) with (27) gave the ketone (31) (70%) which led to (15) (64%).



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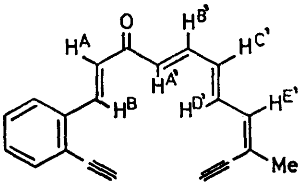

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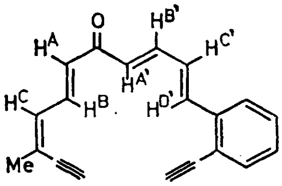

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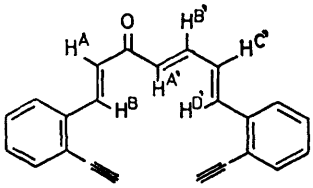

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The structures of these new compounds were established from spectral properties and elemental analyses.

Treatment of the annulenones (8)—(15) with trifluoroacetic acid or deuteriotrifluoroacetic acid gave the corresponding protonated or deuteriated carbonyl species (8′)—(15′): (8′) red, (9′) red, (10′) red, (11′) red brown, (12′) red, (13′) dark green, (14′) red purple, and (15′) purple. Reaction of (8′)—(15′) with aqueous sodium hydrogencarbonate resulted in regeneration of (8)—(15), respectively.

The electronic spectra of the annulenones (4)—(15) in ether are given in Table 1. The main maxima of these tetradehydro[15]annulenones exhibit bathochromic shifts compared to those of the corresponding tetradehydro[13]annulenones.[1,2] However, the difference between the [15]annulenones and the [17]annulenones is small.[3] This is considered to be due to the occurrence of the same sort of alternation between the main maxima of ($4n$ − 2) and $4n$ systems, as has been observed for the annulenes and dehydroannulenes.[7,14] As is also seen from Table 1, the longest wavelength band of the annulenones (12)—(15) shifts to longer wavelength along the series (12) > (13) ≈ (14) > (15), *i.e.* with increasing number of fused benzene rings on the macrocyclic system, demonstrating the degree of extended conjugation of the π-electron system in the tetradehydro[15]annulenone ring, in accord with the results obtained from examination of ^{1}H n.m.r. spectra (see below). A similar observation is made for the annulenones (4)—(7) and (8)—(11) [(4) > (5) ≈ (6) > (7); (8) > (9) ≈ (10) > (11); see ref. 6].

The electronic spectra of the annulenones (4)—(15) in trifluoroacetic acid are given in Table 2. The main maxima of these protonated species shift to longer wavelengths (by 9—70 nm), and it is noted that much larger bathochromic shifts of the main maxima, caused by protonation, are observed in the cases of the alkylated annulenones (4), (8), and (12) (50—70 nm) than in those of the corresponding tetradehydro-[13]- and -[17]-annulenones (5—30 nm).[1-3]

TABLE 3

^{1}H-N.m.r. parameters of compounds (4)—(15), (18), (20), (22), (23), (26), (28), (30)—(35) (in $CDCl_3$) and (4′)—(15′) (in CF_3CO_2D) at 90 MHz, determined at 35 °C (τ-values)

	H^A	$H^{A'}$	H^B	$H^{B'}$	H^C	$H^{C'}$	$H^{D'}$	$H^{E'}$	Ar-H	Me
(32)	3.40—	—3.72	2.27	2.60	3.40—	—3.72	2.87	3.40—3.72		7.93, 7.97
(4)	3.35	4.37	4.17	2.44	2.75	3.19	4.53	2.75		7.76, 7.82
(4′)	1.31	10.10	9.92	0.29	0.89	1.28	10.15	0.89		6.73, 6.82
Δ(4)—(32)			+1.90	−0.16			+1.66			−0.11 to −0.21
Δ(4′) − (32)			+7.65	−2.31			+7.28			−1.11 to −1.24
(33)	2.30—	—3.80	1.97	2.30—					—3.80	8.05
(5)	2.26—								—3.54	7.90
(5′)	1.92	5.55	4.75	1.35		2.55	5.43	2.17	1.98—2.05 1.96—2.08 1.32—1.47	7.47
(34)	2.14—								—3.61	7.95
(6)	2.36—								—3.64	7.87
(6′)	2.60	4.91	4.80	1.90—		—2.35	4.87		2.12—2.23 1.90—2.35 1.58—1.70	7.40
(35)[a]	1.90—						—3.40		1.90—3.40	
(7)[a]	2.0—						—3.3		2.3—3.3	
(7′)[a]	2.1—						—3.2		2.1—3.2	
(18)	3.13		2.25	2.82	3.50	2.95	3.36	3.52		7.97
(8)	3.33		4.38	4.53	2.73	2.87	4.61	2.91		7.79, 7.90, 7.95
(8′)	1.60		8.52	8.05	1.30	1.25	8.95	1.33		6.89, 7.07, 7.12
Δ(8) − (18)	+0.20		+2.13	+1.71	−0.77	−0.08	+1.25	−0.61		−0.02 to −0.18
Δ(8′) − (18)	−1.53		+6.27	+5.23	−2.20	−1.70	+5.59	−2.19		−0.85 to −1.08
(20)	2.23—2.78		1.90	2.23—2.78		2.92	3.35	3.55	2.23—2.78	7.97, 8.00
(9)	2.97		3.20	3.58		3.05	3.72	2.90	2.07—2.20 2.30—2.65	7.93, 7.98
(9′)[b]	1.60—4.73		1.60—						—4.73	7.70, 7.80
(22)	3.10		2.06—	—2.80	3.47	2.06—	—2.80		2.06—2.80	7.90, 7.95
(10)	2.3—3.8		2.3—				—3.8		2.3—3.8	7.90, 7.95
(10′)	2.68		4.65	4.55	2.45	1.8—2.4	4.43		1.8—2.4	7.52, 7.60
(23)	2.17—2.83		1.82	2.17—			—2.83		2.13—2.83	7.83
(11)	2.13—3.32		2.13—				—3.32		2.13—3.32	7.92
(11′)	2.2—3.4		2.2—				—3.4		2.2—3.4	7.78
(26)		3.13	2.44	2.57	3.25	3.52	2.87	3.56		7.89, 7.98
(12)		4.50	4.48	2.37	2.57	3.15	4.71	2.75		7.71, 7.79
(12′)		10.57	10.60	0.17	0.60	1.20	10.69	0.80		6.68, 6.75, 6.80
Δ(12) − (26)		+1.37	+2.04	−0.20	−0.68	−0.37	+1.84	−0.81		−0.10 to −0.27
Δ(12′) − (26)		+7.44	+8.16	−2.40	−2.65	−2.32	+7.82	−2.76		−1.09 to −1.30
(30)		3.12	2.22	2.3—2.7		2.85	3.52	3.57	2.3—2.7	7.93, 7.99
(13)		2.00—		—3.67		2.00—			—3.67	7.68, 7.94
(13′)		5.10	4.57	1.8—2.4		3.15	4.90	2.68	1.8—2.4	7.54, 7.77
(28)		2.27—		—3.13	3.27	2.27—	—3.13		2.27—3.13	7.90, 7.98
(14)		3.42	3.23	2.97	2.82	2.37—2.73	3.30		2.37—2.73	7.85, 7.93
(14′)		4.93	4.75	2.43	1.7—2.3	1.82	4.83		1.7—2.3	7.48, 7.60
(31)		3.01	2.17	2.97		2.1—	—2.7		2.1—2.7	7.88
(15)		2.10—	—2.75	3.20		2.10—2.75	2.95		2.10—2.75	7.73
(15′)		3.30	3.01	3.20		2.1—2.8	2.95		2.1—2.8	7.72

[a] See ref. 5. [b] In the spectrum of (9′), the signals due to olefinic protons show a rather puzzling pattern and the analysis is not complete.

The n.m.r. spectra of the annulenones (4)—(15) are listed in Table 3, together with those of the corresponding acyclic ketones (32)—(35), (18), (20), (22), (23), (26), (28), (30), and (31). Data for the deuteriated species (4′)—

(15') are also given in Table 3. Individual assignments, some of which are tentative, were made on the basis of multiplicities, coupling constants (see Experimental section), and comparison with the data of closely related compounds.[4a]

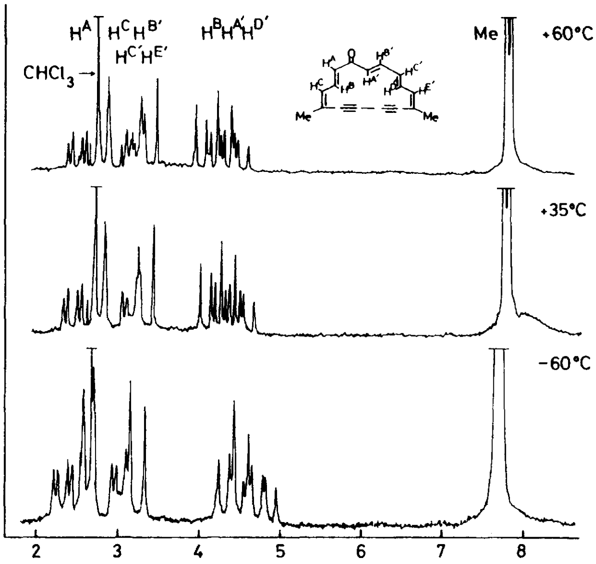

FIGURE 1 90-MHz Fourier-transform ^{1}H n.m.r. spectra of the [15]annulenone (4) in CDCl$_3$

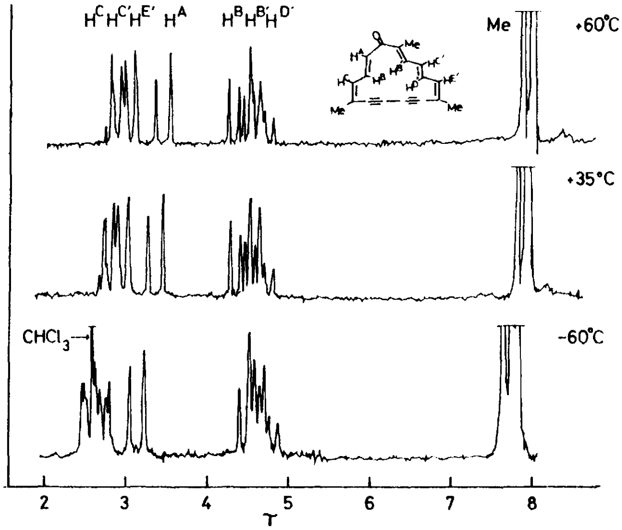

FIGURE 2 90-MHz ^{1}H N.m.r. spectra of the [15]annulenone (8) in CDCl$_3$

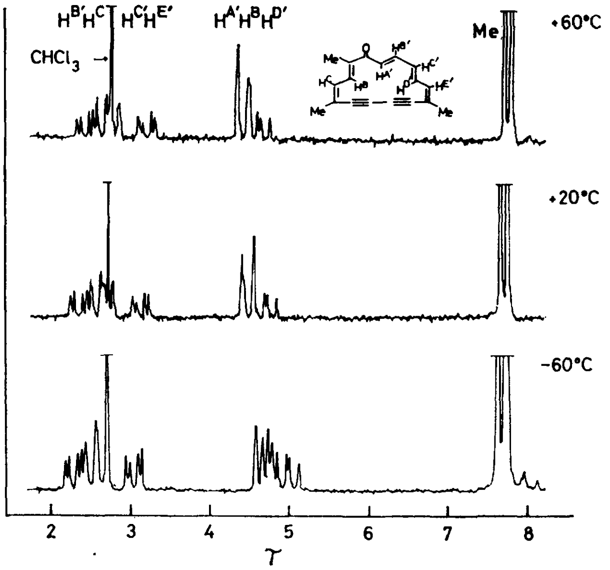

FIGURE 3 100-MHz Fourier-transform ^{1}H n.m.r. spectra of the [15]annulenone (12) in CDCl$_3$

From Table 3, if we judge the tropicity of these annulenones from the differences in chemical shifts between the various resonances for the cyclic ketone (annulenone) and the corresponding acyclic model (upfield shift for the inner protons and downfield for the outer) (Table 3), the annulenones (4), (8), and (12) are seen to be diatropic, while (5)—(7), (9)—(11), and (13)—(15) are atropic. This readily seen from Figures 1—3 (centre portion of the spectra) and 4, which show the ^{1}H n.m.r. spectra of (4), (8), (12), and (13)—(15) at room temperature, respectively. The spectra of (5)—(7) and (9)—(11) are not illustrated since these are similar to those of (13)—(15) (see Table 3). In the spectra of (13)—(15), compared with those of (4), (8), and (12), the high- and low-field shifts of the resonances of the inner and outer protons, respectively, are not observed, although (13)—(15) have rather rigid molecular skeletons compared with (5)—(7) and (9)—(11) (see below). On

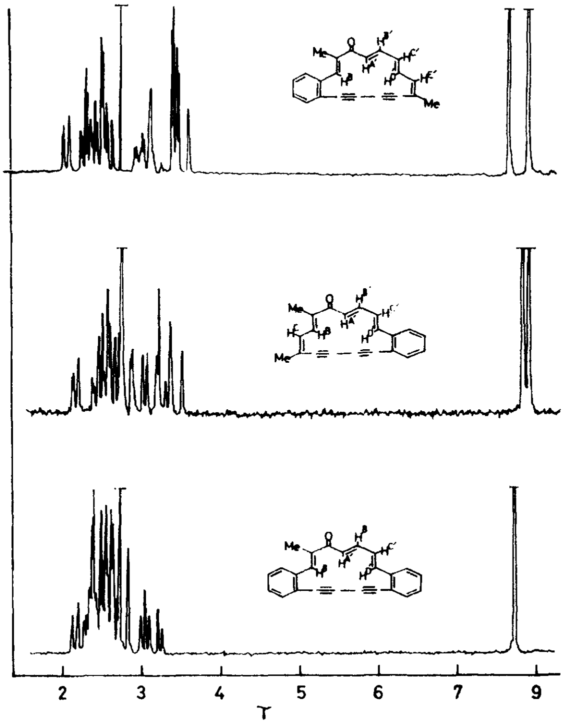

FIGURE 4 100-MHz Fourier-transform ^{1}H n.m.r. spectra of the [15]annulenones (13), (14), and (15) in CDCl$_3$ at 20 °C the other hand, the deuteriated species, (4′), (8′), and (12′) are strongly diatropic, (5′), (6′), (9′), (10′), (13′), and (14′) are diatropic, and (7′), (11′), and (15′) are atropic (Table 3). Thus, the diatropicity of both the annulenones and the deuteriated species decreases in the sequence (4) ≈ (8) ≈ (12), [(4′) ≈ (8′) ≈ (12′)] > (5) ≈ (6) ≈ (9) ≈ (10) ≈ (13) ≈ (14), [(5′) ≈ (6′) ≈ (9′) ≈ (10′) ≈ (13′) ≈ (14′)] > (7) ≈ (11) ≈ (15), [(7′) ≈ (11′) ≈ (15′)], *i.e.* with increasing number of fused benzene rings on the tetradehydro[15]annulenone system, which is in accord with the result found for the bis-(cyclohexene)-annelated compounds.[4a]

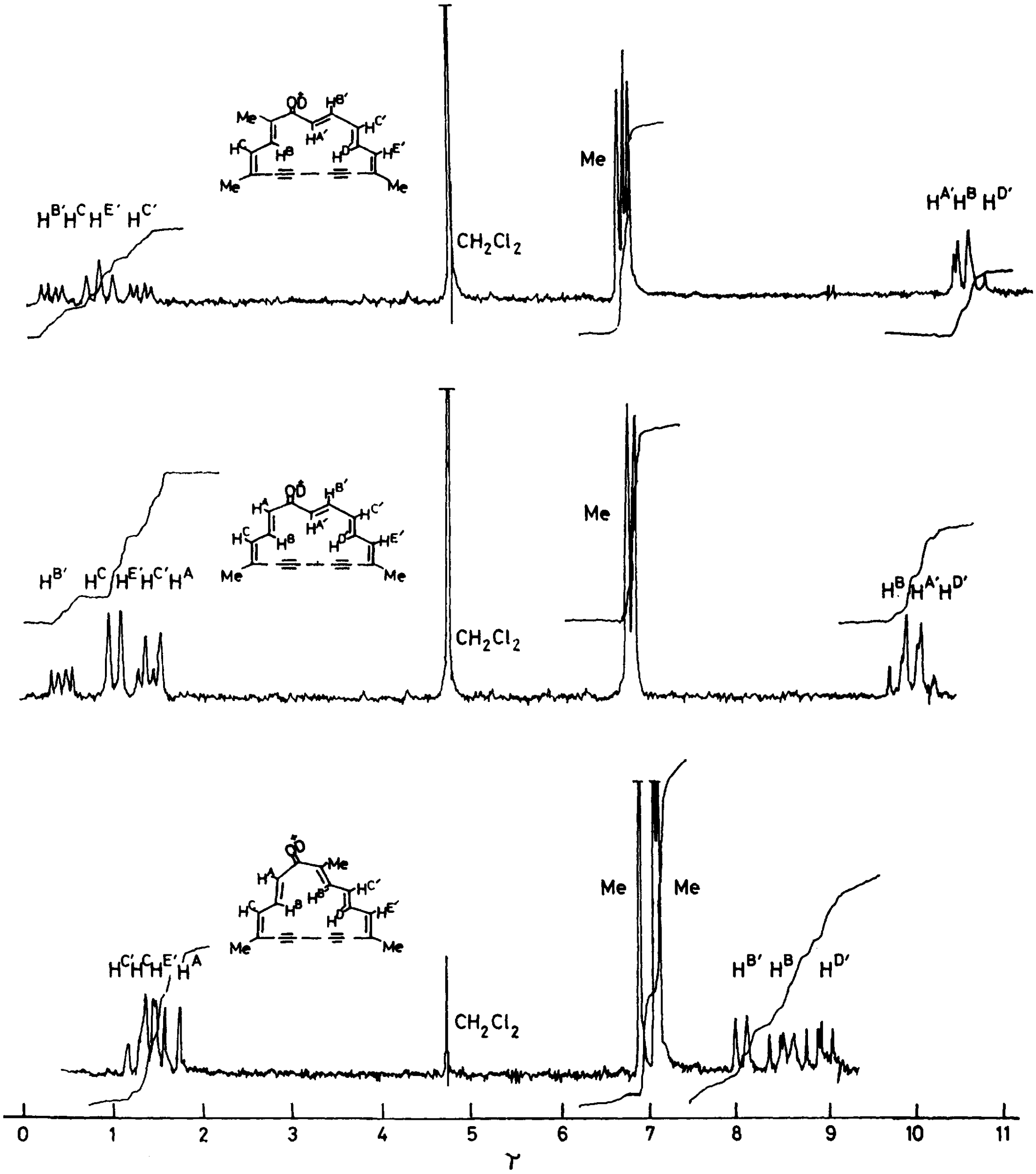

FIGURE 5 90-MHz ^{1}H N.m.r. spectra of the [15]annulenones (4), (8), and (12) in CF$_3$CO$_2$D at 35 °C

Variable-temperature ^{1}H n.m.r. spectra of (4)—(15) were run over the range −60 to +60 °C, the results of which, summarized in Table 4, show the spectra of all the annulenones (4)—(15) to be essentially temperature-independent. The spectra of the trimethyltetradehydro[15]annulenone (8) which is the higher analogue of the conformationally mobile compound (1), are shown in Figure 2. On cooling, the resonances of the inner protons ($\mathrm{H^B}$, $\mathrm{H^{B'}}$, $\mathrm{H^{D'}}$) of (8) move to slightly higher field, whereas those of the outer protons ($\mathrm{H^A}$, $\mathrm{H^C}$, $\mathrm{H^{C'}}$, $\mathrm{H^{E'}}$) and three methyl protons move to slightly lower field. However, the $J_{\mathrm{B,C}}$ value (11 Hz), indicating an *s-trans* relationship of the $\mathrm{H^B}$ and $\mathrm{H^C}$ bonds, does not vary from −60 to +60 °C, thus excluding a change of conformation of (8) due to rotation of the $\mathrm{CH^A{=}CH^B}$ double bond over this temperature range, in contrast to the case for the trimethyltetradehydro[13]annulenone (1). The spectra of the dimethyltetradehydro[15]-annulenone (4) and the trimethylannulenone (12) are illustrated in Figures 1 and 3, respectively, which show that the signals of both the inner and outer protons of (4) and (12) vary less than those of (8) between −60 and +60 °C (see also Table 4), reflecting the rigidity of the molecular skeleton. This observation is manifested very markedly in the spectra of (4), (8), and (12) in deuteriotrifluoroacetic acid (Figure 5). As also seen from Table 3, it is to be noted that the inner protons of these annulenones resonate at lower field in the sequence (12′) > (4′) > (8′), while the outer and methyl protons resonate at higher field in the same sequence. This result suggests that the planarity, *i.e.* the rigidity, of the molecular skeleton of the tetradehydro[15]annulenone ring system decreases in the sequence (12) > (4) > (8), reflecting the effect of perturbation caused by introduction of the α-methyl substituent. This observation is supported by the fact that a bathochromic shift of the main maximum as well as the longest wavelength band, is seen in the u.v. spectra of these annulenones in both ether and deuteriotrifluoroacetic acid (Tables 1 and 2).

TABLE 4

Variable-temperature ^{1}H n.m.r. parameters for the compounds (4)—(15) at 100 MHz (τ values)

Compound	T (°C)	H^A	$H^{A'}$	H^B	$H^{B'}$	H^C	$H^{C'}$	$H^{D'}$	$H^{E'}$	Ar-H	Me
(4)	+60	3.38	4.30	4.11	2.49	2.82	3.22	4.45	2.82		7.78, 7.84
	+35	3.33	4.35	4.17	2.45	2.77	3.17	4.52	2.77		7.76, 7.82
	−30	3.28	4.48	4.33	2.37	2.68	3.08	4.73	2.68		7.72, 7.77
	−60	3.25	4.52	4.40	2.33	2.64	3.05	4.82	2.64		7.68, 7.75
(5)	+60	2.28	—	—	—	—	—	—	—	—3.53 1.92—2.10	7.92
	−60	2.08	—	—	—	—	—	—	—	—3.67 1.82—2.00	7.83
(6)	+60	2.17	—	—	—	—	—	—	—	—3.70	7.90
	−60	2.05	—	—	—	—	—	—	—	—3.60	7.82
(7)	+60	2.03	—	—	—	—	—	—	—	—3.23	
	−60	2.00	—	—	—	—	—	—	—	—3.28	
(8)	+60	3.39		4.35	4.52	2.82	2.90	4.60	3.00		7.84, 7.95, 7.99
	+35	3.37		4.45	4.58	2.78	2.90	4.68	2.98		7.83, 7.93, 7.97
	−30	3.28		4.56	4.67	2.69	2.76	4.76	2.89		7.78, 7.88, 7.94
	−60	3.24		4.65	4.69	2.63	2.70	4.83	2.84		7.77, 7.87, 7.93
(9)	+60	3.09		3.22	3.60		3.13	3.74	3.01	2.13—2.77	7.97, 8.03
	−60	2.97		3.30	3.63		2.98	3.82	2.88	2.05—2.52	7.94
(10)	+60	2.30	—	—	—	—	—	—	—	—3.80	7.92, 7.97
	−60	2.20	—	—	—	—	—	—	—	—3.83	7.82, 7.92
(11)	+60	2.2	—	—	—	—	—	—	—	—3.3	7.95
	−60	2.1	—	—	—	—	—	—	—	—3.2	7.91
(12)	+60		4.44	4.43	2.42	2.63	3.22	4.63	2.81		7.74, 7.83
	+20		4.51	4.52	2.37	2.59	3.15	4.74	2.75		7.72, 7.81
	−30		4.61	4.66	2.32	2.54	3.09	4.91	2.68		7.68, 7.78
	−60		4.66	4.72	2.26	2.48	3.04	4.98	2.62		7.64, 7.76
(13)	+60		3.47	3.06	2.02	—	—	—	—	—2.70	7.68, 7.93
	−60		3.72	3.34	2.00	—	—	—2.60	2.91	2.00—2.60	7.66, 7.88
(14)	+60		3.41	3.18	3.03	2.84	2.40—2.80	3.25		2.16—2.25 2.40—2.80	7.85, 7.92
	−60		3.51	3.38	2.86	2.72	2.32—2.59	3.43		2.0—2.1 2.32—2.59	7.77, 7.88
(15)	+60		2.12—2.78		3.22		2.12—2.78	2.90		2.12—2.78	7.74
	−60		2.13—2.80		3.12		2.13—2.80	2.99		2.13—2.80	7.72

In conclusion, these results obtained from this study suggest that the skeleton of the tetradehydro[15]annulenone system is more planar and less strained than that of tetradehydro[13]annulenone,[1,2] as has been observed for the corresponding tetradehydro[17]annulenone.[3]

EXPERIMENTAL

Deoxygenated ether was used and prepared as reported.[3] The ethanolic sodium ethoxide solution used for aldol condensation was prepared from sodium (380 mg) and dry ethanol (50 ml) immediately before use. M.p.s were determined with a hot-stage apparatus. I.r. spectra were taken as KBr discs with a Hitachi EPI-S2 spectrophotometer. U.v. spectra were measured in ether solution on a Hitachi 124 spectrophotometer. Mass spectra were recorded with a JEOL JMS-OI-SG-2 spectrometer operating at 75 eV using a direct inlet system. N.m.r. spectra were run with Varian EM-390 or Hitachi R-900 (90 MHz) or JEOL FX-100 (100 MHz) spectrometers, in $CDCl_3$ solution unless stated otherwise. Merck alumina (activity II—III) was used for column chromatography, sodium sulphate was used as drying agent, and solvents were evaporated at water-pump pressure.

3,13-*Dimethylpentadeca*-3,5,8,10,12-*pentaen*-1,14-*diyn*-7-*one* (32).[7]—Ethanolic sodium ethoxide (4.0 ml) was added to a solution of 6-methylocta-3,5-dien-7-yn-2-one [1] (1.72 g, 12.8 mmol) in deoxygenated ether (99 ml), and a solution of the dienyne aldehyde (25) [10] (2.00 g, 16.6 mmol) in deoxygenated ether (26 ml) was added dropwise during 35 min with stirring at 5 °C. After stirring for a further 6 h at the same temperature, the reaction was quenched by addition of aqueous oxalic acid. The solution was poured into water and extracted with benzene. The benzene extracts were washed successively with water, aqueous sodium hydrogencarbonate, and brine, and then dried. The semi-solid obtained after removal of solvent was chromatographed on alumina (80 g). The initial fractions gave the unchanged aldehyde (25) (100 mg). Later fractions (45% ether–hexane as eluant) gave the ketone (32) (1.11 g, 37%) as a solid. Recrystallization from hexane–benzene afforded yellow *needles*, m.p. 104—105 °C (lit.,[7] 105—106 °C); for u.v. and i.r. data see ref. 7; τ 2.27 (1 H, dd, *J* 15 and 11 Hz, H^{B}), 2.60 (1 H, dd, *J* 15 and 11 Hz, $H^{B'}$), 2.87 (1 H, dd, *J* 15 and 11 Hz, $H^{D'}$), 3.40—3.72 (5 H, m, H^{A}, $H^{A'}$, H^{C}, $H^{C'}$, and $H^{E'}$), 6.48 (1 H, s, $-C\equiv CH$), 6.55 (1 H, s, $-C\equiv CH$), 7.93 (3 H, s, Me), and 7.96 (3 H, s, Me) (Found: C, 86.25; H, 7.0. Calc. for $C_{17}H_{16}O$: C, 86.4; H, 6.8%).

5,10-*Dimethyl*-6,7,8,9-*tetradehydrocyclopentadecenone* (4).[7]—The compound was prepared from (32) by the previously described method [7] as yellow *needles* from hexane–benzene, m.p. 164—165 °C (decomp.) [lit.,[7] 162—163 °C (decomp.)]; for u.v. data see Tables 1 and 2; τ 2.44 (1 H, dd, *J* 15 and 5 Hz, $H^{B'}$), 2.75 (2 H, d, *J* 11 Hz, H^{C} and $H^{E'}$), 3.19 (1 H, dd, *J* 16 and 5 Hz, $H^{C'}$), 3.35 (1 H, d, *J* 16 Hz, H^{A}), 4.17 (1 H, dd, *J* 16 and 11 Hz, H^{B}), 4.37 (1 H, d, *J* 15 Hz, $H^{A'}$), 4.53 (1 H, dd, *J* 15 and 12 Hz, $H^{D'}$), 7.76 (3 H, s, Me), and 7.82 (3 H, s, Me) (see also Figure 1); τ (CF_3CO_2D, CH_2Cl_2 as internal standard) 0.29 (1 H, dd, *J* 15 and 6 Hz, $H^{B'}$ or $H^{C'}$), 0.89 (2 H, d, *J* 12 Hz, H^{C} and $H^{E'}$), 1.28 (1 H, dd, *J* 15 and 6 Hz, $H^{B'}$ or $H^{C'}$), 1.31 (1 H, d, *J* 15 Hz, H^{A}), 6.73 (3 H, s, Me), 6.82 (3 H, s, Me), 9.92 (1 H, dd, *J* 15 and 12 Hz, H^{B} or $H^{D'}$), 10.10 (1 H, d, *J* 15 Hz, $H^{A'}$), and 10.15 (1 H, dd, *J* 15 and 12 Hz, H^{B} or $H^{D'}$) (see also Figure 5) (Found: C, 87.3; H, 6.0. Calc. for $C_{17}H_{14}O$: C, 87.15; H, 6.0%).

1-(o-*Ethynylphenyl*)-9-*methylundeca*-1,4,6,8-*tetraen*-10-*yn*-3-*one* (33).—This compound was prepared as reported.[6]

13-*Methyl*-14,15,16,17-*tetradehydrobenzocyclopentadecen*-7-*one* (5).—The annulenone (5) was prepared from (33) by the same procedure as described for the preparation of (8). The yield could not be improved over that previously reported.[6]

1-(o-*Ethynylphenyl*)-9-*methylundeca*-1,3,6,8-*tetraen*-10-*yn*-5-*one* (34).—This compound was prepared as reported.[6]

13-*Methyl*-14,15,16,17-*tetradehydrobenzocyclopentadecen*-9-*one* (6).—This compound was prepared from (34) employing anhydrous copper(II) acetate (instead of monohydrate [6]) in pyridine–dry ether as in the preparation of (8); yield 65%.

1,7-*Bis*-(o-*ethynylphenyl*)*hepta*-1,4,6-*trien*-3-*one* (35).—This compound was prepared as reported.[4]

16,17,18,19-*Tetradehydrodibenzo*[a,g]*cyclopentadecen*-7-*one* (7).[4]—This compound was prepared as reported.[4] A solution of (35) (2.57 g, 8.33 mmol) in nitrogen-flushed *NN*-dimethylformamide (321 ml) was added dropwise during 4.5 h to a stirred solution of copper(II) acetate monohydrate (32.1 g) in nitrogen-flushed *NN*-dimethylformamide (1 285 ml) at 51—56 °C. The reaction mixture was stirred at the same temperature for a further 30 min, and cooled. The mixture was poured into 4N-hydrochloric acid (643 ml) and brine (1 930 ml), and extracted with benzene. The benzene extracts were washed successively with saturated sodium hydrogencarbonate and brine, and dried. The residue obtained after solvent removal was chromatographed on alumina (80 g). Elution with ether gave the annulenone (7) (332 mg, 13%), obtained as yellow cubes from hexane–benzene, m.p. 204—206 °C (decomp.), [lit.,[4] *ca.* 150 °C (decomp.)]; for u.v. data see Tables 1 and 2; for n.m.r. data see Table 3 (Found: C, 89.9; H, 4.7. Calc. for $C_{23}H_{13}O$: C, 90.2; H, 4.6%).

This compound was also prepared from (35) employing anhydrous copper(II) acetate in pyridine–dry ether as described for the preparation of (8). However, the yield could not be improved.

3,8,13-*Trimethylpentadeca*-3,5,8,10,12-*pentaen*-1,14-*diyn*-7-*one* (18).—A solution of ethanolic sodium ethoxide (1.5 ml) was added to a solution of the ketone (16) [3] (344 mg, 1.69 mmol) in deoxygenated ether (15 ml), and a solution of the enyne aldehyde (17) [11] (372 mg, 3.95 mmol) in deoxygenated ether (6 ml) was then added dropwise during 10 min with stirring in an ice-bath. After stirring for a further 15 h at room temperature, the reaction was quenched by addition of aqueous oxalic acid. The mixture was poured into water and extracted with benzene. After the usual work-up, the yellow liquid obtained was chromatographed on alumina (100 g). Initial fractions gave the unchanged ketone (16) (184 mg). Later fractions, eluted with hexane–ether (4 : 1), gave the ketone (18) (217 mg, 51%) as a solid. Recrystallization from hexane–benzene afforded yellow *needles*, m.p. 97—98 °C; *m/e* 250 (M^+, 100%); *M*, 250.3; $\nu_{max.}$ 3 320, 3 280 ($C\equiv C-H$), 2 120 ($C\equiv C$), 1 650 (C=O), 1 600, 1 590 (C=C), 975, and 965 cm^{-1} (*trans* C=C); $\lambda_{max.}$ 224 (ε 10 100), 237sh (9 400), 252sh (12 000), 265sh (13 900), 280sh (16 700), 288 (18 100), 301 (17 500), 347sh (31 700), 359 (36 800), and 374sh nm (30 400); τ 2.25 (1 H, dd, *J* 15 and 12 Hz, H^{B}), 2.82 (1 H, d, *J* 12 Hz, $H^{B'}$), 2.95 (1 H, dd, *J* 15 and 12 Hz, $H^{C'}$ or $H^{D'}$), 3.13 (1 H, d, *J* 15 Hz, H^{A}), 3.36 (1 H, dd, *J* 15 and 12 Hz, $H^{C'}$ or $H^{D'}$), 3.50 (1 H, d, *J* 12 Hz, H^{C} or $H^{E'}$), 3.52 (1 H, d, *J* 12 Hz, H^{C} or $H^{E'}$), 6.53 (1 H, s, $-C\equiv CH$), 6.57 (1 H, s, $-C\equiv CH$), and 7.97 (9 H, s, Me) (Found: C, 86.6; H, 7.4. $C_{18}H_{18}O$ requires C, 86.4; H, 7.25%).

5,10,15-*Trimethyl*-6,7,8,9-*tetradehydrocyclopentadecenone* (8).—A solution of the ketone (18) (320 mg, 1.3 mmol) in pyridine–dry ether (3 : 1, 28 ml) was added dropwise during 40 min to a stirred solution of anhydrous copper(II) acetate (1.6 g) in pyridine–dry ether (3 : 1, 60 ml) at 48—50 °C. The solution was stirred at 48—50 °C for a further 1.5 h and cooled. After addition of benzene (100 ml), the mixture was filtered through Hyflo SuperCel. The precipitates formed were washed with benzene (35 ml × 2), and the filtrate was poured into 3N-hydrochloric acid. The organic layer, combined with the benzene extracts from the aqueous layer, was washed with 3N-hydrochloric acid, water, aqueous sodium hydrogencarbonate, and brine, and then dried. After removal of solvent, the residue obtained was chromatographed on alumina (100 g) with hexane–ether (3 : 2) to give the annulenone (8) (140 mg, 44%) as a solid. Recrystallization from hexane–benzene afforded yellow *cubes*, m.p. 136—137 °C; *m/e* 248 (M^+, 36%) and 233 (100); *M*, 248.3; $\nu_{max.}$ 2 150 ($C\equiv C$), 1 635 (C=O), 1 595 (C=C), and 980 cm^{-1} (*trans* C=C); for u.v. data see Tables 1 and 2; τ 2.73 (1 H, d, *J* 11 Hz, H^{C} or $H^{E'}$), 2.87 (1 H, dd, *J* 16 and 11 Hz, $H^{C'}$), 2.91 (1 H, d, *J* 11 Hz, H^{C} or $H^{E'}$), 3.33 (1 H, d, *J* 16 Hz, H^{A}), 4.38 (1 H, dd, *J* 16 and 11 Hz, H^{B}), 4.53 (1 H, d, *J* 11 Hz, $H^{B'}$), 4.61 (1 H, dd, *J* 16 and 11 Hz, $H^{D'}$), 7.79 (3 H, s, Me), 7.90 (3 H, s, Me), and 7.95 (3 H, s, Me) (see also Figure 2); τ (CF_3CO_2D, CH_2Cl_2 as internal standard) 1.25 (1 H, dd, *J* 15 and 12 Hz, $H^{C'}$), 1.30 (1 H, d, *J* 12 Hz, H^{C} or $H^{E'}$), 1.33 (1 H, d, *J* 12 Hz, H^{C} or $H^{E'}$), 1.60 (1 H, d, *J* 15 Hz, H^{A}), 6.89 (3 H, s, Me), 7.07 (3 H, s, Me), 7.12 (3 H, s, Me), 8.05 (1 H, d, *J* 12 Hz, $H^{B'}$), 8.52 (1 H, dd, *J* 15 and 12 Hz, H^{B} or $H^{D'}$), and 8.95 (1 H, dd, *J* 15 and 12 Hz, H^{B} or $H^{D'}$) (see also Figure 5) (Found: C, 86.9; H, 6.35. $C_{18}H_{16}O$ requires C, 87.1; H, 6.5%).

1-(o-*Ethynylphenyl*)-4,9-*dimethylundeca*-1,4,6,8-*tetraen*-10-*yn*-3-*one* (20).—A solution of ethanolic sodium ethoxide (3.9 ml) was added to a solution of the ketone (16) (1.13 g, 6.5 mmol) in deoxygenated ether (50 ml), and a solution of *o*-ethynylbenzaldehyde (19) [12] (800 mg, 8.4 mmol) in deoxygenated ether (13 ml) was added dropwise during 20 min with stirring in an ice-bath. After stirring for a further 5 h at room temperature, the reaction was quenched by addition of aqueous oxalic acid. After the usual work-up, the dark brown liquid obtained was chromatographed on alumina (100 g). Initial fractions gave the ketone (16) (50 mg). Later fractions, eluted with hexane–ether (1 : 1), gave the ketone (20) (1.29 g, 69%) as a solid. It formed orange *needles* from hexane–benzene, m.p. 130—131 °C; *m/e* 286 (M^+, 100%); *M* 286.4; $\nu_{max.}$ 3 270 (C≡C–H), 2 150, 2 130 (C≡C), 1 645 (C=O), 1 580 (C=C), 985, and 975 cm^{-1} (*trans* C=C); $\lambda_{max.}$ 227 (ε 22 600), 252 (14 000), 283sh (19 500), 291 (19 900), 339sh (28 100), 356 (33 500), and 369sh nm (29 100); τ 1.90 (1 H, d, *J* 16 Hz, H^{B}), 2.23—2.78 (6 H, m, H^{A}, $H^{B'}$, and Ar-H), 2.92 (1 H, dd, *J* 15 and 11 Hz, $H^{C'}$ or $H^{D'}$), 3.35 (1 H, dd, *J* 15 and 11 Hz, $H^{C'}$ or $H^{D'}$), 3.55 (1 H, d, *J* 11 Hz, $H^{E'}$), 6.59 (2 H, s, C≡CH), 7.97 (3 H, s, Me), and 8.00 (3 H, s, Me) (Found: C, 87.9; H, 6.1. $C_{21}H_{18}O$ requires C, 88.1; H, 6.3%).

8,13-*Dimethyl*-14,15,16,17-*tetradehydrobenzocyclopentadecen*-7-*one* (9).—A solution of the ketone (20) (1.01 g, 3.5 mmol) in pyridine–dry ether (3 : 1, 188 ml) was added dropwise during 1.5 h to a stirred solution of anhydrous copper(II) acetate (5.0 g) in pyridine–dry ether (3 : 1, 188 ml) at 51—55 °C. After stirring for a further 45 min at the same temperature, the solution was cooled. Work-up as for the isolation of (8) gave a semi-solid which was chromatographed on alumina (80 g) with hexane–ether as eluant to give the annulenone (9) (0.76 g, 76%) as a solid. Recrystallization from benzene afforded yellow *rods*, m.p. 150 °C (decomp.); *m/e* 284 (M^+, 57%) and 269 (100); *M*, 284.3; $\nu_{max.}$ 2 200, 2 150 (C≡C), 1 620, 1 605, 1 595 (C=O, C=C), and 970 cm^{-1} (*trans* C=C); for u.v. data see Tables 1 and 2; τ 2.07—2.20 (1 H, m, Ar-H), 2.30—2.65 (3 H, m, Ar-H), 2.90 (1 H, d, *J* 10.5 Hz, $H^{E'}$), 2.97 (1 H, d, *J* 16 Hz, H^{A}), 3.05 (1 H, dd, *J* 15 and 10.5 Hz, $H^{C'}$), 3.20 (1 H, d, *J* 16 Hz, H^{B}), 3.58 (1 H, d, *J* 10.5 Hz, $H^{B'}$), 3.72 (1 H, dd, *J* 15 and 10.5 Hz, $H^{D'}$), 7.93 (3 H, s, Me_3), and 7.98 (3 H, s, Me); τ (CF_3CO_2D), see Table 3 (Found: C, 88.9; H, 5.7. $C_{21}H_{16}O$ requires C, 88.7; H, 5.7%).

1-(o-*Ethynylphenyl*)-4,9-*dimethylundeca*-1,3,6,8-*tetraen*-10-*yn*-5-*one* (22).—A solution of ethanolic sodium ethoxide (1.3 ml) was added to a solution of the ketone (21) [3] (450 mg, 2.1 mmol) in deoxygenated ether (17 ml), and a solution of the enyne aldehyde (17) [11] (300 mg, 3.2 mmol) in deoxygenated ether (4 ml) was added dropwise during 8 min with stirring in an ice-bath. After stirring for a further 6.5 h at room temperature, the reaction was quenched by addition of aqueous oxalic acid. After the usual work-up, the product was chromatographed on alumina (80 g). Initial fractions gave the unchanged ketone (21) (180 mg). Later fractions, eluted with hexane–ether (3 : 2), gave the ketone (22) (220 mg, 36%), which was recrystallized from hexane–benzene to afford yellow *cubes*, m.p. 125 °C (decomp.); *m/e* 286 (M^+, 100%); *M*, 286.4; $\nu_{max.}$ 3 260 (C≡C–H), 2 130 (C≡C), 1 640, 1 620, 1 595 (C=O, C=C), 980, and 960 cm^{-1} (*trans* C=C); $\lambda_{max.}$ 234 (ε 15 300), 249sh (15 600), 255 (17 300), 264sh (15 800), 294sh (13 200), 340sh (31 100), 352 (34 200), and 370sh nm (26 000); τ 2.06—2.80 (8 H, m, H^{B}, $H^{B'}$, $H^{C'}$, $H^{D'}$, and Ar-H), 3.10 (1 H, d, *J* 16 Hz, H^{A}), 3.47 (1 H, d, *J* 12 Hz, H^{C}), 6.52 (1 H, s, C≡CH), 6.57 (1 H, s, –C≡H), 7.90 (3 H, s, Me), and 7.95 (3 H, s, Me) (Found: C, 87.8; H, 6.4. $C_{21}H_{18}O$ requires C, 88.1; H, 6.3%).

8,13-*Dimethyl*-14,15,16,17-*tetradehydrobenzocyclopentadecen*-9-*one* (10).—A solution of the ketone (22) (230 mg, 0.80 mmol) in pyridine–dry ether (3 : 1, 18 ml) was added dropwise during 25 min to a stirred solution of anhydrous copper(II) acetate (1.0 g) in pyridine–dry ether (3 : 1, 38 ml) at 50—55 °C. The solution was stirred for a further 45 min at the same temperature and cooled. After work-up as for the isolation of (8), the product was chromatographed on alumina (80 g) with hexane–ether (3 : 2) as eluant to give the annulenone (10) (110 mg, 48%) as a solid. Recrystallization from hexane–benzene afforded yellow *needles*, m.p. 160—161 °C, *m/e* 284 (M^+, 48%) and 270 (100); *M*, 284.3; $\nu_{max.}$ 2 200 (C≡C), 1 605, 1 580 (C=O, C=C), and 975 cm^{-1} (*trans* C=C); for u.v. data see Tables 1 and 2; n.m.r., see Table 3; τ (CF_3CO_2D) 1.8—2.4 (5 H, m, $H^{C'}$ and Ar-H), 2.45 (1 H, d, *J* 12 Hz, H^{C}), 2.68 (1 H, d, *J* 15 Hz, H^{A}), 4.43 (1 H, d, *J* 15 Hz, $H^{D'}$), 4.55 (1 H, d, *J* 12 Hz, $H^{B'}$), 4.65 (1 H, dd, *J* 15 and 12 Hz, H^{B}), 7.52 (3 H, s, Me), and 7.60 (3 H, s, Me) (Found: C, 88.5; H, 5.45. $C_{21}H_{16}O$ requires C, 88.7; H, 5.7%).

1,7-*Bis*-(o-*ethynylphenyl*)-4-*methylhepta*-1,4,6-*trien*-3-*one* (23).—A solution of ethanolic sodium ethoxide (1.4 ml) was added to a solution of the ketone (21) [3] (450 mg, 2.1 mmol) in deoxygenated ether (17 ml), and then a solution of *o*-ethynylbenzaldehyde (19) [12] (364 mg, 2.8 mmol) in deoxygenated ether (4.3 ml) was added dropwise during 10 min with stirring in an ice-bath. After stirring at room temperature overnight, the reaction was quenched by addition of aqueous oxalic acid. After the usual work-up, the product obtained was chromatographed on alumina (120 g). Fractions eluted with 35% ether–hexane gave the ketone (23) (326 mg, 49%) as a solid, which was recrystallized from hexane–benzene to give yellow *cubes*, m.p. 111—112 °C; *m/e* 322 (M^+, 100%); *M*, 322.4; $\nu_{max.}$ 3 300, 3 250 (C≡C–H), 2 150 (C≡C), 1 640 (C=O), 1 615, 1 600, 1 595 (C=C), 975, and 960 cm^{-1} (*trans* C=C); $\lambda_{max.}$ 226 (ε 27 500), 248sh (21 300), 254 (21 300), 266sh (14 700), 287sh (13 700), 338sh (27 700), 350 (31 500), and 370sh nm (20 700); τ 1.82 (1 H, d, *J* 16 Hz, H^{B}), 2.17—2.83 (12 H, m, H^{A}, $H^{B'}$, $H^{C'}$, $H^{D'}$, and Ar-H), 6.55 (1 H, s, C≡CH), 6.57 (1 H, s, C≡CH), and 7.83 (3 H, s, Me) (Found: C, 89.3; H, 5.9. $C_{24}H_{18}O$ requires C, 89.4; H, 5.6%).

8-*Methyl*-16,17,18,19-*tetradehydrodibenzo*[a,g]*cyclopentadecen*-7-*one* (11).—A solution of the ketone (25) (326 mg, 1.0 mmol) in pyridine–dry ether (3 : 1) (24 ml) was added dropwise during 40 min to a stirred solution of anhydrous copper(II) acetate (1.3 g) in pyridine–dry ether (3 : 1) (49 ml) at 48—50 °C. The solution was stirred for a further 30 min at 50—55 °C and cooled. The reaction mixture was poured into water (200 ml) and extracted with benzene. After work-up as for the isolation of (8), the product obtained was chromatographed on alumina (80 g) with hexane–ether (3 : 2) to give the annulenone (11) (220 mg, 68%). Recrystallization from benzene afforded light yellow *cubes*, m.p. 182—183 °C; *m/e* 320 (M^+, 45%) and 280 (100); *M*, 320.4; $\nu_{max.}$ 2 240, 2 170 (C≡C), 1 625, 1 615, 1 600 (C=O, C=C), and 975 cm^{-1} (*trans* C=C); for u.v. data see Tables 1 and 2; for n.m.r. data see Table 3 (Found: C, 89.9; H, 5.0. $C_{24}H_{16}O$ requires C, 90.0; H, 5.00).

3,6,13-*Trimethylpentadeca*-3,5,8,10,12-*pentaen*-1,14-*diyn*-7-*one* (16).—A solution of ethanolic sodium ethoxide (4.0 ml) was added to a solution of the ketone (24) [1] (1.23 g, 8.30 mmol) in deoxygenated ether (65 ml), and a solution of the aldehyde (25) [10] (2.00 g, 16.6 mmol) in deoxygenated ether (65 ml) was added dropwise during 30 min with stirring in an ice-bath. After stirring for a further 2.5 h at room temperature, further portions of ethanolic sodium ethoxide (each 2.0 ml) were added after every 30 min. After stirring for a total of 10 h, the reaction was quenched by addition of aqueous oxalic acid. The mixture was poured into water (400 ml) and extracted with benzene. After work-up as usual, the dark red liquid obtained by solvent removal was chromatographed on alumina (150 g). The ketone (26) (0.75 g, 36%) was eluted with hexane–ether (9 : 1). Recrystallization from hexane–benzene afforded orange *needles*, m.p. 101—102 °C; *m/e* 250 (M^+, 46%) and 282 (100); *M*, 250.3; $\nu_{max.}$ 3 230 (C≡C–H), 2 150 (C≡C), 1 640, 1 610, 1 585 (C=O, C=C), and 1 000 cm^{-1} (*trans* C=C); $\lambda_{max.}$ 231 (ε 9 600), 248sh (14 800), 254sh (17 400), 260sh (19 700), 265sh (20 400), 276 (20 900), 290 (22 000), 304 (23 300), 340sh (32 600), 355 (36 500), and 372sh nm (31 200); τ 2.44 (1 H, d, *J* 11 Hz, H^B), 2.57 (1 H, dd, *J* 15 and 11 Hz, $H^{B'}$), 2.87 (1 H, dd, *J* 15 and 11 Hz, $H^{D'}$), 3.13 (1 H, d, *J* 15 Hz, $H^{A'}$), 3.25 (1 H, d, *J* 11 Hz, H^C or $H^{E'}$), 3.52 (1 H, dd, *J* 15 and 11 Hz, $H^{C'}$), 3.56 (1 H, d, *J* 11 Hz, H^C or $H^{E'}$), 6.45 (1 H, s, C≡CH), 6.54 (1 H, s, C≡CH), 7.89 (3 H, s, Me), and 7.98 (6 H, s, Me) (Found: C, 86.1; H, 7.3. $C_{18}H_{18}O$ requires C, 86.4; H, 7.25%).

2,5,10-*Trimethyl*-6,7,8,9-*tetradehydrocyclopentadecenone* (12).—A solution of the ketone (26) (0.70 g, 2.80 mmol) in pyridine–dry ether (3 : 1, 67 ml) was added dropwise to a stirred solution of anhydrous copper(II) acetate (3.4 g) in pyridine–dry ether (3 : 1) (135 ml) during 2 h at 48—52 °C. The solution was stirred for a further 30 min at the same temperature and cooled. After work-up as described for the isolation of (8), the dark red semi-solid obtained was chromatographed on alumina (110 g). The annulenone (12) (333 mg, 48%) was eluted with hexane–ether (7 : 3). Recrystallization from hexane–benzene afforded yellow *needles*, m.p. 190—191 °C, *m/e* 248 (M^+, 40%) and 233 (100); *M*, 248.3; $\nu_{max.}$ 2 200 (C≡C), 1 625 (C=O), 1 595 (C=C), and 970 cm^{-1} (*trans* C=C); for u.v. data see Tables 1 and 2; τ 2.37 (1 H, dd, *J* 16 and 5 Hz, $H^{B'}$), 2.57 (1 H, d, *J* 11 Hz, H^C), 2.75 (1 H, d, *J* 11 Hz, $H^{E'}$), 3.15 (1 H, dd, *J* 16 and 5 Hz, $H^{C'}$), 4.48 (1 H, d, *J* 11 Hz, H^B), 4.50 (1 H, d, *J* 16 Hz, $H^{A'}$), 4.71 (1 H, dd, *J* 16 and 11 Hz, $H^{D'}$), 7.71 (3 H, s, Me), and 7.79 (6 H, s, Me) (see also Figure 3); τ (CF_3CO_2D, CH_2Cl_2 as internal standard) 0.17 (1 H, dd, *J* 16 and 7 Hz, $H^{B'}$), 0.60 (1 H, d, *J* 12 Hz, H^C), 0.80 (1 H, d, *J* 12 Hz, $H^{E'}$) 1.20 (1 H, dd, *J* 16 and 7 Hz, $H^{C'}$), 6.68 (3 H, s, Me), 6.75 (3 H, s, Me), 6.80 (3 H, s, Me), 10.57 (1 H, d, *J* 16 Hz, $H^{A'}$), 10.60 (1 H, d, *J* 12 Hz, H^B), and 10.69 (1 H, dd, *J* 16 and 12 Hz, $H^{D'}$) (see also Figure 5) (Found: C, 86.85; H, 6.6. $C_{18}H_{16}O$ requires C, 87.1; H, 6.5%).

1-(o-*Ethynylphenyl*)-2,9-*dimethylundeca*-1,4,6,8-*tetraen*-10-*yn*-3-*one* (30).—A solution of ethanolic sodium ethoxide (7.6 ml) was added to a solution of the ketone (29)[2] (1.62 g, 9.50 mmol) in deoxygenated ether (75 ml), and a solution of the dienyne aldehyde (25)[10] (1.70 g, 14.2 mmol) in deoxygenated ether (19 ml) was added dropwise during 80 min at 2—3 °C with stirring. After stirring for a further 6 h at room temperature, the reaction was quenched by addition of aqueous oxalic acid. After work-up as for the isolation of (26), the product obtained was chromatographed on alumina (100 g). Fractions eluted with hexane–ether (17 : 3) gave the recovered ketone (29) (112 mg). The following fractions eluted with hexane–ether (17 : 3) gave the ketone (30) (1.59 g, 60%). Recrystallization from hexane–benzene afforded orange *plates*, m.p. 98—99 °C, *m/e* 286 (M^+, 42%) and 228 (100); *M*, 286.4; $\nu_{max.}$ 3 280, 3 250 (C≡C–H), 2 120 (C≡C), 1 645, 1 615, 1 585 (C=O, C=C), and 1 010 cm^{-1} (*trans* C=C); $\lambda_{max.}$ 226 (ε 25 700), 246 (19 800), 343 (36 000), and 361sh nm (30 000); τ 2.22 (1 H, s, H^B), 2.3—2.7 (5 H, m, $H^{B'}$ and Ar-H), 2.85 (1 H, dd, *J* 15 and 11 Hz, $H^{C'}$), 3.12 (1 H, d, *J* 15 Hz, $H^{A'}$), 3.52 (1 H, dd, *J* 15 and 11 Hz, $H^{D'}$), 3.57 (1 H, d, *J* 11 Hz, $H^{E'}$), 6.52 (1 H, s, C≡CH), 6.57 (1 H, s, C≡CH), 7.93 (3 H, d, *J* 1 Hz, Me), and 7.99 (3 H, s, Me) (Found: C, 87.9; H, 6.6. $C_{21}H_{18}O$ requires C, 88.1; H, 6.3%).

6,13-*Dimethyl*-14,15,16,17-*tetradehydrobenzocyclopentadecen*-7-*one* (13).—A solution of the ketone (30) (1.60 g, 5.7 mmol) in pyridine–dry ether (3 : 1) (137 ml) was added dropwise to a stirred solution of anhydrous copper(II) acetate (6.9 g) in pyridine–dry ether (3 : 1) (275 ml) during 2 h at 47—50 °C. After stirring for a further 1 h at the same temperature, the reaction mixture was chilled and then poured into water and extracted with benzene. After work-up as for the isolation of (8), the product was chromatographed on alumina (110 g). The annulenone (13) (0.69 g, 43%) was eluted with hexane–ether (3 : 2). Recrystallization from benzene afforded yellow *needles*, m.p. 165—166 °C; *m/e* 284 (M^+, 20%) and 240 (100); *M*, 284.3; $\nu_{max.}$ 2 180 (C≡C), 1 635 (C=O), 1 605 (C=C), and 975 cm^{-1} (*trans* C=C); for u.v. data see Tables 1 and 2; τ 2.00—3.67 (10 H, m, olefinic and Ar-H), 7.68 (3 H, s, Me), and 7.94 (3 H, s, Me) (see also Figure 4); τ (CF_3CO_2D) 1.80—2.40 (5 H, m, $H^{B'}$ and Ar-H), 2.68 (1 H, d, *J* 12 Hz, $H^{E'}$), 3.15 (1 H, dd, *J* 15 and 6 Hz, $H^{C'}$), 4.57 (1 H, s, H^B), 4.90 (1 H, dd, *J* 15 and 12 Hz, $H^{D'}$), 5.10 (1 H, d, *J* 15 Hz, $H^{A'}$), 7.54 (3 H, s, Me), and 7.77 (3 H, s, Me) (Found: C, 88.6; H, 5.4. $C_{21}H_{16}O$ requires C, 88.7; H, 5.7%).

1-(o-*Ethynylphenyl*)-6,9-*dimethylundeca*-1,3,6,8-*tetraen*-10-*yn*-5-*one* (28).—A solution of ethanolic sodium ethoxide (15 ml) was added to a solution of the ketone (24)[1] (2.00 g, 13.5 mmol) in deoxygenated ether (105 ml), and a solution of o-ethynylcinnamaldehyde (27)[13] (2.00 g, 12.8 mmol) in deoxygenated ether (30 ml) was added dropwise during 30 min with stirring in an ice-bath. After stirring at room temperature overnight, the reaction was quenched by addition of aqueous oxalic acid. The mixture was poured into water and extracted with benzene. After work-up as for the isolation of (26), the dark red liquid obtained was chromatographed on alumina (120 g). The ketone (28) (1.94 g, 53%) was eluted with hexane–ether (17 : 3). Recrystallization from hexane–benzene afforded light yellow *needles*, m.p. 102—103 °C, *m/e* 286 (M^+, 20%) and 228 (100); *M*, 286.4; $\nu_{max.}$ 3 280, 3 230 (C≡C–H), 2 100 (C≡C), 1 645, 1 610, 1 585 (C=O, C=C), and 998 cm^{-1} (*trans* C=C); $\lambda_{max.}$ 234 (ε 24 400), 256 (29 200), 263 (28 700), 296sh (23 200), 338sh (35 700), 349 (37 100), and 372sh nm (25 200); τ 2.27—3.13 (9 H, m, $H^{A'}$, H^B, $H^{B'}$, $H^{C'}$, $H^{D'}$, and Ar-H), 3.27 (1 H, d, *J* 12 Hz, H^C), 6.42 (1 H, s, C≡CH), 6.57 (1 H, s, C≡CH), 7.90 (3 H, s, Me), and 7.98 (3 H, s, Me) (Found: C, 88.0; H, 6.3. $C_{21}H_{18}O$ requires C, 88.1; H, 6.3%).

10,13-*Dimethyl*-14,15,16,17-*tetradehydrobenzocyclopentadecen*-9-*one* (14).—A solution of the ketone (28) (985 mg, 3.4 mmol) in pyridine–dry ether (3 : 1) (84 ml) was added dropwise during 1.5 h to a stirred solution of anhydrous copper(II) acetate (4.2 g) in pyridine–dry ether (3 : 1) (166 ml) at 53—55 °C. The mixture was stirred for a further 1 h at 55 °C and cooled. The mixture was poured into water, and extracted with benzene. After usual work-up as for the isolation of (8), the yellow semi-solid obtained was chromatographed on alumina (100 g). The annulenone (14) (0.57 g, 58%) was eluted with hexane–

ether (3 : 2). Recrystallization from hexane–benzene afforded yellow *needles*, m.p. 187—188 °C; *m/e* 284 (M^+, 34%) and 239 (100); *M*, 284.3; $\nu_{max.}$ 2 200 (C≡C), 1 650, 1 625, 1 580 (C=O, C=C), and 970 cm^{-1} (*trans* C=C); for u.v. data see Tables 1 and 2; τ 2.10—2.20 (1 H, m, Ar-H), 2.37—2.73 (4 H, m, $H^{B'}$ or $H^{C'}$, and Ar-H), 2.82 (1 H, d, *J* 12 Hz, H^B or H^C), 2.97 (1 H, dd, *J* 16 and 6 Hz, $H^{B'}$ or $H^{C'}$), 3.23 (1 H, d, *J* 12 Hz, H^B or H^C), 3.30 (1 H, d, *J* 16 Hz, $H^{D'}$), 3.42 (1 H, d, *J* 16 Hz, $H^{A'}$), 7.85 (3 H, s, Me), and 7.93 (3 H, s, Me) (see also Figure 4); τ (CF_3CO_2D) 1.82 (1 H, dd, *J* 16 and 6 Hz, $H^{C'}$), 1.73—2.33 (5 H, m, H^C and Ar-H), 2.43 (1 H, dd, *J* 16 and 6 Hz, $H^{B'}$), 4.75 (1 H, d, *J* 12 Hz, H^B), 4.83 (1 H, d, *J* 16 Hz, $H^{D'}$), 4.93 (1 H, d, *J* 16 Hz, $H^{A'}$), 7.48 (3 H, s, Me), and 7.60 (3 H, s, Me) (Found: C, 88.6; H, 5.4. $C_{21}H_{16}O$ requires C, 88.7; H, 5.7%).

1,7-*Bis*-(o-*ethynylphenyl*)-2-*methylhepta*-1,4,6-*trien*-3-*one* (31).—A solution of ethanolic sodium ethoxide (7.0 ml) was added to a solution of the ketone (29) [2] (1.80 g, 9.8 mmol) in deoxygenated ether (75 ml), and a solution of *o*-ethynylcinnamaldehyde (27) [13] (1.90 g, 12.3 mmol) in deoxygenated ether (29 ml) was added dropwise during 25 min with stirring at 9—10 °C. After stirring for a further 5 h at 10—15 °C, the reaction was quenched by addition of aqueous oxalic acid. The mixture was poured into water, and extracted with benzene. After work-up as for the isolation of (26), the product was chromatographed on alumina (125 g). Initial fractions gave the unchanged ketone (29) (0.23 g). Later fractions, eluted with hexane–ether (17 : 3), gave the ketone (31) (2.20 g, 70%). Recrystallization from hexane–benzene afforded yellow *needles*, m.p. 105—107 °C; *m/e* 322 (M^+, 11%) and 279 (100); *M*, 322.4; $\nu_{max.}$ 3 300, 3 230 (C≡C–H), 2 150 (C≡C), 1 640 (C=O), 1 580 (C=C), and 1 005 cm^{-1} (*trans* C=C); $\lambda_{max.}$ 227 (ε 36 400), 250 (27 500), 263sh (22 900), 327sh (33 000), and 338 nm (35 000); τ 2.17 (1 H, s, H^B), 2.1—2.7 (10 H, m, $H^{C'}$, $H^{D'}$, and Ar-H), 2.97 (1 H, dd, *J* 15 and 12 Hz, $H^{B'}$), 3.01 (1 H, d, *J* 15 Hz, $H^{A'}$), 6.53 (1 H, s, C≡CH), 6.56 (1 H, s, C≡CH), and 7.88 (3 H, s, Me) (Found: C, 89.2; H, 5.5. $C_{24}H_{18}O$ requires C, 89.4; H, 5.6%).

6-*Methyl*-16,17,18,19-*tetradehydrodibenzo*[a,g]*cyclopentadecen*-7-*one* (15).—A solution of the ketone (31) (2.60 g, 8.07 mmol) in pyridine–dry ether (3 : 1) (194 ml) was added dropwise to a stirred solution of anhydrous copper(II) acetate (9.7 g) in pyridine–dry ether (3 : 1) (387 ml) during 3 h at 48—52 °C. After stirring for a further 1 h at 50—55 °C, the chilled reaction mixture was poured into water, and extracted with benzene. After work-up as for the isolation of (8), the product was chromatographed on alumina (130 g). The annulenone (15) (1.70 g, 64%) was eluted with hexane–ether (1 : 1—1 : 9). Recrystallization from benzene afforded yellow *needles*, m.p. 168—169 °C; *m/e* 320 (M^+, 58%) and 276 (100); *M*, 320.4; $\nu_{max.}$ 2 250 (C≡C), 1 650, 1 620, 1 580 (C=O, C=C), and 970 cm^{-1} (*trans* C=C); for u.v. data see Tables 1 and 2; τ 2.10—2.75 (11 H, m, H^B, $H^{A'}$, or $H^{D'}$, $H^{B'}$ or $H^{C'}$, and Ar-H), 2.95 (1 H, d, *J* 16 Hz, $H^{A'}$ or $H^{D'}$), 3.20 (1 H, dd, *J* 16 and 5 Hz, $H^{B'}$ or $H^{C'}$), and 7.73 (3 H, s, Me) (see also Figure 4); τ (CF_3CO_2D) 2.08—2.80 (9 H, m, $H^{B'}$ or $H^{C'}$, and Ar-H), 2.95 (1 H, d, *J* 16 Hz, $H^{D'}$), 3.01 (1 H, s, H^B), 3.20 (1 H, dd, *J* 15 and 6 Hz, $H^{B'}$ or $H^{C'}$), 3.30 (1 H, d, *J* 16 Hz, $H^{A'}$), and 7.72 (3 H, s, Me) (Found: C, 89.9; H, 5.1. $C_{24}H_{16}O$ requires C, 90.0; H, 5.0%).

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