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Syntheses and Properties of α-Ethyl-substituted Bisdehydro-[15]annulenones

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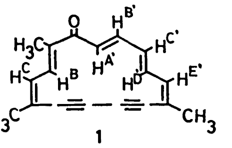
2-Ethyl-5,10-dimethyl- and 15-ethyl-5,10-dimethyl-6,8-bisdehydro[15]annulenone were synthesized. Influence of α-ethyl substitution upon the skeleton of the bisdehydro[15]annulenone ring system is discussed on the basis of ^{1}H NMR and UV spectra of these annulenones and their α-methyl-substituted derivatives.

In a previous paper[1)] we reported the synthesis of the diatropic bisdehydro[15]annulenones **1**—**3** and showed that the planarity, *i.e.*, the rigidity of molecular skeleton, of bisdehydro[15]annulenone ring system decreases in the sequence of **1**>**2**>**3**, reflecting the effect of perturbation caused by the introduction of α-methyl substituent. Since 3-ethyl-2-alkanones **6**[2)] and **9** were made available, we examined the effect of α-ethyl group on the molecular skeleton of bisdehydro[15]annulenone ring system.



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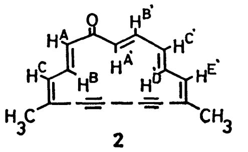

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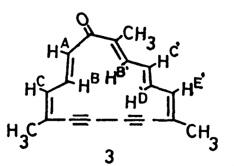

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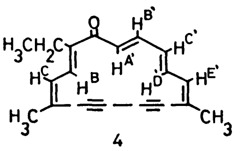

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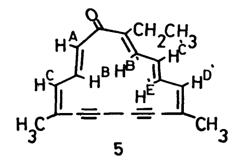

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Results and Discussion

Synthesis. Annulenones **4** and **5** were synthesized by a reaction sequence similar to that used for their corresponding α-methyl derivatives.[1)] Condensation of ketone **6**,[2)] obtained from aldehyde **10**[3)] and 2-pentanone, with (2*E*,4*Z*)-5-methyl-2,4-heptadien-6-ynal **7**[4)] in the presence of ethanolic sodium ethoxide in ether gave the acyclic ketone **8** in 75% yield. Oxidative coupling of **8** with anhydrous copper(II) acetate in pyridine and dry ether at 50 °C[5)] gave annulenone **4** in 38% yield. Acid-catalyzed aldol condensation of **7** with 2-pentanone yielded ketone **9** in 34% yield. Reaction of **9** and **10**, under the same conditions as for **6** and **7**, afforded ketone **11** in 36% yield. Oxidation of **11**, as with **8**, afforded another annulenone **5** in 34% yield. 2-Ethyl-5,10-dimethyl-**4** and 15-ethyl-5,10-dimethyl-6,8-bisdehydro[15]annulenone **5** formed yellow needles (mp 145—146 °C) and orange cubes (mp 97—98 °C), respectively; both **4** and **5** appear to be considerably stable. All the new compounds gave spectral data consistent with the assigned structures and satisfactory results of elemental analysis were obtained except for the unstable acyclic ketone **11**.

Treatment of annulenone **4** or **5** with trifluoroacetic acid or trifluoroacetic acid-*d* gave a red solution indicating formation of the protonated or deuteronated species **4′** or **5′**, respectively. Quenching of **4′** or **5′** with aqueous sodium hydrogencarbonate resulted in regeneration of **4** or **5**, respectively.

Properties. Electronic absorption maxima of these annulenones **4** and **5** as well as related derivatives **1**—**3**[1)] are listed in Table 1. As expected, the spectra are similar to one another. However, the main and longest wavelength bands exhibit a small bathochromic shift in the sequence of **4**>**1**>**2** as the α-substituent at C_2-position passes from ethyl *via* methyl to hydrogen, whereas in the spectra of **3** and **5**, the positions of these maxima are in relatively short wavelengths and appear to be independent of alkyl substitution at C_{15}-position, reflecting that the molecular skeletons of **3** and **5** are less planar than those of **1**, **2**, and **4**. The absorption maxima of these annulenones **1**—**5** in tri-

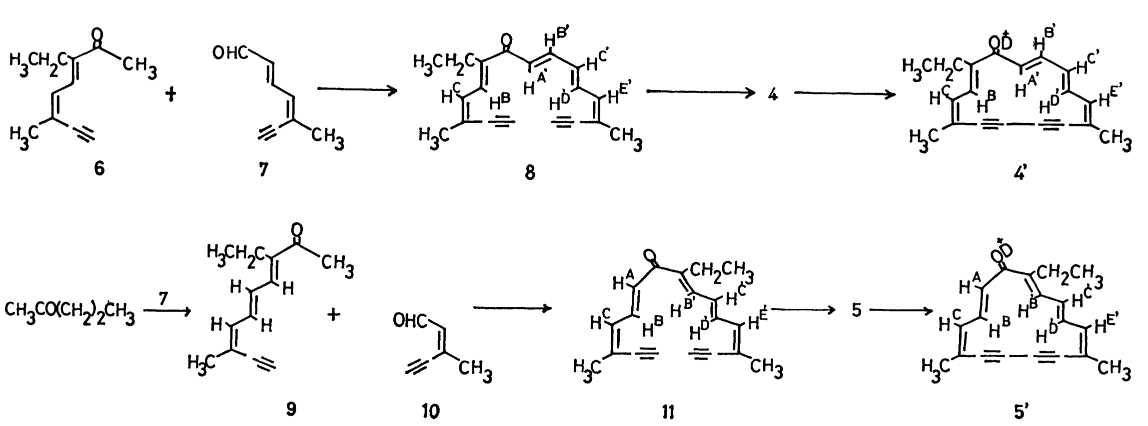


Table 1. Electronic absorption maxima of bisdehydro[15]annulenones in ether λ_{max}/nm (ε_{max})

1[a)]	**2**[a)]	**3**[a)]	**4**	**5**
232 sh (13400)	247 sh (13000)	247 sh (12500)	221 sh (17500)	247 sh (12600)
246 (13800)	258 (14300)	257 sh (14200)	247 (12200)	252 sh (13300)
258 (14800)	301 (33200)	298 (40500)	258 (13700)	258 sh (14700)
304 (42600)	382 (5700)	366 (6530)	308 (41200)	297 (37800)
310 sh (41200)			387 (7350)	369 (6540)
384 (7880)				

a) See Ref. 1.

Table 2. Electronic absorption maxima of bisdehydro[15]annulenones in trifluoroacetic acid λ_{max}/nm (Relative extinction coefficient)

1[a)]	**2**[a)]	**3**[a)]	**4**	**5**
298 sh (0.08)	292 (0.08)	350 (1.00)	356 sh (0.72)	350 (1.00)
356 sh (0.72)	352 sh (0.68)	366 sh (0.72)	371 (1.00)	366 sh (0.74)
370 (1.00)	367 (1.00)	502 (0.35)	470 sh (0.07)	502 (0.34)
470 sh (0.11)	496 sh (0.15)	536 (0.35)	500 sh (0.16)	536 (0.33)
500 sh (0.18)	513 (0.19)		524 (0.20)	
524 (0.23)	555 (0.34)		562 (0.25)	
562 (0.29)				

a) See Ref. 1.

Table 3. ^{1}H NMR chemical shifts of **1**—**5**, **8**, **11** (in $CDCl_3$), and **1′**—**5′** (in CF_3COOD) at 90 MHz, determined at 35 °C (τ Value; Internal standard, Me_4Si)

Compd	H^A	$H^{A'}$	H^B	$H^{B'}$	H^C	$H^{C'}$	$H^{D'}$	$H^{E'}$	CH_3	$-C\underline{H}_2CH_3$	$-CH_2C\underline{H}_3$
1[a)]		4.50	4.48	2.37	2.57	3.15	4.71	2.75	7.71, 7.79		
1′[a)]		10.57	10.60	0.17	0.60	1.20	10.69	0.80	6.68, 6.75, 6.80		
2[a)]	3.35	4.37	4.17	2.44	2.75	3.19	4.53	2.75	7.76, 7.82		
2′[a)]	1.31	10.10	9.92	0.29	0.89	1.28	10.15	0.89	6.73, 6.82		
3[a)]	3.33		4.38	4.53	2.73	2.87	4.61	2.91	7.79, 7.90, 7.95		
3′[a)]	1.60		8.52	8.05	1.30	1.25	8.95	1.33	6.89, 7.07, 7.12		
8		3.12	2.48	2.57	3.26	3.52	2.87	3.56	7.90, 7.98	7.47	8.97
4		4.47	4.50	2.36	2.56	3.14	4.69	2.73	7.70, 7.80	7.25	8.84
4′[b)]		10.53	10.58	0.17	0.60	1.20	10.67	0.77	6.60, 6.73	6.18	8.30
Δ(**4**−**8**)		+1.35	+2.02	−0.21	−0.70	−0.38	+1.82	−0.83	−0.10—−0.28	−0.22	−0.13
Δ(**4′**−**8**)		+7.41	+8.10	−2.40	−2.66	−2.22	+7.80	−2.79	−1.17—−1.38	−1.29	−0.67
11	3.15		2.25	2.85	3.50	2.93	3.35	3.50	7.97	7.47	8.97
5	3.30		4.38	4.58	2.73	2.82	4.62	2.90	7.80, 7.92	7.42	9.00
5′[b)]	1.60		8.46	8.02	1.30	1.23	8.83	1.30	6.93, 7.07	6.60	8.50
Δ(**5**−**11**)	+0.15		+2.13	+1.73	−0.77	−0.11	+1.27	−0.60	−0.05—−0.17	−0.05	+0.03
Δ(**5′**−**11**)	−1.55		+6.21	+5.17	−2.20	−1.70	+5.48	−2.20	−0.90—−1.04	−0.87	−0.47

a) See Ref. 1. b) Determined with CH_2Cl_2 as an internal standard.

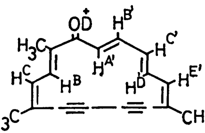
Table 4. ^{1}H NMR chemical shifts of compounds **4** and **5** (in $CDCl_3$) at 100 MHz (τ Value; Internal standard, Me_4Si)

Compd	T/°C	H^A	$H^{A'}$	H^B	$H^{B'}$	H^C	$H^{C'}$	$H^{D'}$	$H^{E'}$	$-C\underline{H}_2CH_3$	CH_3	$-CH_2C\underline{H}_3$
4	+60		4.44	4.46	2.45	2.66	3.24	4.62	2.83	7.30	7.75, 7.84	8.88
	+22		4.51	4.54	2.42	2.64	3.20	4.73	2.80	7.30	7.73, 7.82	8.88
	−30		4.60	4.68	2.36	2.58	3.14	4.89	2.73	7.29	7.69, 7.79	8.88
	−60		4.63	4.74	2.32	2.54	3.09	4.95	2.68	7.28	7.65, 7.76	8.88
5	+60	3.40		4.33	4.59	2.86	2.94	4.58	3.01	7.46	7.84, 7.96	9.01
	+22	3.36		4.43	4.63	2.81	2.90	4.66	2.98	7.45	7.82, 7.92	9.02
	−30	3.30		4.60	4.74	2.76	2.80	4.78	2.92	7.44	7.77, 7.88	9.02
	−60	3.26		4.68	4.77	2.72	2.75	4.83	2.88	7.41	7.74, 7.83	9.02

fluoroacetic acid are given in Table 2, and it is evident that protonation of **4** and **5** with this acid causes shift of main maxima to longer wavelengths, similarly to the case of **1**—**3**. The main maxima of these annulenones in trifluoroacetic acid exhibit a bathochromic shift in the order of $\mathbf{4}\simeq\mathbf{1}>\mathbf{2}>\mathbf{3}\simeq\mathbf{5}$, suggesting that the positions of main maxima do not depend on alkyl substitution, but on molecular planarity (*vide infra*). Also, the bathochromic shifts (53—63 nm) of the main maxima of **4** and **5** by protonation are much larger than that observed for their corresponding α-ethyl-substituted bisdehydro[13]annulenone (7 nm);[2] similar relations have been observed between [4*n*—2]- and [4*n*]annulenes and dehydroannulenes.[6]

^{1}H NMR chemical shifts of the protons of **4**, **5**, **8**, and **11**, together with those of **1**—**3** reported by us[1] are summarized in Table 3. The individual assignments, some of which are tentative, were made on the basis of multiplicity, coupling constants (Experimental), and data of closely related compounds.[1]

A comparison of the ^{1}H NMR chemical shifts of various protons of annulenones **4** and **5** with those of their corresponding acyclic ketones **8** and **11** indicates that both **4** and **5** are diatropic, as might be expected with 14π-electron systems. This follows from the fact that all the inner protons in **4** and **5** resonate at higher fields than their corresponding protons in **8** and **11**, respectively, whereas essentially all the outer protons (including allylic methylene and methyl protons) in **4** and **5** resonate at lower fields.



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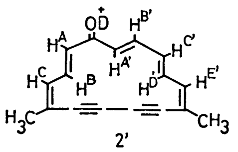

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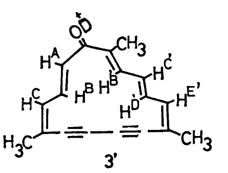

3'

^{1}H NMR chemical shifts of the deuteronated species **1'**—**5'**, obtained through dissolution in trifluoroacetic acid-*d*, are also given in Table 3. It is evident that the conformations of **4** and **5** are unchanged. A comparison of the chemical shifts of various protons of **4'** and **5'** with those of their corresponding acyclic models **8** and **11**, as with **4** and **5** mentioned above, indicates that the diatropicities of the deuteronated species **4'** and **5'** are much more marked than those of annulenones **4** and **5**, respectively.

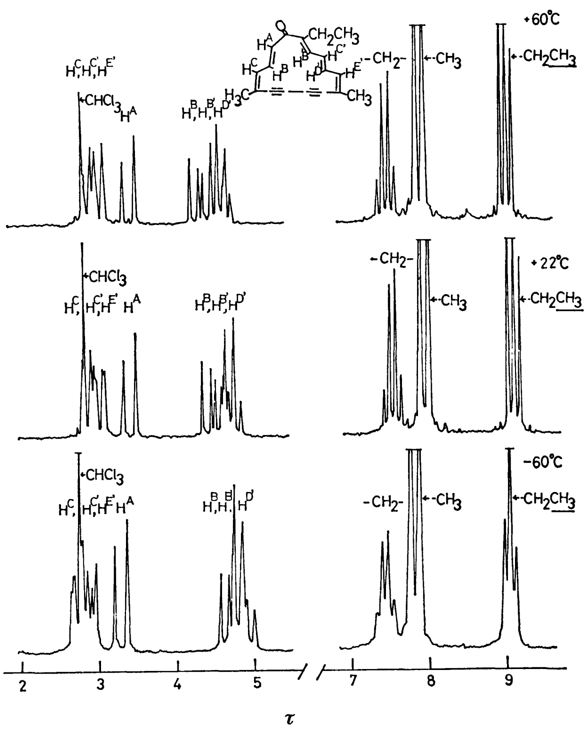

Fig. 1. The ^{1}H NMR FT spectra of **5** in $CDCl_3$ at 100 MHz (internal standard, TMS).

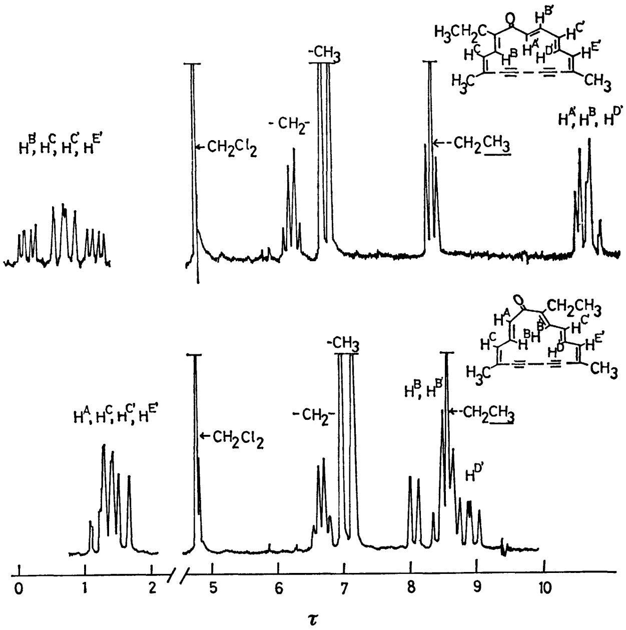

Fig. 2. The 90 MHz ^{1}H NMR spectra of **4** and **5** in CF_3COOD at 35 °C.

Variable-temperature ^{1}H NMR spectra of **4** and **5**, recorded over the range of −60 to 60 °C and summarized in Table 4, show that temperature has essentially no effect on spectra of **4** or **5**. Spectra of ethyldimethylbisdehydro[13]annulenone **5**, expected to be more mobile than **4**, are shown in Fig. 1. On cooling, the resonance of the inner (H^B, $H^{B'}$, $H^{D'}$) protons of **5** shifts to a slightly higher field, whereas that of the outer (H^A, H^C, $H^{C'}$, $H^{E'}$) protons (including allylic methylene and methyl protons) 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 in the range −60—60 °C, excluding any change in conformation due to rotation of the $CH^A{=}CH^B$ double bond over this temperature range, in contrast to the case of α-ethyl-substituted bisdehydro[13]annulenones.[2] The signals of both the inner and outer protons of **4** exhibit less temperature dependence than those of **5** in the range −60—60 °C (Table 4), reflecting an enhanced rigidity in the molecular skeleton of **4**. This tendency is manifested very markedly in the spectra of **4** and **5** in trifluoroacetic acid-*d*, illustrated in Fig. 2. It is to be noted that the magnitudes of upfield shifts of the inner protons and of downfield shifts of the outer and methyl protons decrease in the order of **4**>**5**. Also, the chemical shifts of the olefinic and methyl protons of **4′** are almost the same with those of their corresponding protons of **1′**. Similar relations in chemical shift are seen between **3′** and **5′** (Table 3). This fact suggests that the planarity, *i.e.*, the rigidity, of this bisdehydro[15]annulenone ring system decreases in the sequence of $\mathbf{4}\simeq\mathbf{1}>\mathbf{2}>\mathbf{3}\simeq\mathbf{5}$. This interpretation, already presented on a different basis, is supported by the fact that their bathochromic shifts in main maxima as well as the longest wavelength bands are in the same sequence in both ether and trifluoroacetic acid (Tables 1 and 2).

Thus, the difference in behavior observed for the bisdehydro[15]annulenone ring system against the α-ethyl and α-methyl substitutions is not so large as that for the corresponding bisdehydro[13]annulenone system,[2] reflecting higher planarity of the molecular skeleton of the former system.

Experimental

Deoxygenated ether was prepared and used as reported.[1,2] Melting points were uncorrected. IR spectra were taken with a Hitachi EPI-S2 spectrophotometer. UV spectra were measured on a Hitachi 124 spectrophotometer and recorded in nm. ε-Values are given in parentheses, shoulders being denoted by sh. Mass spectra were recorded with a JEOL JMS-200 spectrometer operating at 75 eV. ^{1}H NMR spectra were recorded with a Varian EM-390 (90 MHz) or a JEOL FX-100 (100 MHz) spectrometer. Data taken with a Varian EM-390 instrument at 35 °C are specified by τ-value for $CDCl_3$ solution, TMS being used as an internal standard unless otherwise stated. Coupling constants (J) are given in Hz. Merck alumina (Act. II—III) was used for column chromatography. Sodium sulfate was used as drying agent, and solvents were evaporated at the water aspirator pressure.

*6-Ethyl-3,13-dimethyl-3,5,8,10,12-pentadecapentaene-1,14-diyn-7-one (**8**).* A solution of aldehyde **7**[4] (1.10 g, 9.3 mmol) in deoxygenated ether (17 ml) was added dropwise during 30 min to a stirred ice-cooled solution of ketone **6**[2] (1.0 g, 6.2 mmol) in deoxygenated ether (47 ml) containing ethanolic sodium ethoxide (6.7 ml) [from sodium (760 mg) and absolute ethanol (50 ml)]. After stirring for 5 h, portions of the ethanolic sodium ethoxide (each 2.0 ml) were added every 2 h. After stirring for a total 8 h, 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 aqueous sodium hydrogencarbonate and brine, and then dried. The semi-solid obtained after removal of the solvent was chromatographed on alumina (80 g). The early fractions gave the recovered ketone **6** (188 mg). The later fractions eluted with hexane–ether (4:1) gave ketone **8** (1.23 g, 75%) as a solid. Recrystallization from hexane–benzene afforded orange needles: mp 69—70 °C; MS, *m*/*e*, 264 (M^+, 74%) and 192 (100); mol wt 264.3; IR (KBr disk) 3300 ($-C\equiv CH$), 2100 ($-C\equiv C-$), 1640 (C=O), 1610, 1585 (C=C), and 1085 cm^{-1} (*trans* C=C); UV_{max} (ether) 225 sh (10300), 231 (10900), 253 sh (16100), 266 (20500), 277 (20800), 290 (21400), 304 (22800), 340 sh (32000), 356 (36100), and 373 nm sh (29600); NMR $\tau=2.48$ (d, 11, 1H, H^B), 2.57 (dd, 15, 11, 1H, $H^{B'}$ or $H^{C'}$ or $H^{D'}$), 2.87 (dd, 15, 11, 1H, $H^{B'}$ or $H^{C'}$ or $H^{D'}$), 3.12 (d, 15, 1H, $H^{A'}$), 3.26 (d, 11, 1H, H^C or $H^{E'}$), 3.52 (dd, 15, 11, 1H, $H^{B'}$ or $H^{C'}$ or $H^{D'}$), 3.56 (d, 11, 1H, H^C or $H^{E'}$), 6.43 (s, 1H, $-C\equiv CH$), 6.53 (s, 1H, $-C\equiv CH$), 7.47 (q, 8, 2H, $-C\underline{H}_2CH_3$), 7.90 (s, 3H, CH_3), 7.98 (s, 3H, CH_3), and 8.97 (t, 8, 3H, $-CH_2C\underline{H}_3$). Found: C, 86.05; H, 7.43%. Calcd for $C_{19}H_{20}O$: C, 86.32; H, 7.63%.

*2-Ethyl-5,10-dimethyl-6,8-bisdehydro[15]annulenone (**4**).* A solution of ketone **8** (1.17 g, 4.4 mmol) in pyridine (79 ml) and dry ether (27 ml) was added dropwise to a stirred solution of anhydrous copper(II) acetate (5.3 g) in pyridine (159 ml) and dry ether (53 ml) during 6 h at 49—52 °C. The solution was stirred for a further 30 min at the same temperature, and then cooled. After addition of benzene (300 ml), the mixture was filtered through a Hyflo Super-Cel. The precipitates formed were washed with benzene (100 ml × 3) and the filtrate was poured into water. The organic layer was separated and the aqueous layer was extracted with benzene. The combined organic extracts were washed successively with 7% hydrochloric acid, aqueous sodium hydrogencarbonate, and brine, and then dried. The semi-solid obtained after removal of the solvent was chromatographed on alumina (80 g). The fractions eluted with hexane–ether (7:3) gave annulenone **4** (434 mg, 38%). Recrystallization from hexane–benzene afforded yellow needles: mp 145—146 °C; MS, *m*/*e*, 262 (M^+, 27%) and 203 (100); mol wt 262.3; IR (KBr disk) 2170 ($-C\equiv C-$), 1635 (C=O), 1610 (C=C), and 975 cm^{-1} (*trans* C=C); UV, see Tables 1 and 2; NMR $\tau=2.36$ (dd, 16, 5, 1H, $H^{B'}$ or $H^{C'}$), 2.56 (d, 11, 1H, H^C or $H^{E'}$), 2.73 (d, 11, 1H, H^C or $H^{E'}$), 3.14 (dd, 16, 5, 1H, $H^{B'}$ or $H^{C'}$), 4.47 (d, 16, 1H, $H^{A'}$), 4.50 (d, 11, 1H, H^B), 4.69 (dd, 16, 11, 1H, $H^{D'}$), 7.25 (q, 8, 2H, $-C\underline{H}_2CH_3$), 7.70 (s, 3H, CH_3), 7.80 (s, 3H, CH_3), and 8.84 (t, 8, 3H, $-CH_2C\underline{H}_3$); NMR (CF_3COOD, determined with CH_2Cl_2 as an internal standard) $\tau=0.17$ (dd, 15, 7, 1H, $H^{B'}$ or $H^{C'}$), 0.60 (d, 12, 1H, H^C or $H^{E'}$), 0.77 (d, 12, 1H, H^C or $H^{E'}$), 1.20 (dd, 15, 7, 1H, $H^{B'}$ or $H^{C'}$), 6.18 (q, 8, 2H, $-C\underline{H}_2CH_3$), 6.60 (s, 3H, CH_3), 6.73 (s, 3H, CH_3), 8.30 (t, 8, 3H, $-CH_2C\underline{H}_3$), 10.53 (d, 15, 1H, $H^{A'}$), 10.58 (d, 12, 1H, H^B), and 10.67 (dd, 15, 11, 1H, $H^{D'}$), and see Fig. 2. Found: C, 87.15; H, 6.84%. Calcd for $C_{19}H_{18}O$: C, 86.98; H, 6.91%.

*3-Ethyl-8-methyl-3,5,7-decatrien-9-yn-2-one (**9**).* A solution of aldehyde **7**[4] (3.0 g, 25 mmol) in acetic acid (13 ml) was added dropwise during 20 min to a stirred solution of 2-pentanone (15.1 g, 0.175 mol) and concentrated sulfuric acid (4.7 ml) in acetic acid (95 ml) at 8—9 °C. The solution was stirred for a further 3 h, and then cautiously poured into saturated aqueous potassium carbonate (200 ml). The mixture was diluted with water, and extracted with benzene. The extracts were washed with saturated aqueous sodium chloride solution, and then dried. The dark red liquid obtained was chromatographed on alumina (80 g). The fractions eluted with hexane–ether (9:1—4:1) gave ketone **9** (1.59 g, 34%) as a yellow liquid: MS, *m*/*e*, 188 (M^+, 80%) and 159 (100); mol wt 188.2; IR (neat) 3250 ($-C\equiv CH$), 2100 ($-C\equiv C-$), 1655 (C=O), 1610, 1595 (C=C), and 980 cm^{-1} (*trans* C=C); UV_{max} (ether) 227 (5600), 236 (5710), 310 sh (23700), 331 (32800), and 341 nm sh (32500); NMR $\tau=2.89$ (d, 11, 1H, H^B), 2.95 (dd, 15, 11, 1H, H^D), 3.38 (dd, 15, 11, 1H, H^C), 3.52 (d, 11, 1H, H^E), 6.55 (s, 1H, $-C\equiv CH$), 7.56 (q, 8, 2H, $-C\underline{H}_2CH_3$), 7.63 (s, 3H, CH_3), 7.98 (s, 3H, CH_3), and 8.01 (t, 8, 3H, $-CH_2C\underline{H}_3$). Found:

C, 82.68; H, 8.29%. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57%.

*8-Ethyl-3,13-dimethyl-3,5,8,10,12-pentadecapentaene-1,14-diyn-7-one (**11**).* A solution of ethanolic sodium ethoxide (2.4 ml) [from sodium (760 mg) and absolute ethanol (50 ml)] was added to a solution of ketone **9** (1.0 g, 5.3 mmol) in deoxygenated ether (47 ml), and a solution of aldehyde **10**[3] (1.0 g, 11 mmol) in deoxygenated ether (16 ml) was then added dropwise during 15 min with stirring and ice-bath cooling. After stirring for a further 14.5 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 working up as in the preparation of **8**, the semi-solid obtained after removal of the solvent was chromatographed on alumina (100 g). The early fractions gave the recovered ketone **9** (438 mg). The following fractions eluted with hexane–ether (4:1) gave ketone **11** (498 mg, 36%). Recrystallization from hexane–benzene afforded brown needles: mp 92—93 °C; MS, *m/e*, 264 (M^+, 100%); mol wt 264.3; IR (KBr disk) 3250 ($-C\equiv CH$), 2100 ($-C\equiv C-$), 1640 (C=O), 1580 (C=C), and 985 cm^{-1} (*trans* C=C); UV_{max} (ether) 233 sh (12600), 250 sh (18500), 260 sh (22400), 275 sh (26600), 287 (29900), 299 (29300), 342 sh (44900), 358 (50100), and 375 nm sh (43800); NMR $\tau=2.25$ (dd, 15, 12, 1H, H^{B}), 2.85 (d, 12, 1H, $H^{B'}$), 2.93 (dd, 15, 12, 1H, $H^{C'}$), 3.15 (d, 15, 1H, H^{A}), 3.35 (dd, 15, 12, 1H, $H^{D'}$), 3.50 (d, 12, 2H, H^{C} and $H^{E'}$), 6.53 (s, 1H, $-C\equiv CH$), 6.60 (S, 1H, $-C\equiv CH$), 7.47 (q, 8, 2H, $-C\underline{H}_2CH_3$), 7.97 (s, 6H, CH_3), and 8.97 (t, 8, $-CH_2C\underline{H}_3$).

Crystals of **11** decomposed rapidly on exposure to diffused light and air at room temperature. Compound **11** gave unsatisfactory results of elemental analysis, which seems attributable to its instability. Found: C, 85.64; H, 7.35%. Calcd for $C_{19}H_{20}O$: C, 86.32; H, 7.63%.

*15-Ethyl-5,10-dimethyl-6,8-bisdehydro[15]annulenone (**5**).* A solution of ketone **11** (370 mg, 1.4 mmol) in pyridine–dry ether (3:1, 32 ml) was added dropwise during 2.5 h to a stirred solution of anhydrous copper(II) acetate (1.8 g) in pyridine–dry ether (3:1, 64 ml) at 48—50 °C. The solution was stirred at 49—51 °C for a further 30 min and then cooled. After working up as in the preparation of **4**, the semi-solid obtained after removal of the solvent was chromatographed on alumina (70 g). The fractions eluted with hexane–ether (3:1—2:3) gave annulenone **5** (124 mg, 34%) as a yellow liquid. Crystallization from hexane–benzene afforded orange cubes: mp 97—98 °C; MS, *m/e*, 262 (M^+, 25%) and 203 (100); mol wt 262.3; IR (KBr disk) 2150, 2100 ($-C\equiv C-$), 1620 (C=O), 1590 (C=C), 1000, and 970 cm^{-1} (*trans* C=C); UV, see Tables 1 and 2; NMR $\tau=2.73$ (d, 11, 1H, H^{C}), 2.82 (dd, 16, 11, 1H, $H^{C'}$), 2.90 (d, 11, 1H, $H^{E'}$), 3.30 (d, 16, 1H, H^{A}), 4.38 (dd, 16, 11, 1H, H^{B}), 4.58 (d, 11, 1H, $H^{B'}$), 4.62 (dd, 16, 11, 1H, $H^{D'}$), 7.42 (q, 8, 2H, $-C\underline{H}_2CH_3$), 7.80 (s, 3H, CH_3), 7.92 (s, 3H, CH_3), and 9.00 (t, 8, 3H, $-CH_2C\underline{H}_3$), and see Fig. 1; NMR (CF_3COOD, determined with CH_2Cl_2 as an internal standard) $\tau=1.23$ (dd, 15, 11, 1H, $H^{C'}$), 1.30 (d, 11, 2H, H^{C} and $H^{E'}$), 1.60 (d, 15, 1H, H^{A}), 6.60 (q, 8, 2H, $-C\underline{H}_2CH_3$), 6.93 (s, 3H, CH_3), 7.07 (s, 3H, CH_3), 8.02 (d, 11, 1H, $H^{B'}$), 8.46 (dd, 15, 11, 1H, H^{B}), 8.50 (t, 8, 3H, $-CH_2C\underline{H}_3$), and 8.83 (dd, 15, 11, 1H, $H^{D'}$), and see Fig. 2. Found: C, 87.18; H, 6.82%. Calcd for $C_{19}H_{18}O$: C, 86.98; H, 6.91%.

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