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-methyldibenzo[d,j]-6,8-bisdehydro[15]annulenone 9 are described. As observed for the corresponding [17]annulenone, the ¹H-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 2,5010-trimethyl-6,8-bisdehydro[13]annulenone \downarrow 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 \downarrow .²⁾ In contrast, for the corresponding [17]annulenone series, the α -methyl substituent and benzannelation exerts no significant influence upon



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-trimethy1-6,8-bisdehydro[15] annulenone δ and its benzannelated derivatives 7-2, and the properties of the annulenones 3-5 which were prepared previously.^{4,5}

The successful syntheses of the annulenones $\mathfrak{Z}-\mathfrak{Z}, \mathfrak{Z}, \mathfrak{Z$

The syntheses of the annulenones 6-2 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°C⁸⁾ yielded the annulenone 5^{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 (-----) & (-----), and 9 (-----) in ether

Fig. 2. The 90 MHz NMR spectra of $\underset{2}{(5)}$ in ${\rm CDC1}_{3}^{(11)}$

Table 1.	The	¹ H-NMR	data	\mathbf{of}	3-9	(in	CDC1,) and	3'_9'	(in C	CF_COOD)	at	90 MH	z ([,]	τ values)	,12)
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	н ^А	HA'	н ^В	H ^B '	н ^С	H ^C	HD,	н ^Е '	benzenoid H	CH3		
3	3.35	4.37	4.17	2.44	2.85	3.19	4.53	2.85	, <u>,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,</u>	7.76,	7.82	
<u>.</u> 3'	1.31	10.10	9.92	0.29	0.89	1.28	10.15	0.89		6.73,	6.82	
4	·											
4'	1.92	5.55	4.75	1.35		2.55	5.43	2.17	1.32-2.08	7.47		
<u>5</u>	← 2.10 → 3.62 →											
<u>~</u> 5'	2.60	4.91	4.80	(1.9	$0 \sim 2$	2.35)	4.87	(1.90-2.3	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
<u>,6</u> '	1.60		8.52	8.05	1.30	1.25	8.95	1.33		6.89,	7.07,	7.12
2	2.97		3.20	3.58		3.05	3.72	2.90	2.07-2.80	7.93,	7.98	
Z' ¹³	⁵⁾ ←				1.60 ~	4.80	0		\longrightarrow	7.70,	7.80	
8	<i>(</i>				2.3 ~	3.8			>	7.90,	7.95	
<mark>8</mark> '	2.68		4.65	4.55	2.45 ((1.8-2.4)	4.43		1.8-2.4	7.52,	7.60	
2	<i>(</i>			······································	2.13	3.32	2		>	7.92		
2'	(2.2	<u> </u>				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 dibenzamnulenone 9 (light yellow cubes, mp. 182-183°C, 68%).

The UV spectra of $\xi - 2$ are illustrated in Fig. 1. The longest wavelength band of these annulenones exhibits absorption toward longer wavelength in the sequence of $\xi > 7 > 8 > 2$, demonstrating the degree of extended conjugation of π -electron system in bisdehydro[15]annulenone ring.

The ¹H-NMR spectra of \mathfrak{Z} 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 \mathfrak{Z} proved to be essentially temperature-independent. The spectra of the trimethylbisdehydro[15]annulenone \mathfrak{g} which is the higher analogue of the conformationally mobile compound \mathfrak{l} , 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 & 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 & 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 ¹H-NMR data of the annulenones \mathfrak{Z} are listed in Table 1, altogether with those of deuteronated species $\mathfrak{Z}'-\mathfrak{L}'$ which were obtained by dissolving in deuteriotrifluoroacetic acid.¹²) Examination of the ¹H-NMR spectra of \mathfrak{Z} - \mathfrak{L} as well as the comparison with those of the respective acyclic ketones,¹⁴) indicates that the methylated annulenones \mathfrak{Z} , \mathfrak{L} are diatropic, whereas monobenz- \mathfrak{L} , \mathfrak{Z} , \mathfrak{L} and dibenzannulenone \mathfrak{L} are atropic. On the other hand, in the corresponding deuteronated species \mathfrak{Z}' , \mathfrak{L}' are strongly diatropic, \mathfrak{L}' , \mathfrak{Z}' , \mathfrak{L}' , \mathfrak{L}' are diatropic, and \mathfrak{L}' is atropic, in accord with the result obtained for the related compounds.¹⁵

It is also noted that the inner protons of δ' resonate at a lower field than those of \mathfrak{Z}' , presumably reflecting less planarity of the skeleton of δ' due to the perturbation caused by the extra methyl group, as compared with that of \mathfrak{Z}' .

References and Notes

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- 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 Z', 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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