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SYNTHESES AND PROPERTIES OF TRIMETHYLBISDEHYDRO[21]ANNULENONE AND THE BENZANNELATED DERIVATIVES

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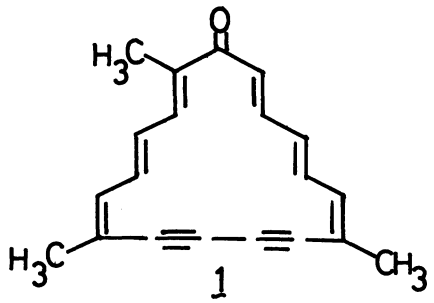
Syntheses of 2,9,14-trimethyl- 2, 14-methylbenzo[h]- 4, and 2-methyldibenzo[h,n]-10,12-bisdehydro[21]annulenone 5 are described. The effect of α-methyl substitution and benzannelation for the bisdehydro[21]annulenone ring sytem are discussed.

In the previous paper, we reported a synthesis of the paratropic 2,7,12-trimethyl-8,10-bisdehydro[17]annulenone 1 and its benzannelated derivatives, and showed that both α-methyl substitution and benzannelation exert no significant influence for the molecular skeleton of the bisdehydro[17]annulenone ring system of type 1,[1] in contrast to the case of the corresponding bisdehydro[13]annulenone.[2]

In view of the result as well as the effect of benzannelation on a ring current, we were interested in examining the properties of the higher analogue of 1 and the benzannelated compounds, *i.e.*, 2,9,14-trimethyl- 2, 9,14-dimethyl- 3,[3] 14-methylbenzo[h]- 4, and 2-methyldibenzo[h,n]-10,12-bisdehydro[21]annulenone 5.



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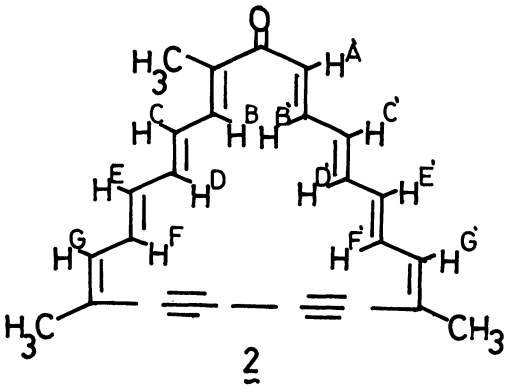

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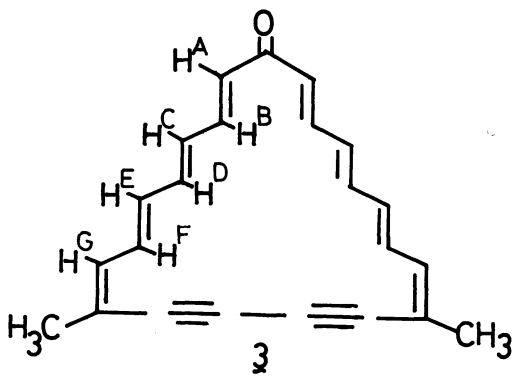

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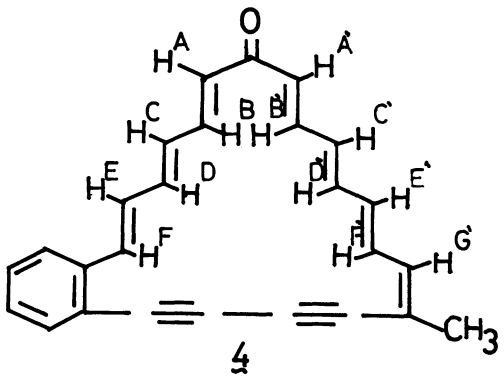

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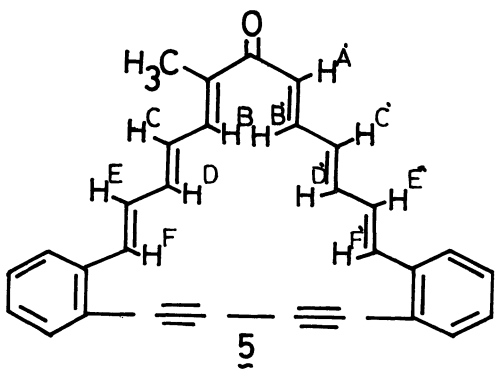

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Examination of the structure 2 by the Dreiding molecular model led us to infer that the annulenone 2 has a considerable steric strain due to a bent 1,3-diacetylene linkage and is less paratropic than the annulenone 1.

The syntheses of the annulenones 2,4,5 were carried out by the same procedure as previously reported.[1–3] Condensation of 3,10-dimethyl-3,5,7,9-dodecatetraen-11-yn-2-one 6[4] with 7-methyl-2,4,6-nonatrien-8-ynal 7[5] in the presence of ethanolic sodium ethoxide in ether for 7 h at 0°C gave the acyclic ketone 8 (mp. 106°C (dec), 53%).[6] Oxidative coupling of 8 with anhydrous copper(II) acetate in pyridine and ether for 5 h at 50°C[7] yielded the annulenone 2 (dark red needles, mp. 168°C (dec), 6.8%). Condensation of 8-(*o*-ethynylphenyl)-3,5,7-octatrien-2-one 9[8] with the aldehyde 7 as that between 6 and 7 gave the ketone 10 (mp. 130°C (dec), 61%), which was oxidized to yield the annulenone 4 (orange needles, mp. 175°C (dec), 4.9%). The acid-catalysed aldol condensation of 2-butanone with 5-(*o*-ethynylphenyl)-2,4-pentadienal 12[8] afforded the ketone 11 (mp. 142–144°C, 67%). Condensation of 11 with 12 in the presence of ethanolic sodium ethoxide in tetrahydrofuran gave the ketone 13 (mp.

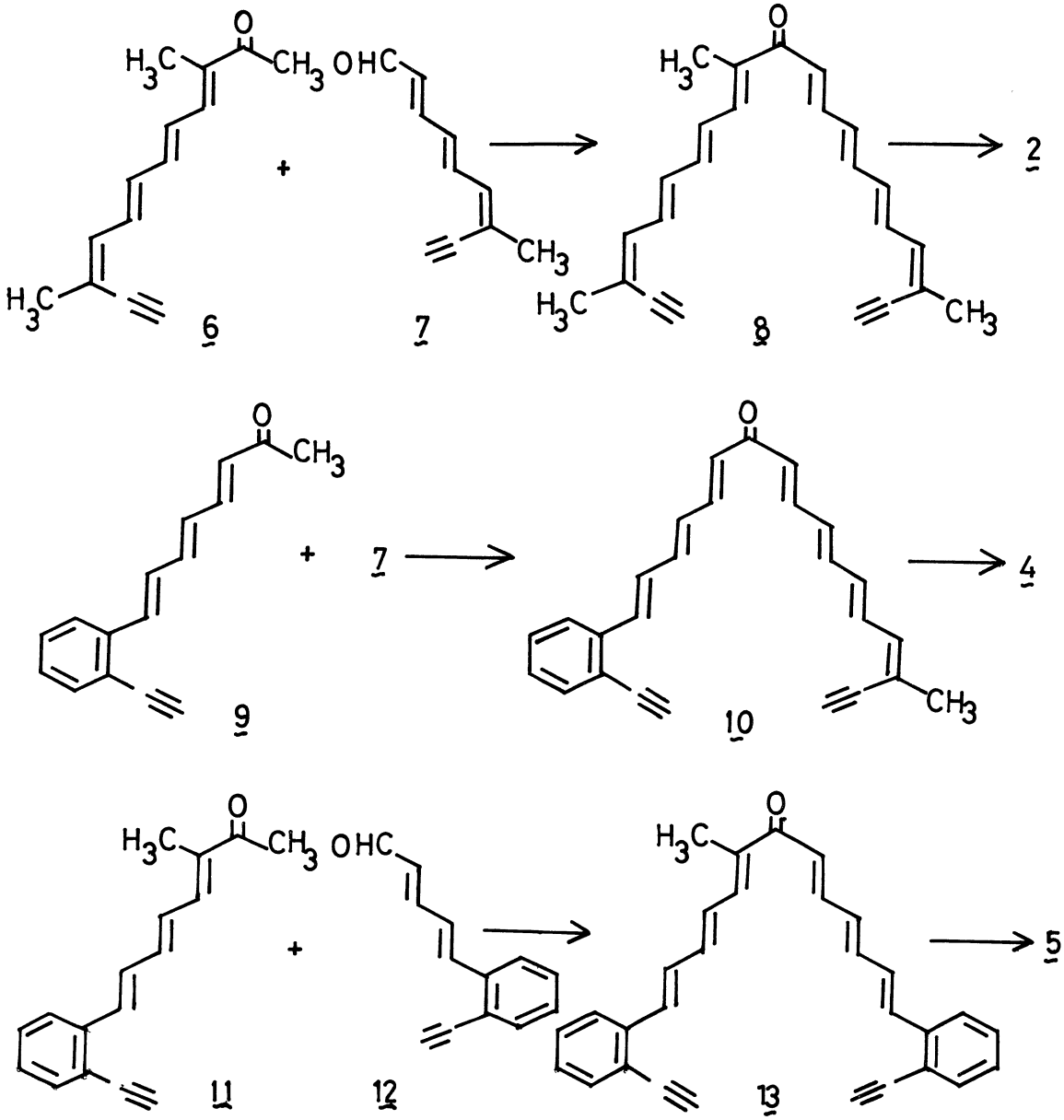

Table 1. The ^{1}H-NMR data of 2–5 (in $CDCl_3$) and 2'–5' (in CF_3COOD) at 90 MHz (τ values)

	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	CH_3
2		4.07	3.82	3.88	3.73	3.79	3.63	3.63	1.99	1.93	2.07	1.98	2.32	2.32		8.18
2'		4.25	4.38	4.23	4.55	4.55	4.30	4.30	-1.98	-1.55	-1.59	-1.80	-1.17	-1.30		8.28, 8.49
3	4.16		3.88		3.84		3.63		2.36		1.94		1.94			8.17
3'	(4.3–4.8)		(4.3–4.8)		(4.3–4.8)		(4.3–4.8)		-1.62		-2.22		-2.10			8.52
4	4.03		(3.4–3.8)		3.25	(3.4–3.8)		(3.4–3.8)	(2.2–2.9)				2.10	(2.3–2.9)		8.05
4'	3.85		3.72	3.79	3.50	3.93		3.79	0.13	0.28	0.30	0.29	0.15	0.69	(2.6–2.9)	8.17
5		3.92	(2.2–3.7)						(2.2–3.7)							8.02
5'		(3.1–3.8)							(1.2–1.9)						(2.4–2.8)	7.94

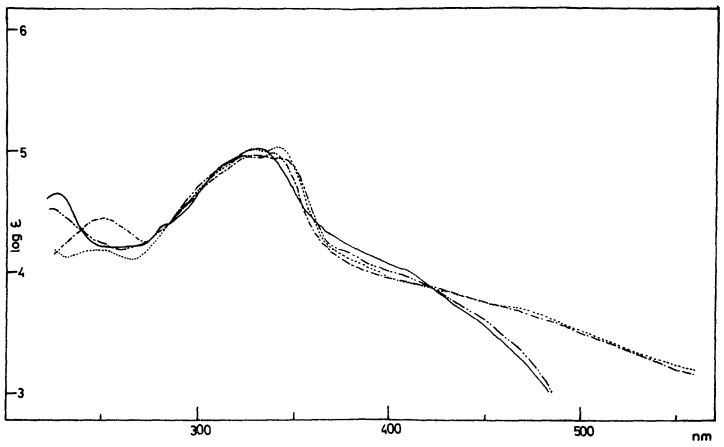

Fig. 1. The UV spectra of 2 (·····), 3 (– – – –), 4 (– · – · –), and 5 (————) in tetrahydrofuran

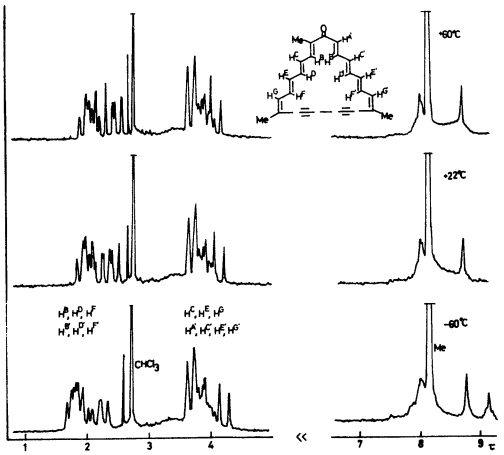

Fig. 2. The 100 MHz ^{1}H-NMR spectra of 2 in $CDCl_3$[9]

144–145°C, 79%), which was led to the dibenzannulenone 5 (yellow needles, mp. 197–198°C, 26%).

The UV spectra of the annulenones 2–5 are illustrated in Figure 1. As expected, the spectra are similar to those of the corresponding [17]annulenone[1] except that each band exhibits a bathochromic shift.

The ^{1}H-NMR spectra of 2–5 at a variable temperature were taken at 100 MHz in the range of -60 to 60°C,[9] and the spectra of all these annulenones 2–5 proved to be essentially temperature-independent. The spectra of the trimethylbisdehydro-[21]annulenone 2 which is the higher analogue of 1, are indicated in Figure 2. On cooling, the resonances of the inner protons (H^B, $H^{B'}$, H^D, $H^{D'}$, H^F, $H^{F'}$) of 2 move to a slightly lower field, whereas those of the outer ($H^{A'}$, H^C, $H^{C'}$, H^E, $H^{E'}$, H^G, $H^{G'}$) and three methyl protons are nearly unchanged. However, the expected first-order pattern is observed at -60°C, and the

$J_{B',C'}$ value (11 Hz) of the $H^{B'}$, $H^{C'}$ bond which is the potentially mobile bond in view of the case of the corresponding [13]annulenone,[2] points to the s-*trans* relationship of the bond from -60 to 60°C, excluding a change of conformation of 2 at this temperature range. Thus, the extra methyl substituent adjacent to the carbonyl group exerts no significant influence upon the skeleton of this bisdehydro[21]annulenone system, as observed for the [17]annulenone.[1]

The ^{1}H-NMR data of these annulenones 2–5 at 90 MHz[10] are listed in Table 1 together with those of the deuteronated species 2'–5' which were obtained by dissolving in deuteriotrifluoroacetic acid. Examination of the ^{1}H-NMR data as well as the comparison with those of the respective acyclic ketones,[11] indicates that the methylated annulenones 2, 3 are paratropic, monobenz- 4 is weakly paratropic, and the dibenzannulenone 5 is atropic. On the other hand, in the corresponding deuteronated species 2', 3' are strongly paratropic, 4', 5' are paratropic. Also, comparison of the chemical shifts of olefinic and methyl protons of each column exhibits that the paratropicities of both annulenones and their deuteronated species decrease in the sequence of 2≃3 (2'≃3') > 4 (4') > 5 (5') with increasing number of fused benzene ring on bisdehydro[21]annulenone system, which is in accord with the result recognized on [17]annulenone[1] and some examples.[12]

The results above described indicate that the molecular skeleton of this bisdehydro[21]annulenone ring is rather rigid, as has been observed for the corresponding [17]annulenone, although examination from the Dreiding molecular model predicts a considerable strained system containing nonlinear 1,3-diacetylene linkage.

References and Notes

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2) J. Ojima and M. Fujiyoshi, *Chem. Lett.*, 1978, 569; *Idem, J. Chem. Soc., Perkin Trans. I*, 1980, 466.

3) J. Ojima, Y. Shiroishi, K. Wada, and F. Sondheimer, *J. Org. Chem.*, in press.

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

9) The ^{1}H-NMR spectra at a variable temperature were taken on a JEOL FX-100 spectrometer.

10) 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, 3) although these being in part tentative.

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

12) *Inter alia*, a) M. Iyoda and M. Nakagawa, *Chem. Lett.*, 1975, 813; b) R. T. Weavers, R. R. Jones, and F. Sondheimer, *Tetrahedron Lett.*, 1975, 1043.

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