

AROMATIC LINEARLY ANNELATED DIBENZOCYCLONONATETRAENYL ANION

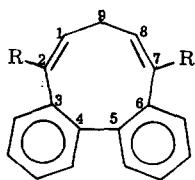
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(Received in UK 22 October 1974; accepted for publication 8 November 1974)

The question whether  $\pi$  delocalization will persist in nonbenzenoid aromatic systems when perturbed by fusion with benzene rings is a central problem in the study of these systems.<sup>1,2</sup> It has previously been observed that unlike the monobenzannelated cyclononatetraene<sup>2a</sup> the deprotonation of 3,4;5,6-dibenzocyclononatetraene system (I)<sup>2b</sup> showed only a gradual development of a delocalized  $\pi$  frame. This difference between mono- and dibenzannelation could be attributed either to the higher degree of annelation or to the presence of the biphenyl backbone in (I). A promising model compound for such a study, would be the linearly annelated 1,2;5,6-dibenzocyclononatetraenyl anion (II). We describe the generation and direct observation of (II) and its precursor 1,2;5,6-dibenzocyclononatetraene (III).

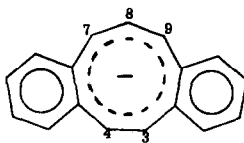
Ozonolysis of indene<sup>3,4</sup> followed by reduction gave homophtholyl alcohol (IVa) which was transformed into the dibromide (IVb).<sup>5</sup> Reaction of (IVb) with triphenylphosphine (boiling, DMF, 3 hrs.) afforded the diphosphonium salt (IVc), m.p. 148°, 93% yield. The Wittig reaction<sup>6</sup> of (IVc) and phthalaldehyde in the presence of lithium ethoxide (DMF, 80°, 3 hrs., inert atmosphere)



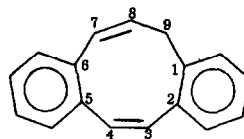
I

R = H

R = Ph



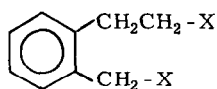
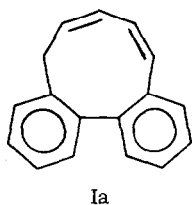
II



III

afforded, after repeated chromatographies on Florisil, 1,2;5,6-dibenzocyclononatetraene (III), (m.p. 20°, 10%); mass spectrum,  $m/e$  218 (M, 100%), 217, 215, 203, 191, 165, 163, 152;  $\nu_{\max}^{\text{CHCl}_3}$  ( $\text{cm}^{-1}$ ) 1490, 1430, 1100, 805, 750, 735, 710;  $\lambda_{\max}^{\text{EtOH}}$  250 sh ( $\epsilon$  9,600), 320 sh (1,180) and 343 nm (825). The ir band at  $735 \text{ cm}^{-1}$  and the absence of bands in the  $960 \text{ cm}^{-1}$  region point at the cis configuration of the olefinic double bonds. The nmr spectrum<sup>7</sup> confirms the structure of (III)  $\delta$  ppm ( $\text{CDCl}_3$ ) 7.30-6.70 (multiplet, 10H, aromatic,  $\text{H}_3$  and  $\text{H}_4$ ), 6.52 and 6.39 (doublet of triplets, 1H, vinylic  $\text{H}_7$ ,  $J_1 = 12 \text{ Hz}$ ,  $J_2$  (allylic) 2.0 Hz), 5.81 (five lines, 1H, vinylic  $\text{H}_8$ ), 3.42 (double doublet, 2H,  $\text{H}_9$ ,  $J_1 = 5.7 \text{ Hz}$ ,  $J_2 = 2.0 \text{ Hz}$ ). Irradiation at 3.42 ppm<sup>7</sup> transformed the vinylic absorption of  $\text{H}_7$  and  $\text{H}_8$  into an AB spectrum ( $\delta A = 6.40$ ,  $\delta B = 5.78 \text{ ppm}$ ,  $JAB = 12 \text{ Hz}$  verifying a cis configuration of the  $\text{C}_1 - \text{C}_2$  double bond). The hydrocarbon (III) is stable to heat and air, in contrast to the behaviour of the parent hydrocarbon cyclononetetraene which undergoes very easily a symmetry-allowed rearrangement to a dihydroindene system<sup>1</sup>. The dibenzannelated hydrocarbon (I) as well as the monobenzannelated one yield, after treatment with base, two allyl-isomeric hydrocarbons<sup>2b</sup> (e.g., hydrocarbon (I) forms isomer (Ia)). However, hydrocarbon (II) does not form allyl isomers.

Treatment of III in [ $^2\text{H}_8$ ]tetrahydrofuran with n-butyl lithium in cyclohexane at  $-20^\circ$  gave instantaneously a deep red solution with the following nmr parameters<sup>8</sup>:  $\delta$  ppm 7.62 (2H, singlet,  $\text{H}_3$  and  $\text{H}_4$ ), 6.60-6.10 (11H, multiplet, benzenoid protons,  $\text{H}_7$ ,  $\text{H}_8$  and  $\text{H}_9$ ). On the basis of the chemical shifts we assign this spectrum to the planar delocalized aromatic ion (II)<sup>9</sup>. The spectrum did not show any change with time. Its immediate formation contrasts with the slow transformation of (I) into its delocalized anion (ca. 30 hrs. at room temperature)<sup>2b</sup>. Thus, it appears that in the case of (I), it is the biphenyl backbone and not the annelation which retards the process of delocalization in the anion. The relatively high field shift of the benzenoid protons of (II) indicates that charge delocalization is not limited to the cyclononatetraenyl portion but extends into the benzene moieties as well.



a, X = OH

b, X = Br

c, X = P<sup>+</sup>(Ph<sub>3</sub>)Br<sup>-</sup>

Acknowledgment: This work was supported by a grant from The Israel Commission for Basic Research.

### References

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7. Proton nmr spectra were recorded at 100 MHz.  $^1\text{H}$  Chemical shifts are reported in ppm downfield from  $\text{Me}_4\text{Si}$ . The decoupling was carried out with a Hewlett-Packard model 4204A oscillator.
8. Quenching (II) with EtOH gave unchanged (III).
9. At  $-30^\circ$  an intermediary short-lived allylic anion was observed,  $\delta$  ppm = 6.85-6.35 (10H, multiplet, benzenoid protons,  $\text{H}_3$  and  $\text{H}_4$ ), 5.67 (1H, triplet,  $\text{H}_8$ ,  $J = 5.5$  Hz), 3.99 (2H, doublet,  $\text{H}_7$  and  $\text{H}_9$ ,  $J = 5.5$  Hz). Irradiation<sup>7</sup> at 5.67 ppm rendered the doublet at 3.99 ppm into a singlet. This ion undergoes a fast transformation into (II) ( $\tau_{1/2} = 3$  min. at  $-30^\circ$ ). However, at  $-20^\circ$  an instantaneous formation of (II) was observed.