

LAYERED COMPOUNDS. VII  SIXFOLD-LAYERED CYCLOPHANE

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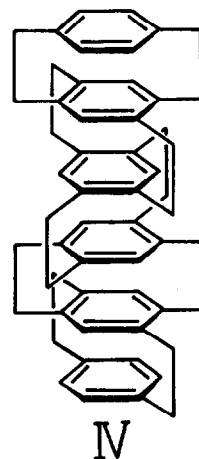
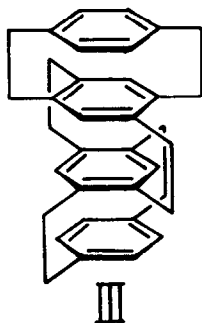
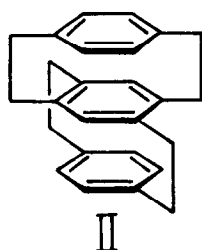
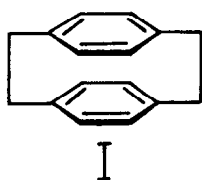
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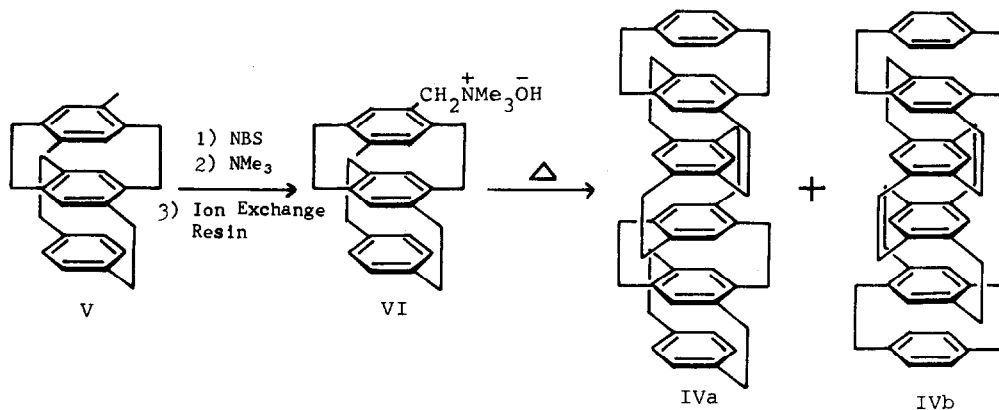
(Received in Japan 2 June 1972; received in UK for publication 12 June 1972)

Aromatic compounds in which more than two benzenoid aromatic rings are closely bound in a manner of face-to-face by methylene bridges, i.e., layered cyclophanes, are known as quite suitable models for the study of the transannular electronic interaction. And the more the number of layers increases, e.g., single-layered compound (such as p-xylene or durene), double-layered one (I), triple-layered one (II), and quadruple-layered one (III), the larger the transannular interaction has been observed^{2,3}.

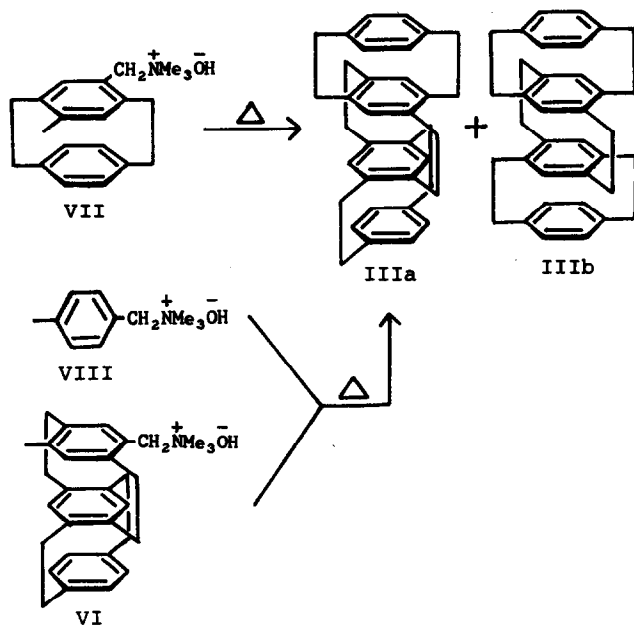
In the present communication, we will report the synthesis of sixfold-layered cyclophane (IV), which is expected to exhibit more remarkable electronic interaction and magnetic shielding effects of multiple benzene rings.



A quaternary ammonium hydroxide (VI) was synthesized from dimethyl triple-layered compound (V)^{2a)}. Pyrolysis of VI in boiling toluene afforded sixfold-layered compound (IV) together with polymers. After column chromatography on neutral alumina, the readily soluble product (3.7% yield based on V) was separated from the sparingly soluble one (1.9%) by treatment with benzene. Recrystallization of the 3.7% product from toluene gave colorless plates, decomp. > 250°C, mol. wt., calcd. 729; found 737 (osmometry in benzene). On the other hand, recrystallization of the 1.9% one from xylene gave colorless fine crystals, decomp. > 250°C. Satisfactory elemental analysis has been obtained for both new compounds. The NMR, IR, and UV spectra of the readily soluble crystals are the nearly same as those of the sparingly soluble one; the IR spectra are characterized by 898 (m), 673 (s) cm^{-1} for the former and 894 (m), 677 (s) cm^{-1} for the latter. So, these facts indicate that both are isomeric with each other.



On the Hofmann elimination reaction of VI, IVa (D_2 symmetry) and IVb (C_{2h} symmetry) are considered as the producible isomers of sixfold-layered cyclophane IV. We have also encountered two isomers of quadruple-layered one (III)^{2b)} in the previous study, where the pyrolysis of VII in boiling xylene afforded a mixture of the readily soluble major product and the sparingly soluble minor one. The former was assigned to the structure IIIa (D_2 symmetry) by direct comparison with an independently synthesized sample (IIIa by the cross-breeding reaction of VI and VIII), and then the sparingly soluble isomer was assigned to the isomeric structure IIIb



(C_{2h} symmetry). On analogy with III

it is presumed that in the case of sixfold-layered cyclophane, the structure of the readily soluble major isomer is IVa with less steric crowding, whereas the sparingly soluble one is IVb with more steric crowding.

As shown in Fig. 1, the NMR spectrum of IVa reveals a striking feature that all the aromatic protons

appear at remarkably higher field. Especially, two types of inner protons are more shielded due to the anisotropies of the upper and lower benzene rings. For comparison the NMR spectra of the multilayered cyclophanes together with p-xylene are included in Table 1. There exists an additivity among the chemical shifts of the aromatic protons depending upon the number of sandwiching benzene layers. Thus, as the number of layers increases, the resonance positions of the aromatic protons shift to more higher field with decreasing magnitude of the shifts, indicating that the shielding effect of additional benzene ring becomes less effective.

The UV spectra of the multilayered cyclophanes exhibit strong bathochromic and hyperchromic effects as the number of layers increases successively (see Fig. 2). In particular, such

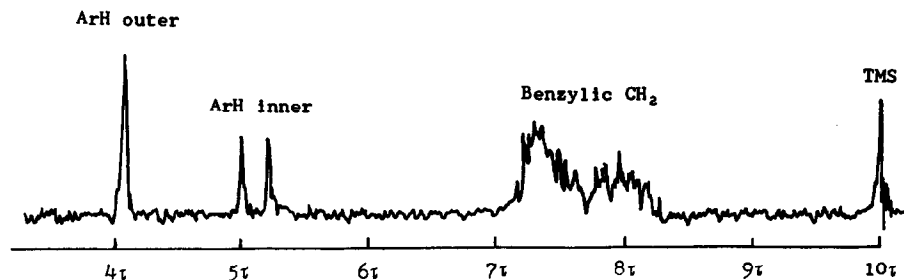


Fig. 1. NMR spectrum of sixfold-layered cyclophane (IVa) in CCl_4 .

Table 1. NMR spectra of layered cyclophanes in CCl_4 (τ value)

	outer	Ar H	inner	benzylic CH_2
p-xylene	3.05 (s)			
I	3.65 (s)			6.99 (s)
II	3.92 (s)		4.65 (s)	6.8~7.7 (m)
IIIa	4.02 (s)		4.88 (s)	6.7~7.9 (m)
IVa	4.06 (s)	5.00 (s), 5.20 (s)		7.1~8.3 (m)

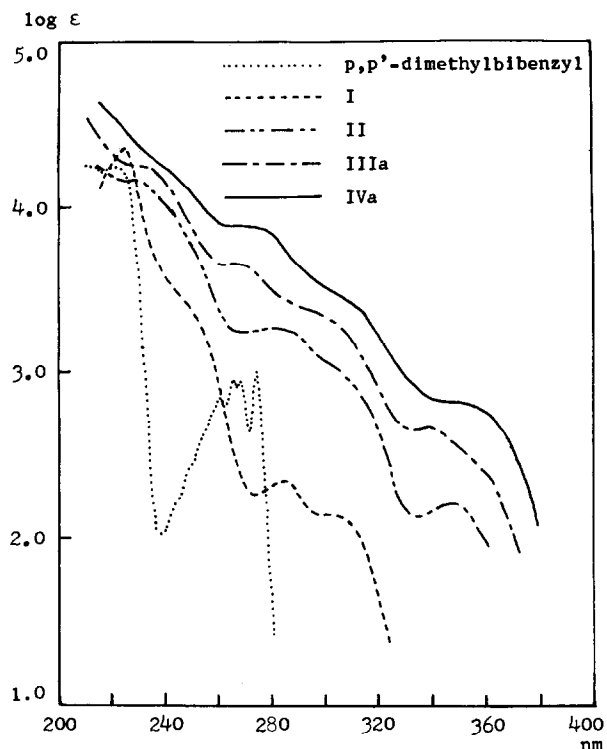


Fig. 2. UV spectra of layered cyclophanes in cyclohexane

effects are prominent as the layer is varied up to the tripled one(II). The absorption curves of the tripled (II), the quadrupled (IIIa), and the sixfolded (IVa) become broader generally and become similar in shape with each other, but the intensity per the unit chromophore in longer wavelength region increases with the number of layers. These phenomena are attributable to the increase of the transannular electronic interaction among benzene rings. To obtain further information of the interaction, a study of the emission spectra is under way.

References

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