

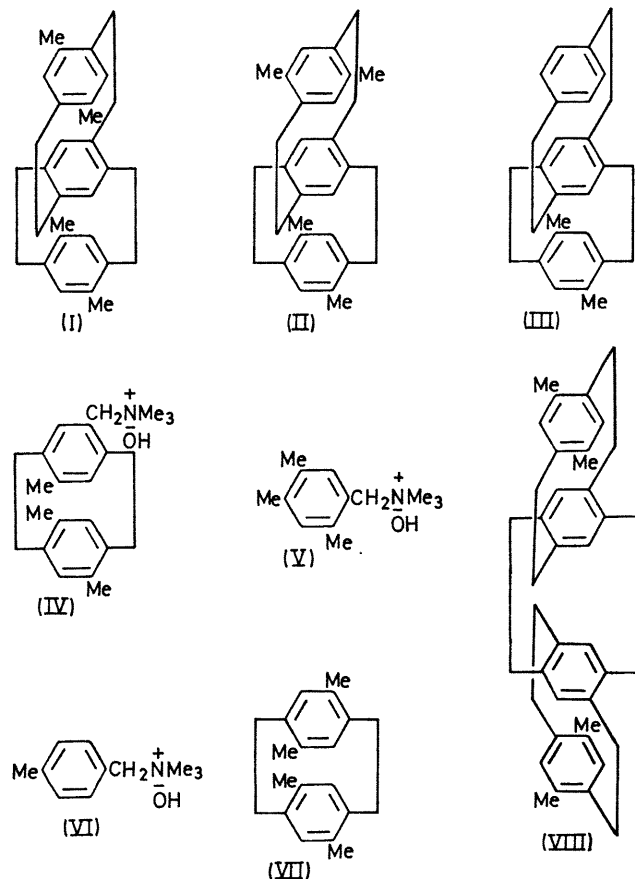
Layered Cyclophanes

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Summary New triple-layered cyclophanes (I)—(III), which show remarkable transannular electronic interaction between the benzene rings, have been synthesised.

A WIDE variety of aromatic compounds in which aromatic rings are closely bound by methylene bridges, *i.e.* layered cyclophanes, have been investigated, especially from the view-point of transannular interaction.¹ However, almost all the cyclophanes studied so far have been of the double-layered aromatic-nuclei-type and there have been few of more than three layers,^{2,3} which should exhibit remarkable π -electron interaction. We report the synthesis of new triple-layered cyclophanes of the 1,2,4,5-tetramethylbenzene(durene)-durene-durene-type (I) and (II), and xylene-durene-durene, (III).



The triple-layered cyclophanes (I) and (II) were synthesized by pyrolysis of an equimolar mixture of (IV) and

(V) in boiling xylene. The crude product was separated by chromatography (silica gel or neutral alumina) from the double-layered (VII)^{2,4} and quadruple-layered (VIII).² Recrystallization from acetone-ethanol (1:1) gave colourless plates of (I) (1.1%), m.p. 245–246 °C (sealed tube), τ (CDCl₃) 3.88 (2H, s, ArH), 4.21 (4H, s, ArH), 6.7–7.7 (16H, m, CH₂), and 8.07 (12H, s, CH₃), and colourless plates of (II) (1.1%), m.p. 204–205 °C, τ 4.17 (2H, s, ArH), 4.21 (2H, s, ArH), 4.28 (2H, s, ArH), 6.7–7.8 (16H, m, CH₂), and 8.10 (12H, s, CH₃).[†]

The triple-layered compound (III) was prepared from (IV) and (VI) similarly (1.8%), m.p. 147–148 °C (from light petroleum), τ (CCl₄) 3.88 (4H, s, ArH), 4.30 (2H, s, ArH), 4.36 (2H, s, ArH), 6.8–8.1 (16H, m, CH₂), and 8.17 (6H, s, CH₃). As the number of layers increases, the shielding effect due to anisotropy of benzene rings becomes more effective, especially evident with chemical shifts of aromatic protons.

The u.v. spectrum of the cyclophane (I) exhibits strong bathochromic and hyperchromic effects as compared with that of the double-layered (VII) (see Figure). This is

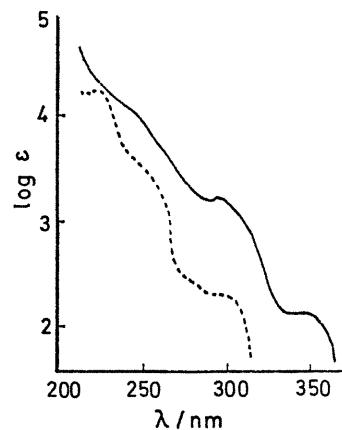


FIGURE. U.v. spectra of the triple-layered cyclophane (I) (—) and the double-layered cyclophane (VII) (---) in cyclohexane.

probably attributable to the significant increase of the transannular electronic interaction between benzene rings. The electronic interaction is also reflected in the absorption maxima of longest wavelength of tetracyanoethylene cyclophane complexes, which shift to longer wavelength with increasing numbers in the layer, *e.g.* durene⁵ 480 nm, (VII)² 580 nm, (I) 655 nm, and (VIII)² 690 nm in CH₂Cl₂.

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[†] Satisfactory elemental analysis and mass spectral data have been obtained for all new compounds.

¹ For summary and references, see (a) B. H. Smith, 'Bridged Aromatic Compounds,' Academic Press, New York, 1964; (b) D. J. Cram, N. L. Allinger and H. Steinberg, *J. Amer. Chem. Soc.*, 1954, **76**, 6132; (c) D. J. Cram and R. H. Bauer, *ibid.*, 1959, **81**, 5971; (d) M. Sheehan and D. J. Cram, *ibid.*, 1969, **91**, 3553.

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