

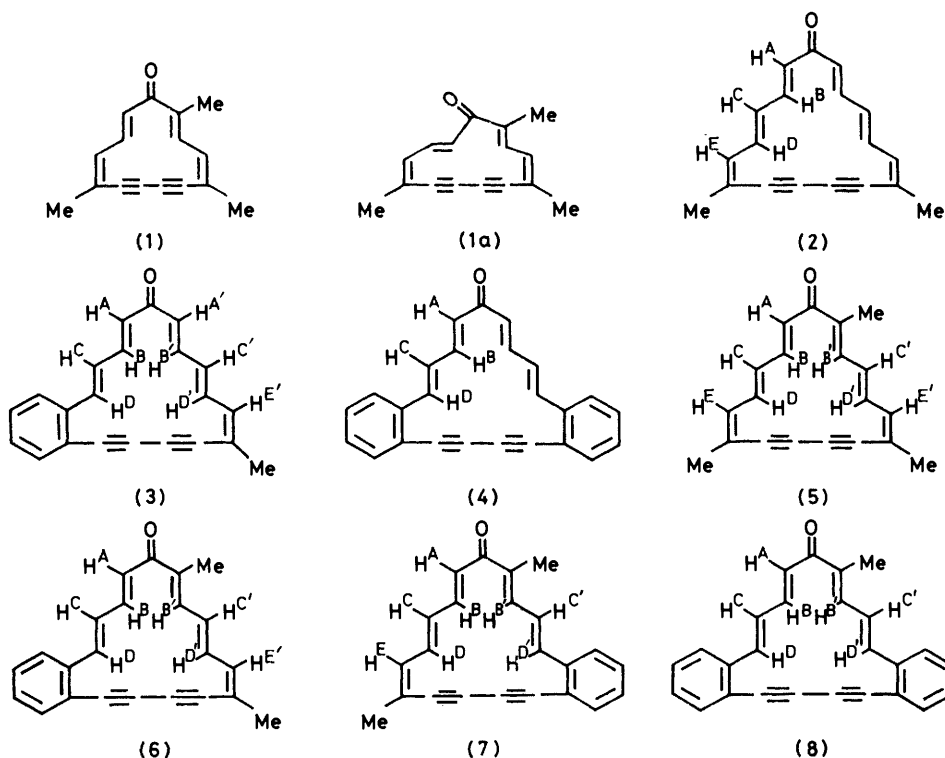
Synthesis and Properties of a Trimethyltetradehydro[17]annulenone and its Benzannelated Derivatives

By Juro Ojima,* Keiko Kanazawa, Kiyomi Kusaki, and Kazuyo Wada, Department of Chemistry, Faculty of Science, Toyama University, Gofuku, Toyama 930, Japan

Syntheses of 2,7,12-trimethyl-8,9,10,11-tetradehydrocycloheptadecenone (5), 10,15- (6) and 8,15-dimethyl-16,17,18,19-tetradehydrobenzocycloheptadecen-9-one (7), and 8-methyl-18,19,20,21-tetradehydrodibenzo[*a,g*]cycloheptadecen-9-one (8) are described. The ^1H n.m.r. spectra of these annulenones and related compounds indicate that the skeleton of the tetradehydro[17]annulenone ring system is more planar and less strained than that of the corresponding [13]annulenones.

It has been found that the methyl substituent adjacent to the ketone group of the paratropic [13]annulenone 2,5,10-trimethyl-6,7,8,9-tetradehydrotridecenone (1) causes a change of conformation due to a rotation of the opposite *trans* double bond so that the molecule exists essentially in the conformation (1a) at -60°C .¹ In the preceding paper, one of us reported the preparation of the benzannelated derivatives of (1), and showed that

ations of the properties of the α -methyl-unsubstituted compounds (2)—(4).⁴ The annulenones (3) and (4) were obtained by a modification of the reported procedure.³ Condensation of 6-(*o*-ethynylphenyl)-3,5-hexadien-2-one³ with (2*E*,4*Z*)-5-methylhepta-2,4-dien-6-ynal (10)³ in the presence of methanolic sodium methoxide gave the corresponding crystalline acyclic ketone (19) in 47% yield.³ The ketone (19) was



both methyl substitution and benzannelation exert a considerable influence on the development of the paratropicity in tetradehydro[13]annulenones of type (1).²

In view of the paratropicity and conformational mobility observed on this tetradehydro[13]annulenone system, we were interested in examining the higher analogue of (1) and its benzannelated derivatives, and with examining further the α -methyl-unsubstituted annulenones (2)—(4), prepared previously.³ This paper is concerned with the syntheses and properties of the title compounds (5)—(8), together with further examin-

oxidatively coupled with anhydrous copper(II) acetate in pyridine-ether at 50°C ⁵ to afford the annulenone (3) in 21% yield. The dibenzannulenone (4) was prepared as reported,³ except that anhydrous copper(II) acetate was used instead of monohydrate in the oxidative coupling step.²

The syntheses of the annulenones (5)—(8) were carried out by reported procedure.^{1,2} Condensation of butan-2-one (9) with (2*E*,4*Z*)-5-methylhepta-2,4-dien-6-ynal (10)³ in the presence of sulphuric acid in acetic acid gave the ketone (11) in 35% yield; this was condensed

TABLE I

Electronic absorption maxima of tetrahydro[17]annulenones in tetrahydrofuran [λ_{\max} , (ϵ_{\max}) values]

(2) ^a	(3)	(4) ^a	(5)	(6)	(7)	(8)
264sh (19 300)			280sh (42 900)	286sh (38 400)	280sh (32 900)	
279sh (42 100)			298 (68 800)	301 (46 100)	297 (42 500)	298sh (44 500)
296 (63 400)	298 (51 900)	296sh (38 400)	307 (70 100)	312 (38 400)	320 (38 600)	314 (49 900)
306 (66 900)	315sh (47 000)	312 (47 000)	356sh (7 900)	402sh (4 100)	405sh (3 500)	373sh (4 700)

^a See ref. 3.

with another mol of (10) using ethanolic potassium hydroxide in tetrahydrofuran to give the acyclic ketone (12) in 45% yield. Oxidation of (12) as before gave the annulenone (5) in 34% yield. Similarly, condensation of (11) with *o*-ethynylcinnamaldehyde (13)⁶ gave the ketone (14) in 30% yield, which was oxidized to the benzannulenone (6) in 20% yield. Reaction of (9) and (13), under the conditions described for that between (9) and (10), afforded the ketone (15) in 50% yield, which was condensed with (10) in the presence of ethanolic potassium hydroxide to give the acyclic ketone (16) in 20% yield. Oxidation of (16) as before afforded the

benzannulenone (7) in 28% yield. Similarly, condensation between (13) and (15) gave the acyclic ketone (17) in 53% yield, which was used to form the dibenzannulenone (8) in 21% yield. The structures of these new compounds were established from their spectral properties as well as elemental analyses.

Treatment of the annulenones (2)–(8) with trifluoroacetic acid or deuteriotrifluoroacetic acid gave the corresponding protonated or deuteriated carbonyl species (2')–(8'): (2') was dark green, (3') deep green, (4') dark red, (5') dark green, (6') deep green, (7') deep green, and (8') dark red. Quenching of (2')–(8') with aqueous

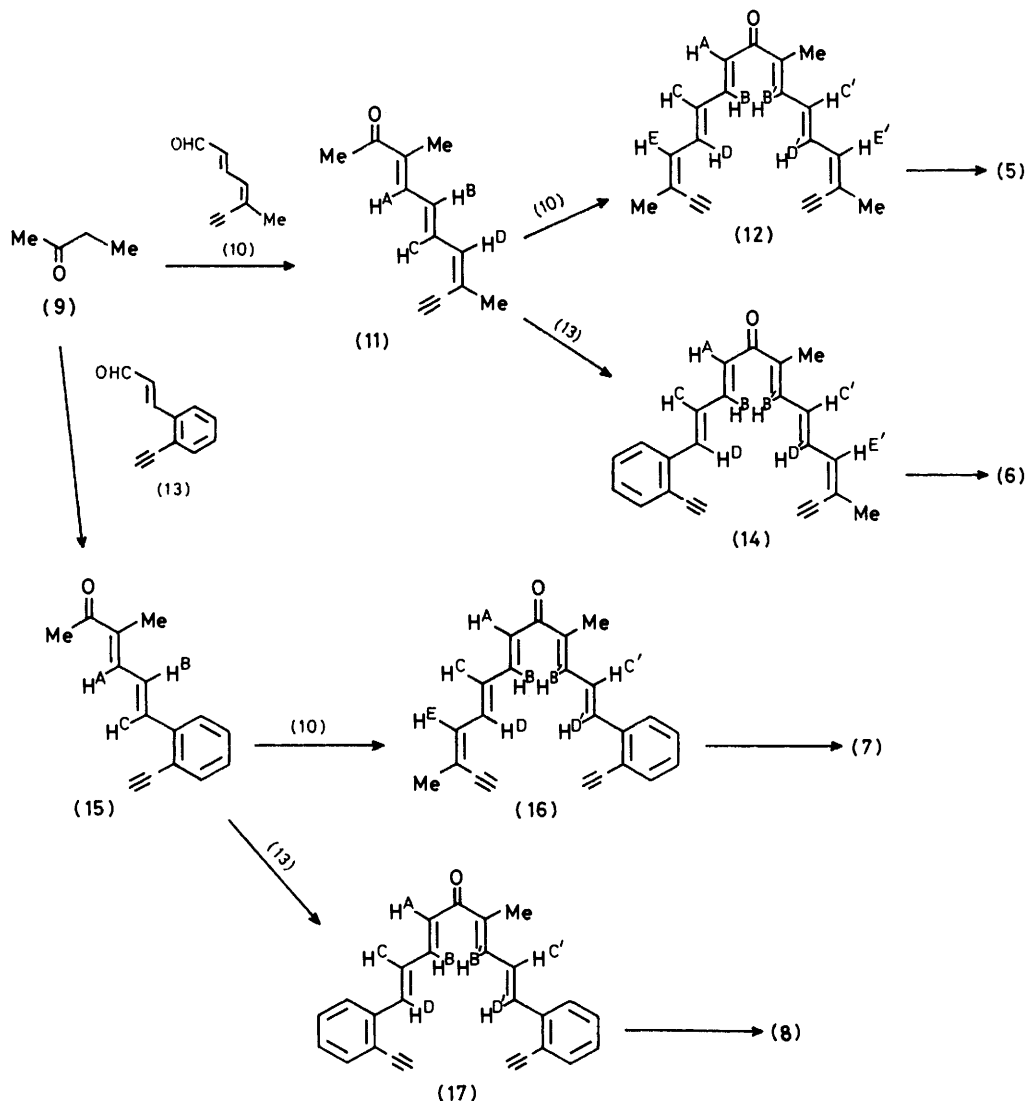


TABLE 2
Electronic absorption maxima of tetradecahydro[17]annulenes in trifluoroacetic acid [λ_{\max} (relative extinction coefficients)]

(2) ^a	(3)	(4)	(5)	(6)	(7)	(8)
		275sh (0.60)				275sh (0.58)
	288 (0.75)	292 (0.71)		286 (0.67)	290 (0.67)	293 (0.69)
		309 (0.81)	316 (0.52)			311 (0.80)
331 (1.00)	332 (1.00)	328 (1.00)	334 (1.00)	335 (1.00)	334 (1.00)	329 (1.00)
343sh (0.92)	341 (0.99)	355sh (0.49)			340 (0.99)	364sh (0.47)
380 (0.21)	404sh (0.53)	395sh (0.41)	393 (0.23)	393sh (0.56)	420 (0.41)	402 (0.40)
	655 (0.05)	572 (0.04)		661 (0.06)	630 (0.07)	581 (0.03)

^a See ref. 3.

TABLE 3

¹H N.m.r. parameters of compounds (2)—(8), (12), (14), (16)—(20) (in CDCl₃) and (2')—(8') (in CF₃CO₂D) at 90 MHz, determined at 35 °C (τ values, internal standard Me₄Si)

	HA	HA'	H ^B	H ^{B'}	H ^C	H ^{C'}	H ^D	H ^{D'}	H ^E	H ^{E'}	ArH	CH ₃
(18)	3.37		2.62 ^a		3.59		2.90 ^a		3.58			7.99
(2)	4.20		1.37 ^b		3.98		1.40 ^b		3.65			8.20
(2')	4.29		-1.68 ^c		4.36		-1.75 ^c		4.09			8.42
$\Delta(2) - (18)$	+0.83		-1.25		+0.39		-1.50		+0.07			+0.21
$\Delta(2') - (18)$	+0.92		-4.30		+0.77		-4.65		+0.51			+0.43
(19)	3.52 ^a	3.45 ^a	(2.3—2.7)		3.02 ^b	3.60 ^b	2.95	(2.3—2.7)		3.54	2.3—2.7	8.00
(3)	4.00 ^c	3.90 ^c	1.79	1.79	3.40 ^d	3.73 ^d	1.95	1.92		3.52	2.4—2.8	8.08
(3')	3.86 ^e	3.83 ^e	0.33 ^f	0.29 ^f	3.49 ^g	3.70 ^g	0.25	0.35		3.75	2.4—2.8	8.15
$\Delta(3) - (19)$	+0.48	+0.53			+0.38	+0.13	-1.00		-0.02			+0.08
$\Delta(3') - (19)$	+0.34	+0.38			+0.47	+0.10	-2.70		+0.21			+0.15
(20)	3.43		(2.3—2.8)		3.05		(2.3—2.8)				2.3—2.8	
(4)	3.92		2.28		3.33		2.08				2.5—2.8	
(4')	3.60		1.18		3.20		1.03				2.4—2.7	
$\Delta(4) - (20)$	+0.49				+0.28							
$\Delta(4') - (20)$	+0.17				+0.15							
(12)	3.17		2.67	2.85	3.50 ^a	3.62 ^a	2.90 ^b	2.92 ^b	3.52 ^c	3.60 ^c		8.00
(5)	3.95		1.31 ^d	1.45	3.81 ^e	3.99 ^e	1.38 ^d	1.62 ^d	3.67 ^f	3.80 ^f		8.16
(5')	4.20		-1.67 ^g	-2.07 ^e	4.45 ^h	4.27 ^h	-1.85 ^g	-1.98 ^g	4.13 ⁱ	4.11 ⁱ		8.21
$\Delta(5) - (12)$	+0.78		-1.36	-1.40	+0.31	+0.37	-1.52	-1.30	+0.15	+0.20		8.23
$\Delta(5') - (12)$	+1.03		-4.34	-4.92	+0.95	+0.65	-4.75	-4.90	+0.61	+0.51		8.43
(14)	(2.30—3.53)											8.12
(6)	4.00		1.93 ^a	2.03	3.53 ^b	3.61 ^b	1.84	2.09 ^a		3.42	2.6—2.8	8.15
(6')	3.85		0.43 ^c	0.33	3.60 ^d	3.73 ^d	0.42	0.63 ^c		3.67	2.7—3.0	8.12
$\Delta(6) - (14)$												8.23
$\Delta(6') - (14)$												+0.15—+0.18—+0.15—+0.26
(16)	3.13		2.47 ^a	3.50	2.90 ^b	(2.4—2.8) ^b	2.43 ^a	2.45	3.65		(2.4—2.8)	7.93
(7)	3.80		1.98 ^c	2.03	3.82 ^d	3.25 ^d	2.17 ^c	1.76	3.53		2.5—2.8	8.01
(7')	3.75		0.36 ^e	0.45	3.87 ^f	3.30 ^f	0.50 ^e	0.22	3.65		2.6—2.9	8.03
$\Delta(7) - (16)$	+0.67		-0.49	-1.47	+0.92		-0.26	-0.69	-0.12			8.13
$\Delta(7') - (16)$	+0.62		-2.11	-3.05	+0.97		-1.93	-2.23	0.00			7.97
(17)	2.99		(2.23—2.82)		2.97 ^a	(2.23—2.82) ^a					2.2—2.8	8.17
(8)	3.85		(2.27—2.77)		3.10 ^b	3.33 ^b	2.07	2.07			2.3—2.8	7.97
(8')	3.67		1.48	1.42	3.10 ^c	3.35 ^c	1.19 ^d	1.23 ^d			2.4—2.7	7.90
$\Delta(8) - (17)$	+0.86				+0.13							+0.08
$\Delta(8') - (17)$	+0.68				+0.13							+0.01

^{a-i} Assignments may be reversed in each group of the column (see Experimental section). However, most probable values are given in Table 3 by referring to the chemical shifts of the related compounds (see refs. 2 and 3).

sodium hydrogencarbonate resulted in regeneration of (2)—(8), respectively.

The electronic absorption maxima of the annulenones (2)—(8) are given in Table 1. As expected, the spectra are similar to those of the corresponding [13]-annulenones^{1,2} except that each band exhibits a bathochromic shift. The absorption maxima of the annu-

lenones (3)—(8) in trifluoroacetic acid are given in Table 2. It is evident that the main maxima of these protonated species shift to longer wavelength, as has been observed for [13]annulenones.^{1,2}

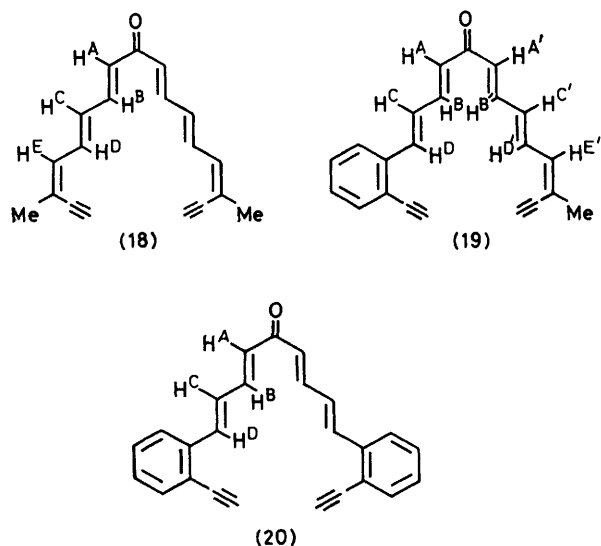
TABLE 4

¹H N.m.r. parameters for compounds (2)—(8) at 100 MHz (τ values)

Compd.	<i>T</i> (°C)	H ^A	H ^{A'}	H ^B	H ^{B'}	H ^C	H ^{C'}	H ^D	H ^{D'}	H ^E	H ^{E'}	ArH	Me
(2)	60	4.20		1.43		3.98		1.52		3.68			8.24
	20	4.21		1.42		4.00		1.44		3.70			8.22
	-60	4.29		1.16		3.98		1.20		3.66			8.20
(3)	60	4.01	4.03	2.04	2.06	3.46	3.78	1.84	2.08		3.52	2.5—2.8	8.14
	20	4.04	4.04	1.85	1.85	3.46	3.78	1.80	2.02		3.52	2.5—2.9	8.12
	-60	4.04	4.08	(1.74—2.00)		3.42	3.74	1.72	(1.74—2.00)		3.45	2.5—2.8	8.10
(4)	60	3.92		2.32		3.34		2.12				2.4—2.8	
	20	3.92		2.30		3.32		2.09				2.5—2.8	
	-60	3.87		2.18		3.26		2.01				2.4—2.7	
(5)	60	3.94		1.41	1.43	(3.62—4.16)		1.45	1.78	(3.62—4.16)			8.19 8.24
	20	3.99		1.36	1.49	3.85	4.03	1.42	1.68	3.67	3.80		8.19 8.24
	-60	4.18		(1.02—1.42)	1.14	(3.60—4.14)		(1.02—1.42)		(3.60—4.14)			8.18 8.22
(6)	60	4.02		2.02	2.09	3.52	3.62	1.88	2.16		3.50	2.6—2.9	8.10 8.14
	20	4.02		1.99	2.05	3.52	3.62	1.86	2.13		3.50	2.6—2.9	8.12 8.15
	-60	4.02		1.97	1.93	3.46	3.56	1.78	1.90		3.42	2.6—2.8	8.10
(7)	60	3.78		2.02	2.10	3.82	3.26	2.26	1.83	3.55		2.5—2.9	8.05 8.16
	20	3.82		2.02	2.07	3.79	3.26	2.19	1.79	3.52		2.4—2.8	8.03 8.14
	-60	3.98		(1.8—2.1)	1.71	3.76	3.25	(1.8—2.1)		3.49		2.4—2.8	8.02 8.12
(8)	60	3.88		(2.3—2.8)		3.14	3.38	2.14	2.16			2.3—2.8	7.99
	20	3.87		(2.3—2.8)		3.11	3.36	2.12	2.14			2.3—2.8	7.97
	-60	3.87		(2.0—2.8)		3.11	3.36	2.06	2.08			2.0—2.8	7.96

The chemical shifts of the olefinic, aromatic, and

(annulenone) and the corresponding acyclic model (up-field shift for the outer protons and downfield for the inner) (Table 3), both the annulenones (2)—(8) and their protonated species (2')—(8') * are seen to be paratropic



methyl protons of these annulenones (2)—(8) at 90 MHz are listed in Table 3, together with those of the corresponding acyclic ketones (12), (14), and (16)—(20). Data for the deuteriated species (2')—(8') of these annulenones, obtained by dissolution in deuteriotrifluoroacetic acid,

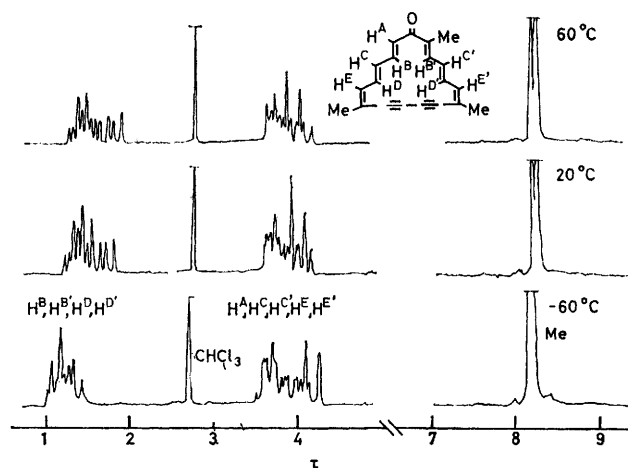


FIGURE 1 100-MHz N.m.r. spectra of [17]annulenone (5) in CDCl_3

molecules. This can be seen from Figures 1 (centre portion of spectrum) and 2 which show the 100-MHz ¹H n.m.r. spectra of (2)—(8) at room temperature. In the spectra of (2)—(8) high- and low-field shifts are

* The small downfield shift of all protons expected to be caused by the positive charge does not significantly affect the argument.

observed for the inner and outer protons, respectively. Also, comparison of the chemical shifts of the olefinic and methyl protons of the annulenones (Table 3 and Figures 1 and 2) shows that the paratropicity of both these annulenones and their deuteriated species decreases in the order (2) \simeq (5), [(2') \simeq (5')] $>$ (3) \simeq

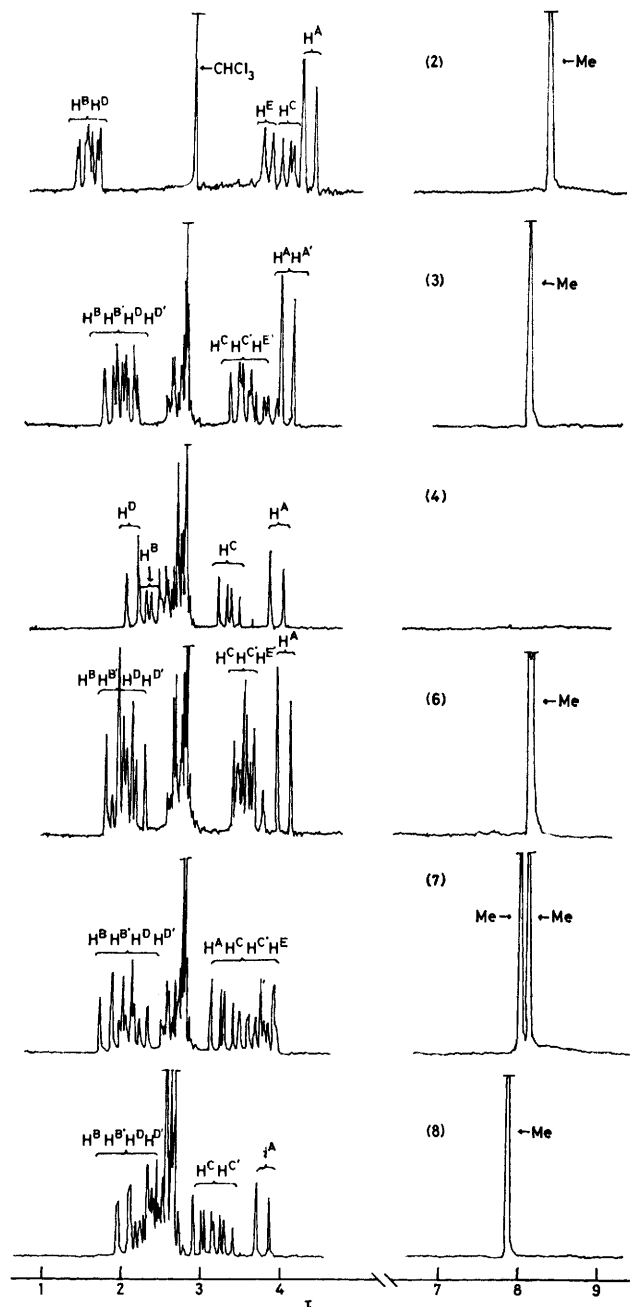


FIGURE 2 100 MHz N.m.r. spectra of the [17]annulenones (2)—(4) and (6)—(8) in CDCl_3 at 20°C

(6) \simeq (7), [(3') \simeq (6') \simeq (7')] $>$ (4) \simeq (8), [(4') \simeq (8')] *i.e.* with increasing number of fused benzene rings on the tetrahydro[17]annulenone system, in accord with results elsewhere.⁷ In contrast, the corresponding methyl-substituted tetrahydro[13]annulenones do not

adhere to this trend, presumably due to the conformational mobility and/or steric strain of the [13]-annulenone ring skeleton, as previously reported.²

Variable-temperature ^1H n.m.r. spectra of (2)—(8) were run at 100 MHz over the range -60 to $+60^\circ\text{C}$, the results of which, summarized in Table 4, show the spectra of all the annulenones (2)—(8) to be essentially temperature-independent. The spectra of the trimethyl-tetrahydro[17]annulenone (5), the higher analogue of the conformationally mobile compound (1), are shown in Figure 1. On cooling, the resonances of the inner protons (H^{B} , $\text{H}^{\text{B}'}$, H^{D} , $\text{H}^{\text{D}'}$) of (5) move to slightly lower field and become unresolved at -60°C . For the outer protons (H^{A} , H^{C} , $\text{H}^{\text{C}'}$, H^{E} , $\text{H}^{\text{E}'}$), however, the expected first-order pattern is observed, and the $J_{\text{B,C}}$ value (11 Hz) of the potentially mobile $\text{H}^{\text{B}}-\text{H}^{\text{C}}$ bond points to an *s-trans* relationship over the range -60 to $+60^\circ\text{C}$, thus excluding any conformational change of (5) between these temperatures. The methyl substituent adjacent to the carbonyl group thus exerts no significant influence upon the skeleton of this tetrahydro[17]annulenone ring system, in contrast to the case for the [13]-annulenone system.^{1,2}

In conclusion, the results suggest that the skeleton of the tetrahydro[17]annulenone system is more planar and less strained than that of the [13]annulenones, in accordance with predictions using molecular models.

EXPERIMENTAL

Deoxygenated ether and tetrahydrofuran (THF) were used and prepared as described.² I.r. and u.v. spectra were taken with Hitachi EPI S-2 and 124 spectrophotometers respectively. N.m.r. spectra were recorded with a Varian EM-390 or a JEOL FX-100 spectrometer at 100 MHz (Me_4Si as an internal standard). Merck alumina (activity II—III) was used for column chromatography.

1-(*o*-Ethynylphenyl)-11-methyltrideca-1,3,6,8,10-pentaen-12-yn-5-one (19).—This compound was prepared by a modification of the previously described method.³ A solution of the diene aldehyde (10) (0.80 g, 6.7 mmol) in deoxygenated ether (10 ml) was added dropwise over 40 min to a stirred solution of 6-(*o*-ethynylphenyl)hexa-3,5-dien-2-one³ (1.00 g, 5.1 mmol) in ether (40 ml) containing methanolic sodium methoxide (3 ml) [from sodium (380 mg) and dry methanol (100 ml)] in an ice-bath. After stirring for a further 1 h at the same temperature, further sodium methoxide (2 ml) was added. The reaction was allowed to continue for a further 3 h at room temperature and then quenched by addition of aqueous oxalic acid. The mixture was extracted with benzene and the benzene extracts were worked up as usual to afford a liquid which was chromatographed on alumina (100 g). Elution with hexane-ether (7:3) gave the ketone (19) (709 mg, 47%). Recrystallization from hexane-benzene afforded yellow needles, m.p. $127-128^\circ\text{C}$; m/e 298 (M^+ , 100%); M , 298.4; ν_{max} (KBr) 3 300, 3 250 ($-\text{C}=\text{CH}$), 2 100, 2 030 ($-\text{C}=\text{C}-$), 1 655, 1 610, 1 595 ($\text{C}=\text{O}$, $\text{C}=\text{C}$), and 1 010 cm^{-1} (*trans*- $\text{C}=\text{C}$); λ_{max} (THF) 262sh (ϵ 16 400), 271 (18 400), 288sh (16 000), and 378 nm (43 900); $\tau(\text{CDCl}_3; 90 \text{ MHz})$ 2.3—2.7 (7 H, m, H^{B} , $\text{H}^{\text{B}'}$, H^{D} , and ArH), 2.95 (1 H, d, J 16 Hz, H^{D}), 3.02 (1 H, dd, J 16 and 11 Hz, H^{C} or $\text{H}^{\text{C}'}$), 3.45 (1 H, d, J 16 Hz, H^{A} or $\text{H}^{\text{A}'}$), 3.52 (1 H, d, J 16 Hz, H^{A} or $\text{H}^{\text{A}'}$), 3.54 (1 H, d, J

11 Hz, H^E), 3.60 (1 H, dd, *J* 16 and 11 Hz, H^C or H^{C'}), 6.58 (1 H, s, -C≡CH), 6.62 (1 H, s, -C≡CH), and 8.00 (3 H, s, CH₃) (Found: C, 88.6; H, 5.8. C₂₂H₁₈O requires C, 88.6; H, 6.1%).

15-Methyl-16,17,18,19-tetrahydrobenzocycloheptadecen-9-one (3).—A solution of the ketone (19) (277 mg, 9.3 mmol) in pyridine-dry ether (3:1; 22 ml) was added during 50 min to a solution of anhydrous copper(II) acetate (1.2 g) in pyridine-dry ether (3:1; 48 ml) at 52–56 °C (bath temp.). The solution was stirred at the same temperature for a further 2.4 h and cooled. After addition of benzene (100 ml), the mixture was filtered through Hyflo Super-Cel. The precipitates were washed with benzene, and the filtrate was poured into 3*N*-hydrochloric acid (300 ml). The organic layer was separated and the aqueous layer extracted with benzene. The combined organic layer and extracts were washed with 3*N*-hydrochloric acid, aqueous sodium hydrogencarbonate, and brine, and then dried (Na₂SO₄). The semi-solid obtained after removal of solvent was chromatographed on alumina (80 g). Elution with ether-hexane (13:7) afforded the benzannulene (3) (58 mg, 21%), which crystallized as yellow *cubes* from benzene, m.p. 181 °C (decomp.); *m/e* 296 (*M*⁺, 42%) and 252 (100); *M* 296.4; *v*_{max} (KBr) 2 200 (-C≡C-), 1 630 (C=O), 1 590 (C=C), and 998 cm⁻¹ (*trans*-C=C); for u.v. data see Table 1; τ(CDCl₃; 90 MHz) 1.79 (2 H, dd, *J* 16 and 11 Hz, H^B and H^{B'}), 1.92 (1 H, dd, *J* 16 and 11 Hz, H^{D'}), 1.95 (1 H, d, *J* 16 Hz, H^D), 2.4–2.8 (4 H, m, ArH), 3.40 (1 H, dd, *J* 16 and 11 Hz, H^C or H^{C'}), 3.52 (1 H, d, *J* 11 Hz, H^E), 3.73 (1 H, dd, *J* 16 and 11 Hz, H^C or H^{C'}), 3.98 (1 H, d, *J* 16 Hz, H^A or H^{A'}), 4.00 (1 H, d, *J* 16 Hz, H^A or H^{A'}), 8.08 (3 H, s, CH₃) and see Figure 2; τ(CF₃CO₂D; 90 MHz) 0.25 (1 H, d, *J* 16 Hz, H^D), 0.29 (1 H, dd, *J* 16 and 11 Hz, H^B or H^{B'}), 0.33 (1 H, dd, *J* 16 and 11 Hz, H^B or H^{B'}), 0.35 (1 H, dd, *J* 16 and 11 Hz, H^{D'}), 2.4–2.8 (4 H, m, ArH), 3.49 (1 H, dd, *J* 16 and 11 Hz, H^C or H^{C'}), 3.70 (1 H, dd, *J* 16 and 11 Hz, H^C or H^{C'}), 3.75 (1 H, d, *J* 11 Hz, H^{E'}), 3.83 (1 H, d, *J* 16 Hz, H^A or H^{A'}), 3.86 (1 H, d, *J* 16 Hz, H^A or H^{A'}), and 8.15 (3 H, s, CH₃) (Found: C, 89.3; H, 5.6. C₂₂H₁₆O requires C, 89.2; H, 5.4%).

1,9-Bis-(*o*-ethynylphenyl)nona-1,3,6,8-tetraen-5-one (20).—This compound was prepared as previously.³ In our earlier paper H^B and H^C protons were wrongly assigned: τ(CDCl₃; 90 MHz) 2.3–2.8 (12 H, m, H^B, H^D, and ArH), 3.05 (2 H, dd, *J* 15 and 11 Hz, H^C), 3.43 (2 H, d, *J* 15 Hz, H^A), and 6.63 (2 H, s, -C≡CH).

18,19,20,21-Tetrahydrodibenzo[*a,g*]cycloheptadecen-9-one (4).—This compound was prepared from (20) employing anhydrous copper(II) acetate (instead of monohydrate³) in pyridine-dry ether as in the preparation of (3); the yield was 55%.

3,8-Dimethyldeca-3,5,7-trien-9-yn-2-one (11).—A solution of (*2E,4Z*)-5-methylhepta-2,4-dien-6-ynal (10)³ (1.2 g, 10 mmol) in acetic acid (6.5 ml) was added dropwise over 20 min to a stirred solution of butan-2-one (9) (6.0 g, 84 mmol) and concentrated sulphuric acid (1.0 ml) in acetic acid (38 ml) at 6–10 °C. The reaction was continued for a further 6 h at 10 °C. The mixture was then cautiously poured into saturated aqueous potassium carbonate (67 g, 250 ml). After addition of benzene (50 ml), the mixture was filtered through Hyflo Super-Cel. The precipitates were washed with benzene (50 ml × 2) and the organic layer was washed with brine and dried (Na₂SO₄). Chromatography of the product over alumina (150 g) with hexane-ether (7:3) as eluant gave the ketone (11)

(480 mg, 35%) as a solid. Recrystallization from cyclohexane afforded orange *needles*, m.p. 82–83 °C; *m/e* 174 (*M*⁺, 100%); *M*, 174.2; *v*_{max} (KBr) 3 300 (-C≡CH), 2 100 (-C≡C-), 1 655, 1 620, 1 600 (C=O, C=C), 995, and 975 cm⁻¹ (*trans*-C=C); *λ*_{max} (EtOH) 237 (ε 6 400), 332 (34 100), and 343sh nm (33 500); τ(CDCl₃; 90 MHz) 2.93 (1 H, d, *J* 11 Hz, H^A), 3.01 (1 H, dd, *J* 16 and 11 Hz, H^C), 3.50 (1 H, dd, *J* 16 and 11 Hz, H^B), 3.63 (1 H, d, *J* 11 Hz, H^D), 6.67 (1 H, s, -C≡CH), 7.72 (3 H, s, CH₃), 8.07 (3 H, s, CH₃), and 8.17 (3 H, s, CH₃) (Found: C, 82.5; H, 8.2. C₁₂H₁₄O requires C, 82.7; H, 8.1%).

3,8,15-Trimethylheptadeca-3,5,7,10,12,14-hexaen-1,16-diyn-9-one (12).—Potassium hydroxide (0.084 g) in absolute ethanol (1.1 ml) was added to a solution of the ketone (11) (0.35 g, 2.0 mmol) in dry THF (6.0 ml), and a solution of the diyne aldehyde (10)³ (0.35 g, 2.9 mmol) in dry tetrahydrofuran (1.8 ml) was added during 5 min with stirring at 21–24 °C. After stirring for a further 7 h at the same temperature, the reaction was quenched by addition of acetic acid (0.7 ml). The solution was poured into water (100 ml) and the mixture was extracted with benzene. The benzene extracts were filtered through Hyflo Super-Cel to remove polymeric compounds. The filtrate was washed with aqueous sodium hydrogencarbonate and brine, and dried (Na₂SO₄). Removal of the solvent left a dark red liquid which was chromatographed on alumina (90 g). The initial fractions gave the recovered ketone (10) (110 mg). Later fractions (30% ether-hexane as eluant) gave the ketone (12) (250 mg, 45%). Crystallization from hexane-benzene afforded yellow *cubes*, m.p. 102–104 °C; *m/e* 276 (*M*⁺, 88%) and 223 (100); *M*, 276.4; *v*_{max} (KBr) 3 270 (-C≡CH), 2 100 (-C≡C-), 1 635, 1 595, 1 580 (C=O, C=C), 1 000, and 975 cm⁻¹ (*trans*-C=C); *λ*_{max} (THF) 230 (ε 8 900), 270sh (18 100), 284sh (25 500), 295 (26 800), 308 (26 300), 325 (27 500), 359sh (40 300), 378 (46 600), and 396sh nm (39 500); τ(CDCl₃; 90 MHz) 2.67 (1 H, dd, *J* 16 and 11 Hz, H^B), 2.85 (1 H, d, *J* 11 Hz, H^{B'}), 2.90 (1 H, dd, *J* 16 and 11 Hz, H^D or H^{D'}), 2.92 (1 H, dd, *J* 16 and 11 Hz, H^D or H^{D'}), 3.17 (1 H, d, *J* 16 Hz, H^A), 3.50 (1 H, dd, *J* 16 and 11 Hz, H^C or H^{C'}), 3.52 (1 H, d, *J* 11 Hz, H^B or H^{B'}), 3.60 (1 H, d, *J* 11 Hz, H^B or H^{B'}), 3.62 (1 H, dd, *J* 16 and 11 Hz, H^C or H^{C'}), 6.59 (2 H, s, -C≡CH), and 8.00 (9 H, s, CH₃) (Found: C, 86.9; H, 7.2. C₂₀H₂₀O requires C, 86.9; H, 7.3%).

2,7,12-Trimethyl-8,9,10,11-tetrahydrocycloheptadecenone (5).—A solution of the ketone (12) (0.19 g, 0.68 mmol) in pyridine-dry ether (3:1; 15 ml) was added dropwise during 15 min to a stirred solution of anhydrous copper(II) acetate (0.89 g) in pyridine-dry ether (3:1; 32 ml) at 52–54 °C (bath temp.). The solution was stirred at 47–49 °C for a further 2 h and cooled. After work-up as in the isolation of (3), the product was chromatographed on alumina (80 g). Elution with 40% ether-hexane gave the annulene (5) (65 mg, 34%) which crystallized from hexane-benzene as red *needles*, m.p. 163–164 °C; *m/e* 274 (*M*⁺, 100%); *M*, 274.3; *v*_{max} (KBr) 2 170 (-C≡C-), 1 648, 1 620, 1 595 (C=O, C=C), 1 010, 980, and 970 cm⁻¹ (*trans*-C=C); for u.v. data see Table 1; τ(CDCl₃; 90 MHz) 1.31 (1 H, dd, *J* 16 and 11 Hz, H^B, H^D, or H^{D'}), 1.38 (1 H, dd, *J* 16 and 11 Hz, H^B, H^D, or H^{D'}), 1.45 (1 H, d, *J* 11 Hz, H^{B'}), 1.62 (1 H, dd, *J* 16 and 11 Hz, H^B, H^D, or H^{D'}), 3.67 (1 H, d, *J* 11 Hz, H^B or H^{B'}), 3.80 (1 H, d, *J* 11 Hz, H^B or H^{B'}), 3.81 (1 H, dd, *J* 16 and 11 Hz, H^C or H^{C'}), 3.95 (1 H, d, *J* 16 Hz, H^A), 3.99 (1 H, dd, *J* 16 and 11 Hz, H^C or H^{C'}), 8.16 (3 H, s, CH₃), and 8.21 (6 H, s, CH₃) (see also Figure 1);

$\tau(\text{CF}_3\text{CO}_2\text{D}; 90 \text{ MHz}) -2.07$ (1 H, d, J 11 Hz, H^{B}), -1.98 (1 H, dd, J 16 and 11 Hz, H^{B} , H^{D} , or $\text{H}^{\text{D}'}$), -1.85 (1 H, dd, J 16 and 11 Hz, H^{B} , H^{D} , or $\text{H}^{\text{D}'}$), -1.67 (1 H, dd, J 16 and 11 Hz, H^{B} , H^{D} , or $\text{H}^{\text{D}'}$), 4.11 (1 H, d, J 11 Hz, H^{E} or $\text{H}^{\text{E}'}$), 4.13 (1 H, d, J 11 Hz, H^{E} or $\text{H}^{\text{E}'}$), 4.20 (1 H, d, J 16 Hz, H^{A}), 4.27 (1 H, dd, J 16 and 11 Hz, H^{C} or $\text{H}^{\text{C}'}$), 4.45 (1 H, dd, J 16 and 11 Hz, H^{C} or $\text{H}^{\text{C}'}$), 8.23 (3 H, s, CH_3), and 8.43 (6 H, s, CH_3) (Found: C, 87.65; H, 6.5. $\text{C}_{20}\text{H}_{18}\text{O}$ requires C, 87.6; H, 6.6%).

6,11-Dimethyl-1-(*o*-ethynylphenyl)trideca-1,3,6,8,10-penta-en-12-yn-5-one (14).—A solution of potassium hydroxide (0.12 g) in ethanol (1.5 ml) was added to a solution of the ketone (11) (0.72 g, 4.1 mmol) in dry THF (12 ml), and a solution of *o*-ethynylcinnamaldehyde (13)⁹ (0.95 g, 6.0 mmol) in dry THF (3.5 ml) was then added during 10 min with stirring at 24–25 °C. After stirring for a further 4 h at the same temperature, the reaction was quenched by addition of acetic acid (1.1 ml). The solution was then poured into water (100 ml), and the mixture extracted with benzene. After the usual work-up, the dark red liquid obtained was chromatographed on alumina (150 g). Initial fractions gave the recovered ketone (11) (210 mg). Later fractions, eluted with hexane–ether (7 : 3), gave the desired ketone (14) (380 mg, 30%) as a solid. Recrystallization from hexane–benzene afforded yellow cubes, m.p. 81–83 °C; m/e 312 (M^+ , 60%) and 175 (100); M , 312.4; ν_{max} (KBr) 3 250 ($-\text{C}=\text{CH}$), 2 100 ($-\text{C}\equiv\text{C}-$), 1 635, 1 610, 1 595 ($\text{C}=\text{O}$, $\text{C}=\text{C}$), 995, and 970 cm^{-1} (*trans*- $\text{C}=\text{C}$); λ_{max} (THF) 236 (ϵ 19 700), 260sh (19 600), 268 (22 000), 290sh (25 100), 302 (27 500), 315 (27 400), 359sh (39 800), 374 (44 000), and 392sh nm (36 000); $\tau(\text{CDCl}_3; 90 \text{ MHz})$ 2.30–3.53 (12 H, m, olefinic and aromatic H), 6.55 (1 H, s, $-\text{C}=\text{CH}$), 6.59 (1 H, s, $-\text{C}=\text{CH}$), and 7.97 (6 H, s, CH_3) (Found: C, 88.6; H, 6.6. $\text{C}_{23}\text{H}_{20}\text{O}$ requires C, 88.4; H, 6.45%).

10,15-Dimethyl-16,17,18,19-tetradehydrobenzocycloheptadecen-9-one (6).—A solution of the ketone (14) (0.18 g, 0.58 mmol) in pyridine–dry ether (3 : 1; 12 ml) was added during 20 min to a stirred solution of anhydrous copper(II) acetate (0.7 g) in pyridine–dry ether (3 : 1; 28 ml) at 50–53 °C (bath temp.). The solution was stirred at 45–47 °C for a further 2 h and cooled. After addition of benzene (50 ml), the mixture was poured into 3*N*-hydrochloric acid (160 ml). The organic layer, combined with the benzene extracts from the aqueous layer, was washed with 3*N*-hydrochloric acid, water, saturated aqueous sodium hydrogencarbonate, and brine and then dried (Na_2SO_4). After removal of solvent, the residual dark red liquid was chromatographed on alumina (160 g). Elution with 30% ether–hexane gave the benzannulenone (6) (36 mg, 20%) as a solid. Recrystallization from benzene afforded orange needles, m.p. 165–166 °C; m/e 310 (M^+ , 100%); M , 310.4; ν_{max} (KBr) 2 200 ($-\text{C}\equiv\text{C}-$), 1 630 ($\text{C}=\text{O}$), 1 595 ($\text{C}=\text{C}$), 1 005, 990, and 970 cm^{-1} (*trans*- $\text{C}=\text{C}$); for u.v. data see Table 1; $\tau(\text{CDCl}_3; 90 \text{ MHz})$ 1.84 (1 H, d, J 16 Hz, H^{D}), 1.95 (1 H, dd, J 16 and 11 Hz, H^{B} or H^{D}), 2.03 (1 H, d, J 11 Hz, H^{B}), 2.09 (1 H, dd, J 16 and 11 Hz, H^{B} or H^{D}), 2.6–2.8 (4 H, m, ArH), 3.42 (1 H, d, J 11 Hz, H^{E}), 3.53 (1 H, dd, J 16 and 11 Hz, H^{C} or $\text{H}^{\text{C}'}$), 3.61 (1 H, dd, J 16 and 11 Hz, H^{C} or $\text{H}^{\text{C}'}$), 4.00, (1 H, d, J 16 Hz, H^{A}), 8.12 (3 H, s, CH_3), and 8.15 (3 H, s, CH_3) (see also Figure 2); $\tau(\text{CF}_3\text{CO}_2\text{D}; 90 \text{ MHz})$ 0.33 (1 H, d, J 11 Hz, H^{B}), 0.42 (1 H, d, J 15 Hz, H^{D}), 0.43 (1 H, dd, J 15 and 11 Hz, H^{B} or H^{D}), 0.63 (1 H, dd, J 15 and 11 Hz, H^{B} or H^{D}), 2.7–3.0 (4 H, m, ArH), 3.60 (1 H, dd, J 15 and 11 Hz, H^{C} or $\text{H}^{\text{C}'}$), 3.67 (1 H, d, J 11 Hz, H^{E}), 3.73 (1 H, dd, J 15 and 11 Hz, H^{C} or $\text{H}^{\text{C}'}$), 3.85 (1 H, d, J 15 Hz, H^{A}),

8.12 (3 H, s, CH_3), and 8.23 (3 H, s, CH_3) (Found: C, 89.0; H, 5.9. $\text{C}_{23}\text{H}_{18}\text{O}$ requires C, 89.0; H, 5.85%).

6-(*o*-Ethynylphenyl)-3-methylhexa-3,5-dien-2-one (15).—A solution of *o*-ethynylcinnamaldehyde (13) (2.0 g, 12.8 mmol) in acetic acid (10 ml) was added dropwise over 20 min to a stirred solution of butan-2-one (9) (3.9 g, 55 mmol) and concentrated sulphuric acid (1.1 ml) in acetic acid (50 ml). The resultant dark red solution was stirred for a further 24 h at room temperature, and then cautiously poured into saturated aqueous potassium carbonate. After work-up as for the isolation of (11), the residue was chromatographed on alumina (180 g) with light petroleum–ether (7 : 3) as eluant, giving the ketone (15) (1.34 g, 50%), which crystallized as yellow cubes from hexane–benzene, m.p. 80–81 °C; m/e 210 (M^+ , 100%); M , 210.3; ν_{max} (KBr) 3 250 ($-\text{C}=\text{CH}$), 2 100 ($-\text{C}\equiv\text{C}-$), 1 650 ($\text{C}=\text{O}$), 1 620 ($\text{C}=\text{C}$), and 995 cm^{-1} (*trans*- $\text{C}=\text{C}$); λ_{max} (EtOH) 220 (ϵ 10 900), 233 (8 900), 248sh (9 400), 255 (12 700), 263 (12 100), 327 (25 100), and 331 nm (25 500); $\tau(\text{CDCl}_3; 90 \text{ MHz})$ 2.25–2.85 (7 H, m, olefinic and aromatic H), 6.60 (1 H, s, $-\text{C}=\text{CH}$), 7.58 (3 H, s, CH_3), and 8.00 (3 H, s, CH_3) (Found: C, 85.4; H, 6.4. $\text{C}_{15}\text{H}_{14}\text{O}$ requires C, 85.7; H, 6.7%).

4,11-Dimethyl-1-(*o*-ethynylphenyl)trideca-1,3,6,8,10-penta-en-12-yn-5-one (16).—Potassium hydroxide (0.17 g) in absolute ethanol (3 ml) was added to a solution of the ketone (15) (1.34 g, 6.4 mmol) in dry THF (19 ml). A solution of the dienyne aldehyde (10)³ (1.1 g, 9.4 mmol) in dry THF (6 ml) was then added during 15 min with stirring at 24–26 °C. After stirring for a further 4 h at the same temperature, the reaction was quenched by addition of acetic acid (1.0 ml). The mixture was poured into water (200 ml) and extracted with benzene. After the usual work-up, the red liquid obtained was chromatographed on alumina (110 g) with hexane–ether (1 : 1) to give the ketone (16) (0.40 g, 20%), obtained as yellow cubes from hexane–benzene, m.p. 122–123 °C; m/e 312 (M^+ , 100%); M , 312.4; ν_{max} (KBr) 3 300 ($-\text{C}=\text{CH}$), 2 100 ($-\text{C}\equiv\text{C}-$), 1 645, 1 620, 1 590 ($\text{C}=\text{O}$, $\text{C}=\text{C}$), and 995 cm^{-1} (*trans*- $\text{C}=\text{C}$); λ_{max} (THF) 260sh (ϵ 16 300), 268 (18 100), 288 (17 700), and 317sh nm (19 900); $\tau(\text{CDCl}_3; 90 \text{ MHz})$ 2.4–2.8 (5 H, m, H^{C} or $\text{H}^{\text{C}'}$, and ArH), 2.43 (1 H, dd, J 16 and 11 Hz, H^{B} or H^{D}), 2.45 (1 H, d, J 16 Hz, H^{D}), 2.47 (1 H, dd, J 16 and 11 Hz, H^{B} or H^{D}), 2.90 (1 H, dd, J 16 and 11 Hz, H^{C} or $\text{H}^{\text{C}'}$), 3.13 (1 H, d, J 16 Hz, H^{A}), 3.50 (1 H, d, J 11 Hz, H^{B}), 3.65 (1 H, d, J 11 Hz, H^{E}), 6.57 (2 H, s, $-\text{C}=\text{CH}$), 7.93 (3 H, s, CH_3), and 8.01 (3 H, s, CH_3) (Found: C, 88.6; H, 6.4. $\text{C}_{23}\text{H}_{20}\text{O}$ requires C, 88.4; H, 6.45%).

8,15-Dimethyl-16,17,18,19-tetradehydrobenzocycloheptadecen-9-one (7).—A solution of the ketone (16) (0.27 g, 0.86 mmol) in pyridine–dry ether (3 : 1, 19 ml) was added dropwise during 1 h to a stirred solution of anhydrous copper(II) acetate (1.1 g) in pyridine–dry ether (3 : 1; 40 ml) at 45–50 °C (bath temp.). After stirring for a further 2 h at 43–45 °C, the solution was cooled. After addition of benzene (50 ml), the reaction mixture was filtered through Hyflo Super-Cel. The precipitates formed were washed with benzene (35 ml \times 2), and the filtrate was poured into 3*N*-hydrochloric acid (300 ml). The organic layer was combined with benzene extracts from the aqueous layer and washed with 3*N*-hydrochloric acid until it turned acidic, and then with water, aqueous sodium hydrogencarbonate, and brine. Drying (Na_2SO_4) followed by removal of solvent gave a residue which was chromatographed on alumina (110 g) with hexane–ether (45 : 55) as eluant to give the benzannulenone (7) (74 mg, 28%), which crystal-

lized from benzene as yellow *cubes*, m.p. 160–161 °C; m/e 310 (M^+ , 100%); M , 310.4; ν_{\max} (KBr) 2 200 ($-\text{C}\equiv\text{C}-$), 1 645, 1 620, 1 595 ($\text{C}=\text{O}$, $\text{C}=\text{C}$), 1 005, 975, and 960 cm^{-1} (*trans*- $\text{C}=\text{C}$); for u.v. data see Table 1; $\tau(\text{CDCl}_3; 90 \text{ MHz})$ 1.76 (1 H, d, J 16 Hz, H^{D}), 1.98 (1 H, dd, J 16 and 11 Hz, H^{B} or H^{D}), 2.03 (1 H, d, J 11 Hz, H^{B}), 2.17 (1 H, dd, J 16 and 11 Hz, H^{B} or H^{D}), 2.45–2.83 (4 H, m, ArH), 3.25 (1 H, dd, J 16 and 11 Hz, H^{C} or $\text{H}^{\text{C}'}$), 3.53 (1 H, d, J 11 Hz, H^{E}), 3.80 (1 H, d, J 16 Hz, H^{A}), 3.82 (1 H, dd, J 16 and 11 Hz, H^{C} or $\text{H}^{\text{C}'}$), 8.03 (3 H, s, CH_3), and 8.13 (3 H, s, CH_3) (see also Figure 2); $\tau(\text{CF}_3\text{CO}_2\text{D}; 90 \text{ MHz})$ 0.22 (1 H, d, J 15 Hz, H^{D}), 0.36 (1 H, dd, J 15 and 11 Hz, H^{B} or H^{D}), 0.45 (1 H, d, J 11 Hz, $\text{H}^{\text{B}'}$), 0.50 (1 H, dd, J 15 and 11 Hz, H^{B} or H^{D}), 2.60–2.89 (4 H, m, ArH), 3.30 (1 H, dd, J 15 and 11 Hz, H^{C} or $\text{H}^{\text{C}'}$), 3.65 (1 H, d, J 11 Hz, H^{E}), 3.75 (1 H, d, J 15 Hz, H^{A}), 3.87 (1 H, dd, J 15 and 11 Hz, H^{C} or $\text{H}^{\text{C}'}$), 7.97 (3 H, s, CH_3), and 8.17 (3 H, s, CH_3) (Found: C, 88.8; H, 5.7. $\text{C}_{23}\text{H}_{18}\text{O}$ requires C, 89.0; H, 5.85%).

1,9-Bis-(*o*-ethynylphenyl)-4-methylnona-1,3,6,8-tetraen-5-one (17).—Potassium hydroxide (0.17 g) in absolute ethanol (3 ml) was added to a solution of the ketone (11) (1.3 g, 6.4 mmol) in dry THF (19 ml). A solution of *o*-ethynylcinnamaldehyde (13) (1.5 g, 9.4 mmol) in dry THF (6.4 ml) was then added during 15 min with stirring at 23–25 °C. The reaction was continued for a further 4 h at the same temperature and then quenched by addition of acetic acid (1.4 ml). The resultant solution was poured into water (160 ml), and the reaction mixture was extracted with benzene. The usual work-up gave a liquid which was chromatographed on alumina (180 g) with light petroleum–ether (4 : 6) as eluant to give the ketone (17) (1.18 g, 53%), which crystallized from hexane–benzene as yellow *cubes*, m.p. 130–131 °C; m/e 348 (M^+ , 100%); M , 348.4; ν_{\max} (KBr) 3 300 ($-\text{C}\equiv\text{CH}$), 2 100 ($-\text{C}\equiv\text{C}-$), 1 640, 1 620, 1 580 ($\text{C}=\text{O}$, $\text{C}=\text{C}$), and 1 005 cm^{-1} (*trans*- $\text{C}=\text{C}$); λ_{\max} (THF) 265 (ϵ 13 000) and 367 (23 600); $\tau(\text{CDCl}_3; 90 \text{ MHz})$ 2.23–2.82 (13 H, m, H^{C} or $\text{H}^{\text{C}'}$, H^{B} , $\text{H}^{\text{B}'}$, H^{D} , $\text{H}^{\text{D}'}$, and ArH), 2.97 (1 H, dd, J 15 and 11 Hz, H^{C} or $\text{H}^{\text{C}'}$), 2.99 (1 H, d, J 15 Hz, H^{A}), 6.60 (1 H, s, $-\text{C}\equiv\text{CH}$), 6.61 (1 H, s, $-\text{C}\equiv\text{CH}$), and 7.89 (3 H, s, CH_3) (Found: C, 89.6; H, 5.6. $\text{C}_{26}\text{H}_{20}\text{O}$ requires C, 89.6; H, 5.8%).

8-Methyl-18,19,20,21-tetrahydrodibenzo[*a,g*]cycloheptadecen-9-one (8).—A solution of the ketone (17) (0.98 g,

2.8 mmol) in pyridine–dry ether (3 : 1, 60 ml) was added dropwise during 1.5 h to a stirred solution of anhydrous copper(II) acetate (3.5 g) in pyridine–dry ether (3 : 1; 130 ml) at 48–53 °C (bath temp.). After stirring for a further 2 h at this temperature, the solution was cooled. Work-up as for the isolation of (7) gave a semi-solid which was chromatographed on alumina (120 g) with light petroleum–ether (7 : 3) as eluant to give the dibenzannulene (8) (0.21 g, 21%), which crystallized from benzene as yellow *cubes*, m.p. 206–207 °C; m/e 346 (M^+ , 65%) and 303 (100); M , 346.4; ν_{\max} (KBr) 2 200 ($-\text{C}\equiv\text{C}-$), 1 630, 1 590 ($\text{C}=\text{O}$, $\text{C}=\text{C}$), and 1 005 cm^{-1} (*trans*- $\text{C}=\text{C}$); for u.v. data see Table 1; $\tau(\text{CDCl}_3; 90 \text{ MHz})$ 2.07 (2 H, d, J 16 Hz, H^{D} and $\text{H}^{\text{D}'}$), 2.27–2.77 (10 H, m, H^{B} or $\text{H}^{\text{B}'}$, and ArH), 3.10 (1 H, dd, J 16 and 11 Hz, H^{C} or $\text{H}^{\text{C}'}$), 3.33 (1 H, dd, J 16 and 11 Hz, H^{C} or $\text{H}^{\text{C}'}$), 3.85 (1 H, d, J 16 Hz, H^{A}), 7.97 (3 H, s, CH_3) (see also Figure 2); $\tau(\text{CF}_3\text{CO}_2\text{D}; 90 \text{ MHz})$ 1.19 (1 H, d, J 15 Hz, H^{D} or $\text{H}^{\text{D}'}$), 1.23 (1 H, d, J 15 Hz, H^{D} or $\text{H}^{\text{D}'}$), 1.42 (1 H, d, J 11 Hz, $\text{H}^{\text{B}'}$), 1.48 (1 H, dd, J 15 and 11 Hz, H^{B}), 2.45–2.72 (8 H, m, ArH), 3.10 (1 H, dd, J 15 and 11 Hz, H^{C} or $\text{H}^{\text{C}'}$), 3.35 (1 H, dd, J 15 and 11 Hz, H^{C} or $\text{H}^{\text{C}'}$), 3.67 (1 H, d, J 15 Hz, H^{A}), and 7.90 (3 H, s, CH_3) (Found: C, 90.3; H, 5.5. $\text{C}_{26}\text{H}_{18}\text{O}$ requires C, 90.1; H, 5.2%).

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