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LAYERED COMPOUNDS. XIII[1] FIVEFOLD-LAYERED CYCLOPHANES

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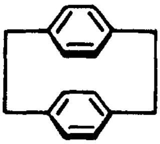
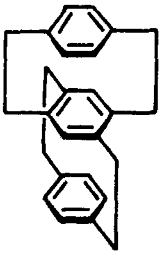
Our previous papers of this series have been concerned with the transannular electronic interaction of the aromatic compounds in which more than two benzene rings are closely stacked by methylene bridges, namely, layered cyclophanes.[2] As the number of layers increases successively, e.g., double-layered compound (I), triple-layered one (II), quadruple-layered one (III), and sixfold-layered one (V), larger intramolecular interaction of the chromophores has been observed, especially in the electronic spectra In the present communication, we will report the synthesis and properties of fivefold-layered cyclophane (IV) for further investigations of the transannular electronic interaction and magnetic shielding effect of layered benzene rings.


I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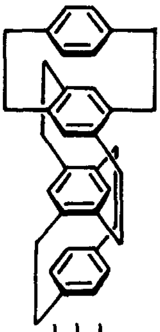
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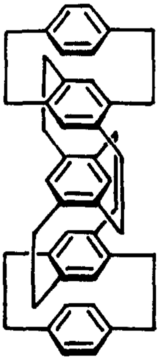
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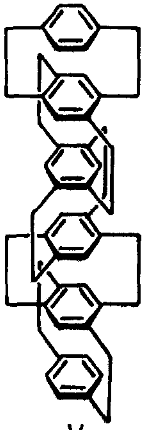
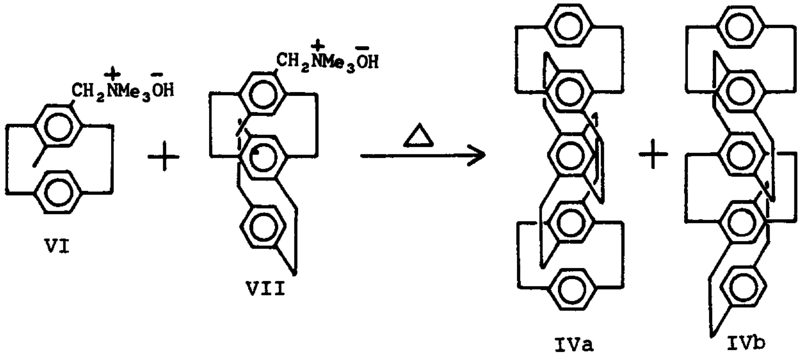
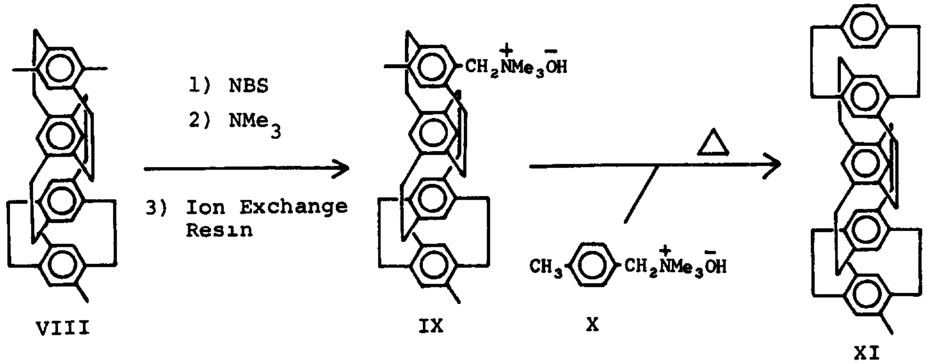
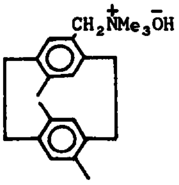

V

Pyrolysis of an equimolar mixture of quaternary ammonium hydroxides, VI and VII, in boiling xylene afforded fivefold-layered compound (IV) in a 4.3% yield along with quadruple-layered one (III) and polymers. Separation by liquid chromatography gave pure IV, colorless microcrystals from carbon tetrachloride-acetone (1:3), [decomp. >240°C; mass m/e 598(M^+)], which is probably a mixture of two isomers, IVa (D_2 symmetry) and IVb (C_2 symmetry).

Dimethyl derivative (XI) of IVa was obtained together with [2.2]paracyclophane (I), [2.2.2]paracyclophane, and polymers by pyrolysis of an excess of ammonium hydroxide X with IX which was synthesized from tetramethyl quadruple-layered cyclophane (VIII) having D_2 symmetry configuration.³⁾ Column chromatography on neutral alumina gave a 0.8% yield of XI in a pure state, colorless plates from carbon tetrachloride-acetone (1:3), [decomp. >250°C; mass m/e 626(M^+)]. Dimethyl derivative of fivefold-layered cyclophane also yielded by pyrolysis of a mixture of VII and XII. This product is considered a mixture of two isomers, XI and dimethyl derivative of IVb, as in the case of non-substituted one (IV).







XII

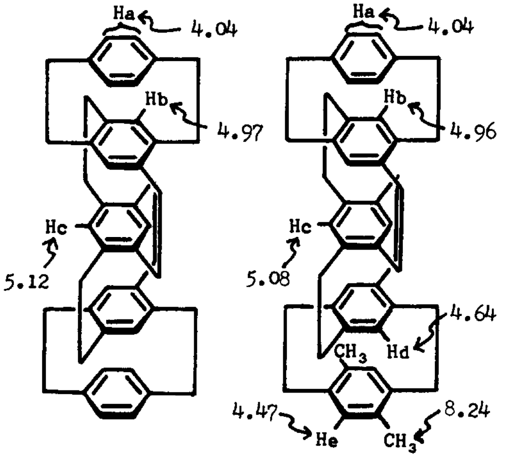


Fig. 1 NMR spectra (τ value) of fivefold-layered cyclophanes (in CCl_4). Methylene protons appear at τ 6.8~8.1 (m).

The NMR spectra of fivefold-layered cyclophanes are depicted in Fig. 1. The aromatic protons, Ha, Hb, and Hc, of non-substituted compound IV are easily assigned by means of integral strength Of aromatic protons in dimethyl derivative XI, the assignment of Ha, Hb, and Hc was established by comparison with the corresponding protons of IV, and the proton which appeared at lower field by ca. 0.3 ppm than Hb was assigned to be Hd on the basis of the steric compression effect caused by methyl group at pseudo-gem position in the adjacent benzene ring.2a, 4)

One can obviously see on the spectra of multilayered cyclophanes that all the aromatic protons progressively appear at higher field with the increasing number of layers. Hereupon, it is anticipated that there may exist some regularity among the chemical shifts of those aromatic protons. On an examination of those spectral data[2], the shielding effects of additionally stacked benzene rings were empirically estimated as shown in Table 1. Thus, the chemical shift of a given aromatic proton is calculated by adding these values of the shielding effects to the chemical shift of the aromatic protons in standard alkyl benzene, τ 3.05 (p-xylene) or τ 3.26 (durene). For example, a calculated value of Ha in IV is τ 4.09 ($3.05 + \sigma_1 + \sigma_2 + \sigma_3 + \sigma_4$), for Hb τ 4.96 ($3.26 + 2\sigma_1 + \sigma_2 + \sigma_3$), and for Hc τ 5.08 ($3.26 + 2\sigma_1 + 2\sigma_2$), respectively

Table 1. Shielding effect of additional benzene rings (ppm)

	Empirical	Calculated*
σ_1 (neighbouring ring)	0.69	0.417
σ_2 (next ring but one)	0.22	0.157
σ_3 (next ring but two)	0.10	0.059
σ_4 (next ring but three)	0.03	0.028
σ_5 (next ring but four)	0.02	0.014

* Values were calculated according to the Johnson-Bovey's method.5)

in excellent agreement with the observed values. Similarly, we observed good agreements in the cases of the other multilayered cyclophanes (I, II, III, and V) and also in the cases of those methyl derivatives by considering secondary effects such as steric compression effect of methyl groups As seen in Table 1, it is notable that the shielding effects above estimated are not quite equal but in a good correlation with the values calculated from the ring current equation of Johnson-Bovey[5] , where a value of 3.03 Å is used for an average distance between two adjacent benzene rings, which was derived from X-ray crystallography of quadruple-layered cyclophane.[3] This denotes that our data may be generalized on similarly constructed compounds.

In the previous paper,[2b] it has been reported that the electronic spectra of multilayered cyclophanes exhibit strong bathochromic and hyperchromic effects with the increasing number of layers owing to the transannular electronic interaction among benzene rings However, the spectra of fivefold-layered cyclophanes show that their curve and intensity per unit chromophore are nearly identical with that of sixfold-layered one V. Consequently, it may be concluded from those spectra that no further increase of the transannular electronic interaction is observed in more than five layered cyclophanes in contrast to appreciable changes in the interaction up to fivefold-layered one.

References

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