Syntheses and Properties of a Trimethyltetradehydro[21]annulenone and its Benzannulated Derivatives

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The syntheses of 2,9,14-trimethyl-10,11,12,13-tetradehydrocycloheneicosenone (3), 19-methyl-20,21,22,23-tetradehydrobenzocycloheneicosen-11-one (4), and 10-methyl-22,23,24,25-tetradehydrodibenzo[a,g]cycloheneicosen-11-one (5) are described. The influence of α-methyl substitution and benzannulation on the structure and tropicity of the tetradehydro[21]annulenone ring system is discussed in view of the ¹H n.m.r. and u.v. spectra of these annulenones, as well as those of the dimethylannulenone (2).

In the previous paper, we reported the syntheses of the paratropic 2,7,12-trimethyl-8,9,10,11-tetradehydrocycloheptadecenone (1) and its benzannulated derivatives, and showed that both α-methyl substitution and benzannulation exert no significant influence upon the

with examining further the dimethylannulenone (2), prepared previously.[3] This paper deals with the syntheses and properties of the title compounds (3)—(5), together with further examination of the properties of the dimethyl compound (2).[4]

(1)   (2)   (3)   (4)   (5)
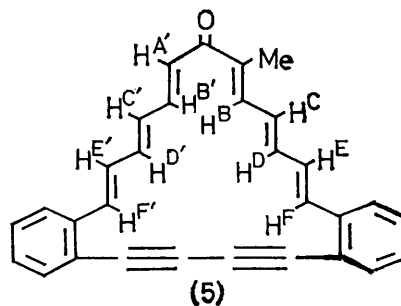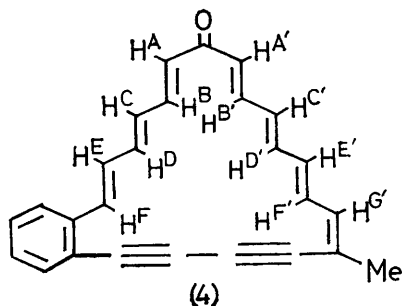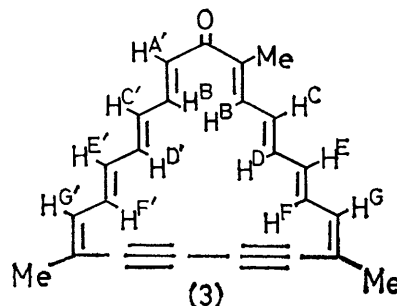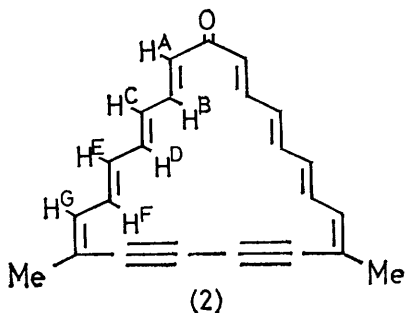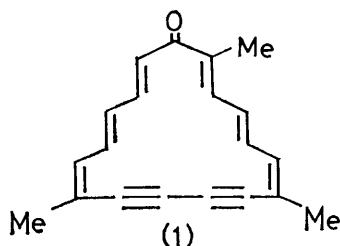
molecular skeleton of a tetradehydro[17]annulenone ring system of type (1),[1] in contrast to the corresponding tetradehydro[13]annulenone.[2]

In view of the paratropicity and the skeletal rigidity observed in the tetradehydro[17]annulenone system, we were interested in examining the properties of the higher analogue of (1) and its benzannulated derivatives, and

RESULTS AND DISCUSSION

The syntheses of the annulenones (3)—(5) were carried out by the reported method.[1] The ketone (6) was prepared from butan-2-one and (2E,4E,6Z)-7-methylnona-2,4,6-trien-8-ynal (7)[5] as reported.[6] This was condensed with another 1 mol of (7) using ethanolic
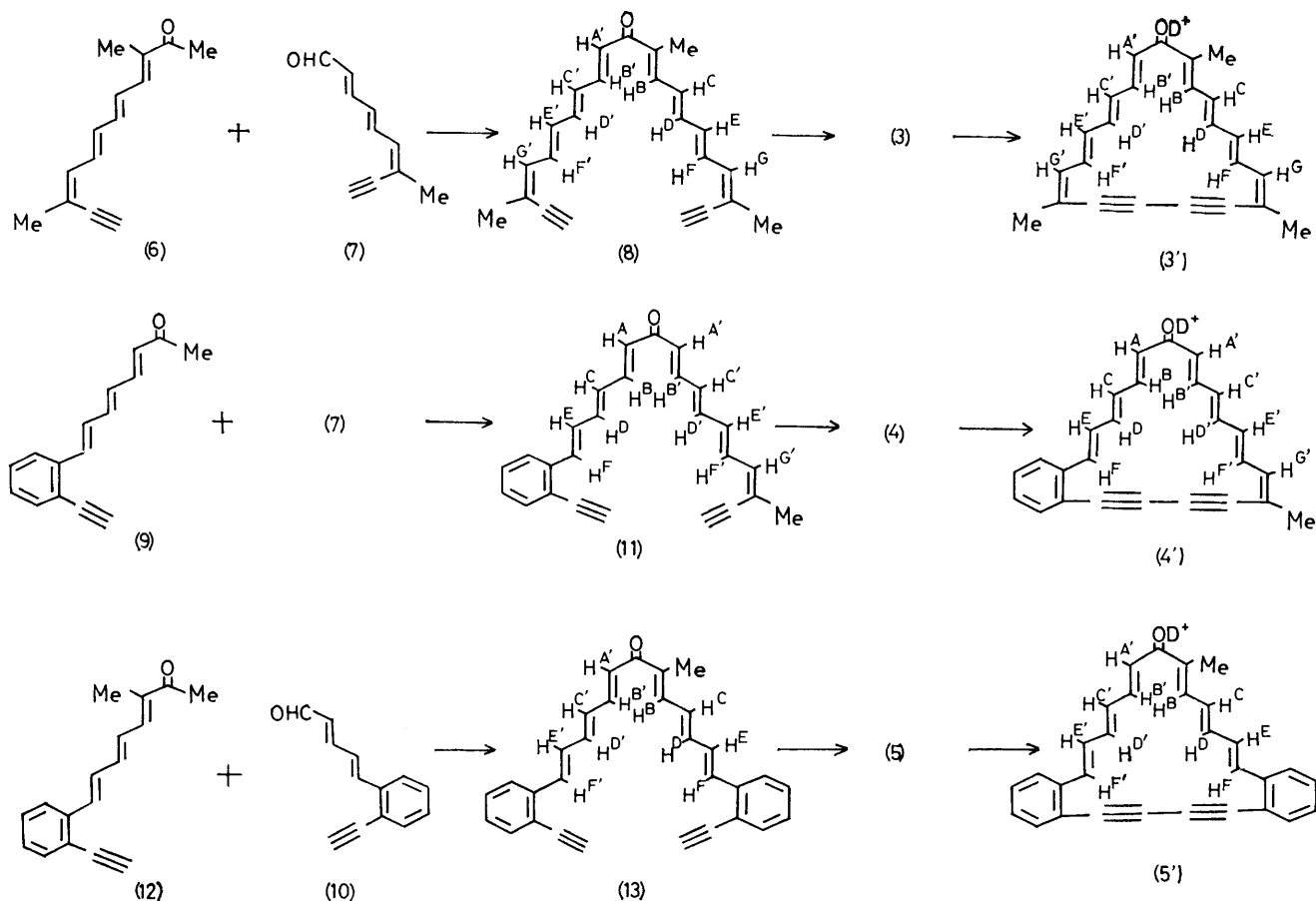
sodium ethoxide in ether to give the acyclic ketone (8) in 53% yield. The ketone (8) was oxidatively coupled with anhydrous copper(II) acetate in pyridine–dry ether at 50 °C [7] to afford the annulenone (3) in 6.8% yield. Similarly, condensation of (9),[3] which was prepared from acetone and the trienyne aldehyde (7), with 5-(o-ethynylphenyl)penta-2,4-dienal (10) [8] gave the ketone (11) in 61% yield, which was oxidized to the benzannulenone (4) in 4.9% yield. The acid-catalysed aldol condensation of butan-2-one with the aldehyde (10) afforded the ketone (12) in 67% yield, which was condensed with another 1 mol of (10) in the presence of ethanolic sodium ethoxide in tetrahydrofuran to give

the ketone (13) in 79% yield. Oxidation of (13) as before gave the dibenzannulenone (5) in 26% yield. The dimethylannulenone (2) was prepared via (14) as reported.[3] Although the dimethylannulenone (2) is rather unstable, it is noted that the trimethylannulenone (3) is more stable than (2). The structures of these new compounds were established from their spectral properties as well as elemental analyses.

Treatment of the annulenones (2)—(5) with trifluoroacetic acid or deuteriotrifluoroacetic acid gave the corresponding protonated or deuteriated species (2')—(5'): (2') [3] was dark green, (3') dark green, (4') yellow, and (5') yellow. Quenching of (2')—(5') with aqueous
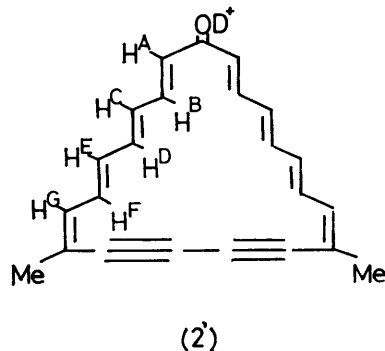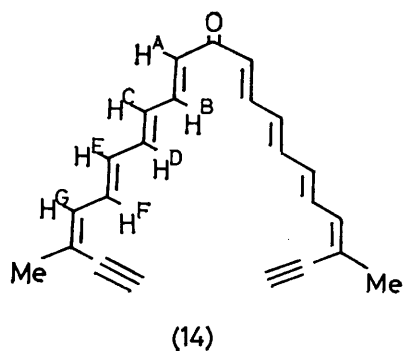
sodium hydrogencarbonate resulted in regeneration of (2)—(5), respectively.

TABLE 1

Electronic absorption maxima of tetradehydro[21]annulenones in tetrahydrofuran [$\lambda_{max.}$/nm ($\varepsilon_{max.}$)]

(2) [a]	(3)	(4)	(5)
245 (14 800)	245 (15 000)	223 (33 200)	226 (44 700)
255sh (14 000			260 (16 400)
307sh (52 200)	308sh (71 700)	317sh (84 800)	283sh (24 300)
327 (84 200)	328 (102 000)	330 (93 000)	310sh (72 900)
340 (92 300)	341 (109 000)	344 (86 900)	332 (105 000)
415sh (7 110)	469sh (4 750)	434sh (6 800)	414sh (9 200)

[a] See ref. 3.

The electronic absorption maxima of the annulenones (2)—(5) in tetrahydrofuran are given in Table 1. The main maxima of these tetradehydro[21]annulenones exhibit bathochromic shifts of 18—34 nm compared with those of the corresponding tetradehydro[17]-annulenones.[1] However, large bathochromic shifts of the main maxima are not observed between these tetradehydro[21]annulenones and the corresponding tetradehydro[19]annulenones [6] (<11 nm). This is considered to be due to the occurrence of the same sort of alternation between the main maxima of ($4n$—2) and $4n$ π-systems, as has been observed for the annulenes and dehydroannulenes.[9] As is seen from their absorption curves (see ref. 4), the longest wavelength band of the annulenes (2)—(5) exhibits absorption toward longer wavelength in the sequence (2) $\simeq$ (3) > (4) > (5), i.e.

with increasing number of fused benzene ring(s) on the macrocyclic system, demonstrating the degree of extended conjugation of the π-electron system in the tetradehydro[21]annulenone ring, in accordance with the result from an examination of the ^{1}H n.m.r. spectra of these annulenones (see below).

TABLE 2

Electronic absorption maxima of tetradehydro[21]annulenones in trifluoroacetic acid; [$\lambda_{max.}$/nm (relative extinction coefficients)]

(2) [a]	(3)	(4)	(5)
271 (0.67)		261 (0.65)	
308 (0.67)	310 (0.41)	290sh (0.79)	304 (0.95)
	358sh (0.80)	310 (0.84)	
374 (1.00)	376 (1.00)	375 (1.00)	341 (1.00)
425 (0.54)			394 (0.92)
450sh (0.39)	452 (0.30)	445sh (0.64)	453 (0.72)
486sh (0.29)	489sh (0.20)	665 (0.07)	636 (0.11)

[a] See ref. 3.

The absorption maxima of the annulenones (2)—(5) in trifluoroacetic acid are given in Table 2. It is evident that the main maxima of these protonated species shift to longer wavelengths (9—47 nm) in every case. It is noted that much smaller bathochromic shifts of the main maxima, caused by the protonation, are observed in the cases of the methylated annulenones (2) and (3) (35—47 nm) than in those of the corresponding tetradehydro[19]-annulenones (68—79 nm).[6]

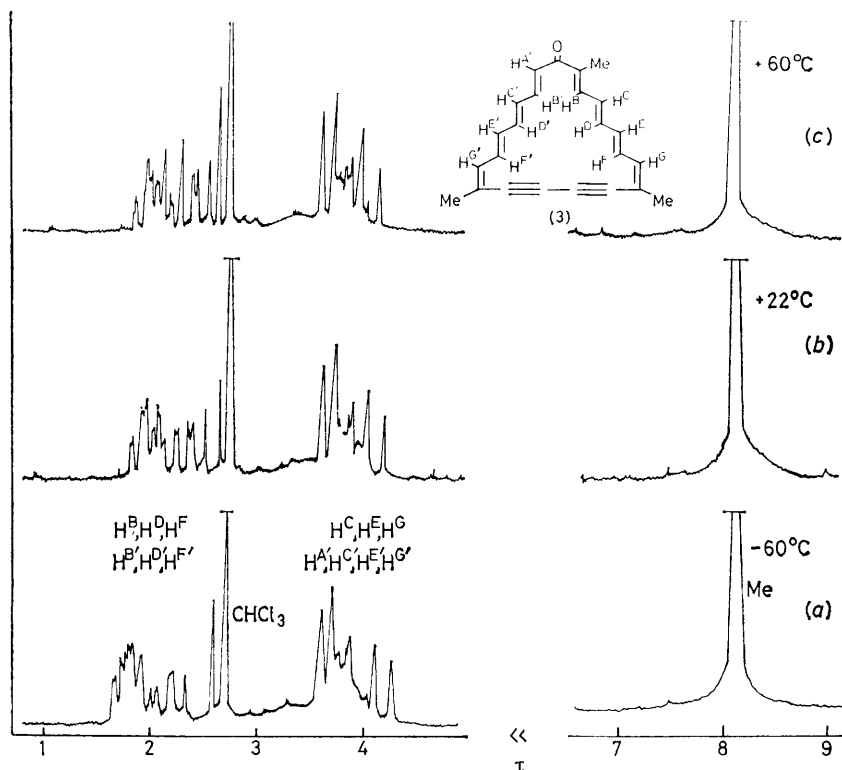The chemical shifts of the olefinic, aromatic, and methyl protons of the annulenones (2)—(5) are listed in

FIGURE 1   100-MHz Fourier-transform ^{1}H n.m.r. spectra of the [21]annulenone (3) in CDCl$_3$

TABLE 3

^{1}H-n.m.r. parameters of compounds (2)—(5), (8), (11), (13), (14) (in CDCl$_3$) and (2')—(5') (in CF$_3$CO$_2$D) at 90 MHz, determined at 35 °C (τ-values)

Compound	H^A	$H^{A'}$	H^C	$H^{C'}$	H^E	$H^{E'}$	H^G	$H^{G'}$	H^B	$H^{B'}$	H^D	$H^{D'}$	H^F	$H^{F'}$	Ar-H	Me
(14)[a]	2.53													3.78		8.02
(2)[a]	4.16		3.88[b]		3.84[b]		3.63		2.36		1.94		1.94			8.17
(2')[a]	4.28—4.80		4.28—4.80		4.28—4.80		4.28—4.80		−1.62		−2.22[c]		−2.10[c]			8.52
Δ[(2)—(14)]																+0.15
Δ[(2')—(14)]																+0.50
(8)	2.5						3.63	3.63						3.8		7.98
(3)	4.07[d]		3.82[d]	3.88[d]	3.73[d]	3.79[d]	3.63		1.99	1.93[e]	2.07[e]	1.98[e]	2.32	2.32		8.18
(3')	4.25		4.38[f]	4.23[f]	4.55	4.55	4.30		−1.98	−1.55[g]	−1.59[g]	−1.80[g]	−1.17[g]	−1.30[g]		8.28, 8.49
Δ[(3)—(8)]																+0.20
Δ[(3')—(8)]																+0.30, +0.51
(11)	2.3						3.80[h]	3.80[h]						3.8		8.00
(4)	4.03		3.40	3.85	3.25[h]	3.40	3.79	3.79	2.25[h]				2.10	2.25	2.90	8.05
(4')	3.85		3.72[i]	3.79[i]	3.50[i]	3.93[i]			0.13[j]	0.28[j]	0.30[j]	0.29[j]	0.15	0.69[j]	2.62—2.83	8.17
Δ[(4)—(11)]																+0.05
Δ[(4')—(11)]																+0.17
(13)	2.30		2.22				3.77	3.77							3.63	7.97
(5)	3.92														3.68	8.02
(5')	3.05								1.17					1.92	2.4—2.8	7.94
Δ[(5)—(13)]																+0.05
Δ[(5')—(13)]																−0.03

[a] At 100 MHz, see ref. 3.   [b-j] Assignments may be reversed in each group (see Experimental section).
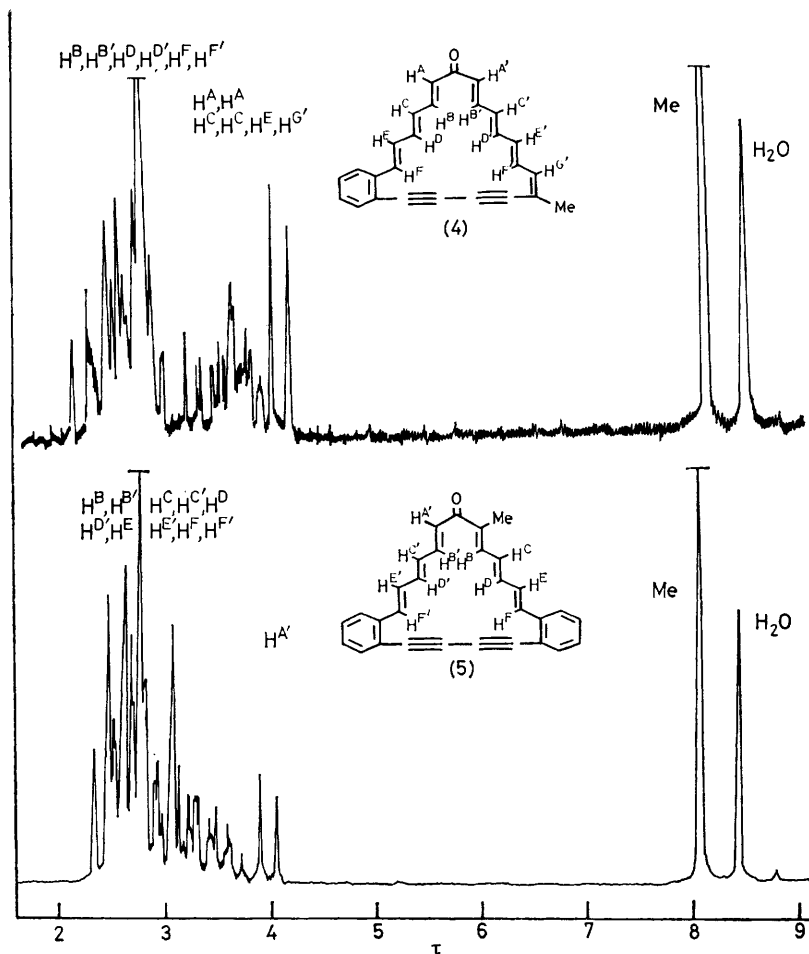
Figure 2 100-MHz Fourier-transform ^{1}H n.m.r. spectra of the [21]annulenones (4) and (5) in CDCl$_3$ at 22 °C

Table **3**, together with those of the corresponding acyclic ketones (8), (11), (13), and (14). Data for the deuteriated species (2')—(5'), 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.[1]

If we judge the tropicity of these annulenones from the difference in chemical shifts between the various protons for the cyclic ketone (annulenone) and the corresponding

TABLE 4

Variable-temperature ^{1}H-n.m.r. parameters for the compounds (2)—(5) at 100 MHz (τ-values)

Compound	T (°C)	H^A	H$^{A'}$	H^C	H$^{C'}$	H^E	H$^{E'}$	H^G	H$^{G'}$	H^B	H$^{B'}$	H^D	H$^{D'}$	H^F	H$^{F'}$	ArH	Me
(2) [a]	+60	4.15		3.87		3.83		3.60		2.40		1.97		1.97			8.17
	+22	4.17		3.87		3.83		3.63		2.34		1.90		1.90			8.16
	−30	4.21		3.88		3.84		3.64		2.24		1.80		1.83			8.16
	−60	4.23		3.99		3.85		3.64		2.19		1.74		1.79			8.18
(3)	+60		4.08	3.86	3.95	3.74	3.80	3.70	3.70	2.02	2.11	2.04	2.20	2.46	2.46		8.18
	+22		4.13	3.86	3.90	3.78	3.84	3.72	3.72	1.98	2.04	2.03	2.12	2.42	2.42		8.18
	−30		4.18	3.84	3.94	3.83	3.83	3.70	3.70	1.86	1.93	1.94	1.96	2.25	2.25		8.17
	−60		4.19	3.87	3.92	3.80	3.85	3.70	3.70	1.82	1.88	1.88	1.96	2.22	2.22		8.16
(4)	+60	4.06	4.03	3.47—3.88		3.27	3.47———3.88			2.29———————2.97				2.17	2.29—2.97		8.08
	+22	4.05	4.05	3.47—3.88		3.27	3.47———3.88			2.24———————2.92				2.14	2.24—2.92		8.08
	−30	4.05	4.05	3.42—3.84		3.25	3.42———3.84			2.20———————2.88				2.09	2.20—2.88		8.06
	−60	4.04	4.04	3.41—3.82		3.24	3.41———3.82			2.10———————2.84				2.05	2.10—2.84		8.05
(5)	+60		3.95	2.34———————————————————————————————3.73													8.03
	+22		3.95	2.32———————————————————————————————3.73													8.03
	−30		3.95	2.25———————————————————————————————3.70													8.02
	−60		3.94	2.25———————————————————————————————3.68													8.01

[a] At 200 MHz.

acyclic model (upfield shift for the outer protons and downfield shift for the inner) (Table 3), the annulenones (2) and (3) are seen to be paratropic, (4) is weakly paratropic, and (5) is atropic. This is more readily seen from Figs 1(*b*) and 2, which show the ^{1}H n.m.r. spectra of (3), (4), and (5) at room temperature. In the spectra of (5), compared with those of (3) and (4), the high- and low-field shifts of the resonances of the outer and the inner protons, respectively, are not observed. On the other hand, the deuteriated species, (2') and (3') are strongly paratropic, (4') is paratropic, and (5') is atropic (Table 3). Thus, the paratropicity of these annulenones and their deuteriated species decreases in the sequence (2) ≃ (3), [(2') ≃ (3')] > (4), [(4')] > (5), [(5')], *i.e.* with increasing number of fused benzene ring(s) upon the tetradehydro[21]annulenone system, which is in accord with other results.[10]

Variable-temperature ^{1}H n.m.r. spectra of (2)—(5) were run over the range −60 to 60 °C, the results of which, summarized in Table 4, show the spectra of all the annulenones (2)—(5) to be essentially temperature-independent. With decreasing temperature the resonances of the inner and outer protons of these annulenones move to a slightly lower and higher field, respectively, reflecting the greater planarity of the tetradehydro[21]annulenone ring system at a low temperature. The spectra of the trimethyltetradehydro[21]annulenone (3), which is the homologue of compound (1), are shown in Figure 1. On cooling, the resonances of the outer protons (H$^{A'}$, H^C, H$^{C'}$, H^E, H$^{E'}$, H^G, H$^{G'}$) and the three methyl groups move to a slightly higher field, whereas those of the inner protons (H^B, H$^{B'}$, H^D, H$^{D'}$, H^F, H$^{F'}$) move to a slightly lower field. However, the $J_{B',C'}$ value (11 Hz), indicating an *s-trans* relationship of the H$^{B'}$ and H$^{C'}$ bonds, does not vary from −60 to 60 °C, thus excluding a change of conformation of (3) due to a rotation of the CH$^{A'}$=CH$^{B'}$ double bond over this temperature range, in contrast to the case for the trimethyltetradehydro[13]annulenone.[2a] The methyl substituent adjacent to the carbonyl group and benzannulation exert no significant influence upon the skeleton of this tetradehydro[21]annulenone system, in contrast to the case for the tetradehydro[13]annulenone system.[2]

In conclusion, the results obtained from this study suggest that the molecular skeleton of this tetradehydro-[21]annulenone system is rather rigid, as has been observed for the corresponding [17]annulenone, although examination of Dreiding molecular model predicts a very strained system, since it contains a non-linear 1,3-diacetylene linkage.

EXPERIMENTAL

Deoxygenated ether and tetrahydrofuran were used and prepared as described previously.[1] M.p.s were determined with a hot-stage apparatus and are uncorrected. I.r. spectra were taken as KBr discs with a Hitachi EPI-S2, and u.v. spectra were measured in tetrahydrofuran solution on a Hitachi 124. Mass spectra were recorded with a JEOL-OI-SG-2 at 75 eV using a direct-inlet system. N.m.r.

spectra were run with Varian EM-390 (90 MHz), XL-200 (200 MHz), or JEOL FX-100 (100 MHz) spectrometers, in CDCl$_3$ solution unless otherwise stated. Merck alumina (activity II–III) was used for column chromatography, sodium sulphate was used as drying agent, and solvents were evaporated under water-pump pressure.

3,19-Dimethylheneicosa-3,5,7,9,12,14,16,18-*octaen*-1,20-*diyn*-11-*one* (14).—The compound was prepared from (7) and (9) as reported previously.[3]

9,14-Dimethyl-10,11,12,13-*tetradehydrocycloheneicosenone* (2).—This compound was prepared from (14) as reported previously.[3]

3,10,19-Trimethylheneicosa-3,5,7,9,12,14,16,18-*octaen*-1,20-*diyn*-11-*one* (8).—A solution of ethanolic sodium ethoxide (43 ml) [from sodium (760 mg) and dry ethanol (100 ml)] was added to a solution of the ketone (6)[6] (1.18 g, 5.89 mmol) in deoxygenated ether (47 ml), and a solution of the aldehyde (7)[5] (1.38 g, 9.42 mmol) in deoxygenated ether (15 ml) was added dropwise during 50 min with stirring at 2—3 °C. After stirring for a further 1.5 h at the same temperature, further portions of ethanolic sodium ethoxide (each 5.0 ml) were added every 1.5 h. After stirring for a total of 7 h, the reaction was quenched by the addition of aqueous oxalic acid. The mixture was poured into water and extracted with benzene. The extracts were washed successively with aqueous sodium hydrogencarbonate and brine, and then dried. After removal of solvent, the residue obtained was chromatographed on alumina (120 g). Initial fractions gave the unchanged ketone (6) (183 mg) and the following fractions gave the unchanged aldehyde (7) (137 mg). Later fractions (10% ether in hexane) gave the ketone (8) (1.03 g, 53%) as a solid. Recrystallization from hexane–benzene afforded brown *needles*, m.p. 106 °C (decomp.); *m/e* 328 (*M*$^+$, 100%); *M*, 328.4; $\nu_{max.}$ 3 250 (C≡C–H), 2 100 (C≡C), 1 655, 1 635, 1 615 (C=O, C=C), 995, and 980 cm^{-1} (*trans*-C=C); $\lambda_{max.}$ 226 (ε 6 330), 253 (5 880), 310sh (21 900), 325sh (25 200), 339 (26 400), 360sh (28 000), 388sh (36 500), 408 (42 500), and 430sh nm (33 600); τ *ca.* 2.5—3.8 (13 H, m, olefinic H), 6.57 (2 H, s, C≡CH), and 7.98 (9 H, s, Me) (Found: C, 87.5; H, 7.6. C$_{24}$H$_{24}$O requires C, 87.8; H, 7.4%).

2,9,14-Trimethyl-10,11,12,13-*tetradehydrocycloheneico-senone* (3).—A solution of the ketone (8) (1.70 g, 5.18 mmol) in pyridine–dry ether (3 : 1, 109 ml) was added dropwise during 4 h to a stirred solution of anhydrous copper(II) acetate (6.4 g) in pyridine–dry ether (3 : 1, 243 ml) at 50—55 °C. The solution was stirred for a further 1 h at the same temperature and then cooled. After addition of benzene (100 ml), the solution was filtered through Hyflo Super-Cel. The precipitates formed were washed with benzene (100 ml × 3), and the filtrate poured into water. The organic layer, combined with the benzene extracts from the aqueous layer, was washed successively with 3M-hydrochloric acid, aqueous sodium hydrogencarbonate, and brine, and then dried. After removal of solvent, the dark red liquid obtained was chromatographed on alumina (100 g). Fractions, eluted with hexane–ether (2 : 3), gave the annulenone (3) (115 mg, 6.8%) as a solid. It formed dark red *needles* from hexane–benzene, m.p. 168 °C (decomp.), *m/e* 326 (*M*$^+$, 66%) and 253(100); *M*, 326.4; $\nu_{max.}$ 2 150 (C≡C), 1 630, 1 615 (C=O), 1 590 (C=C), and 985 cm^{-1} (*trans*-C=C); for u.v. data see Tables 1 and 2; τ 1.93 (1 H, dd, *J* 16 and 11 Hz, H$^{B'}$ or H^D or H$^{D'}$), 1.98 (1 H, dd, *J* 16 and 11 Hz, H$^{B'}$ or H^D or H$^{D'}$), 1.99 (1 H, d, *J* 11 Hz, H^B), 2.07 (1 H, dd, *J* 16 and 11 Hz, H$^{B'}$ or H^D or H$^{D'}$), 2.32 (2 H,

dd, J 16 and 12 Hz, H^F and $H^{F'}$), 3.63 (2 H, d, J 12 Hz, H^G and $H^{G'}$), 3.73 (1 H, dd, J 16 and 11 Hz, H^E or $H^{E'}$), 3.79 (1 H, dd, J 16 and 11 Hz, H^E or $H^{E'}$), 3.82 (1 H, dd, J 16 and 11 Hz, H^C or $H^{C'}$), 3.88 (1 H, dd, J 16 and 11 Hz, H^C or $H^{C'}$), 4.07 (1 H, d, J 16 Hz, $H^{A'}$), and 8.18 (9 H, s, Me) (see also Figure 1); $\tau(CF_3CO_2D)$: -1.98 (1 H, d, J 11 Hz, H^B), -1.80 (1 H, dd, J 16 and 11 Hz, $H^{B'}$ or H^D or $H^{D'}$), -1.59 (1 H, dd, J 16 and 11 Hz, $H^{B'}$ or H^D or $H^{D'}$), -1.55 (1 H, dd, J 16 and 11 Hz, $H^{B'}$ or H^D or $H^{D'}$), -1.30 (1 H, dd, J 16 and 11 Hz, H^F or $H^{F'}$), -1.17 (1 H, dd, J 16 and 11 Hz, H^F or $H^{F'}$), 4.23 (1 H, dd, J 16 and 11 Hz, H^C or $H^{C'}$), 4.25 (1 H, d, J 16 Hz, $H^{A'}$), 4.30 (2 H, d, J 11 Hz, H^G and $H^{G'}$), 4.38 (1 H, dd, J 16 and 11 Hz, H^C or $H^{C'}$), 4.55 (2 H, dd, J 16 and 11 Hz, H^E and $H^{E'}$), 8.28 (3 H, s, Me), and 8.49 (6 H, s, Me) (Found: C, 88.55; H, 7.0. $C_{24}H_{22}O$ requires C, 88.3; H, 6.8%).

1-(o-*Ethynylphenyl*)-15-*methylheptadeca*-1,3,5,8,10,12,14-*heptaen*-16-*yn*-7-*one* (11).—A solution of ethanolic sodium ethoxide (3.0 ml) [from sodium (380 mg) and dry ethanol (100 ml)] was added to a mixture of the ketone (9) [3] (514 mg, 3.06 mmol) and 5-(o-ethynylphenyl)penta-2,4-dienal (10) [8] (556 mg, 3.06 mmol) in deoxygenated ether (29 ml) with stirring at 2—3 °C. After stirring for a further 6.5 h at the same temperature, the reaction was quenched by addition of aqueous oxalic acid. After work-up as for the isolation of (8), the product was chromatographed on alumina (100 g). Initial fractions gave the unchanged aldehyde (10) (56 mg). Later fractions, eluted with hexane–ether (1 : 3), gave the ketone (11) (657 mg, 61%) as a solid. Recrystallization from hexane–ethyl acetate afforded reddish brown *microcrystals*, m.p. 130 °C (decomp.); m/e 350 (M^+, 100%); M, 350.4; $\nu_{max.}$ 3 250, 3 200 (C≡C–H), 2 110 (C≡C), 1 660 (C=O), 1 610, 1 585 (C=C) and 1 005 cm^{-1} (*trans*-C=C); $\lambda_{max.}$ 226 (ε 17 100), 266sh (14 800), 277sh (16 200), 305 (23 300), 316 (23 300), and 400 nm (61 200); τ *ca.* 2.3—3.8 (17 H, m, olefinic and Ar-H), 6.57 (1 H, s, C≡CH), 6.60 (1 H, s, C≡CH), and 8.00 (3 H, s, Me) (Found: C, 89.4; H, 6.4. $C_{26}H_{22}O$ requires C, 89.1; H, 6.3%).

19-*Methyl*-20,21,22,23-*tetradehydrobenzocycloheneicosen*-11-*one* (4).—A solution of the ketone (11) (2.52 g, 7.19 mmol) in pyridine–dry ether (3 : 1, 152 ml) was added dropwise during 4.5 h to a stirred solution of anhydrous copper(II) acetate (8.9 g) in pyridine–dry ether (3 : 1, 339 ml) at 49—53 °C. The solution was stirred for a further 1 h at the same temperature and cooled. After work-up as for the isolation of (3), the dark red semi-solid obtained was chromatographed on alumina (90 g). Fractions, eluted with hexane–ether (1 : 1), gave the annulenone (4) (122 mg, 4.9%) as a solid. It formed orange *needles* from hexane–benzene, m.p. 175 °C (decomp.); m/e 349 (M^+, 48%) and 289 (100); M, 348.4; $\nu_{max.}$ 2 240 (C≡C), 1 620 (C=O), 1 595 (C=C), and 1 000 cm^{-1} (*trans*-C=C); for u.v. data see Tables 1 and 2; τ 2.10 (1 H, d, J 16 Hz, H^F), 2.25—2.90 (9 H, m, H^B, $H^{B'}$, H^D, $H^{D'}$, $H^{F'}$, and ArH), 3.25 (1 H, dd, J 16 and 11 Hz, H^E or $H^{E'}$), 3.40—3.85 (4 H, m, H^C, $H^{C'}$, H^E or $H^{E'}$, and $H^{G'}$), 4.03 (2 H, d, J 16 Hz, H^A and $H^{A'}$), and 8.05 (3 H, s, Me) (see also Figure 2); $\tau(CF_3CO_2D)$: 0.13 (1 H, dd, J 16 and 12 Hz, H^B or $H^{B'}$ or H^D or $H^{D'}$ or $H^{F'}$), 0.15 (1 H, d, J 16 Hz, H^F), 0.28 (1 H, dd, J 16 and 12 Hz, H^B or $H^{B'}$ or H^D or $H^{D'}$ or $H^{F'}$), 0.29 (1 H, dd, J 16 and 12 Hz, H^B or $H^{B'}$ or H^D or $H^{D'}$ or $H^{F'}$), 0.30 (1 H, dd, J 16 and 12 Hz, H^B or $H^{B'}$ or H^D or $H^{D'}$ or $H^{F'}$), 0.69 (1 H, dd, J 16 and 12 Hz, H^B or $H^{B'}$ or H^D or $H^{D'}$ or $H^{F'}$), 2.62—2.83 (4 H, m, Ar-H), 3.50 (1 H, dd, J 16 and 12 Hz, H^C or $H^{C'}$ or

H^E or $H^{E'}$), 3.72 (1 H, dd, J 16 and 12 Hz, H^C or $H^{C'}$ or H^E or $H^{E'}$), 3.79 (1 H, d, J 12 Hz, $H^{G'}$), 3.79 (1 H, dd, J 16 and 12 Hz, H^C or $H^{C'}$ or H^E or $H^{E'}$), 3.85 (2 H, d, J 16 Hz, H^A and $H^{A'}$), 3.93 (1 H, dd, J 16 and 12 Hz, H^C or $H^{C'}$ or H^E or $H^{E'}$), and 8.17 (3 H, s, Me) (Found: C, 89.6; H, 5.8. $C_{26}H_{20}O$ requires C, 89.6; H, 5.8%).

8-(o-*Ethynylphenyl*)-3-*methylocta*-3,5,7-*trien*-2-*one* (12).—A solution of the aldehyde (10) [8] (1.0 g, 5.5 mmol) in acetic acid (19 ml) was added dropwise during 40 min at 15 °C to a stirred solution of butan-2-one (2.8 g, 38 mmol) and concentrated sulphuric acid (0.9 ml) in acetic acid (44 ml). The solution was stirred for a further 3 h at room temperature, and then cautiously poured into saturated aqueous potassium carbonate (67 g, 200 ml). This solution was then poured into water and extracted with benzene, and the benzene extracts were washed with brine. The residue obtained after solvent removal was chromatographed on alumina (100 g). The fractions, eluted with hexane–ether (4 : 1), gave the ketone (12) (872 mg, 67%) as a solid. Recrystallization from hexane–benzene afforded yellow *needles*, m.p. 142—143 °C; m/e 236 (M^+, 24%) and 178 (100); M, 236.3; $\nu_{max.}$ 3 250 (C≡C–H), 2 100 (C≡C), 1 640 (C=O), 1 615, 1 590 (C=C), and 990 cm^{-1} (*trans*-C=C); $\lambda_{max.}$ 224 (ε 14 100), 230 (14 100), 257 (9 110), 265 (10 300), 275 (9 700), 337sh (40 100), 354 (53 900), and 371 nm (41 600); τ 2.29—3.32 (9 H, m, olefinic and Ar-H), 6.57 (1 H, s, C≡CH), 7.63 (3 H, s, Me), and 8.03 (3 H, s, Me) (Found: C, 86.3; H, 6.6. $C_{17}H_{16}O$ requires C, 86.4; H, 6.8%).

1,13-*Bis*-(o-*ethynylphenyl*)-6-*methyltrideca*-1,3,5,8,10,12-*hexaen*-7-*one* (13).—A solution of ethanolic sodium ethoxide (12 ml) [from sodium (380 mg) and dry ethanol (50 ml)] was added to a solution of the ketone (12) (796 mg, 3.37 mmol) in deoxygenated tetrahydrofuran (26 ml), and a solution of the aldehyde (10) [8] (736 mg, 4.04 mmol) in deoxygenated tetrahydrofuran (9.4 ml) was added dropwise during 20 min with stirring at 2—3 °C. After stirring for a further 7 h at the same temperature, the reaction was quenched by addition of aqueous oxalic acid. After work-up as for the isolation of (8), the dark red liquid obtained was chromatographed on alumina (140 g). Initial fractions gave the unchanged aldehyde (10) (191 mg). Later fractions, eluted with hexane–ether (7 : 3), gave the ketone (13) (1.07 g, 79%) as a solid. It formed yellow *cubes* from hexane–benzene, m.p. 144—145 °C, m/e 400 (M^+, 25%) and 179 (100); M, 400.5; $\nu_{max.}$ 3 270 (C≡C–H), 2 100 (C≡C), 1 635 (C=O), 1 600 (C=C), 1 000, and 990 cm^{-1} (*trans*-C=C); $\lambda_{max.}$ 226 (ε 27 400), 237sh (22 700), 256 (17 600), 265 (19 200), 275 (19 000), 304sh (25 400), 316sh (32 000), 332sh (36 000), 348 (40 500), 384sh (59 100), 398 (63 400), and 416sh (54 600); τ 2.30—3.63 (19 H, m, olefinic and Ar-H), 6.57 (2 H, s, C≡CH), and 7.97 (3 H, s, Me) (Found: C, 89.9; H, 6.1. $C_{30}H_{24}O$ requires C, 90.0; H, 6.0%).

10-*Methyl*-22,23,24,25-*tetradehydrodibenzo*[a,g]*cycloheneicosen*-11-*one* (5).—A solution of the ketone (13) (1.32 g, 3.30 mmol) in pyridine–dry ether (3 : 1, 70 ml) was added dropwise during 4.5 h to a stirred solution of anhydrous copper(II) acetate (4.1 g) in pyridine–dry ether (3 : 1, 155 ml) at 49—53 °C. After stirring for a further 1 h at the same temperature, the solution was cooled. After work-up as for the isolation of (3), the product was chromatographed on alumina (80 g). Fractions, eluted with hexane–ether (2 : 3), gave the annulenone (5) (347 mg, 26%) as a solid. Recrystallization from hexane–benzene afforded yellow *needles*, m.p. 197—198 °C; m/e 398 (M^+, 100%); M, 398.5; $\nu_{max.}$ 2 200 (C≡C), 1 635 (C=O), 1 605, 1 590 (C=C),

and 990 cm^{-1} (*trans*-C=C); for u.v. data see Tables 1 and 2; τ 2.22—3.68 (18 H, m, H^B, H$^{B'}$, H^C, H$^{C'}$, H^D, H$^{D'}$, H^E, H$^{E'}$, H^F, H$^{F'}$, and Ar-H), 3.92 (1 H, d, 16, H$^{A'}$), and 8.02 (3 H, s, Me) (see also Figure 2); τ(CF$_3$CO$_2$D): 1.17—1.92 (6 H, m, H^B, H$^{B'}$, H^D, H$^{D'}$, H^F, and H$^{F'}$), *ca.* 2.4—2.8 (8 H, m, Ar-H), 3.05—3.77 (5 H, m, H$^{A'}$, H^C, H$^{C'}$, H^E, and H$^{E'}$), and 7.94 (3 H, s, Me) (Found: C, 90.3; H, 5.6. C$_{30}$H$_{22}$O requires C, 90.4; H, 5.6%).

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