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SYNTHESIS OF DIBENZO[d,j]-6,8-BISDEHYDRO[13]ANNULENONE

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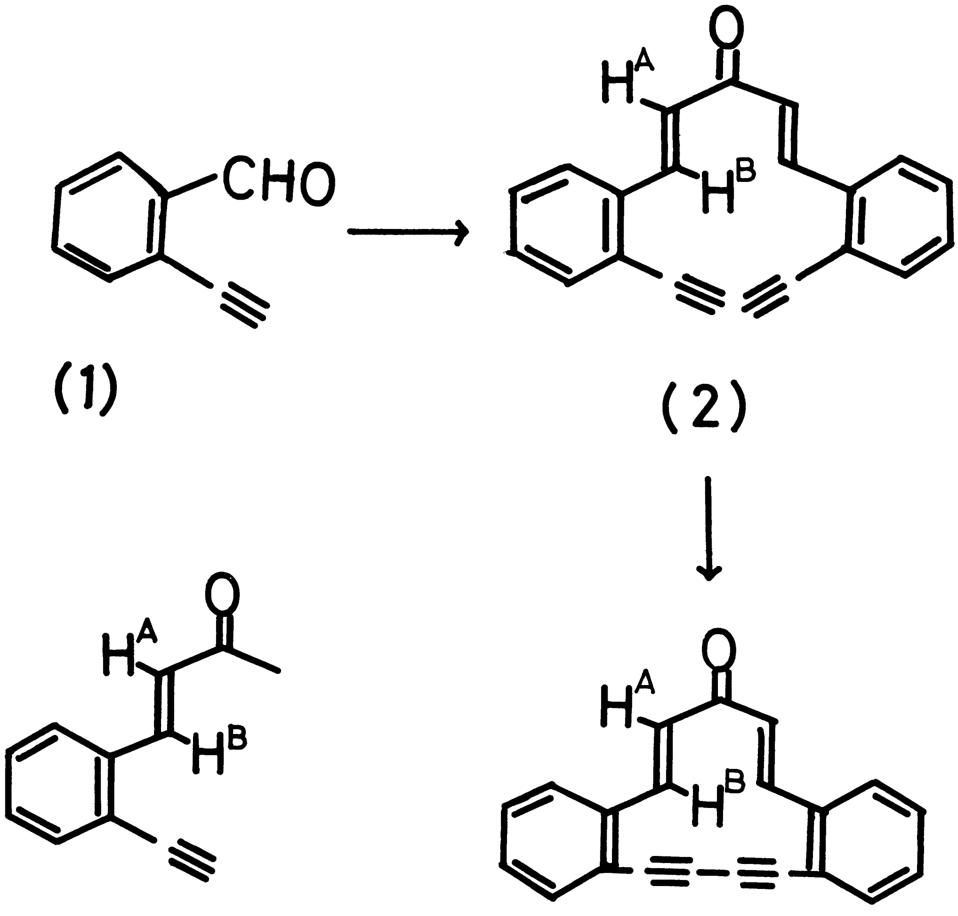
An annelated[13]annulenone (3) was prepared starting from o-ethynylbenzaldehyde (1) in order to examine the effect of annelation on the ring current of the inner thirteen membered ring. It was found that two benzene rings reduce a paramagnetic ring current arising from polarization of a carbonyl group in the inner ring.

A series of fully conjugated monocyclic monoketone, annulenone, are expected to be diatropic or paratropic owing to polarization of carbonyl group provided they contain (4n+3) membered ring or (4n+1) membered ring, respectively. Recently, F. Sondheimer et al. have showed a simple general synthetic method of [13]- and [17]-membered dehydroannulenones.1) It was of considerable interest to investigate the effect on the ring current produced by benzoannelation of these systems. We now describe the synthesis of dibenzo[d,j]-6,8-bisdehydro[13]annulenone (3), and show that two benzene rings reduce, but do not completely suppress, the paramagnetic ring current of [13]-membered ring.

Condensation of the o-ethynylbenzaldehyde (1) (2 mol)2) with acetone (1 mol) by means of methanolic potassium hydroxide in peroxide-free ether for 3 hours at room temperature afforded 35% yield of an acyclic ketone (2) as yellow plates, m.p. 101.3-101.7°C3) Found: C, 89.18; H, 4.76; Calcd: C, 89.33; H, 5.00; Mass: m/e 282 (M^+, 20%), 155 (base); IR (KBr) 3250(-C≡CH), 2100(-C≡C-), 1660(>C=O), 1595 (>C=C<), 985, 965 $\mathrm{cm^{-1}}$ ($^{H}\!>$C=C$<_{H}$); UV (EtOH) $\lambda_{max}(\varepsilon)$ 250nm(24,400), 332(24,500); NMR in Table 1.

Oxidative coupling of (2) by Eglinton's method4) gave the desired cyclic compound (3) 5) in 61% yield as yellow plates m.p. 194°C(dec).3) Mass: m/e 280 (M^+, base); IR (KBr): 2150(-C≡C-), 1640, 1620, 1590(>C=O, >C=C<), 970 $\mathrm{cm^{-1}}$ ($^{H}\!>$C=C$<_{H}$); UV (EtOH) $\lambda_{max}(\varepsilon)$ 284nm(3,900), 298(46,000), 379sh(3,820), 468sh(1,380); NMR in Table 1.

Treatment of (3) with trifluoroacetic acid gave the corresponding carbonyl protonated species (yellow-brown; λ_{max} 285sh nm, 301, 348sh, 413sh, >700; NMR in Table 1.



(1) (2) (4) (3)

Table 1. ^{1}H-NMR parameters of (2),(3), and (4) at 60MHz (τ-values, internal standard TMS, J in Hz)

	(2) in $CDCl_3$ a)	(3) in $CDCl_3$	(3) in CF_3COOD	(4) in $CDCl_3$ b) 6)	Δ(3)-(2)	Δ(3)-(4)
H_A	2.84 d J=16	3.24 d J=16	3.00	3.33 d J=16	+0.40	-0.09
H_B	1.82 d J=16	1.53 d J=16	0.98	2.02 d J=16	-0.29	-0.51
benzene ring	2.22-2.76	2.5-2.8	2.6-2.8	2.32-2.80		

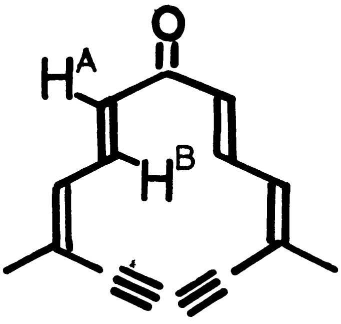
a) In addition, a singlet at 6.54 ($-C\equiv CH$)

b) In addition, a singlet at 6.57 ($-C\equiv CH$) and a singlet at 7.59(CH_3)

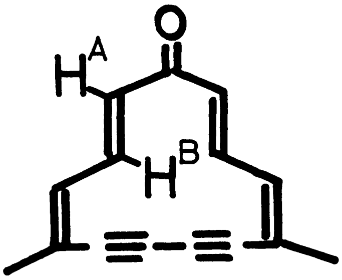
From the comparison of the NMR spectra of (2) and (3) in CDCl$_3$ (Table 1), compound (3) suggests to be paratropic, as expected for a potential 12π-electron system by the polarization of the carbonyl group, H_A resonance having moved to higher field, and H_B resonance to lower field.

However, the chemical shift of outer proton H_A in (2) is at considerably lower field than that of proton H_A in (3), in contrast to somewhat same position of both protons H_A in (3) and (4). This might be presumably due to complementary effects of two styrylethynyl moieties of the acyclic ketone (2). Furthermore, S. Misumi et al.7) noted the outer protons and benzenoid protons show little difference in the chemical shift between the acyclic system and the cyclic system on dibenzo-fused [14]-membered annulenedione, in contrast to the chemical shift of the inner protons. From these points, it seems to be appropriate to use the chemical shift difference of inner protons to compare the ring current effect of benzo-fused system with that of no-fused system.

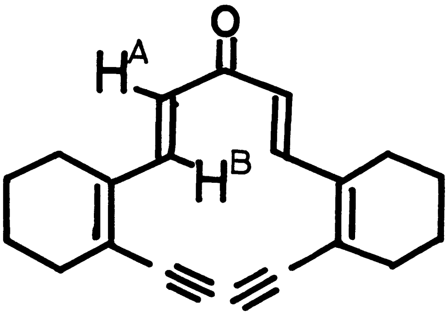
In order to obtain quantitative data regarding the paramagnetic ring current in (3), the ^{1}H-NMR spectral data of the model compounds (6) and (8) which were prepared by Sondheimer group,1)8) are also given in Table 2, as well as the chemical shift differences for the various resonances on passing from (5) to (6) and from (7) to (8). This shows the magnitude of the upfield shift of the outer proton signals and the downfield shift of the inner proton signals.



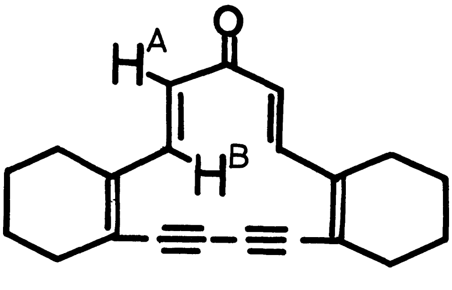
(5)



(6)



(7)



(8)

Table 2. ^{1}H-NMR parameters of (5), (6), (7), and (8) in $CDCl_3$ at 60MHz (τ-values, internal standard TMS)

	(5)	(6)	(7)	(8)	Δ(6)-(5)	Δ(8)-(7)
H_A	3.55	3.90	3.63	3.77	+0.35	+0.14
H_B	2.32	0.61	2.02	0.77	-1.71	-1.25

These results show that the macrocyclic ring in the dimethyl compound (6) is strongly paratropic, in the octahydro compound (8) it is moderately paratropic, in the dibenzo-fused compound (3) it is at most weakly paratropic. This is seen by the low field shifts and the chemical shift, as compared with the respective models of the H_B bands [-1.71, -1.25 and -0.29], [0.61, 0.77 and 1.53],respectively.

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5) The elemental analyses of (3) always afforded low values of carbon, but spectral properties clearly support the structure of (3).
6) The details of properties of (4) will be reported elsewhere.
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