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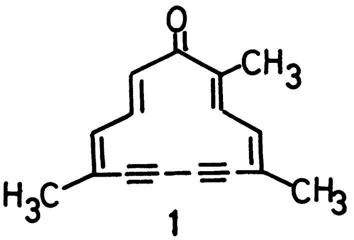
SYNTHESES AND PROPERTIES OF TRIMETHYLBISDEHYDRO[17]ANNULENONE AND ITS BENZANNELATED DERIVATIVES

Jūro OJIMA,* Keiko KANAZAWA, Kiyomi KUSAKI, and Kazuyo WADA
Department of Chemistry, Faculty of Science, Toyama University, Gofuku, Toyama 930

Syntheses of 2,7,12-trimethyl- 5, 12,17-dimethylbenzo[f]- 6, 2,12-dimethylbenzo-[f]- 7, and 2-methyldibenzo[f,l]-8,10-bisdehydro[17]annulenone 8 are described. The ^{1}H-NMR spectra of these annulenones suggest that the skeleton of the bisdehydro[17]-annulenone of this type is more planar and less strained than that of the corresponding [13]annulenone.

It was found that the methyl substituent adjacent to the ketone group of the paratropic 2,5,10-trimethyl-6,8-bisdehydro[13]annulenone 1 causes a change of conformation due to a rotation of the other trans double bond and exist essentially in a conformation of 1a at -60°C.[1] This suggested that the benzannelated derivatives of 1 might also be conformationally mobile, and, quite recently, it was shown that the methyl substituent and benzannelation exert a considerable influence on the development of the paratropic character in bisdehydro[13]annulenone of type 1.[2]



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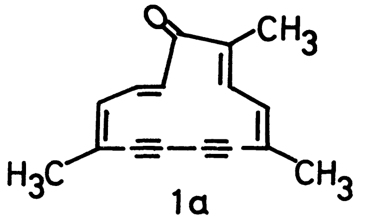

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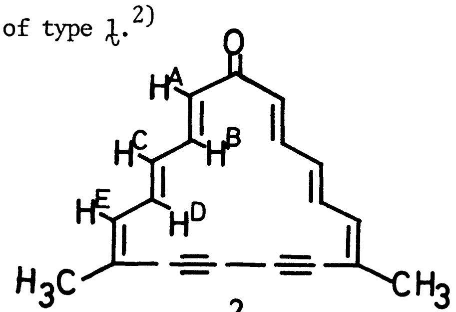

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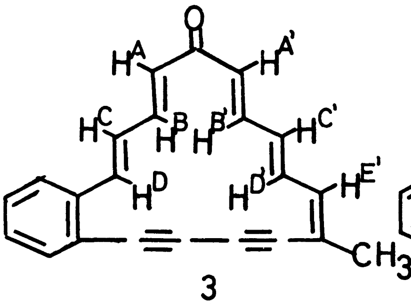

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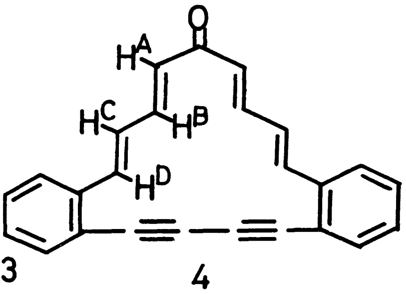

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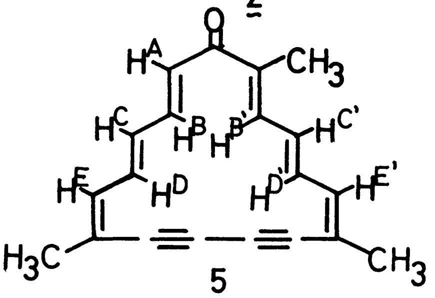

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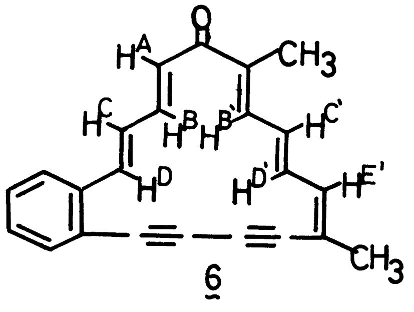

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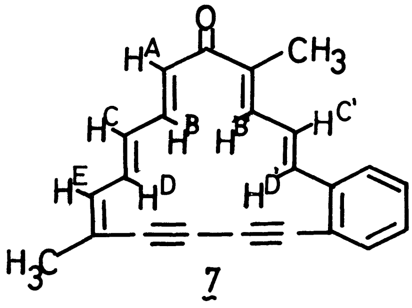

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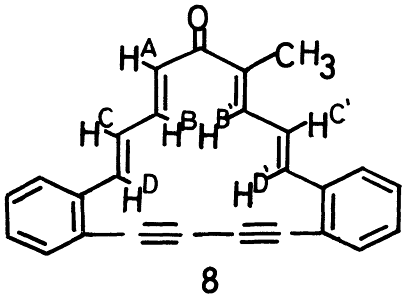

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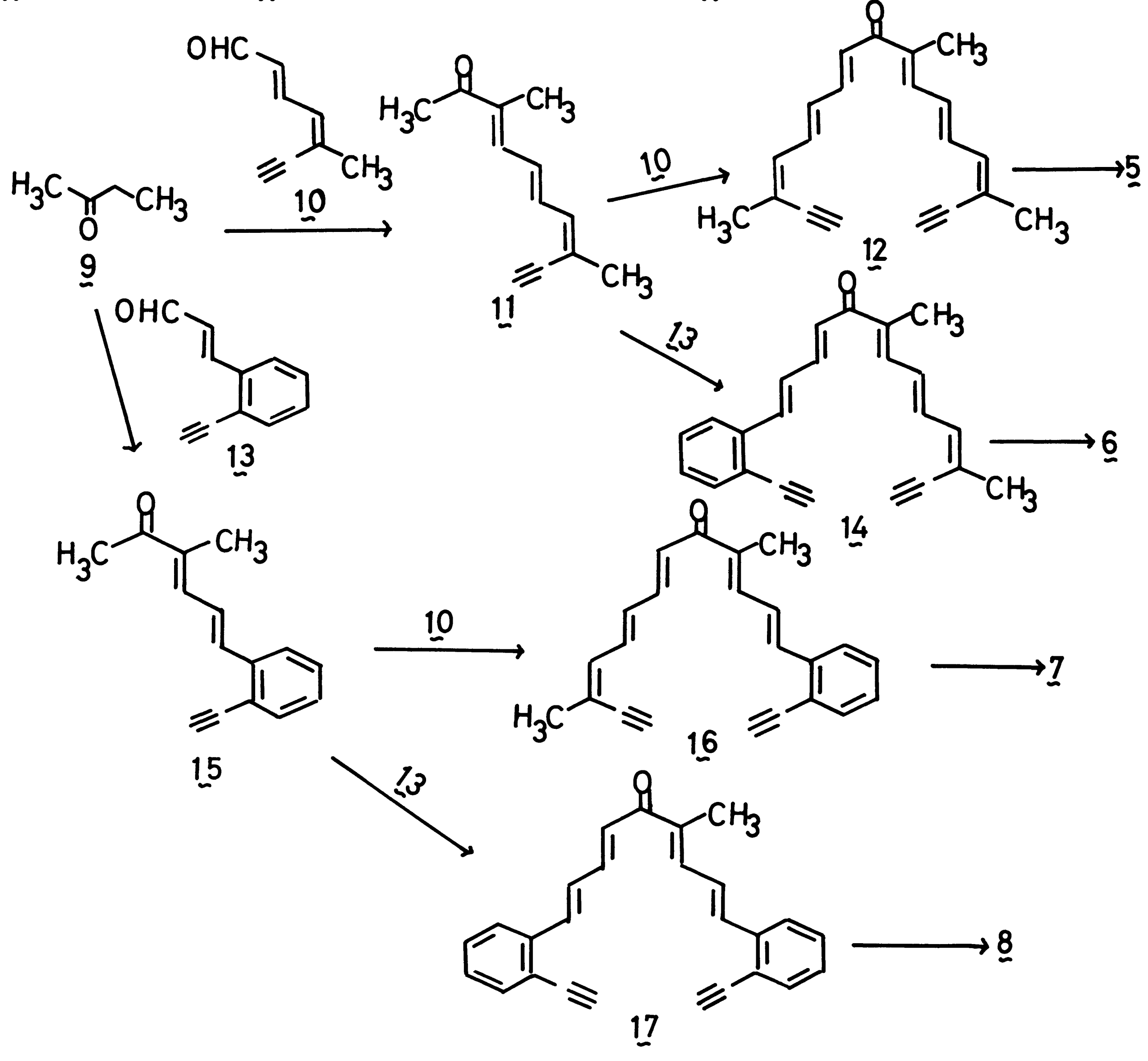
In view of paratropicity and conformational mobility observed on this bisdehydro[13]annulenone system, we were tempted to examine the properties of the title compounds, i.e., the higher analogue of **1** and its benzannelated derivatives (**5**–**8**), and further examination of the properties of the annulenones **2**–**4** which were prepared previously.3)

We now describe the syntheses and properties of the title compounds **5**–**8**, as well as the further examination of the properties of **2**–**4**.

The syntheses of the annulenones **5**–**8** were carried out by the same procedure as previously reported.1,2) Condensation of 2-butanone **9** with 5-methyl-2,4-heptadien-6-ynal **10**3) under acidic conditions afforded the ketone **11** (mp. 82–83°C, 35%),4) which was further condensed with another mole of the aldehyde **10** in the presence of ethanolic potassium hydroxide in tetrahydrofuran, giving the acyclic ketone **12** (mp. 83–86°C, 25%). Oxidative coupling of **12** with anhydrous copper(II) acetate in pyridine and ether at 50°C5) yielded the annulenone **5** (orange crystals, mp. 163–164°C, 34%). Similarly, the condensation of **11** with o-ethynylcinnamaldehyde **13**6) gave the ketone **14** (mp. 80–83°C, 30%), which was oxidized to yield the benzannulenone **6** (orange crystals, mp. 165–166°C, 20%). Reaction of **9** and **13** as that between **9** and **10** afforded the ketone **15** (mp. 80–81°C, 50%), which was condensed with **10**, giving the ketone **16** (mp. 122–123°C, 20%). Oxidation of **16** as before afforded the another benz-



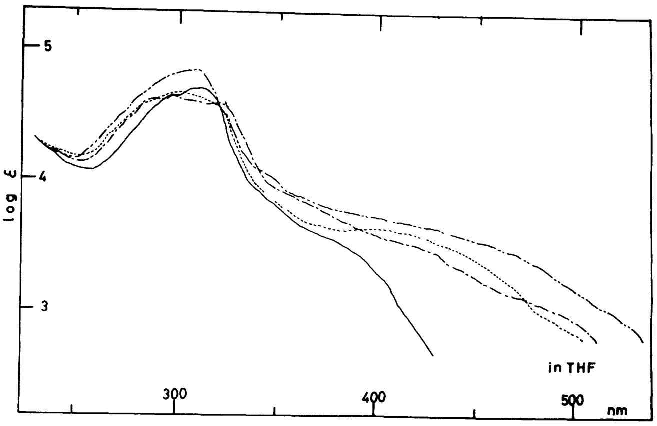


Fig. 1. The UV spectra of 5 (—‧‧—‧‧—), 6 (‧‧‧‧‧‧‧‧), 7 (— — —), and 8 (———)

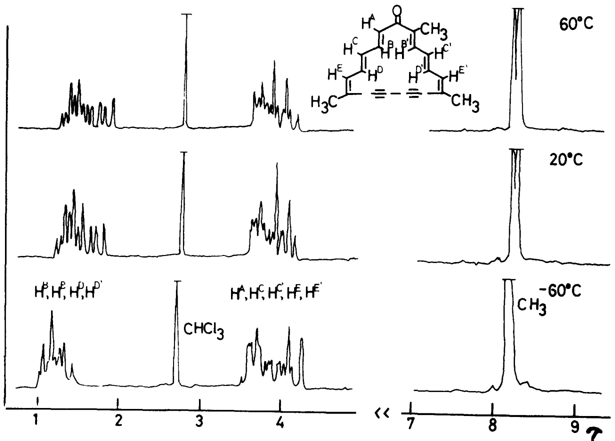


Fig. 2. The 100 MHz NMR spectra of 5 in $CDCl_3$ 7)

Table 1. The ^{1}H-NMR data of 2–8 (in $CDCl_3$) and 2'–8' (in CF_3COOD) at 90 MHz (τ values)8)

	H^A	$H^{A'}$	H^B	$H^{B'}$	H^C	$H^{C'}$	H^D	$H^{D'}$	H^E	$H^{E'}$	benzenoid H	CH_3
2	4.20		1.37		3.98		1.40		3.65			8.20
2'	4.29		-1.64		4.36		-1.71		4.09			8.42
3	4.00	3.98	1.79	1.79	3.40	3.73	1.95	1.92		3.49	2.4–2.8	8.08
3'	3.86	3.83	0.33	0.29	3.49	3.70	0.25	0.35		3.75	2.4–2.8	8.15
4	3.92		2.28		3.33		2.08				2.5–2.8	
4'	3.60		1.18		3.20		1.03				2.4–2.7	
5	3.95		1.31	1.45	3.81	3.99	1.38	1.62	3.67	3.80		8.16 8.21
5'	4.20		-1.67	-2.07	4.27	4.45	-1.85	-1.98	4.11	4.13		8.23 8.43
6	4.00		1.93	2.03	3.53	3.61	1.84	2.09		3.42	2.6–2.8	8.12 8.15
6'	3.85		0.43	0.33	3.60	3.73	0.42	0.63		3.67	2.7–3.0	8.12 8.23
7	3.80		1.98	2.03	3.82	3.25	2.17	1.76	3.53		2.6–2.9	8.03 8.13
7'	3.75		0.36	0.45	3.87	3.30	0.50	0.22	3.65		2.6–2.9	7.97 8.17
8	3.85		2.3–2.8		3.10	3.33	2.07	2.07			2.3–2.8	7.97
8'	3.67		1.48	1.42	3.10	3.35	1.19	1.23			2.4–2.7	7.90

annulenone 7 (yellow crystals, mp. 160–161°C, 28%). Condensation of 15 with 13 gave the acyclic ketone 17 (mp. 130–131°C, 53%), which was led to the dibenzannulenone 8 (yellow crystals, mp. 206–207°C, 21%).

The UV spectra of the annulenones 5–8 are illustrated in Fig. 1. As expected, the spectra are similar to those of the corresponding [13]annulenone1,2) except that each band exhibits a bathochromic shift.

The ^{1}H-NMR spectra of 2–8 at a variable temperature were taken at 100 MHz in the range of -60 to 60°C,7) and the spectra of all these annulenones 2–8 proved to be essentially temperature-independent. The spectra of the trimethylbisdehydro[17]annulenone 5 which is the higher analogue of the conformationally mobile compound 1, are indicated in Fig. 2. On cooling, the resonances of the inner protons (H^B, $H^{B'}$, H^D, $H^{D'}$) of 5 move to a slightly lower field and become unresolved at -60°C. However, in the resonances of the outer protons (H^A, H^C, $H^{C'}$, H^E, $H^{E'}$), the expected first-order pattern is observed and the $J_{B,C}$ value (11 Hz) of H^B, H^C bond which is the potentially mobile bond in view of the case of **1**, points to the s-trans relationship of the bond from -60 to 60°C, excluding a change of conformation of **5** at this temperature range. Thus, the extra methyl substituent adjacent to the carbonyl group exerts no significant influence upon the skeleton of this bisdehydro[17]annulenone system, in contrast to the case of [13]annulenone system.[1,2]

The ^{1}H-NMR data of these annulenones **2**–**8** at 90 MHz[8] are listed in Table 1 together with those of the deuteronated species **2'**–**8'** which were obtained by dissolving in deuteriotrifluoroacetic acid. Comparison of the chemical shifts of olefinic and methyl protons of each column exhibits that the paratropicities[9] of both these annulenones and their deuteronated species decrease in the sequence of **2**≈**5** (**2'**≈**5'**) > **3**≈**6**≈**7** (**3'**≈**6'**≈**7'**) > **4**≈**8** (**4'**≈**8'**) with increasing number of fused benzene ring on bisdehydro[17]annulenone system, which is in accord with the result recognized on some examples.[10] In contrast, in the corresponding methyl-substituted benzannelated bisdehydro[13]annulenone series, the sequence of paratropicities violated the above recognization, presumably due to conformational mobility and/or steric strain of the skeleton of the [13]annulenone system, as previously reported.[2]

These results obtained from this study suggest that the skeleton of bisdehydro[17]annulenone system is more planar and less strained than that of [13]annulenone, in accordance with a prediction from an inspection using molecular model.

References and Notes

1) T. M. Cresp, J. Ojima, and F. Sondheimer, J. Org. Chem., 42, 2130 (1977).

2) J. Ojima and M. Fujiyoshi, Chem. Lett., 1978, 569.

3) J. Ojima, M. Ishiyama, and A. Kimura, Bull. Chem. Soc. Jpn., 50, 1584 (1977), and references cited therein.

4) All the new compounds described in this paper gave IR, NMR, and mass spectral data consistent with the assigned structures and satisfactory elemental analyses were obtained on crystalline compounds except for the rather unstable acyclic ketones **12**, **14**.

5) N. Darby, T. M. Cresp, and F. Sondheimer, J. Org. Chem., 42, 1960 (1977); J. Ojima, Y. Shiroishi, and M. Fujiyoshi, Bull. Chem. Soc. Jpn., 51, 2112 (1978).

6) J. Ojima, A. Kimura, Y. Yokoyama, and T. Yokoyama, Bull. Chem. Soc. Jpn., 48, 367 (1975).

7) The NMR spectra at a variable temperature were taken on JEOL FX-100 spectrometer.

8) These spectra were taken on a Varian EM-390 spectrometer at 35°C and the assignment was made on the basis of multiplicity, coupling constants, and the data of the closely related compounds (Ref. 1,2), albeit it being in part tentative.

9) These annulenones refer to paratropic molecules from the comparison of the chemical shifts of olefinic and methyl protons with those of the respective corresponding acyclic ketones. The details will be reported elsewhere.

10) Inter alia, a) M. Iyoda and M. Nakagawa, Chem. Lett., 1975, 815; b) R. T. Weavers, R. R. Jones, and F. Sondheimer, Tetrahedron Lett., 1975, 1043.

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