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PREPARATION AND PROPERTIES OF METHYL-SUBSTITUTED BENZANNELATED BISDEHYDRO[13]-ANNULENONES

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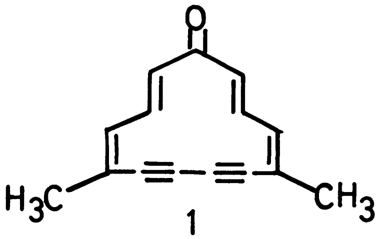
Preparation of methyl-substituted monobenzo- **5**, **6**, and dibenzobisdehydro[13]-annulenone **7** is described. The influence of methyl substituent and benzannelation upon the structure and tropicity of bisdehydro[13]annulenone is discussed.

Recently, Cresp et al. reported the synthesis of methyl-substituted bisdehydro[13]annulenones **1**, **2**, and it was found that the extra methyl group in **2** as compared with **1** causes a change of conformation due to a rotation of the $H^{A'}$, $H^{B'}$ double bond, **2** existing essentially in a conformation of **2a** at -60°C.[1)]

This suggested that the monobenzo- **3** and dibenzobisdehydro[13]annulenone **4** which were prepared previously,[2)] might also be conformationally mobile. In order to investigate this possibility, it was decided to examine the properties of **3**, **4** and to prepare the related methyl-substituted bisdehydro[13]annulenones **5**–**7**.

We now describe the preparation and properties of the title compounds **5**–**7**, as well as the further examination of the properties of **3**, **4**.

The preparation of the annulenones **5**–**7** was carried out by the essentially same procedure as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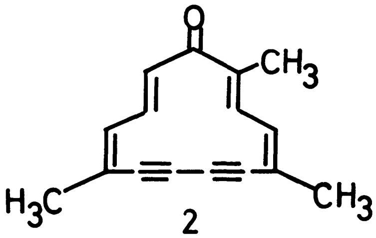
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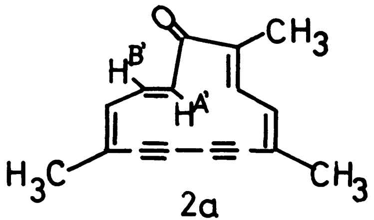
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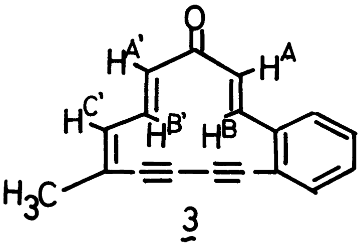
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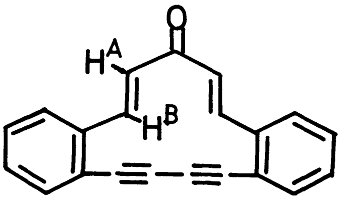
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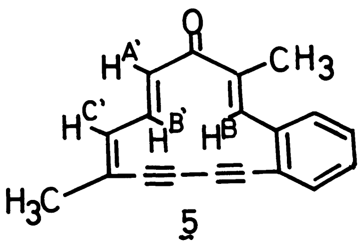
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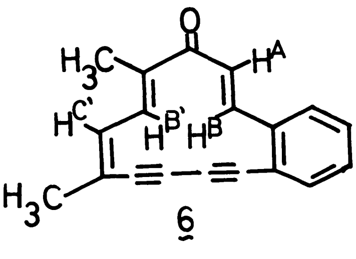
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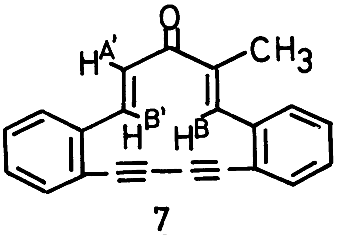
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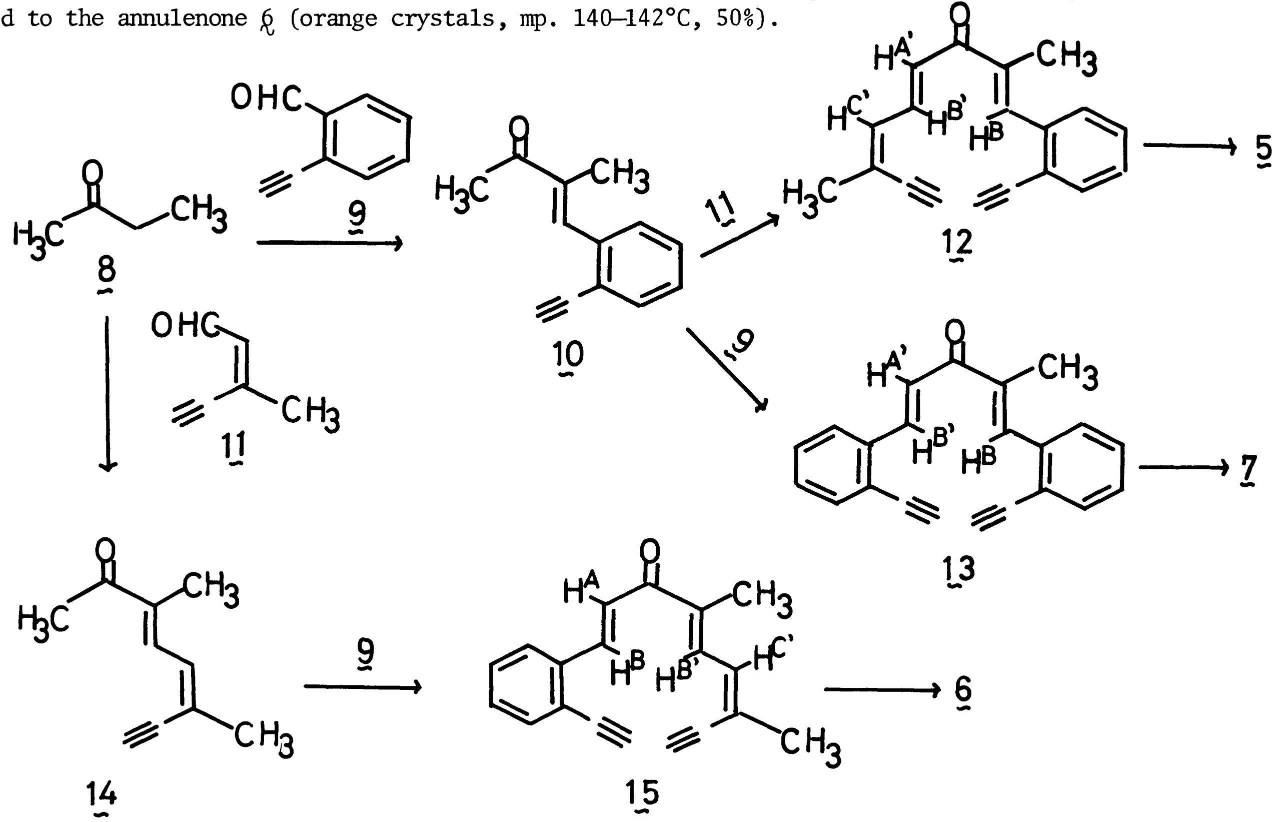
that reported by Cresp et al.$^{1)}$ Condensation of 2-butanone **8** with o-ethynylbenzaldehyde **9**$^{3)}$ under acidic conditions gave the ketone **10** (mp. 33–34°C, 41%),$^{4)}$ which was further condensed with the enyne aldehyde **11**$^{5)}$ in the presence of ethanolic potassium hydroxide, affording the acyclic ketone **12** (mp. 92–93°C, 31%, NMR$^{6)}$: (δ ppm) 7.80 (dd, 15, 10, 1H, $H^{B'}$), 7.77 (s, 1H, H^{B}), 7.25–7.64 (m, 4H, benzenoid H), 6.90 (d, 15, 1H, $H^{A'}$), 6.54 (d, 10, 1H, $H^{C'}$), 3.50 (s, 1H, -C≡CH), 3.42 (s, 1H, -C≡CH), 2.19 (s, 3H, $-CH_3$), 2.07 (s, 3H, $-CH_3$)). Oxidative coupling of **12** with anhydrous copper(II) acetate in pyridine and ether at 50°C$^{7)}$ yielded the annulenone **5** as yellow solid (mp. 144–146°C, 50%). Similarly, the reaction of **10** with **9** gave the ketone **13** (mp. 102–104°C, 52%, NMR: 8.20 (d, 16, 1H, $H^{B'}$), 7.90 (s, 1H, H^{B}), 7.2–7.8 (m, 9H, $H^{A'}$ and benzenoid H), 3.45 (s, 1H, -C≡CH), 3.38 (s, 1H, -C≡CH), 2.13 (s, 3H, $-CH_3$)), which was oxidized to yield the annulenone **7** as yellow crystals (mp. 176–177°C, 88%). Condensation of **14** obtained from **8** and **11** as reported,$^{1)}$ with **9** gave the ketone **15** (mp. 79–80°C, 46%, NMR: 8.10 (d, 16, 1H, H^{B}), 7.23–7.80 (m, 6H, H^{A}, $H^{B'}$, and benzenoid H), 6.75 (d, 12, 1H, $H^{C'}$), 3.52 (s, 1H, -C≡CH), 3.43 (s, 1H, -C≡CH), 2.10 (s, 3H, $-CH_3$), 2.03 (s, 3H, $-CH_3$)), which was led to the annulenone **6** (orange crystals, mp. 140–142°C, 50%).



The UV spectra of the annulenones **5**–**7** are illustrated in Figure 1. The longest wavelength bands of **5** and **6** exhibit the marked intensification as compared with that of **7**, demonstrating that **5** and **6** are more highly delocalized π-electron systems than **7** with two fused benzene rings.

The ^{1}H-NMR spectra of **3**–**7** at a variable temperature were taken at 100 MHz in the range of -60 to 60°C, and the spectra of the annulenones **3**, **4**, **6**, and **7** proved to be essentially temperature independent.$^{8)}$ On the other hand, the spectrum of **5** shows the resonances of H^{A} and benzenoid protons as an unresolved multiplet at 23°C (and above), as indicated in Figure 2. On cooling, the band becomes resolved along with the moving of the $H^{B'}$ band to a lower field, and the expected first-order pattern is observed at -60°C. However, the $J_{B'C'}$ value (10 Hz) pointing to the s-trans relationship of $H^{B'}$ and $H^{C'}$ does not vary from -60 to 60°C, excluding the change of conformation due to the rotation

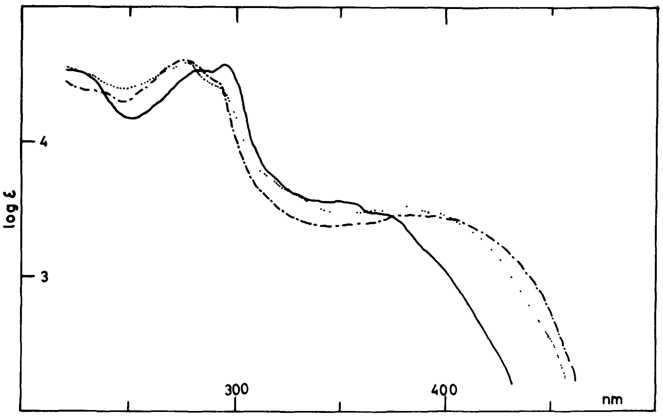


Fig. 1. The UV spectra of 5 (·········), 6 (– – –), and 7 (———) in ether

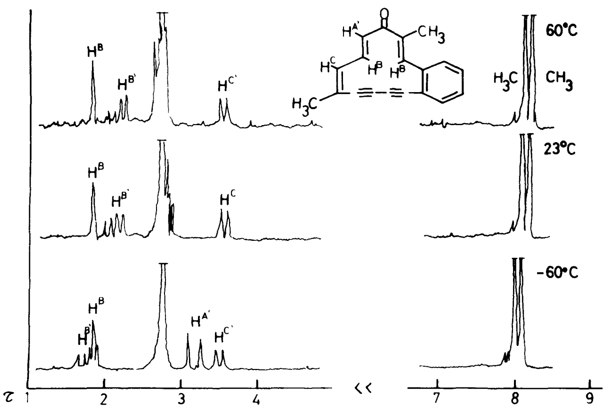


Fig. 2. The 100 MHz NMR spectra of 5 in CDCl$_3$ 8)

Table 1. The ^{1}H-NMR data of 3–7 (in CDCl$_3$) and 3'–7' (in CF$_3$COOD) at 90 MHz (δ ppm) 6)

	H^A	$H^{A'}$	H^B	$H^{B'}$	H^C	benzenoid H	CH_3
3 9)	6.30 d, 16	6.50 d, 16	8.72 d, 16	8.92 dd, 16, 11	6.53 d, 11	7.2–7.4 m	1.87 s
3'	6.43 d, 16	6.73 d, 16	9.55 d, 16	10.00 dd, 16, 11	6.55 d, 11	7.17–7.45 m	1.90 s
4 9.10)	6.83 d, 17		8.53 d, 17			7.24–7.63 m	
4'	7.11 d, 16		9.20 d, 16			7.3–7.6 m	
5		a)	8.27 s	7.95 dd, 16, 10	6.53 d, 10	7.25–7.45 m	2.02, 1.97 s s
5'		7.13 d, 16	8.33 s	8.63 dd, 16, 9	6.65 d, 9	7.3–7.5 m	2.02, 1.94 s s
6	7.41 d, 16		7.88 d, 16	9.07 d, 11	6.70 d, 11	7.11–7.37 m	1.90 broad s
6'	7.81 d, 16		8.23 d, 16	9.91 d, 11	6.71 d, 11	7.1–7.4 m	1.91 broad s
7		7.75 d, 16	8.42 s	8.10 d, 16		7.26–7.53 m	2.10 s
7'		8.18 d, 16	8.95 s	8.65 d, 16		7.3–7.5 m	2.20 s

a) This proton is submerged by those of benzenoid protons.

of the $H^{A'}$, $H^{B'}$ double bond in 5 at this temperature range. Thus, albeit 5 being more flexible than 6 and 7, it is supposed that the benzannelation which is formulated by transformation from 2 to 5, makes the thirteen-membered ring system less mobile. And the annulenones **6**,**7** might experience this effect of benzannelation more highly than **5**, reflecting that in **6** and **7** the "potentially mobile double bond" is flanked by the fused benzene ring.

The ^{1}H-NMR data of the annulenones **5**–**7** are listed in Table 1, altogether with those of **3** and **4** which were reexamined using the same instrument for comparison. The data of the deuterated species, **5'**–**7'**, of these annulenones, obtained by dissolving in deuteriotrifluoroacetic acid, are also given in Table 1. The individual assignment is made on the basis of multiplicity and coupling constants.

From the Table 1, it is noted that the inner proton adjacent to methyl substituent resonates at a lower field than the opposite inner proton except for the case of **5'**, suggesting that the bulky methyl group forces this proton into distinct inner position of the thirteen-membered ring system. And if we consider only the inductive effect of the methyl group, it will be predicted that the expected paratropicities decrease in the sequence of **5**=**6**>**7** with the increasing number of fused benzene ring on macrocyclic system as has been reported.[2,11] However, the data obtained do not show this tendency though it being true for the corresponding carbonyl deuterated species (**5'**=**6'**>**7'**). And also, if we judge the tropicity of these annulenones from the chemical shift differences for the various resonances from the cyclic ketone (annulenone) to the corresponding acyclic model, which indicate the magnitude of the upfield shift of the outer protons and the downfield shift of the inner protons, the annulenones **3**, **4** will refer to paratropic molecules, while **5**–**7** will refer to atropic ones. Although the previous judgement that the dibenzannelated annulenone **4** is paratropic, which was determined from the apparent chemical shift differences,[2] might be exaggerated, as pointed out by Sondheimer et al.,[11b] these results obtained from this study indicate that the extra methyl group and fused benzene ring exert a considerable influence on the development of the paratropic character in bisdehydro[13]annulenone.

References and Notes

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

2) J. Ojima, Y. Yokoyama, and M. Enkaku, Bull. Chem. Soc. Jpn., 50, 1522 (1977), and references cited therein.

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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.

5) J. Ojima, T. Katakami, G. Nakaminami, and M. Nakagawa, Bull. Chem. Soc. Jpn., 49, 292 (1976).

6) All the spectra were taken on a Varian EM-930 spectrometer at 34°C, and refer to $CDCl_3$ solutions unless otherwise stated.

7) N. Darby, T. M. Cresp, and F. Sondheimer, J. Org. Chem., 42, 1960 (1977).

8) The NMR spectra at a variable temperature were taken on a JNM TS-100 spectrometer.

9) The NMR data of the respective acyclic ketones of **3** and **4** in $CDCl_3$ are as follows: (δ) 8.11 (d, 16, 1H, H^B), 7.75 (dd, 16, 11, 1H, $H^{B'}$), 7.2–7.8 (m, 4H, benzenoid H), 7.07 (d, 16, 1H, H^A), 6.54 (d, 16, 1H, $H^{A'}$), 6.51 (d, 11, 1H, $H^{C'}$), 3.55 (s, 1H, -C≡CH), 3.49 (s, 1H, -C≡CH), 2.03 (s, 3H, $-CH_3$); 8.23 (d, 16, 2H, H^B), 7.17–7.75 (m, 8H, benzenoid H), 7.17 (d, 16, 2H, H^A), 3.51 (s, 2H, -C≡CH).

10) The NMR assignment of the H^A and H^B protons of **4** and its corresponding acyclic ketone were established by condensation of **9** with acetone-d_6 to give α,α'-dideuterio acyclic ketone [m/e 284 (M^+); NMR ($CDCl_3$): 8.21 (s, H^B) instead of ABq], which on coupling led to α,α'-dideuterio **4** [m/e 282 (M^+); NMR ($CDCl_3$): 8.51 (s, H^B) instead of ABq].

11) 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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