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SYNTHESES AND PROPERTIES OF TRIMETHYLBISDEHYDRO[19]ANNULENONES AND THE BENZANNELATED DERIVATIVES

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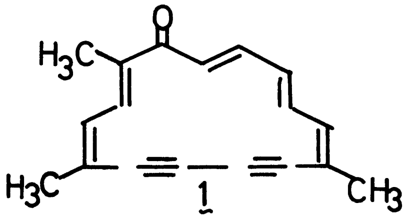
Syntheses of 2,7,12-trimethyl- **5**, 7,12,19-trimethyl-8,10-bisdehydro- **6**, 14-methylbenzo[h]-10,12-bisdehydro- **7**, and 2-methyldibenzo[f,l]-8,10-bisdehydro[19]-annulenone **8** are described. The effects of α-methyl substitution and benzannelation for the bisdehydro[19]annulenone ring system are discussed.

In the previous work,[1)] we reported that the annulenone **3a** (not **3b**) was obtained from the corresponding acyclic ketone by the intramolecular oxidative coupling. Also, it was shown that the planarity of molecular skeleton of bisdehydro[15]annulenone decreases in the order of **1**>**2**>**3a** on the basis of the chemical shifts of olefinic protons of the corresponding deuteronated species.[2)]

In view of these results as well as the effect of benzannelation, we were interested in examining the properties of the higher analogues of the annulenones **1**-**3** and the benzannelated ones,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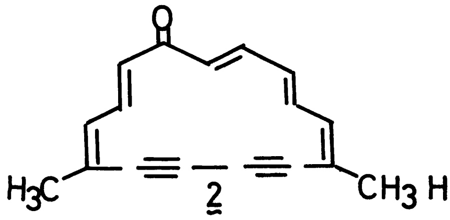
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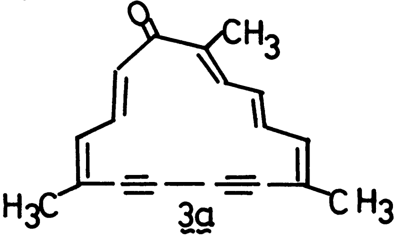
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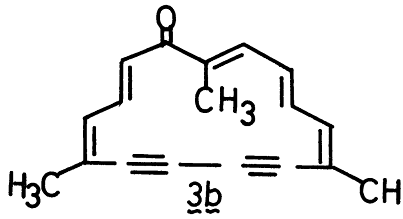
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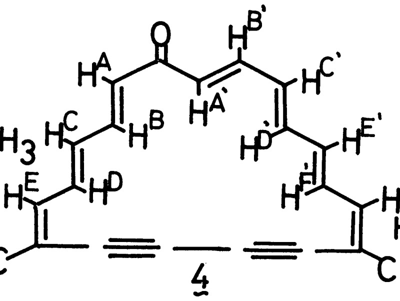
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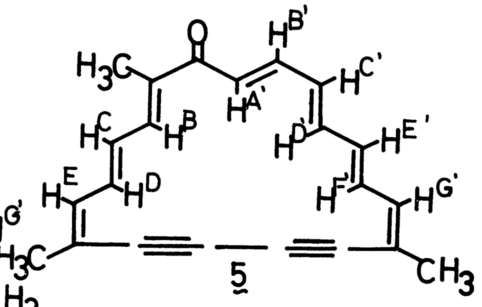
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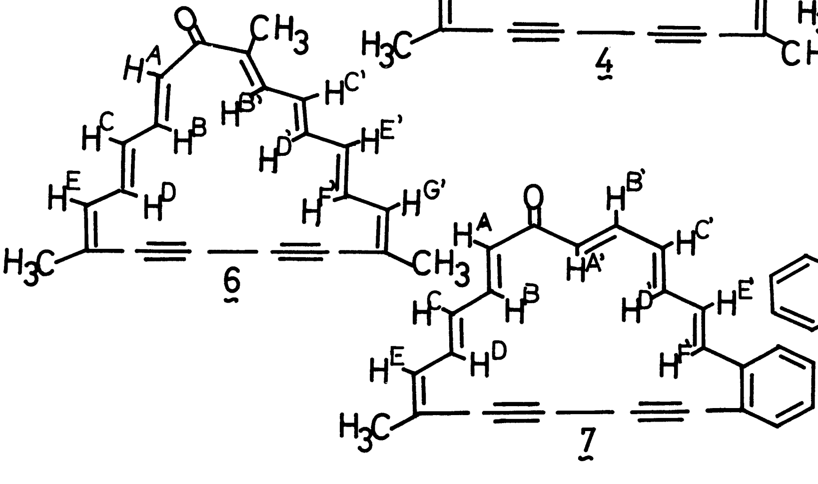
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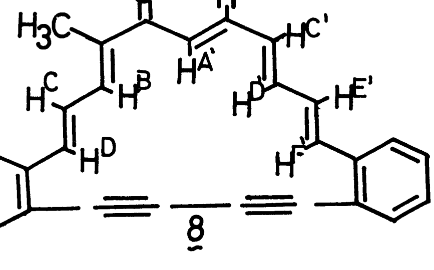
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i.e., 7,12-dimethyl- **4**,3) 2,7,12-trimethyl- **5**, 7,12,19-trimethyl-8,10-bisdehydro[19]annulenone **6**, 14-methylbenzo[h]-10,12-bisdehydro[19]annulenone **7**, and 2-methyldibenzo[f,l]-8,10-bisdehydro[19]-annulenone **8**.

Formation of **3a** from the corresponding acyclic ketone led us to expect that the annulenone having the larger cavity of π-electron cloud might set α-methyl substituent inside the ring. However, the compound obtained from the acyclic ketone **14** proved still to have configuration **6** with α-methyl group outside the ring by an analysis of the ^{1}H-NMR spectra.

The syntheses of the annulenones **5**–**8** were carried out by the same procedure as previously reported.1,4) Condensation of 3,8-dimethyl-3,5,7-decatrien-9-yn-2-one **9**4c) with 7-methyl-2,4,6-nonatrien-8-ynal **10**5) in the presence of ethanolic sodium ethoxide in ether for 7 h at room temperature gave the acyclic ketone **11** (mp. 117°C (dec), 38%).6) Oxidative coupling of **11** with anhydrous copper(II) acetate in pyridine and ether for 5 h at 50°C7) yielded the annulenone **5** (red needles,

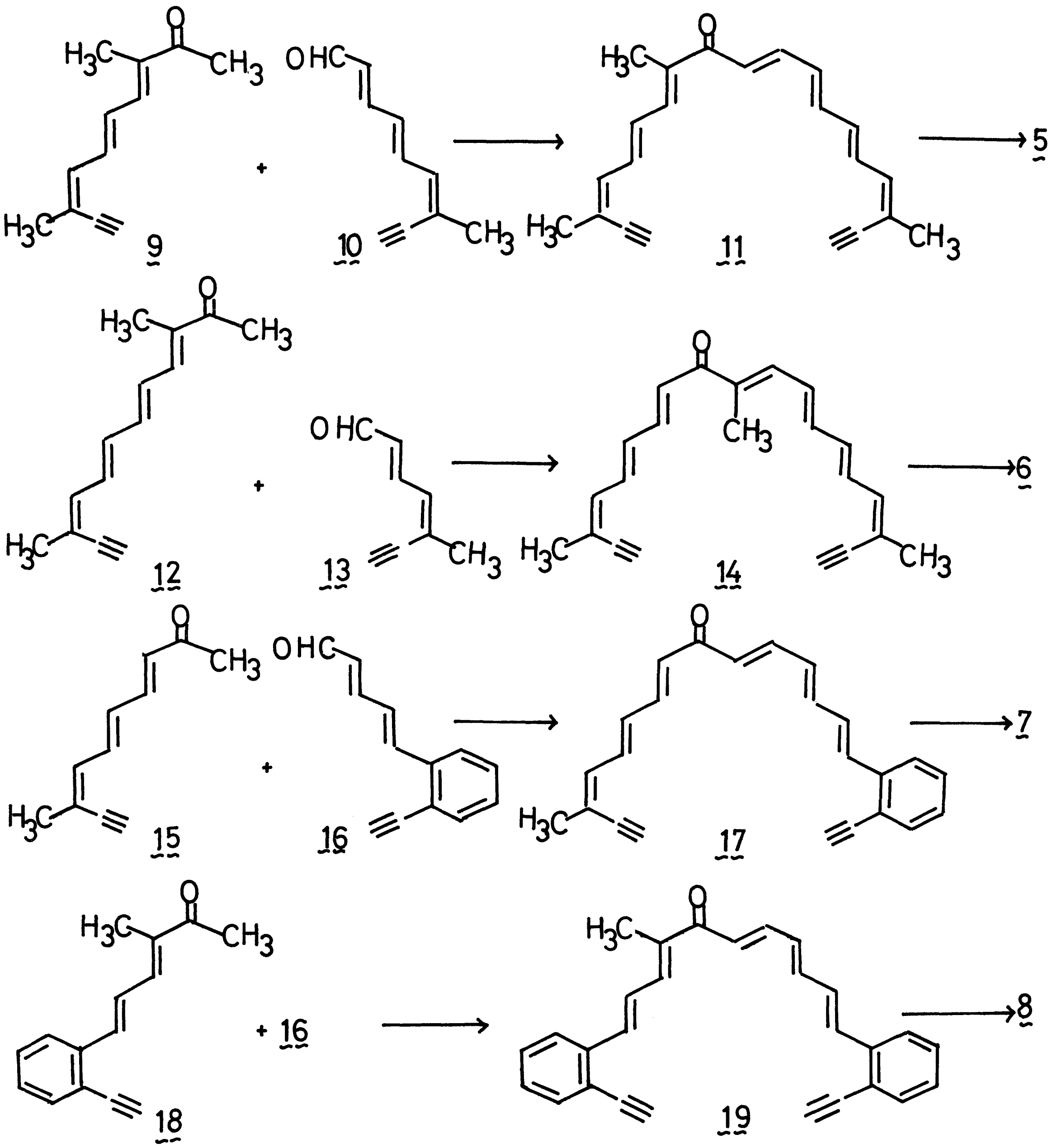


Table 1. The ¹H-NMR data of 4–8 (in $CDCl_3$) and 4'–8' (in CF_3COOD) at 90 MHz (τ values)[11]

	H^A	$H^{A'}$	H^B	$H^{B'}$	H^C	$H^{C'}$	H^D	$H^{D'}$	H^E	$H^{E'}$	$H^{F'}$	$H^{G'}$	ArH	CH_3
4	3.52	3.80	4.10	(2.87–3.22)		3.33	4.15	3.98	(2.87–3.22)		4.35	(2.87–3.22)		7.79, 7.83
4'[13]	(1.2–1.8)	(8.4—9.1)		(1.2———1.8)			(8.4—9.1)		(1.2—1.8)		(8.4–9.1)	(1.2–1.8)		6.96, 7.07
5		3.87	4.22	2.90	2.87	3.40	4.30	4.20	2.97	3.13	4.48	2.97		7.79, 7.83
5'		7.12	9.47	1.56	1.22	2.90	9.52	9.17	1.16	1.31	9.54	0.84		6.84, 6.94
6	(2.8–3.3)		(4.1———4.6)		(2.8———3.3)		(4.1———4.6)		(2.8———3.3)		(4.1–4.6)	(2.8–3.3)		7.80, 7.87, 7.95
6'[13]	(1.3–1.9)		7.69	7.43	(1.3———1.9)		8.12	8.02	(1.3———1.9)		8.42	(1.3–1.9)		7.07, 7.18
7	(2.27————————————————————3.90)													7.89
7'	3.03	5.02	4.87	(1.7—————2.7)			5.15	4.13	(1.7———2.7)		4.60		(1.7–2.7)	7.42
8		(2.40————————————————3.36)												7.87
8'		(1.90————————————————3.85)												7.58

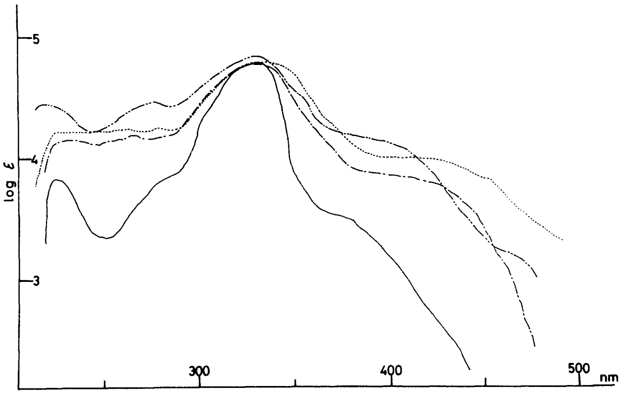


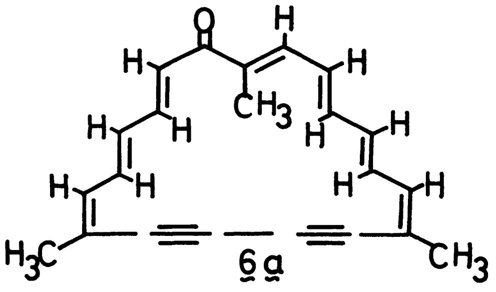
Fig. 1 The UV spectra of 5 (-------), 6 (— - — -), 7 (—·· — ··), and 8 (————) in THF

mp. 201°C (dec), 23%). The acid-catalysed condensation[8] of 2-butanone with 10 afforded the ketone 12 (mp. 76–77°C, 32%). Condensation of 12 with 5-methyl-2,4-heptadien-6-ynal 13[9] as that between 9 and 10 gave the ketone 14 (mp. 187–188°C, 43%), which was oxidized to yield the annulenone 6 (orange needles, mp. 120–121°C, 16%). Similarly, the reaction of 8-methyl-3,5,7-decatrien-9-yn-2-one 15[3b] with 5-(*o*-ethynylphenyl)-penta-2,4-dienal 16[10] afforded the ketone 17 (mp. 141–142°C, 70%). Oxidation of 17 as before gave the benzannulenone 7 (orange needles, mp. 135–136°C, 5.6%). Condensation of 6-(*o*-ethynylphenyl)-3-methyl-3,5-hexadien-2-one 18[4c] with 16 in the presence of ethanolic sodium ethoxide in tetrahydrofuran gave the ketone 19 (mp. 158–159°C, 56%), which was led to the dibenzannulenone 8 (yellow plates, mp. 216°C (dec), 16%).

The UV spectra of 5–8 are illustrated in Fig. 1. The longest wavelength band of these annulenones exhibits absorption toward longer wavelength in the sequence of 5≃6>7>8, demonstrating the degree of extended conjugation of π-electron system in bisdehydro[19]annulenone ring.

The ¹H-NMR data of the annulenones 4–8 are listed in Table 1, altogether with those of deuteronated species 4'–8' which were obtained by dissolving in deuterio-trifluoroacetic acid.[11] Examination of the ¹H-NMR spectra as well as the comparison with those of the respective acyclic ketones,[12] indicates that the methylated annulenones 4, 5, 6 are diatropic, whereas monobenz- 7 and dibenzannulenone 8 are atropic. On the other hand, in the corresponding deuteronated species 4', 5', 6' are strongly diatropic, 7' is diatropic, and 8' is atropic.

Also, comparison of the chemical shifts of olefinic and methyl protons of each column seems to exhibit that the diatropicities of the deuteronated species **4'**–**6'** decrease in the order of **5'**>**4'**[13] >**6'**, reflecting the degree of the planarity of bisdehydro[19]-annulenone skeleton due to perturbation caused by α-methyl substitution in these compounds **4'**–**6'**. This result is similar as that recognized for bisdehydro[15]-annulenone ring system.[2]



6a

In addition, it is noted that the intramolecular oxidative coupling of **14** gave the annulenone **6** with α-methyl substituent outside the ring in bisdehydro[19]annulenone system, as observed for the formation of **3a** in the corresponding [15]annulenone.[1] It suggests that the alternative structure **6a** experiences a considerable steric hindrance between the internal olefinic protons and the methyl protons, which puts the bulky α-methyl group outside the ring. Thus, one may conclude that the behavior is inherent in 1,3-bisdehydroannulenone ring system of this type.

References and Notes

1) J. Ojima, K. Wada, and K. Kanazawa, *Chem. Lett.*, 1979, 1035.

2) For a preliminary report, see J. Ojima *et al.*, Abstracts, 12th Symposium on Nonbenzenoid Aromatic Compound of the Chemical Society of Japan, Matsumoto, September 1979; see also Ref. 1).

3) For a preliminary report, see J. Ojima *et al.*, Abstracts, 11th Symposium on Nonbenzenoid Aromatic Compound of the Chemical Society of Japan, Osaka, October 1978; b) J. Ojima, Y. Shiroishi, and F. Sondheimer, to be published.

4) a) T. M. Cresp, J. Ojima, and F. Sondheimer, *J. Org. Chem.*, 42, 2130 (1977); b) J. Ojima and M. Fujiyoshi, *Chem. Lett.*, 1978, 569: *Idem, J. Chem. Soc., Perkin Trans. I*, in press; c) J. Ojima, K. Kanazawa, K. Kusaki, and K. Wada, *Chem. Lett.*, 1978, 1009: *Idem, J. Chem. Soc., Perkin Trans. I*, in press.

5) J. Ojima, Y. Shiroishi, and M. Fujiyoshi, *Bull. Chem. Soc. Jpn.*, 51, 2112 (1978).

6) All the compounds described in this paper gave IR, NMR, and mass spectral data consistent with the assigned structures and satisfactory elemental analyses were obtained.

7) N. Darby, T. M. Cresp, and F. Sondheimer, *J. Org. Chem.*, 42, 1960 (1977); see also Ref. 5).

8) This condensation was carried out by stirring for 1 h at room temperature using sulfuric acid-acetic acid (Ref. 4a). Prolonged stirring gave less satisfactory yields.

9) J. Ojima, M. Ishiyama, and A. Kimura, *Bull. Chem. Soc. Jpn.*, 50, 1584 (1977).

10) J. Ojima, M. Enkaku, and M. Ishiyama, *J. Chem. Soc., Perkin Trans. I*, 1977, 1548.

11) These spectra were taken on a Varian EM-390 spectrometer at 35°C and the assignments were made on the basis of multiplicity, coupling constants, and the data of the closely related compounds (Ref. 1), although these being in part tentative.

12) This refers to the comparison of the chemical shifts of olefinic protons and methyl protons with those of the respective corresponding acyclic ketones. The details will be reported elsewhere.

13) The ^{1}H-NMR spectrum of the compound **4'** varied along with the elapse of time, suggesting the transformation to a different compound. Similar observation was made for **6'** with a diminished rate. The study on this point is now in progress in our laboratory.

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