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LAYERED COMPOUNDS. XXI.1) MULTILAYERED PARACYCLO-FURANOPHANES AND -THIOPHENOPHANES

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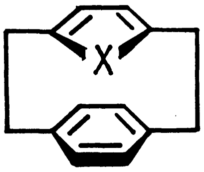
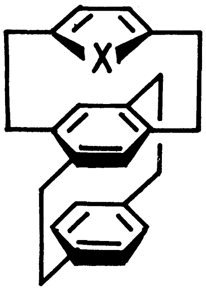
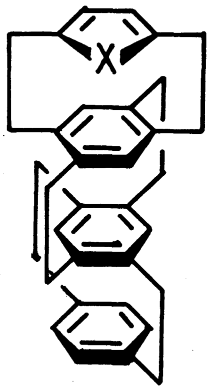
Non-substituted double, triple, and quadruple layered paracycloheterophanes, I∼III, were synthesized. Their nmr spectra demonstrate the fixation of thiophene ring and the internal inversion of furan ring at room temperature. The electronic spectra show transannular electronic interaction among chromophores.

We previously observed larger transannular electronic interaction between chromophores in methyl-substituted triple-layered paracycloheterophanes than in double-layered ones,2) which led our attention to the synthesis of higher member of this series. In this communication we wish to report the synthesis and properties of quadruple-layered paracycloheterophanes IIIa and IIIb, along with the synthesis of non-methylated double- and triple-layered compounds I and II.

Cross-breeding pyrolysis of an ammonium hydroxide V, which was derived from triple-layered paracyclophane (IV)3) in the usual way, with 5-methylfurfuryl- or





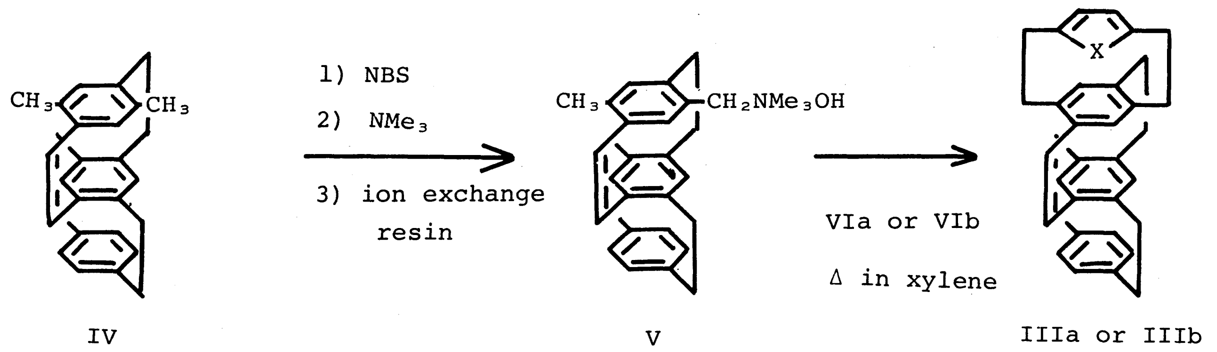


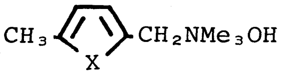
Ia,b

IIa,b

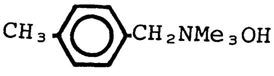
IIIa,b

a : X = O
b : X = S

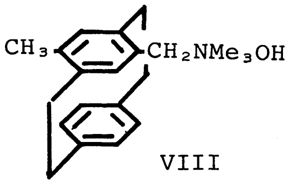




VIa,b a : X = O
b : X = S



VII



VIII

5-methylthenyl-trimethylammonium hydroxide (VIa or VIb) yielded quadruple-layered paracycloheterophane (IIIa or IIIb) together with [2.2](2,5)heterophane and sixfold-layered paracyclophane. Repeated chromatographic separation and recrystallization from carbon tetrachloride-acetone (1:3) gave pure IIIa (colorless plates) and IIIb (colorless prisms), which are relatively unstable, even in crystalline state. Similarly, double- and triple-layered paracycloheterophanes (I and II) were synthesized by the reactions of VI with VII and VIII, respectively. The structures of these new cyclophanes were determined on the basis of nmr, mass, ir, and uv spectra and elemental analysis. Their yields and mp's are summarized in Table 1.

Table 1. Yields and Mp's of Layered Paracycloheterophanes

	Ia	Ib	IIa	IIb	IIIa	IIIb
yield (%)	15	1.6	6.5	0.5	2.8	1.4*
mp (°C)	68.5 ~ 69.5	230 ~ 231**	117.0 ~ 118.0	~175 dec	176.0 ~ 178.0	~195 dec.

*crude **in sealed tube

Nmr spectral data of I ~ III are shown in Fig. 1. All the aromatic protons shift successively to higher field as the number of layers increases, indicating the anisotropy effects due to additional aromatic ring.[4] In addition, it can be seen from Fig. 1 that the protons of the benzene ring faced to thiophene ring in the layered thiophenophanes are unequivalent, while those of the benzene ring

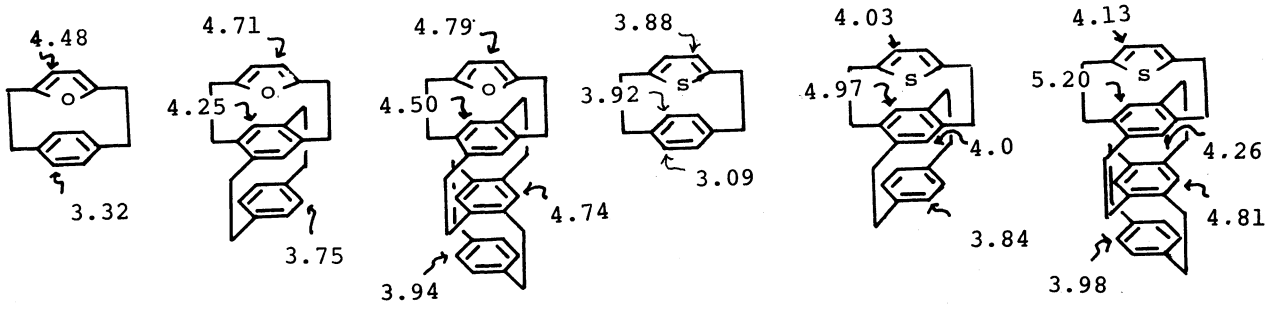


Fig. 1. Nmr data of layered paracycloheterophanes (τ value in CCl_4).

faced to furan ring in the layered furanophanes are equivalent. The signals of the former protons were independent on temperature, being essentially unchanged up to 150°C, while the signals of the latter protons were broadened and finally each of them was separated into two peaks of a 1:1 integral ratio with a decrease in temperature. It clearly shows that the thiophene rings are fixed, whereas the furan rings undergo rapid internal inversion at room temperature. The activation free energies of this inversion were obtained from variable temperature analysis (in CS_2) based on peak separation method;5) Ia, 11.4 kcal/mol (Tc -39°C); IIa, 10.4 kcal/mol (Tc -58°C); IIIa, 10.2 kcal/mol (Tc -62°C). These values for layered paracyclofuranophanes indicate that the inversion of the furan rings becomes easier as the number of layers increases. The value for IIIa is, to our knowledge, the smallest of the values for various [2.2]cyclophanes ever reported.

As shown in Figs. 2 and 3, the electronic spectra of both series of multilayered paracycloheterophanes exhibit strong bathochromic and hyperchromic effects and gradual disappearance of the characteristics due to heteroaromatic ring with the increasing number of layers. These are interpreted by the transannular electronic interactions as in the case of multilayered paracyclophanes, that is, exciton and charge transfer interactions.6) It is particularly noteworthy that the absorption curves of the furanophanes quite resemble to those of metaparacyclophanes7) as the number of layers increases, and the long wavelength region of thiophenophanes also become similar to those of multilayered paracyclophanes.

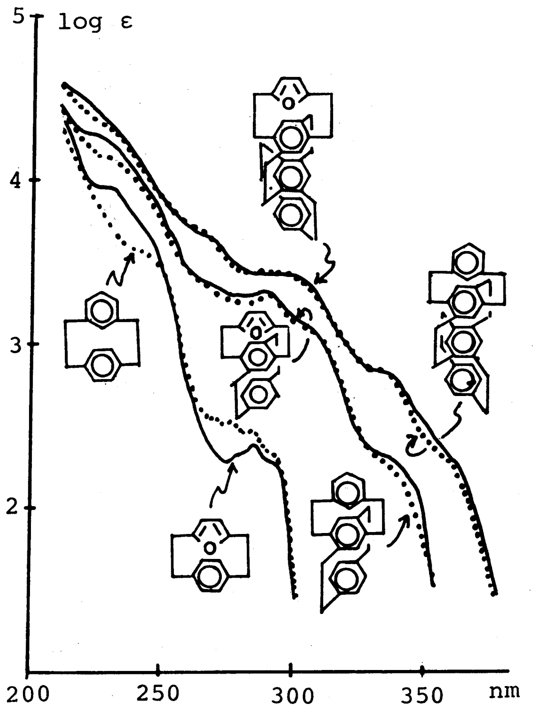


Fig. 2. Uv spectra of layered furanophanes and metaparacyclophanes in cyclohexane.

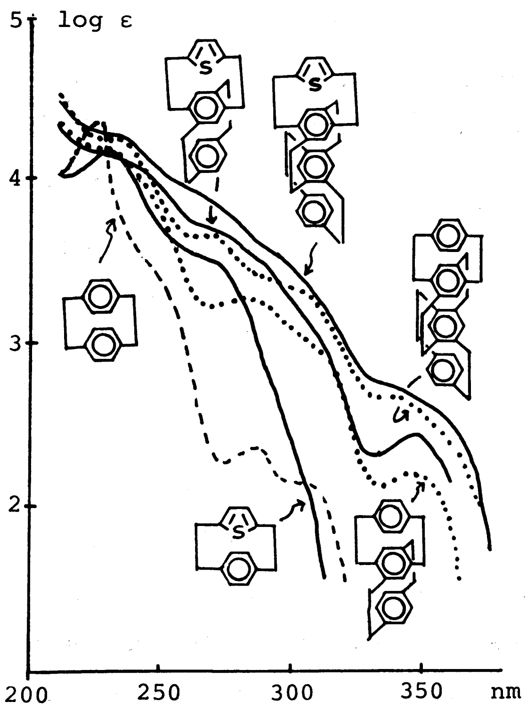


Fig. 3. Uv spectra of layered thiophenophanes and paracyclophanes in cyclohexane.

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