1,2;5,6;9,10-Tribenzocyclododeca-1,5,9-triene-3,7,11-triyne and 1,2;5,6;9,10;13,14-Tetrabenzocyclohexadeca-1,5,9,13-tetraene-3,7,11,15-tetrayne

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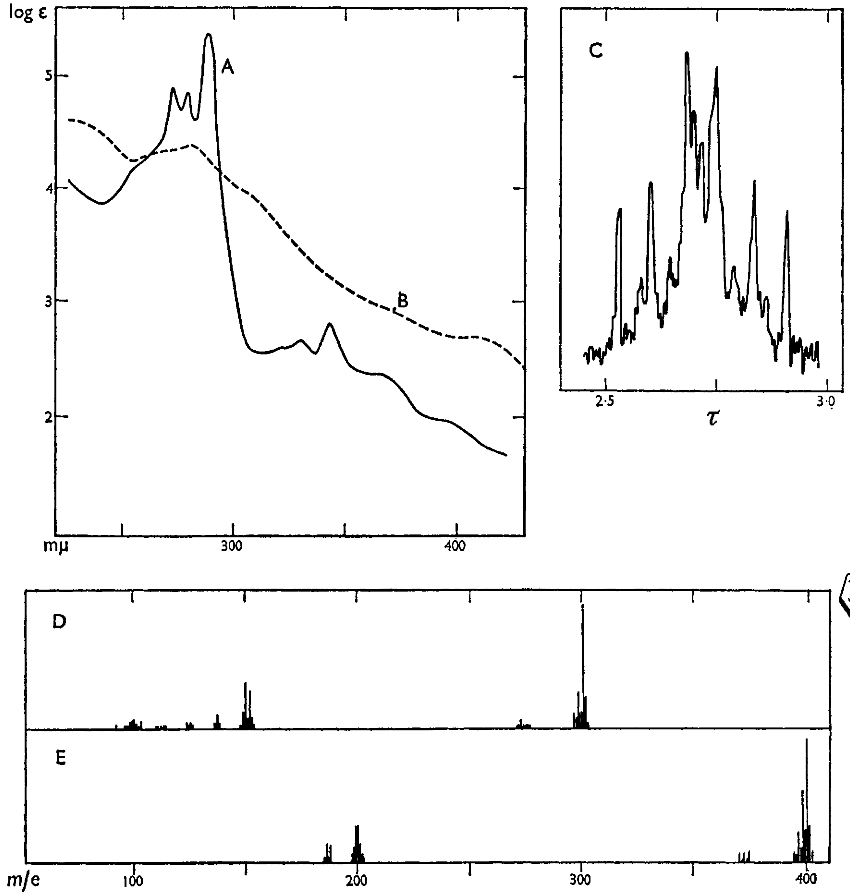
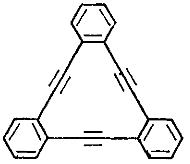
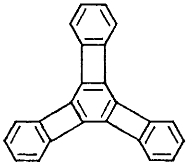
THE recently discovered interaction of cuprous acetylides with aryl iodides to give high yields of arylacetylenes[1] prompted the use of this method for the attempted synthesis of the long-sought strain-free planar triangular molecule (I). Accordingly the cuprous salt of *o*-iodophenylacetylene[2] was heated in anhydrous pyridine under nitrogen for 7 hr. Separation of the hydrocarbon products by preparative thin-layer chromatography gave predominantly (I; 26%) as pale yellow needles m.p. 219—220·5° (no decomposition!) molecular weight 307 ± 10 (osmometry in CCl_4), 300 (mass spectrometry; see Figure, D). The spectroscopic properties were fully compatible with structure (I) although the isomeric (II) could not be ruled out on these data alone. The ultraviolet spectrum shows predominant absorption at 289 mμ (cyclohexane) (ϵ, 244,000) with subsidiary fine structure in the 225—280 mμ and 310—400 mμ regions with vibrationally derived spacings of about 1000 cm.$^{-1}$ and 500 cm.$^{-1}$, respectively (Figure, A). The infrared spectrum is remarkably simple, the most intense band being that due to the γ(CH) mode of the *o*-disubstituted benzene nuclei at 750 cm.$^{-1}$ ($\Delta\nu^a_{\frac{1}{2}}$, 4 cm.$^{-1}$; ϵ, 2000 in CS_2). The n.m.r. spectrum (Figure, C) shows only the expected A_2B_2 system in the aromatic region, centred at τ 2·72, with calculated[3] chemical shifts and coupling constants compatible with such a structure. The mass spectrum (Figure, D) points strongly to a highly stable structure, the base peak being the molecular ion (*m/e* 300) which is surrounded by a cluster of peaks one unit apart. This cluster is paralleled by one at *m/e* 150 with half-unit spacing corresponding to a similar set of doubly charged ions, and a further cluster at 100 with third-unit spacing corresponding to triply-charged ions.




(I)


(II)

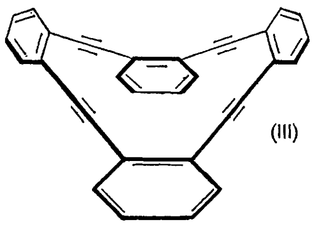

(III)

FIGURE A, B: *Ultraviolet spectra (cyclohexane) of* (I) *and* (III), *respectively.*
C : *N.m.r. spectrum* ($CDCl_3$) *of* (I).
D, E: *Mass spectra of* (I) *and* (III), *respectively.*

Discrimination between the two possible structures in favour of (I) was provided by the results of catalytic hydrogenation (Pd–C), one product of which was shown to be the colourless crystalline hydrocarbon tri-*o*-xylylene by spectroscopic and g.l.c. comparison with an authentic sample.[4]

A by-product of the cyclisation proved to be another yellow crystalline hydrocarbon which decomposed before melting. The strainless saddle-shaped structure (III) of D_{2d} symmetry is assigned to this compound on the following basis. The infrared and n.m.r. spectra were similar to those of (I). The mass spectrum (Figure, E) was again very simple, the strong parent ion occurring at m/e 400 among a cluster of unit-spaced peaks; a similar cluster with a half-unit spacing appeared at 200 and another with third-unit spacing at 133. The ultraviolet spectrum (Figure, B) was, as expected, quite different from that of (I).

The reactions of these novel macrocycles and the scope of this cyclisation procedure are now being explored.

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[1] R. D. Stephens and C. E. Castro, *J. Org. Chem.*, 1963, **28**, 3313; R. E. Atkinson, R. F. Curtis, and G. T. Phillips, *Chem. and Ind.*, 1964, 2101.

[2] R. W. Bott, C. Eaborn, and D. R. M. Walton, *J. Chem. Soc.*, 1965, 384. We thank these workers for a generous gift of the iodoacetylene.

[3] Calculated on a K.D.F. 9 computer using a Freqint IVa programme, kindly provided by Dr. A. L. Porte.

[4] Kindly provided by Dr. F. G. Mann, F.R.S.