Synthesis of a Macrocycle by a One-stage Wittig Reaction

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Summary The macrocycle 7,11:20,24-dimethenotetrabenzo[*a,c,n,p*]cyclohexacosene (I) has been synthesised in a one-stage Wittig reaction from 2,2′-bis(triphenylphosphoniomethyl)biphenyl dibromide (III) and isophthalaldehyde (IV) using sodium ethoxide as base.

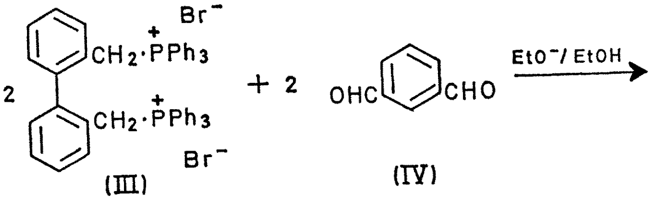
BERGMANN[1] synthesised the macrocycle tetrabenzo[*a,e,i,m*]-cyclohexadecene (II) in a ten-stage synthesis from phthalic anhydride. Griffin[2] synthesised (II) in a four-stage synthesis, the first and last stages being Wittig reactions. However, no synthesis of a macrocycle of this type has been reported from a single reaction involving condensation of four monomeric units.

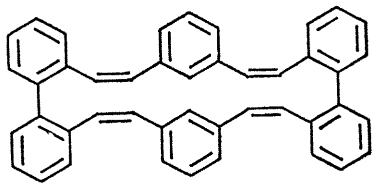
The dibromide (III)[3] was treated with equimolar amounts of isophthalaldehyde (IV) in the presence of sodium ethoxide to give crude hydrocarbon material which on repeated chromatography on alumina gave (I) (12%), m.p. 190° (from benzene–ethanol). Satisfactory analyses were obtained for compounds (I) and (III).

The mass spectrum of (I) showed the molecular ion (*m/e* 560) (2·3%) and several fragmentation series within which the differences in *m/e* values was 13, indicating successive loss of CH. The base peak was due to the phenanthrenyl ion (*m/e* 178). The i.r. spectrum shows strong bands at 958 cm^{-1} (indicative of *trans*-double bonds) and 683 cm^{-1} (indicative of *cis*-double bonds). Other than this, little can be said of the precise stereochemistry of (I); models show that it cannot be planar.

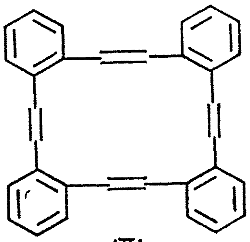
The u.v. spectrum [$\lambda_{\max}$ 221 nm (log ϵ 4·79), 275sh (4·72), 291 (4·78), 318sh (4·60), and 333sh (4·32)] confirms that the molecule is not planar.

Although all the hydrogen atoms in the molecule are more or less within the aromatic region of the n.m.r. spectrum (τ 2·1—3·4), (I) cannot be considered as a derivative of [22]annulene, as one cannot write Kekulé forms of the molecule with alternating double and single bonds round the C$_{22}$ ring. This will limit the delocalisation in the C$_{22}$ ring and eliminate the possibility of resonance, even though (in M.O. terms) continuous overlap of $p\pi$ orbitals is possible.





(I)



(II)

The ease of synthesis of (I) is surprising, as we have tried to synthesise similarly various related cyclic hydrocarbons for which a planar structure is possible and only acyclic products have been obtained.[4]

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[1] E. D. Bergmann and Z. Pelchowicz, *J. Amer. Chem. Soc.*, 1953, **75**, 4281.

[2] C. E. Griffin, K. R. Martin, and B. E. Douglas, *J. Org. Chem.*, 1962, **27**, 1627.

[3] E. D. Bergmann, P. Bracha, I. Agrunat, and M. A. Krauss, *J. Chem. Soc.* (*C*), 1967, 328.

[4] C. D. Tulloch and W. Kemp, unpublished results.