SYNTHESIS OF DIBENZO[f,l]-8,10-BISDEHYDRO[17]ANNULENONE

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An annelated [17]annulenone (3) was prepared starting from o-ethynylcinnamaldehyde (1) in order to examine the effect of anne-lation on the ring current of the inner seventeen 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.

In a previous paper, we reported the synthesis of dibenzo[d,j]-6,8-bisdehydro-[13]annulenone (4), and showed that two benzene rings reduce, but do not completely suppress, the paramagnetic ring current of [13]-membered ring.[1] We now describe the synthesis of the next higher member of (4n+1) membered ring systems, i.e., di-benzo[f,l]-8,10-bisdehydro[17]annulenone which shows the similar result as we got on [13]-membered ring system (4).

Condensation of the o-ethynylcinnamaldehyde (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 26% yield of an acyclic ketone (2) as orange plates, m.p. 129-130°C.[3] Mass: m/e 334 (M^+, 85%), 154 (base); IR (KBr): 3300(-C≡CH), 2100 (-C≡C-), 1660, 1610, 1590($>$C=O, $>$C=C$<$), 990 cm^{-1} ($^H>$C=C$<_H$); UV (THF): $\lambda_{max}(\varepsilon)$ 235nm (26,900), 259(18,800), 266(19,100), 368(37,300); NMR: see Table 1.

Oxidation of (2) with cupric acetate in pyridine[4] gave 17% of the desired cyclic compound (3) as yellow cubes, m.p. 192°C(dec.).[3] Found: C, 90.33; H, 4.97; Calcd: C, 90.33; H, 4.85; Mass: m/e 332 (M^+, 60%), 313 (base); IR (KBr): 1630, 1600 ($>$C=O, $>$C=C$<$), 1000($^H>$C=C$<_H$); UV (THF): $\lambda_{max}(\varepsilon)$ 297nm(63,300), 313(70,000); NMR: see Table 1.

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

	(2) in CDCl$_3$[a)]	(3) in CDCl$_3$	Δ(3)-(2)
H^A	3.33 d J=16	3.88 d J=16	+0.55
H^B		2.16 dd J=16, 12	(-0.01 ~ -0.61)
H^C		3.83 dd J=16, 12	(+1.66 ~ +1.06)
H^D	2.17 ~ 2.77	2.02 d J=16	(-0.15 ~ -0.75)
aromatic protons		2.46 ~ 2.86	

a) In addition, a singlet at 6.55 (-C≡CH).

(1)

(2)

(4)

(3)
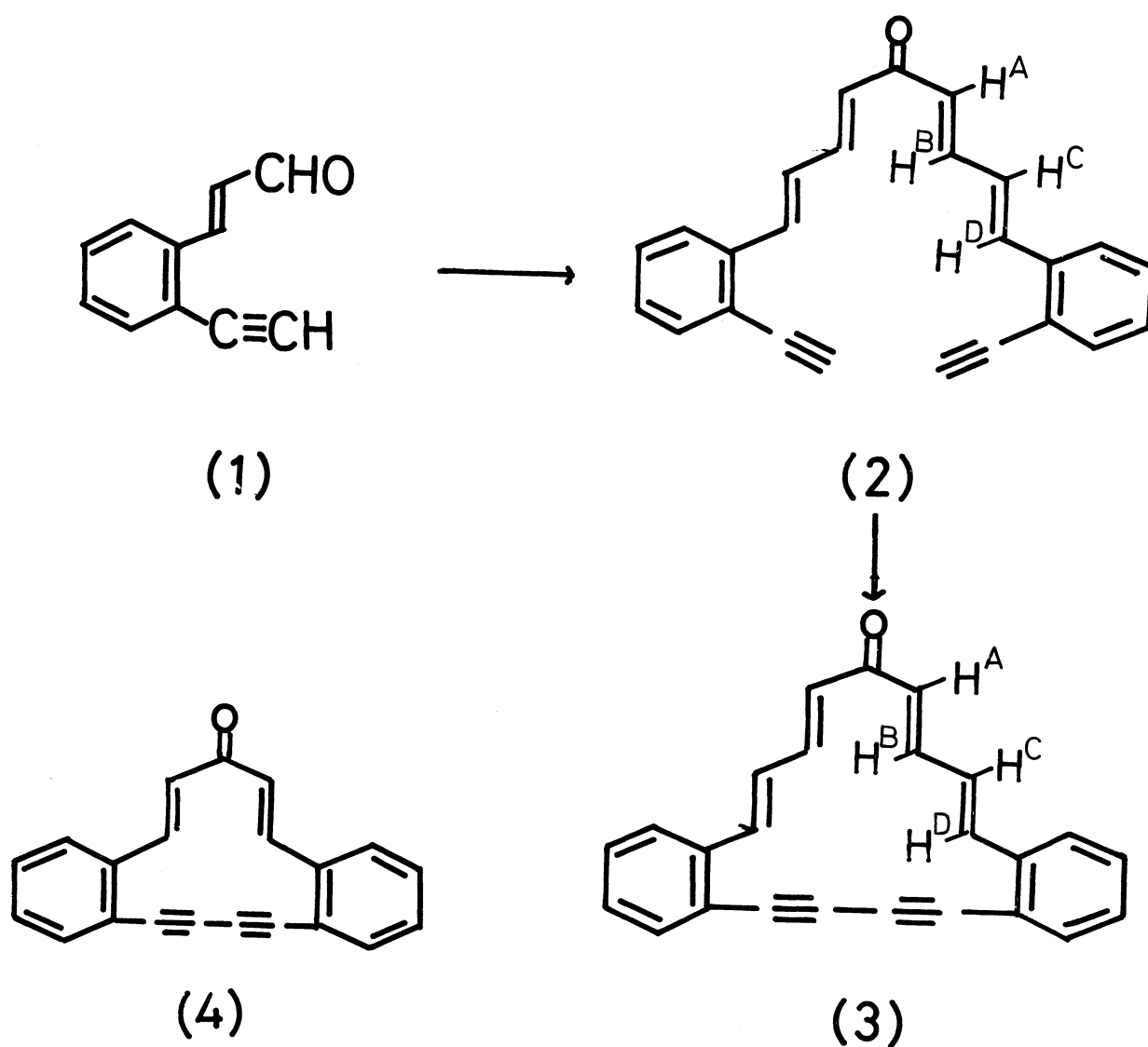
Comparison of the NMR spectra of (2) and (3) in $CDCl_3$ (Table 1) shows there is a little paramagnetic ring current in (3), as expected for a potential 16π-electron system by the polarization of the carbonyl group, the outer proton resonances (H^A, H^C) having moved to a slightly higher field, and the inner proton resonances (H^B, H^D) to a slightly lower field.

Although the downfield shift of the inner protons in (3) as compared to (2) might be due to the anisotropy of the triple bond(s), there is a little corresponding up-field shift of the outer protons. These results suggest the compound (3) to be weakly paratropic.

In order to obtain quantitative data regarding the paramagnetic ring current in (3), the ^{1}H-NMR spectral data of the model compound (6), which was prepared by
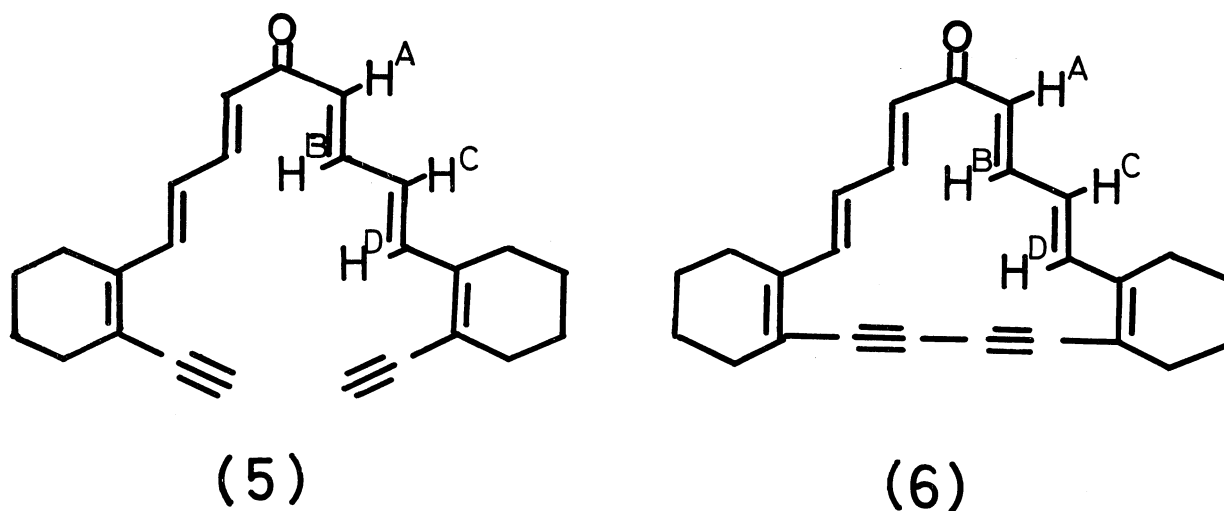

(5)   **(6)**

Table 2. ^{1}H-NMR parameters of (5) and (6) in $CDCl_3$ at 60 MHz

(τ values, internal standard TMS, J in Hz)

	(5)	(6)	Δ(6)-(5)
H^A	3.48 d J=16	4.14 d J=16	+0.66
H^B	2.45 dd J=16,10	1.42 dd J=16,10	-1.03
H^C	3.53 dd J=16,10	3.92 dd J=16,10	+0.39
H^D	2.58 d J=16	1.15 d J=16	-1.43

Sondheimer et al., is also given in Table 2, as well as the chemical shift differ-
ences in the various resonances on passing from (5) to (6). This shows the magni-
tude of the upfield shift of the outer proton signals and the down field shift of
the inner proton signals.

These results show that the paratopic nature of the macrocyclic ring in
dibenzo-fused compound (3) is smaller than that of the macrocyclic ring in octa-
hydro compound (6).

References

1) J. Ojima, Y. Yokoyama, and T. Yokoyama, Chem. Lett., 1261(1974).

2) On the synthesis of compound (1); J. Ojima, A. Kimura, Y. Yokoyama, and
   T. Yokoyama, Bull. Chem. Soc. Japan, in press.

3) All melting points are not corrected.

4) G. Eglinton and A. R. Galbraith, J Chem. Soc., 889(1959).

5) P. D. Howes, E. LeGoff, and F. Sondheimer, Tetrahedron Lett., 3691(1972).