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SYNTHESES AND PROPERTIES OF TRIMETHYLBISDEHYDRO[15]ANNULENONE AND ITS BENZANNELATED DERIVATIVES

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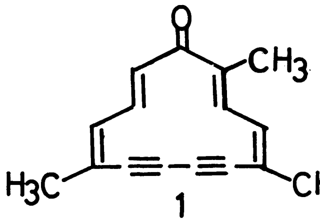
Syntheses of 5,10,15-trimethyl- **6**, 10,15-dimethylbenzo[d]-6,8-bisdehydro[15]-annulenone **7**, 2,12-dimethylbenzo[f]-8,10-bisdehydro[15]annulenone **8**, and 15-methyl-dibenzo[d,j]-6,8-bisdehydro[15]annulenone **9** are described. As observed for the corresponding [17]annulenone, the ^{1}H-NMR spectra of these annulenones suggest that the skeleton of the bisdehydro[15]annulenone of this type is more planar and less strained than that of [13]annulenone.

It was found that the methyl substituent adjacent to the ketone group of the 2,5,10-trimethyl-6,8-bisdehydro[13]annulenone **1** causes a change of conformation due to a rotation of the another *trans* double bond1) and benzannelation also exert a considerable influence on the development of the paratropic character in bisdehydro[13]annulenone of type **1**.2) In contrast, for the corresponding [17]-annulenone series, the α-methyl substituent and benzannelation exerts no significant influence upon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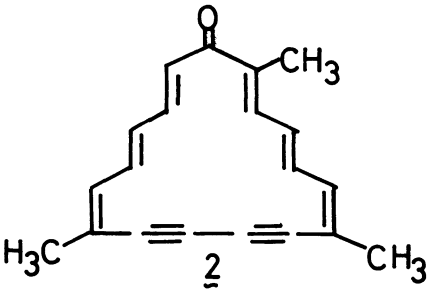
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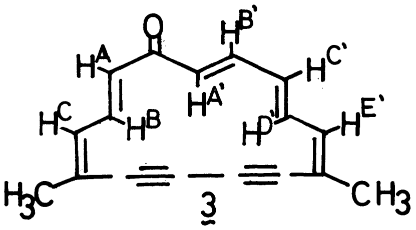
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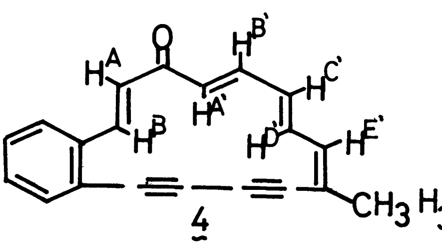
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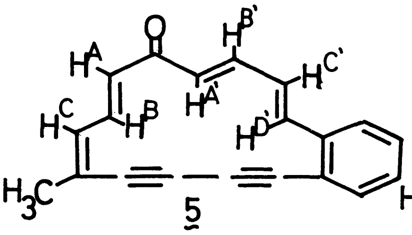
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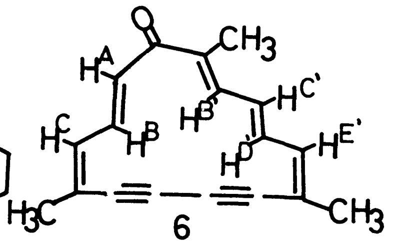
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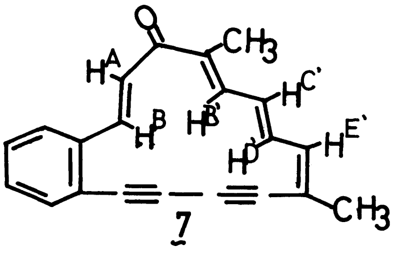
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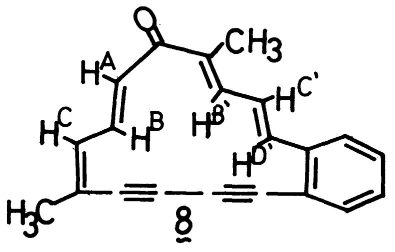
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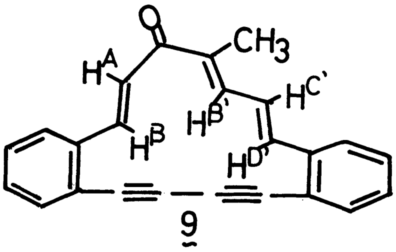
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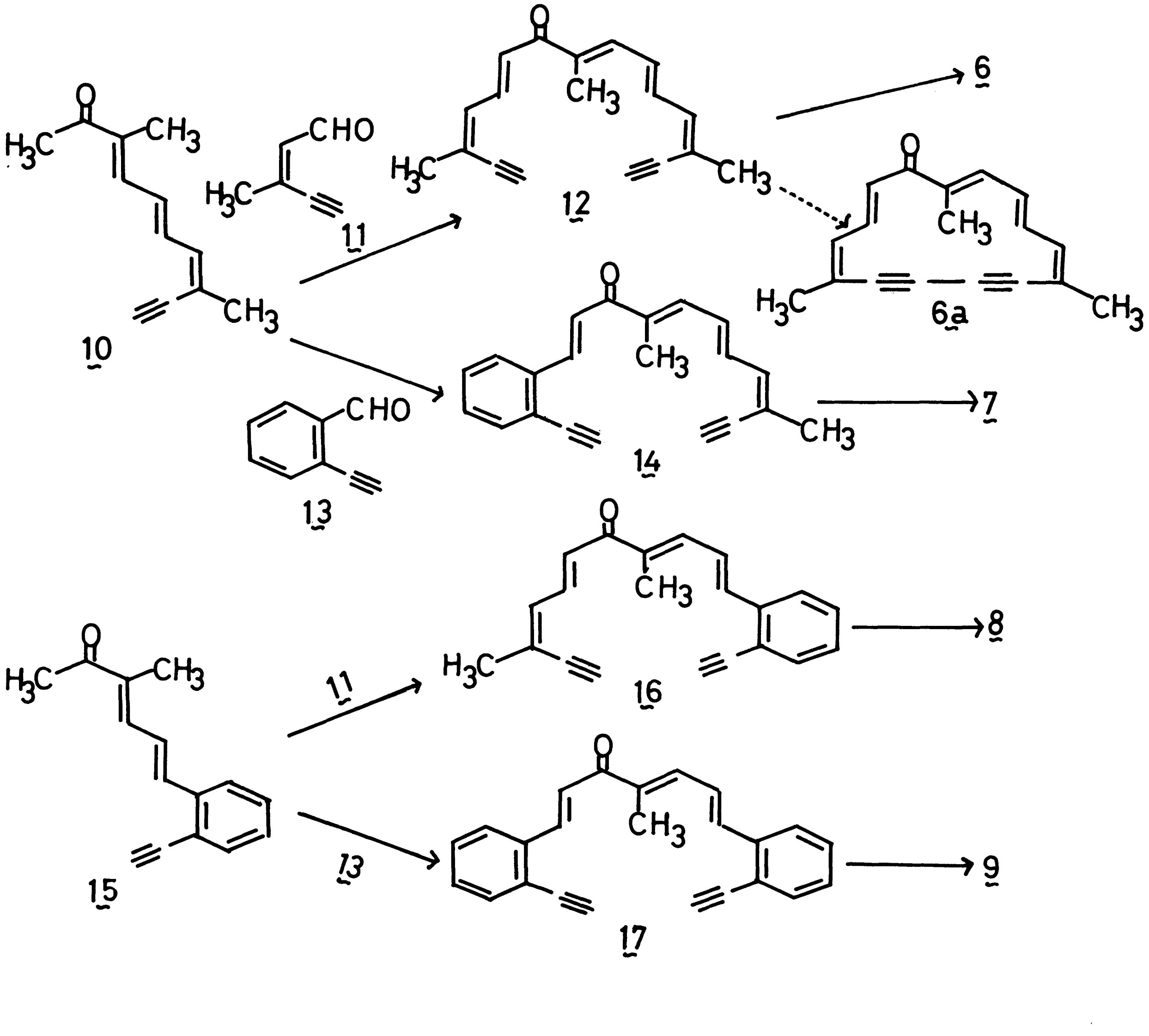
the skeleton of bisdehydro[17]annulenone system of **2**.[3]

In view of the difference observed between [13]- and [17]annulenone system, we were interested in examining the properties of the title compounds, *i.e.*, 5,10,15-trimethyl-6,8-bisdehydro[15]annulenone **6** and its benzannelated derivatives **7**–**9**, and the properties of the annulenones **3**–**5** which were prepared previously.[4,5]

The successful syntheses of the annulenones **3**–**5**,[4,5] together with a prediction from the Dreiding molecular models led us to expect that the annulenones possessing α-methyl group inside the ring might form from the corresponding acyclic ketones by the same approach (*e.g.*, **6a** from **12**). However, all the compounds **6**–**9** obtained proved to have configuration with α-methyl group outside the ring by an analysis of their ^{1}H-NMR spectra.

The syntheses of the annulenones **6**–**9** were carried out by the same procedure as previously reported.[1–3] Condensation of 3,8-dimethyl-3,5,7-decatrien-9-yn-2-one **10**[2] with (Z)-3-methyl-2-penten-4-ynal **11**[6] in the presence of ethanolic sodium ethoxide in ether for 6 h at room temperature gave the acyclic ketone **12** (mp. 97–98°C, 31%).[7] Oxidative coupling of **12** with anhydrous copper(II) acetate in pyridine and ether for 2 h at 50°C[8] yielded the annulenone **6**[9] (yellow cubes, mp. 136–137°C, 44%). Similarly, the condensation of **10** with *o*-ethynylbenzaldehyde **13**,[10] gave the ketone **14** (mp. 130–131°C, 69%), which was oxidized to yield the benzannulenone **7** (yellow rods, mp. 150°C (dec), 76%). Reaction of 6-(*o*-ethynylphenyl)-3-methyl-3,5-hexadien-2-one **15**[3] and **11** as that between **10** and **11** afforded the ketone **16** (mp. 125°C (dec), 36%). Oxidation of **16** as before gave the another benzannulenone **8** (yellow



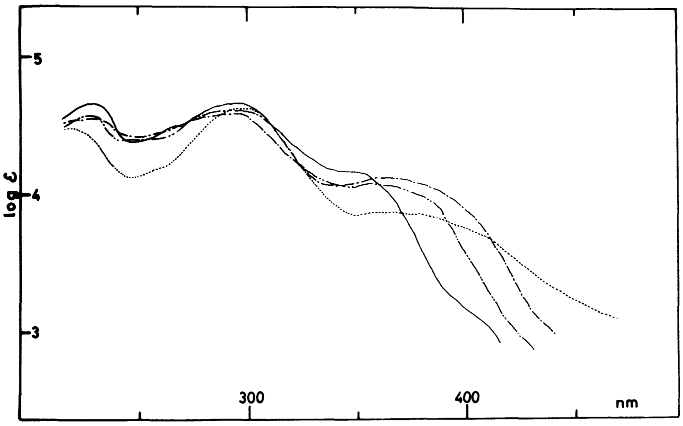


Fig. 1. The UV spectra of 6 (-----------), 7 (—·—·—) 8 (—··—··—), and 9 (————) in ether

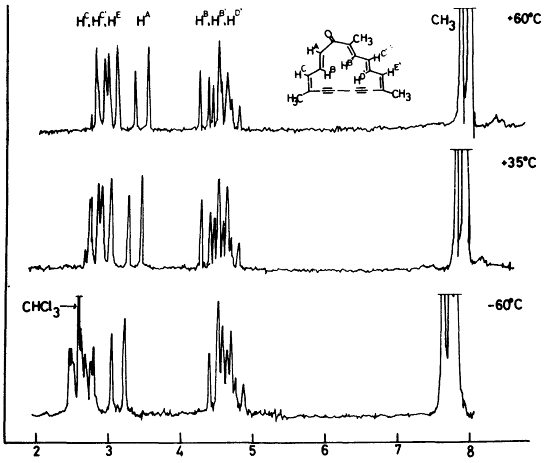


Fig. 2. The 90 MHz NMR spectra of 6 in $CDCl_3$[11)]

Table 1. The ^{1}H-NMR data of 3–9 (in $CDCl_3$) and 3'–9' (in CF_3COOD) at 90 MHz (τ values)[12)]

	H^A	$H^{A'}$	H^B	$H^{B'}$	H^C	$H^{C'}$	$H^{D'}$	$H^{E'}$	benzenoid H	CH_3
3	3.35	4.37	4.17	2.44	2.85	3.19	4.53	2.85		7.76, 7.82
3'	1.31	10.10	9.92	0.29	0.89	1.28	10.15	0.89		6.73, 6.82
4	← 1.96 ∼ 3.52 →									7.88
4'	1.92	5.55	4.75	1.35		2.55	5.43	2.17	1.32–2.08	7.47
5	← 2.10 ∼ 3.62 →									7.85
5'	2.60	4.91	4.80	(1.90 ∼ 2.35)			4.87	(1.90–2.35)	1.58–2.35	7.40
6	3.33		4.38	4.53	2.73	2.82	4.61	2.91		7.79, 7.90, 7.95
6'	1.60		8.52	8.05	1.30	1.25	8.95	1.33		6.89, 7.07, 7.12
7	2.97		3.20	3.58		3.05	3.72	2.90	2.07–2.80	7.93, 7.98
7'[13)]	← 1.60 ∼ 4.80 →									7.70, 7.80
8	← 2.3 ∼ 3.8 →									7.90, 7.95
8'	2.68		4.65	4.55	2.45	(1.8–2.4)	4.43		1.8–2.4	7.52, 7.60
9	← 2.13 ∼ 3.32 →									7.92
9'	← 2.2 ∼ 3.4 →									7.78

needles, mp. 160–161°C, 48%). Condensation of 15 with 13 gave the acyclic ketone 17 (mp. 111–112°C, 49%), which was led to the dibenzannulenone 9 (light yellow cubes, mp. 182–183°C, 68%).

The UV spectra of 6–9 are illustrated in Fig. 1. The longest wavelength band of these annulenones exhibits absorption toward longer wavelength in the sequence of 6>7>8>9, demonstrating the degree of extended conjugation of π-electron system in bisdehydro[15]annulenone ring.

The ^{1}H-NMR spectra of 3–9 at a variable temperature were taken at 90 MHz in the range of -60 to 60°C,[11)] and the spectra of all these annulenones 3–9 proved to be essentially temperature-independent. The spectra of the trimethylbisdehydro[15]annulenone 6 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,

$H^{B'}$, $H^{D'}$) move to a slightly higher field, whereas those of the outer (H^{A}, H^{C}, $H^{C'}$, $H^{E'}$) and three methyl protons do to a slightly lower field. However, the first-order pattern expected for the structure of **6** is observed even at -60°C, 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 **6** at this temperature range. Thus, in analogy with the corresponding [17]annulenones,[3] the extra methyl substituent adjacent to the carbonyl group exerts no significant influence upon the skeleton of this bisdehydro[15]annulenone system, in contrast to the case of [13]annulenone system.[1,2]

The 90 MHz ^{1}H-NMR data of the annulenones **3**–**9** are listed in Table 1, altogether with those of deuteronated species **3'**–**9'** which were obtained by dissolving in deuteriotrifluoroacetic acid.[12] Examination of the ^{1}H-NMR spectra of **3**–**9** as well as the comparison with those of the respective acyclic ketones,[14] indicates that the methylated annulenones **3**, **6** are diatropic, whereas monobenz- **4**, **5**, **7**, **8** and dibenzannulenone **9** are atropic. On the other hand, in the corresponding deuteronated species **3'**, **6'** are strongly diatropic, **4'**, **5'**, **7'**, **8'** are diatropic, and **9'** is atropic, in accord with the result obtained for the related compounds.[15]

It is also noted that the inner protons of **6'** resonate at a lower field than those of **3'**, presumably reflecting less planarity of the skeleton of **6'** due to the perturbation caused by the extra methyl group, as compared with that of **3'**.

References and Notes

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7) 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.

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9) Attempts to prepare the annulenones possessing bulky α-alkyl group, such as ethyl, *iso*propyl, and *t*-butyl were unsuccessful owing to the unsatisfactory result of the preparation of the methyl ketones corresponding to **10**.

10) J. Ojima, T. Yokomachi, and A. Kimura, *Bull. Chem. Soc. Jpn.*, 49, 2840 (1976).

11) The NMR spectra at a variable temperature were taken on a Hitachi R-900 spectrometer.

12) 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. 1–4).

13) In the spectrum of **7'**, the signals due to olefinic protons show rather puzzling pattern and the analysis is not complete yet.

14) This refers to 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.

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