

LAYERED COMPOUNDS. X<sup>1</sup>). MULTILAYERED METACYCLOPHANES

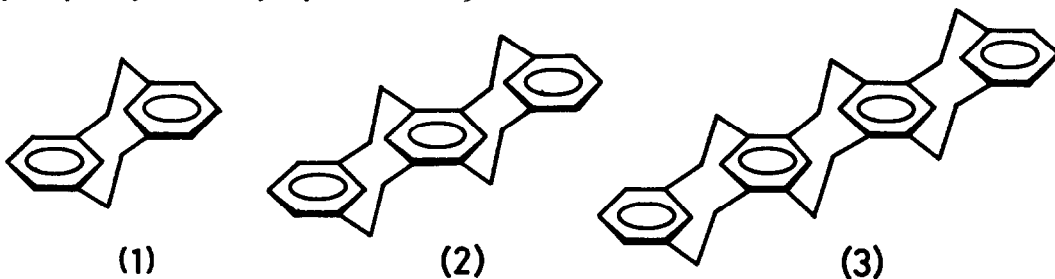
Teruo Umemoto, Tetsuo Otsubo, Yoshiteru Sakata, and Soichi Misumi

The Institute of Scientific and Industrial Research, Osaka University

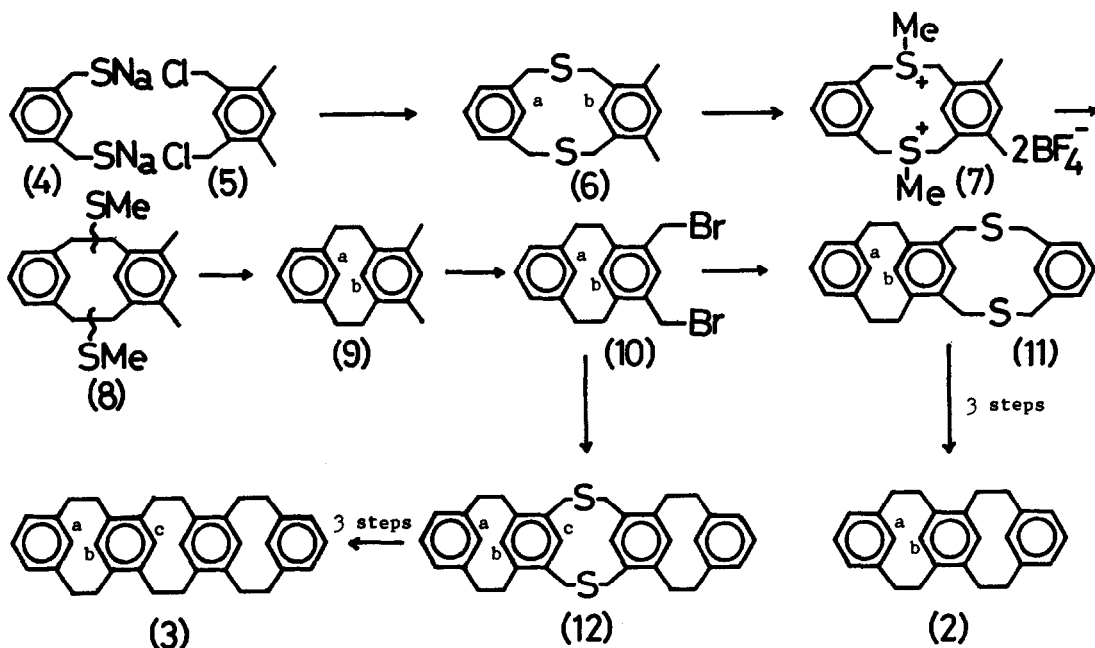
Suita, Osaka, Japan

(Received in Japan 4 December 1972; received in UK for publication 16 January 1973)

Cyclophanes with stacked aromatic nuclei have widely been studied as pertinent model compounds for transannular electronic interactions. From the view of this interaction, we have reported the syntheses and properties of multilayered paracyclophanes and heterophanes.<sup>2)</sup> On the other hand, multilayered metacyclophanes are thought to be other model compounds for the interaction because of partial  $\pi$ -electron overlapping between benzene nuclei in contrast to the paracyclophane systems. We now wish to report the synthesis and properties of triple- and quadruple-layered metacyclophanes (2 and 3).



The synthesis of both layered metacyclophanes was carried out by means of the Stevens rearrangement according to Boekelheide's procedure<sup>3)</sup> followed by a treatment with Raney nickel. Coupling of (4) with (5) in boiling alcohol under dilute conditions<sup>4)</sup> afforded (6) in 71% yield, colorless plates from benzene, m.p. 174~174.5°C. Methylation of (6) with the Borch reagent<sup>5)</sup> followed by the Stevens rearrangement with potassium t-butoxide in tetrahydrofuran gave a sulfide (8) as a mixture of several isomers. The crude sulfide was treated with Raney Ni to afford (9), purified by chromatography over silica gel, in 78% over-all yield from (6), color-



less plates from hexane, m.p.  $77\sim 78^\circ\text{C}$ . Coupling of dibromide (10), obtained by bromination of (9) with NBS in 73% yield, with (4) in boiling alcohol under dilute conditions afforded (11), chromatographed over silica gel, in 71% yield, colorless fine crystals from ligroin, m.p.  $194\sim 195^\circ\text{C}$ . The sulfide (11) was treated in a similar manner to the case of (6) and purified by chromatography over silica gel to give triple-layered metacyclophane (2) in 80% yield, scaly crystals from alcohol, m.p.  $208\sim 209^\circ\text{C}$ . The reaction of (10) with sodium sulfide gave an isomeric mixture of (12), separated by chromatography over silica gel from some polymers, in 17% yield, colorless fine crystals, m.p.  $225\sim 229^\circ\text{C}$ . (12) was similarly treated as in the case of (6) to give quadruple-layered metacyclophane (3), purified by chromatography over alumina, in 17% overall yield, colorless needles from toluene, decomp.  $330^\circ\text{C}$  in sealed tube. All of new compounds above-stated were characterized by NMR, IR, and mass spectra and elemental analysis.

NMR data are shown in Table 1. Assignment of aromatic inner protons in (2), (9), (10), (11), and (12) was based on whether a signal in question broadened due to meta-coupling or not, which was demonstrated by irradiating the aromatic region. As seen in the table, it is noteworthy that  $H_a$  protons are remarkably shifted to lower field, whereas  $H_b$  protons are shifted

Table 1. NMR Spectra of Layered Metacyclophanes in  $\text{CDCl}_3$  ( $\tau$  value)

	aromatic protons					$\text{CH}_3$	- $\text{CH}_2$ - $\text{CH}_2$ -	other - $\text{CH}_2$ -
	inner			outer				
	Ha	Hb	Hc					
(2)	4.97(bs)	5.88(s)		2.5~3.0(m)			6.3~8.3(m)	
(3)	4.90(bs)	5.80(s)	5.05(s)	2.5~2.9(m)			6.3~8.1(m)	
(6)	3.31(bs)	3.92(s)		2.9~3.1(m)	7.80(s)			6.26(s), 6.38(s)
(9)	5.71(bs)	5.79(s)		2.7~3.1(m)	7.68(s)		6.5~8.5(m)	
(10)	5.48(bs)	5.85(s)		2.6~2.9(m)			6.3~8.3(m)	5.42 (s)
(11)	5.79(bs)	6.28(s)		2.5~3.1(m)			6.6~8.5(m)	6.28, 6.06(AB, J=15.0 cps), 6.13(s)
(12)	5.39(bs)	5.93(s)	3.40(s)	2.5~3.1(m)			6.3~8.5(m)	6.15(bs)

toward a little higher field, except for (9) and (11), in comparison with 5.73  $\tau$  for those of [2.2]metacyclophane (1). This suggests that those metacyclophanes (2 and 3) are distorted in such a way that Ha's go away from the faced benzene ring, whereas Hb's somewhat come up to the another benzene ring, possibly due to additional repulsions between the protons of ortho-positioned methylene groups at the inner benzene rings besides the strain held basically in [2.2]-metacyclophane system. The inner protons of (3) were assigned on the basis of broadening due to meta-coupling and of an assumption that the distortion would depend on the same repulsion as in the case of (2). The phenomenon that the inner protons of (11) are abnormally shifted to higher field may be explained by additional anisotropic effect of the third benzene nucleus, which is bridged by sulfide linkages and is conformationally flexible at room temperature. Further details concerning configurational isomers of (2) and (3) will be reported together with results of X-ray crystallographic analysis being under way.

Fig. 1 records the electronic absorption spectra of the layered metacyclophanes as well as that of 3,3'-dimethylbibenzyl as a reference compound. It was suggested on the basis of MO calculations<sup>6)</sup> that the absorption bands in 225~250 nm region and over 280 nm on the spectrum of (1) depend upon the transannular electronic interaction. There are more remarkable changes on the spectra of the multilayered metacyclophanes, (2) and (3), as seen in Fig. 1. Firstly, the whole absorption spectra are shifted to longer wavelength as the number of benzene rings

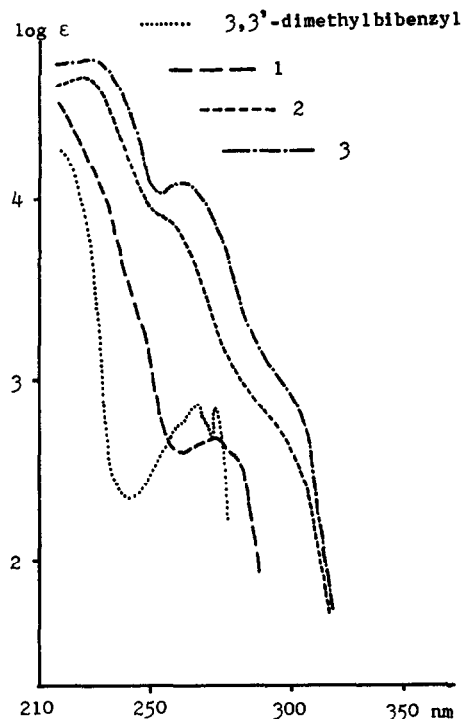


Fig. 1. UV spectra of layered metacyclophanes in tetrahydrofuran

increases, and the change from (1) to (2) is more significant than that between (2) and (3) as well as the change of intensity. Secondly, a further prominent characteristic is seen in 240~260 nm region; a little shoulder near 240 nm in the curve of (1), a more definitive shoulder at 252 nm in (2), and the appearance of a new absorption maximum at 262 nm in (3). This spectral variation can mainly be ascribed to the transannular  $\pi$ -electron interaction together with that of the region over 280 nm. However, the problem how the strain in the layered metacyclophanes contributes on the electronic spectra is ambiguous at present.

#### References

- 1) Part IX. H. Mizuno, K. Nishiguchi, T. Otsubo, S. Misumi, and N. Morimoto, *Tetrahedron Lett.*, (1972) in press.
- 2) T. Otsubo, S. Mizogami, Y. Sakata, and S. Misumi, *Tetrahedron Lett.*, 2791, 4803 (1971); *Chem. Commun.*, 678 (1971); T. Otsubo, Z. Tozuka, S. Mizogami, Y. Sakata, and S. Misumi, *Tetrahedron Lett.*, 2927 (1972)
- 3) R. H. Mitchell and V. Boekelheide, *J. Amer. Chem. Soc.*, 92, 3510 (1970)
- 4) F. Vögtle and L. Schunder, *Chem. Ber.*, 102, 2677 (1969)
- 5) R. F. Borch, *J. Org. Chem.*, 34, 627 (1969)
- 6) N. L. Allinger, M. A. Da Rooze, and R. B. Hermann, *J. Amer. Chem. Soc.*, 83, 1974 (1961)