Syntheses and Properties of a Trimethyltetradehydro[23]annulenone and a Trimethyltetradehydro[25]annulenone

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The syntheses of 2,9,14-trimethyl-10,11,12,13-tetradehydrocyclotricosenone (6) and 2,11,16-trimethyl-12,13,14,-15-tetradehydrocyclopentacosenone (7) are described. Examination of the [1]H n.m.r. spectra indicates that (6) is diatropic, whereas (7) is paratropic, and these ring currents are increased by dissolution in deuteriotrifluoroacetic acid.

SYNTHESES of a series of the paratropic dimethyltetradehydro[13]annulenone (1),[1] trimethyltetradehydro[17]annulenone (3),[2] trimethyltetradehydro[21]annulenone (5),[3] and the diatropic trimethyltetradehydro[15]annulenone (2)[4] and trimethyltetradehydro[19]annulenone (4),[5] have been described previously. It was shown that in tetradehydroannulenones with an unsymmetrical molecular skeleton such as (2) and (4) trimethylannulenones with an α-methyl substituent are superior to the corresponding α-methyl unsubstituted or α'-methyl substituted ones for the investigation of the ring current, since the annulenones with an α-methyl group at C-2 usually have higher conformational stability and molecular planarity than those with a methyl group at another position or with no α-methyl group.[4,5] In contrast, in tetradehydroannulenones with a symmetrical molecular skeleton [e.g. as (3) and (5)] the α-methyl substituent exerts no significant influence upon the molecular skeleton or ring current of the tetradehydroannulenone

ring system. However, it was found that the trimethyltetradehydro[21]annulenone (5) with an α-methyl group was thermally more stable than the α-methyl-unsubstituted dimethyltetradehydro[21]annulenone.[3] Also, it was found that in the tetradehydro[13]annulenone ring system α-methyl substitution caused the change in conformation indicated for the [13]annulenone (1).[1] Thus the dimethyltetradehydro[13]annulenone (1) rather than the corresponding trimethyl derivative with an α-methyl group is shown to have the same conformation as the tetradehydroannulenones (2)—(7) by comparison of their properties (see below).

Bearing these results in mind, we were interested in examining the properties of the higher analogues of (4) and (5), respectively, *i.e.* 2,9,14-trimethyl-10,11,12,13-tetradehydrocyclotricosenone (6) and 2,11,16-trimethyl-12,13,14,15-tetradehydrocyclopentacosenone (7) to test the question of the limiting size for diatropicity and paratropicity in these 1,2,3,4-tetradehydroannulenone


(1)   (2)   (3)   (4)

(5)   (6)   (7)
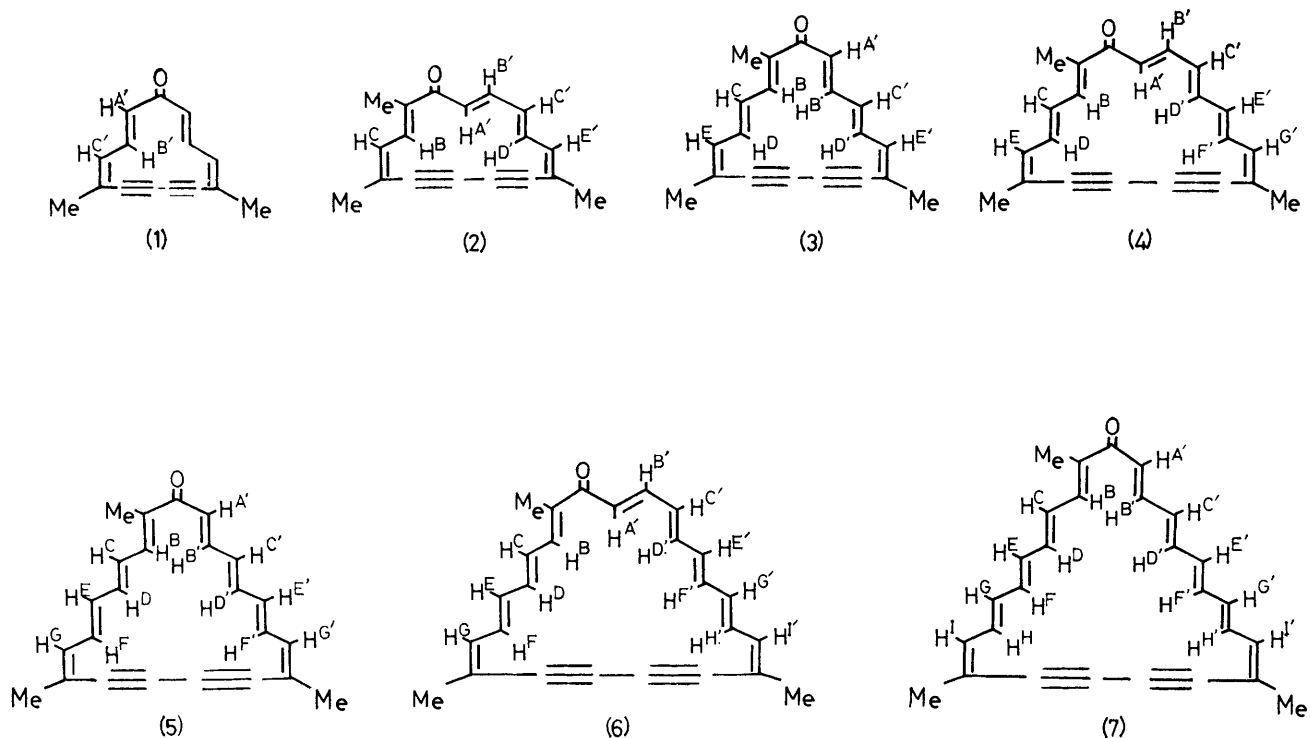
ring systems. This paper deals with the syntheses and properties of the title compounds (6) and (7) [6] which are the largest ring monocyclic annulenone derivatives so far obtained,[7] together with a systematic examination of the properties of the compounds (1)—(5), prepared previously.

RESULTS AND DISCUSSION

The syntheses of the annulenones (6) and (7) were carried out as the reported procedure.[3,5] Attempts to obtain the (2E,4E,6E,8Z)-9-methylundeca-2,4,6,8-tetra-en-10-ynal (10) from the lower homologue, (2E,4E,6Z)-7-methylnona-2,4,6-trien-8-ynal (8),[8] employing Isler's

Treatment of the annulenones (6) and (7) with trifluoroacetic acid or deuteriotrifluoroacetic acid gave the corresponding carbonyl protonated or deuteriated species (6') and (7'), respectively, (6') being green and (7') brown. Quenching of (7') with aqueous sodium hydrogencarbonate resulted in regeneration of (7). Keeping of the species (6') resulted in a change, and the ketone (6) was not recovered from it on quenching.

The electronic absorption spectra (in tetrahydrofuran) of the trimethyltetradehydroannulenones (4)—(7) are illustrated in Figure 1, and the absorption maxima of these annulenones as well as the annulenones (1)—(3) are listed in Table 1. Although the main maxima of
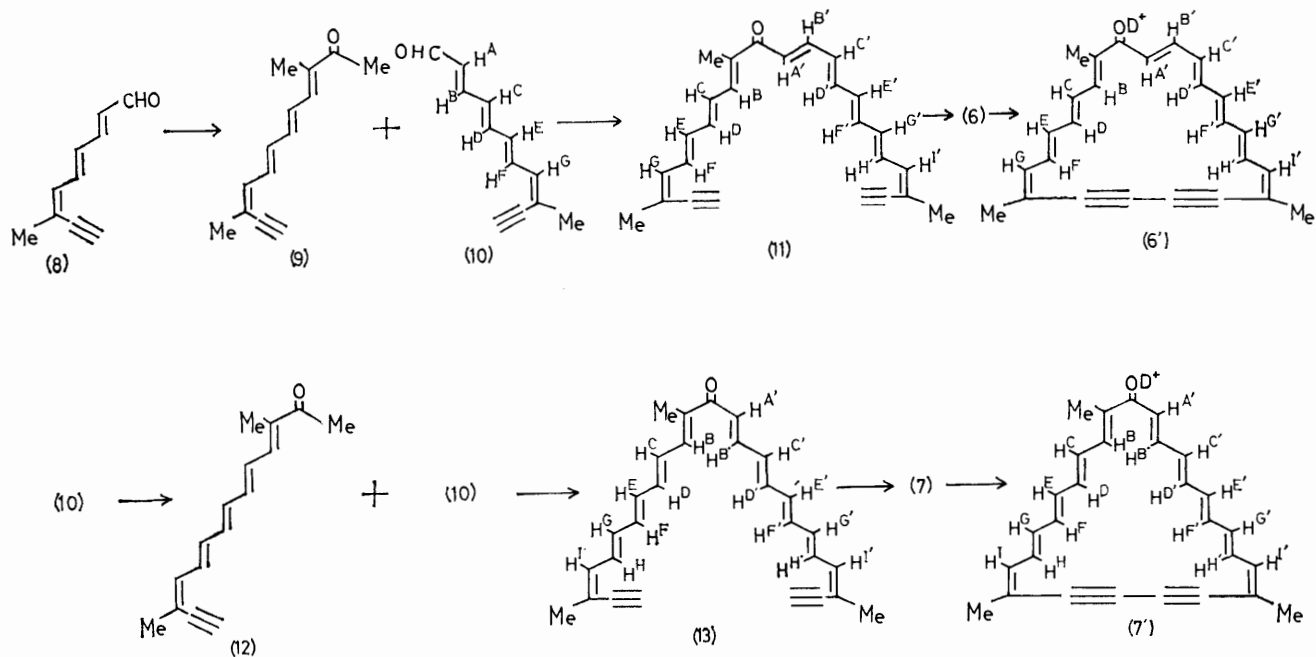
method [9] gave unsatisfactory results. The homologation of (8) to (10) was achieved by Wittig condensation with [(1,3-dioxolan-2-yl)methyl]triphenylphosphonium bromide [10] and lithium ethoxide in NN-dimethylformamide, followed by hydrolysis of the resulting acetal with dilute hydrochloric acid. Aldol condensation of the ketone (9),[3] obtained from butan-2-one and the trienyne aldehyde (8), with the tetraenyne aldehyde (10) in the presence of ethanolic sodium ethoxide in ether gave the acyclic ketone (11) in 66% yield. Oxidative coupling of (11) with anhydrous copper(II) acetate in pyridine–dry ether at 50 °C [11] yielded the tetradehydro[23]-annulenone (6) as red cubes, m.p. 163 °C (decomp.), in 6.6% yield. The acid-catalysed aldol condensation of the aldehyde (10) with butan-2-one in the presence of sulphuric acid–acetic acid gave the pentaenyne ketone (12) in 28% yield; this was condensed with another mol of (10), under the conditions for that between (9) and (10), to afford the ketone (13) in 89% yield. Oxidation of (13) as before gave the tetradehydro[25]-annulenone (7) as purple needles, m.p. 145 °C (decomp.), in 5.0% yield.

these tetradehydroannulenones exhibit a bathochromic shift as the ring size increases, this shift is very small between the [23]annulenone (6) and the [25]annulenone (7), as is also seen between the [15]annulenone (2) and the [17]annulenone (3), and between the [19]annulenone (4) and the [21]annulenone (5). In fact, it is apparent that the electronic spectra of the [4n − 1]annulenones (4) and (6) are rather similar to those of the [4n + 1]-annulenones (5) and (7), respectively. Thus, the occurrence of the same sort of alternation between the maxima of (4n − 2) and 4n systems, as recognized for annulenes and dehydroannulenes,[12,13] is also observed for (6) and (7).

The electronic absorption maxima of the annulenones (1)—(7) in trifluoroacetic acid are given in Table 2, and it is evident that protonation causes the main maxima to shift to longer wavelengths for both (6) and (7), as observed for the annulenones (1)—(5).[12] The bathochromic shift is much larger for the [23]annulenone (6) (76 nm) than for the [25]annulenone (7) (46 nm), as has been observed between the [4n + 1]annulenones (1), (3), and (5), and the [4n − 1]annulenones (2) and (4).[12]
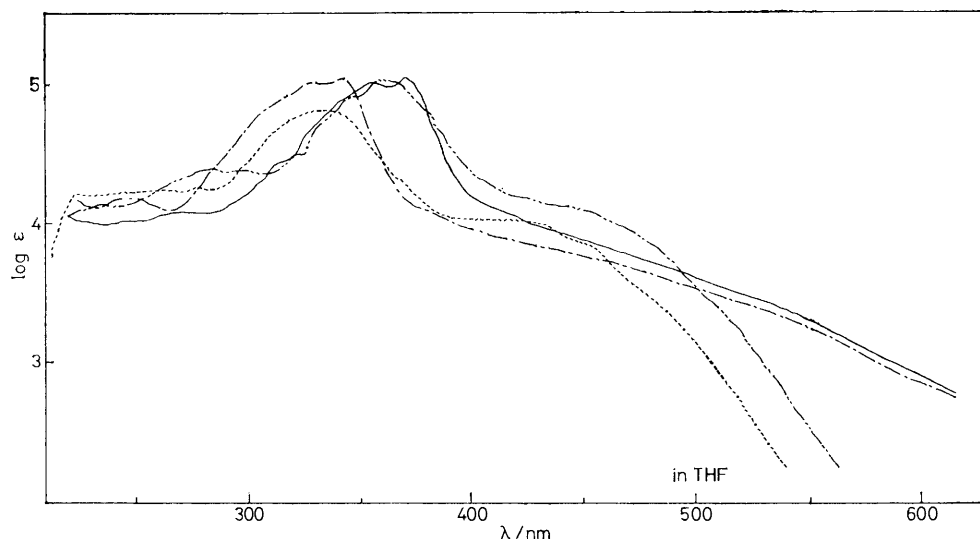
FIGURE 1   U.v. spectra of the [19]annulenone (4) (— — — — —), the [21]annulenone (5) (— · — · —), the [23]annulenone (6)(— ·· — ·· —), and the [25]annulenone (7) (———)

Here, the alternation is much clearer, the main maxima of the tetradehydro[13]-, -[15]-, -[17]-, -[19]-, -[21]-, -[23]-, and -[25]-membered annulenones in trifluoroacetic acid occurring at 281, 370, 334, 406, 376, 438, and 423 nm, respectively.

The ^{1}H n.m.r. chemical shifts of the olefinic and methyl protons of the annulenones (6) and (7) as well as their respective corresponding acyclic ketones (11) and (13)

Comparison of the chemical shifts of the various protons of the [23]annulenone (6) and the [25]annulenone (7) with those of the corresponding acyclic ketones (11) and (13) is difficult owing to overlapping peaks. However, the methyl protons of (6) resonate at a slightly lower field than those of the corresponding acyclic compound (11), whereas the methyl protons of (7) resonate at a slightly higher field than those of the corresponding

TABLE 1

Electronic absorption maxima of the tetradehydroannulenones (1)—(7) in tetrahydrofuran [$\lambda_{max.}$/nm ($\varepsilon_{max.}$)]

(1) [a]	(2) [a]	(3)	(4)	(5)	(6)	(7)
	211 (22 900)		225 (14 700)			
	232sh (13 400)		264 (15 800)	245 (15 000)	237 (13 400)	268 (11 800)
250sh (25 800)	246 (13 800)		279 (16 000)			
262 (37 900)	258 (14 800)				283 (24 800)	
273 (39 900)		280sh (42 900)			299 (24 700)	
	304 (42 600)	298 (68 800)		308sh (71 700)		338sh (65 700)
387 (990)	310sh (41 200)	307 (70 100)	333 (62 500)	328 (100 200)		355 (96 300)
	384 (7 880)	356sh (7 900)	425sh (8 540)	341 (109 000)	362 (102 000)	371 (106 000)
			451sh (6 020)	469sh (4 750)	456sh (11 400)	494sh (4 310)

[a] In ether.

TABLE 2

Electronic absorption maxima of tetradehydroannulenones (1)—(7) in trifluoroacetic acid [$\lambda_{max.}$/nm (relative extinction coefficients)]

(1)	(2)	(3)	(4)	(5)	(6)	(7)
269sh (0.82)	298sh (0.08)	316 (0.52)	270 (0.10)	310 (0.41)	318sh (0.88)	337 (0.67)
281 (1.00)	356sh (0.72)	334 (1.00)	298 (0.61)	358sh (0.80)	331 (0.99)	402sh (0.93)
350sh (0.12)	370 (1.00)	393 (0.23)	407 (1.00)	376 (1.00)	417sh (0.91)	423 (1.00)
	470sh (0.11)		426 (0.84)	452 (0.30)	438 (1.00)	500sh (0.45)
	500sh (0.18)		583 (0.31)	489sh (0.20)	462sh (0.84)	540sh (0.24)
	524 (0.23)		602 (0.31)		649 (0.45)	
	562 (0.29)		661 (0.19)			

are listed in Table 3, together with those of the annulenones (1)—(5). Assignments were made on the basis of multiplicities, coupling constants (see Experimental section), and comparison of the data of closely related compounds.[1-5]

acyclic compound (13) (Table 3). This fact suggests that (6) is diatropic, as might be expected of a 22-π-electron system, while (7) is paratropic, as might be expected of 24-π-electron system.

Support for this interpretation follows from a system-

TABLE 3

^{1}H N.m.r. parameters of compounds (1)—(7), (11), (13) (in CDCl$_3$) and (1')—(7') (in CF$_3$CO$_2$D) (τ-values)

Compound	H$^{A'}$	H^O	H$^{O'}$	H^E	H$^{E'}$	H^G	H$^{G'}$	H^I	H$^{I'}$	H$^{B'}$	H^B	H^D	H$^{D'}$	H^F	H$^{F'}$	H^H	H$^{H'}$	Me
(1)	3.90		3.71							0.61								8.26
(1')	3.85		3.88							−0.79								8.33
(2)	4.50	2.57	3.15		2.75					2.37	4.48		4.71					7.71, 7.79
(2')	10.57	0.60	1.20		0.80					0.17	10.60		10.69					6.68, 6.75, 6.80
(3)	3.95	3.99	3.81	3.80	3.67					1.31	1.45	1.62	1.38					8.16
(3')	4.20	4.27	4.45	4.11	4.13					−1.67	−2.07	−1.98	−1.85					8.23
(4)	3.87	2.90	3.40	2.97	3.13		2.97			2.87	4.22	4.30	4.20		4.48			7.79, 7.83
(4')	7.12	1.22	2.90	1.16	1.31		0.84			1.56	9.47	9.52	9.17		9.54			6.84, 6.94
(5)	4.07	3.82	3.88	3.73	3.79	3.63	3.63			1.93	1.99	2.07	1.98	2.32	2.32			8.18
(5')	4.25	4.38	4.23	4.55	4.55	4.30	4.30			−1.55	−1.98	−1.59	−1.80	−1.17	−1.30			8.28, 8.49
(11)	2.52																3.85	8.00
(6)	3.70	2.95							3.40	3.56	3.88	3.98	4.02	4.14	4.26		4.29	7.86, 7.91
(6') [a]	6.84—7.85	1.35								2.15	6.84						7.85	7.08, 7.12, 7.24
(13)	2.47								3.91	2.24							3.75	8.00
(7)	4.06	3.60															2.82	8.14
(7')	3.97								4.76	−1.43							−0.33	8.23, 8.49

[a] The spectra of (6') changed with time.

atic examination of both the ^{1}H n.m.r. spectral data (Table 3) and the electronic spectra (Tables 1 and 2 and Figure 1) of the compounds (1)—(7), with reference to the results obtained previously.[12]

It is evident from Figure 2 that in the spectra of the [23]annulenone (6), the inner protons resonate at higher field than the outer protons, while in the spectra of the [25]annulenone (7), the inner protons resonate at lower field than the outer protons. This confirms the indicated conformations for the compounds (6) and (7), and shows that the alternation of the ring currents in (6) and (7) can

shifts of (6′) and (7′) with those of the corresponding acyclic compounds (11) and (13), indicates that the ring currents of the deuteriated species (6′) and (7′) are much stronger than in the undeuteriated species, as also occurs for (1′)—(5′). Again, this is seen most simply by inspection of the methyl proton resonances, the alternation of which in (1′)—(7′) is considerably greater than in (1)—(7).

Variable-temperature ^{1}H n.m.r. spectra of (6) and (7) were run over the range —60 to 60 °C, the results of which, summarized in Table 4, show the spectra of both

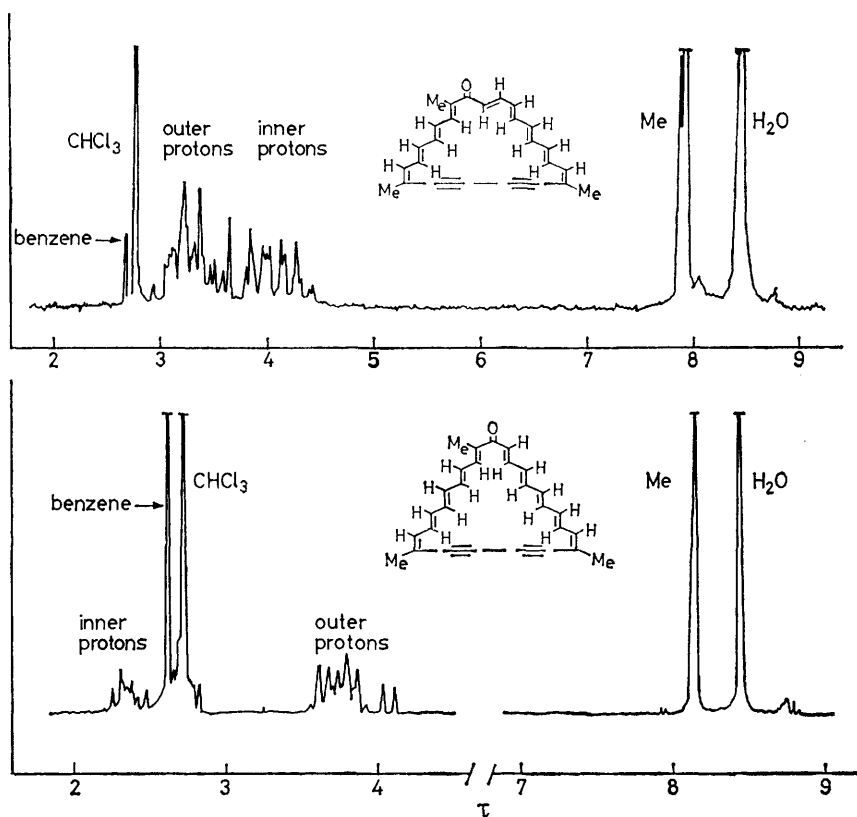FIGURE 2   Fourier-transform ^{1}H n.m.r. spectra of the [23]annulenone (6) (100 MHz) and the [25]annulenone (7) (200 MHz) in CDCl$_3$ at 22 °C

be deduced without reference to the corresponding acyclic compounds (11) and (13). The simplest test for the nature of the ring currents in (1)—(7) which should have similar geometry and planarity, is provided by the chemical shifts of the methyl groups, since these must be outside the ring. The alternation of the methyl proton resonances between the [4n + 1]annulenones (1), (3), (5), and (7) (relatively high field), and the [4n — 1]-annulenones (2), (4), and (6) (relatively low field) confirms the paratropicity of the former and the diatropicity of the latter (Table 3).

The ^{1}H n.m.r. chemical shifts of the deuteriated species (1′)—(7′) obtained by dissolution of (1)—(7) in deuterio-trifluoroacetic acid, are also given in Table 3. It is evident that the conformations of (6′) and (7′) are unchanged. Comparison of the olefinic proton chemical

(6) and (7) to be essentially temperature-independent, although with decreasing temperature the resonances of the inner and outer protons of the [23]annulenone (6) move to slightly higher and lower field, respectively, whereas the resonances of the inner and outer protons of the [25]annulenone (7) move to slightly lower and higher field, respectively, reflecting that both of (6) and (7) have higher planarity at low temperatures.

Also, the ^{1}H n.m.r. spectra of compound (6′) changed with time, suggesting transformation to a different compound (see Experimental section). A similar observation was made for the dimethyl- and trimethyl-tetradehydro[19]annulenones.[5] However, we could not determine the structure of the transformation product from (6′) because of insufficient starting compound.

TABLE 4

Variable-temperature ¹H n.m.r. parameters of compounds (6) and (7) in CDCl₃ (τ-values)

Compound	T (°C)	$H^{A'}$	H^B	H^D	$H^{D'}$	H^F	$H^{F'}$	$H^{H'}$	H^H	$H^{B'}$	H^C	$H^{C'}$	H^E	$H^{E'}$	H^G	$H^{G'}$	$H^{I'}$	H^I	Me
(6) [a]	+60	3.68	3.84	3.94	3.98	4.10	4.22	4.26		3.50	2.98						3.42		7.88, 7.93
	+22	3.70	3.88	3.98	4.02	4.14	4.26	4.29		3.56	2.95						3.40		7.86, 7.91
	−30	3.74	3.94	4.02	4.06	4.18	4.28	4.32		2.88							3.52		7.83, 7.89
	−60	3.75	3.92					4.50		2.80							3.48		7.85
(7) [b]	+60	4.03	2.29							2.86	3.61							3.91	8.14
	+22	4.06	2.24							2.82	3.60							3.91	8.14
	−30	4.12	2.18							2.76	3.61							3.93	8.14
	−60	4.12	2.10							2.70	3.61							3.95	8.14

[a] At 100 MHz. [b] At 200 MHz.

EXPERIMENTAL

Deoxygenated ether was used for aldol condensations, prepared as reported.[12] 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 (measured in tetrahydrofuran solution unless stated otherwise) were taken on a Hitachi 124. N.m.r. spectra were recorded with a Varian EM-390 (90 MHz) or a JEOL FX-100 (100 MHz) or a Varian XL-200 (200 MHz) spectrometer in CDCl$_3$ solution unless specified otherwise (SiMe$_4$ as an internal standard). 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.

(2E,4E,6E,8Z)-9-*methylundeca*-2,4,6,8-*tetraen*-10-*ynal* (10).—Lithium ethoxide [from lithium (209 mg, 0.030 g atom)] in dry ethanol (46 ml) was added dropwise with stirring under nitrogen atmosphere at 65—70 °C during 2 h to (2E,4E,6Z)-7-methyl-2,4,6-trien-8-ynal (8)[8] (3.40 g, 23 mmol) and [(1,3-dioxolan-2-yl)methyl]triphenylphosphonium bromide[10] (12.7 g, 29 mmol) in dry NN-dimethylformamide (96 ml). After an additional 2 h stirring under a slow stream of nitrogen at the same temperature, the mixture was poured into water (500 ml), and extracted with benzene. The combined extracts were washed with saturated brine, dried, and concentrated. The residue was dissolved in tetrahydrofuran (151 ml) and mixed with 10% hydrochloric acid (151 ml), then stirred for 1.5 h at room temperature. The aqueous layer was extracted with benzene, and the organic layer, combined with the extracts, was worked up in the usual fashion. The brown semi-solid was chromatographed on alumina (90 g); elution with hexane–ether (3 : 1) afforded the aldehyde (10) (2.43 g, 60%) as a solid. Recrystallization from hexane–ether gave brown *needles*, m.p. 84—85 °C; m/e 172 (M$^+$, 25%) and 138 (100); M, 172.2; $\nu_{max.}$ 3 250 (C≡C–H), 2 100 (C≡C), 1 680 (CHO), 1 610 (C=C), and 995 cm^{-1} (*trans*-C=C); $\lambda_{max.}$ (ether) 224 (ε 5 030), 253 (6 430), 333sh (32 200), 349 (50 700), and 367 nm (47 900); τ(90 MHz) 0.33 (1 H, d, J 8 Hz, –CHO), 2.80 (1 H, dd, J 15 and 11 Hz, H^F), 3.00 (1 H, dd, J 15 and 11 Hz, H^B), ca. 3.1—3.7 (4 H, m, H^C, H^D, H^E, and H^G), 3.80 (1 H, dd, J 15 and 8 Hz, H^A), 6.53 (1 H, s, C≡CH), and 7.98 (3 H, s, Me) (Found: C, 83.55; H, 7.0. C$_{12}$H$_{12}$O requires C, 83.7; H, 7.0%).

3,10,21-*Trimethyltricosa*-3,5,7,9,12,14,16,18,20-*nonaen*-1,22-*diyn*-11-*one* (11).—A solution of the trienyne aldehyde (8)[8] (1.03 g, 5.98 mmol) in deoxygenated ether (9 ml) was added dropwise over 17 min to a stirred solution of the tetraenone ketone (9)[3] (0.80 g, 3.97 mmol) in deoxygenated ether (32 ml) containing ethanolic sodium ethoxide (47 ml) [from sodium (760 mg) and dry ethanol (100 ml)] at 2—3 °C. After stirring for a further 2 h at the same temperature, further portions of ethanolic sodium ethoxide, each 8.0 ml, were added every 2 h. After stirring for a total of 8 h, the reaction was quenched by the addition of aqueous oxalic acid, poured into water (200 ml), and extracted with benzene. After work-up as usual, the brown semi-solid obtained by solvent removal was chromatographed on alumina (130 g). The initial fractions gave the recovered ketone (9) (132 mg) and the following fractions the recovered aldehyde (10) (170 mg). Later fractions (40% ether–hexane as eluant) gave the ketone (11) (923 mg, 66%) as a solid. Recrystallization from hexane–benzene afforded brown *needles*, m.p. 92 °C (decomp.);

m/e 354 (M$^+$, 42%) and 165 (100); M, 354.4; $\nu_{max.}$ 3 300 (C≡C–H), 2 100 (C≡C), 1 635 (C=O), 1 600 (C=C), 1 010, and 990 cm^{-1} (*trans* C=C); $\lambda_{max.}$ 286sh (ε 11 100), 340sh (29 900), 355sh (33 800), 372sh (35 600), 400sh (44 600), 418 (50 600), and 445sh nm (38 700); τ(90 MHz) 2.52—3.85 (15 H, m, olefinic H), 6.59 (1 H, s, C≡CH), 6.62 (1 H, s, C≡CH), and 8.00 (9 H, s, Me) (Found: C, 87.9; H, 7.6. C$_{26}$H$_{26}$O requires C, 88.1; H, 7.4%).

2,9,14-*Trimethyl*-10,11,12,13-*tetradehydrocyclotricosenone* (6).—A solution of the ketone (11) (1.45 g, 4.09 mmol) in pyridine–dry ether (3 : 1, 88 ml) was added dropwise during 5.5 h to a stirred solution of anhydrous copper(II) acetate (5.1 g) in pyridine–dry ether (3 : 1, 236 ml) at 48—51 °C. After stirring for a further 0.5 h at the same temperature, the solution was cooled. After addition of benzene (200 ml), the reaction mixture was filtered through Hyflo Super-Cel. The precipitates formed were washed with benzene (100 ml × 2), and the filtrate was poured into 3M-hydrochloric acid. The organic layer, combined with the benzene extracts from the aqueous layer, was washed with 3M-hydrochloric acid until it turned acidic, then with water, aqueous sodium hydrogencarbonate, and brine. Drying followed by removal of solvent gave a dark red semi-solid which was chromatographed on alumina (110 g). Fractions eluted with hexane–ether (1 : 1) gave the annulenone (6) (95 mg, 6.6%), which formed red *cubes* from hexane–benzene, m.p. 163 °C (decomp.); m/e 352 (M$^+$, 35%) and 206 (100); M, 352.4; $\nu_{max.}$ 2 150 (C≡C), 1 655 (C=O), 1 620 (C=C), and 980 cm^{-1} (*trans*-C=C); for u.v. data see Tables 1 and 2 and Figure 1; τ(100 MHz) 2.95—3.40 (7 H, m, H^C, H$^{C'}$, H^E, H$^{E'}$, H^G, H$^{G'}$, and H$^{I'}$), 3.56 (1 H, dd, J 15 and 5 Hz, H$^{B'}$), 3.70 (1 H, d, J 15 Hz, H$^{A'}$), 3.88 (1 H, d, J 11 Hz, H^B), 3.98 (1 H, dd, J 15 and 11 Hz, H^D), 4.02 (1 H, dd, J 15 and 11 Hz, H$^{D'}$), 4.14 (1 H, dd, J 15 and 11 Hz, H^F), 4.26 (1 H, dd, J 15 and 11 Hz, H$^{F'}$), 4.29 (1 H, dd, J 15 and 11 Hz, H$^{H'}$), 7.86 (3 H, s, Me), and 7.91 (6 H, s, Me) (see also Table 4 and Figure 2); τ(CF$_3$CO$_2$D, 100 MHz) 1.35—2.15 (8 H, m, H$^{B'}$, H^C, H$^{C'}$, H^E, H$^{E'}$, H^G, H$^{G'}$, and H$^{I'}$), 6.84—7.85 (7 H, m, H$^{A'}$, H^B, H^D, H$^{D'}$, H^F, H$^{F'}$, and H$^{H'}$), 7.08 (3 H, s, Me), 7.12 (3 H, s, Me), and 7.24 (3 H, s, Me). In addition, new signals at τ 3.48 (d, J 15 Hz) and 5.64 (dd, J 15 and 12 Hz) appeared during the course of time (Found: C, 88.3; H, 6.9. C$_{26}$H$_{24}$O requires C, 88.6; H, 6.9%).

3,12-*Dimethyltetradeca*-3,5,7,9,11-*pentaen*-13-*yn*-2-*one* (12).—A solution of the tetraenyne aldehyde (10) (2.25 g, 13 mmol) in acetic acid (14 ml) was added dropwise over 6 min to a stirred solution of butan-2-one (47.2 g, 0.66 mol) and concentrated sulphuric acid (8.5 ml) in acetic acid (127 ml) at 6—7 °C. The resultant dark red solution was stirred for a further 15 min at the same temperature, and the solution was then cautiously added to a stirred aqueous potassium carbonate solution (193 g, 210 ml). The reaction mixture was poured into water (300 ml) and extracted with benzene. The combined extracts were washed with brine and dried. Chromatography of the product over alumina (70 g) with hexane–ether (4 : 1) as eluant gave the ketone (12) (826 mg, 28%) as a solid. Recrystallization from hexane–benzene afforded orange *needles*, m.p. 98—99 °C; m/e 226 (M$^+$, 100%); M, 226.3; $\nu_{max.}$ 3 280 (C≡C–H), 2 100 (C≡C), 1 670, 1 660 (C=O), and 1 620 (C=C), and 1 005 cm^{-1} (*trans*-C=C); $\lambda_{max.}$ 245sh (ε 51 900), 251 (61 300), 255 (60 400), 262sh (46 200), 277sh (10 400), 339sh (19 500), 358sh (39 900), 378 (58 500), and 400 nm (54 800); τ(90 MHz) 2.60—3.85 (8 H, m, olefinic H), 6.60 (1 H, s, C≡CH), 7.64 (3 H, s, Me), 8.02 (3 H, s, Me), and 8.08 (3 H, s, Me)

(Found: C, 85.15; H, 8.0. $C_{16}H_{18}O$ requires C, 84.9; H, 8.0%).

3,12,23-*Trimethylpentacosa*-3,5,7,9,11,14,16,18,20,22-*decaen*-1,24-*diyn*-3-*one* (13).—A solution of ethanolic sodium ethoxide (14 ml) [from sodium (760 mg) and dry ethanol (50 ml)] was added to a solution of the pentaenyne ketone (12) (397 mg, 1.76 mmol) in deoxygenated ether (14 ml), and a solution of the tetraenyne aldehyde (10) (605 mg, 3.52 mmol) in deoxygenated ether (54 ml) was added dropwise during 20 min with stirring at 3—5 °C. After stirring for a further 6 h at the same temperature, the reaction was quenched by addition of aqueous oxalic acid. After work-up as for the isolation of (11), the brown solid obtained was chromatographed on alumina (100 g). Initial fractions gave the recovered aldehyde (10) (149 mg). Later fractions, eluted with hexane–ether (2 : 3), gave the ketone (13) (594 mg, 89%). Recrystallization from hexane–benzene afforded brown *cubes*, m.p. 146 °C (decomp.); m/e 380 (M^+, 71%) and 281 (100); M, 380.5; $\nu_{max.}$ 3 300 (C≡C–H), 2 100 (C≡C), 1 635 (C=O), 1 605 (C=C), 1 005, and 990 cm^{-1} (*trans*-C=C); $\lambda_{max.}$ 256 (ε 6 170), 346sh (42 800), 366 (49 800), 387sh (53 900), 418 (69 600), 432 (72 700), and 456sh nm (58 800); τ(90 MHz) 2.47—3.75 (17 H, m, olefinic H), 6.60 (2 H, s, –C≡CH), and 8.00 (9 H, s, Me) (Found: C, 88.2; H, 7.5. $C_{28}H_{28}O$ requires C, 88.4; H, 7.4%).

2,11,16-*Trimethyl*-12,13,14,15-*tetradehydrocyclopentacos-enone* (7).—A solution of the ketone (13) (784 mg, 2.1 mmol) in pyridine–dry ether (3 : 1, 72 ml) was added dropwise to a stirred solution of anhydrous copper(II) acetate (2.6 g) in pyridine–dry ether (3 : 1, 120 ml) during 5 h at 48—53 °C. The solution was stirred for a further 30 min at the same temperature and cooled. After work-up as for the isolation of (6), the dark red semi-solid obtained was chromatographed on alumina (90 g). Fractions, eluted with hexane–ether (3 : 2), gave the annulenone (7) (39 mg, 5.0%). Recrystallization from hexane–benzene afforded purple *needles*, m.p. 145 °C (decomp.); m/e 378 (M^+, 100%); M, 378.4; $\nu_{max.}$ 2 100 (C≡C), 1 640 (C=O), 1 615, 1 595 (C=C), and 1 000 cm^{-1} (*trans*-C=C); for u.v. data see Tables 1 and 2 and Figure 1); τ(200 MHz) 2.24—2.82 (8 H, m, H^B, $H^{B'}$, H^D, $H^{D'}$, H^F, $H^{F'}$, H^H, and $H^{H'}$), 3.60—3.91 (8 H, m, H^C, $H^{C'}$, H^E, $H^{E'}$, H^G, $H^{G'}$, H^I, and $H^{I'}$), 4.06 (1 H, d, J 16 Hz, $H^{A'}$), and 8.14 (9 H, s, Me) (see also Table 4 and Figure 2); τ(CF$_3$CO$_2$D, 100 MHz) -1.43 to -0.33 (8 H, m, H^B, $H^{B'}$, H^D, $H^{D'}$, H^F, $H^{F'}$, H^H, and $H^{H'}$), 3.97—4.76 (9 H, m, $H^{A'}$, H^C, $H^{C'}$, H^E, $H^{E'}$, H^G, $H^{G'}$, H^I, and $H^{I'}$), 8.23 (3 H, s, Me), and 8.49 (6 H, s, Me) (Found: C, 88.6; H, 7.0. $C_{28}H_{26}O$ requires C, 88.85; H, 6.9%).

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