

LAYERED COMPOUNDS. XVII¹⁾. TRIPLE-LAYERED METAPARACYCLOPHANES

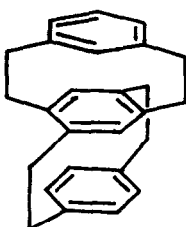
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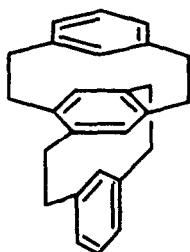
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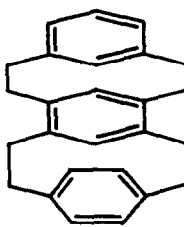
Multilayered paracyclophanes and metacyclophanes have been synthesized for investigation of transannular electronic interactions and showed remarkable interactions in their electronic spectra.^{2,3)} Multilayered cyclophanes with meta-para combined system, which is an intermediate one between meta and para systems, are expected to exhibit interesting properties related to those of meta- and para-cyclophanes. We now wish to report the synthesis and properties of triple-layered metaparacyclophanes (1~4).



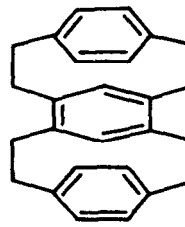
(1)



(2)



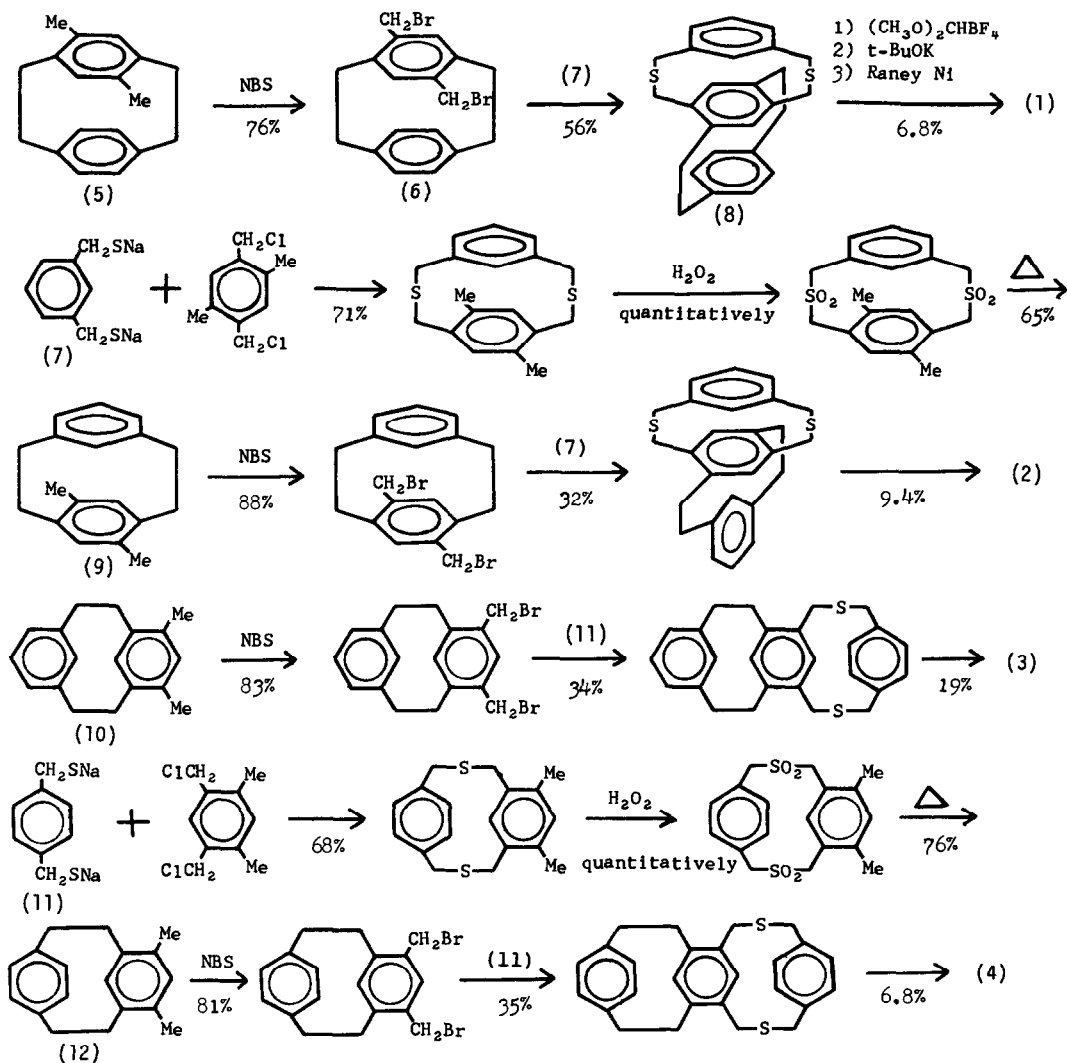
(3)



(4)

Coupling of dibromide (6), obtained by bromination of (5)²⁾ with NBS, with sodium salt of *m*-xylylene dimercaptan (7) in boiling ethanol under dilute conditions afforded (8) in a 56% yield. (1) was obtained from (8) in a 6.8% yield by the Stevens rearrangement according to Boekelheide's procedure⁴⁾ followed by a treatment with Raney nickel, colorless plates from ethanol, m.p. 144~145°C. (3) was obtained from (10)³⁾ in the similar manner, colorless prisms from toluene, m.p. 209~210°C. Dimethyl metaparacyclophanes, (9) and (12), were prepared according to Vögtle's procedure⁵⁾ as shown in the reaction scheme; (9): colorless plates from pentane, m.p. 65~66°C; (12): colorless plates from pentane, m.p. 63~64°C. (9) and (12) thus obtained were led to (2) and (4), respectively, in the usual method; (2): colorless plates from

benzene-ethanol (1:1), m.p. 170–171°C; (4): colorless plates from toluene, m.p. 259–260°C (sealed tube). All new compounds were characterized by NMR, mass, and IR spectra and elemental analysis.



NMR data are shown in Fig. 1. Inner protons of the outside meta-rings are shifted to higher field, for they are situated just above the inside ring and broadened due to meta-coupling. Protons of the inside meta and para rings are also shifted to higher field than the corresponding

protons of double-layered compounds due to the anisotropies of two outside rings. In the metapara system, aromatic protons in the para-ring appear nonequivalently at room temperature and thereby the fixation of the meta-ring is demonstrated. In case of (1), meta-ring undergoes the internal inversion at higher temperature and aromatic protons of the inside para-ring become equivalent ($T_c = 100^\circ\text{C}$). In (2), there are predicted two isomers, (2a) and (2b), by fixation of two meta-rings. In practice, this prediction was ascertained by inspection of the NMR spectrum at room temperature. Thus, two broad singlets with 1:1 integral strength ratio are assigned to the inner protons of the meta-rings of (2a) and (2b), respectively, and a singlet at δ 5.60 is assigned to inside ring protons of (2a) and the remaining two signals to two types of inside ring protons of (2b). Both the inner protons of the meta-rings and the inside ring protons have become equivalent respectively at higher temperature ($T_c = 116^\circ\text{C}$), because of the meta-ring inversion.

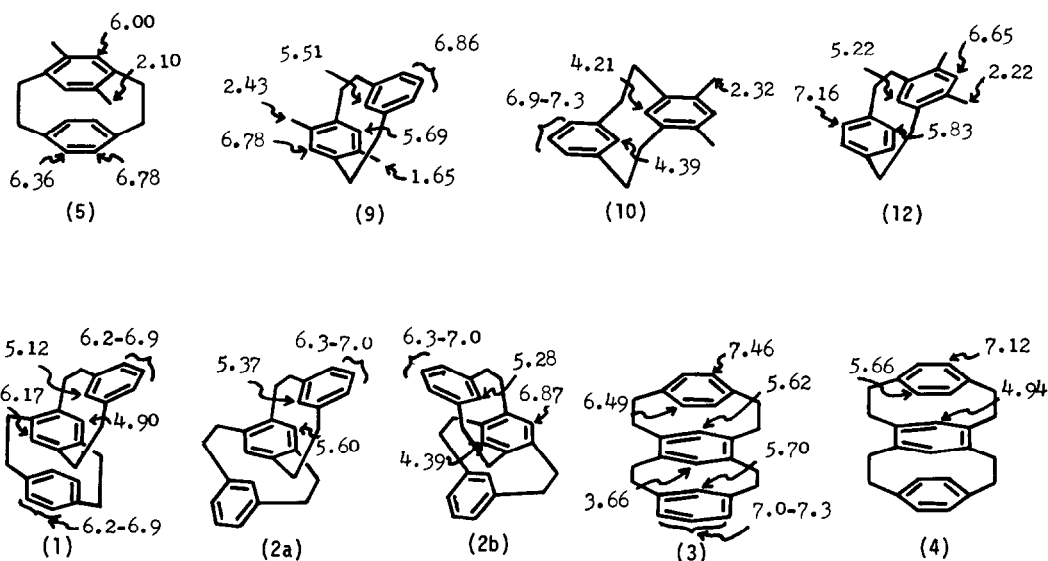


Fig. 1. NMR data of double-layered cyclophanes and triple-layered metaparacyclophanes in deuteriochloroform (ppm).

The electronic spectra of metaparacyclophanes (1-4) are shown in Fig. 2. There has been no evidence of whether transannular electronic interaction between two benzene rings exist in [2.2] metaparacyclophane. The present compounds, (1) and (2), show new bands around 330 and 315

nm, respectively, and increase of intensities of the bands in 260~310 nm region compared with the spectra of double-layered compounds. Thus, their absorption curves are similar to that of triple-layered paracyclophane²⁾ and indicate strongly that obvious transannular electronic interactions exist also between meta and para rings.

On the other hand, the absorption curves of (3) and (4) are rather similar to that of triple-layered metacyclophane³⁾ and therefore, seem to be indicative of electronic interaction different from those of (1) and (2). It can be concluded that substitution modes of methylene bridges in inside rings, para and meta form, serve as a dominant factor on overlapping between benzene rings and hence, on the electronic interaction.

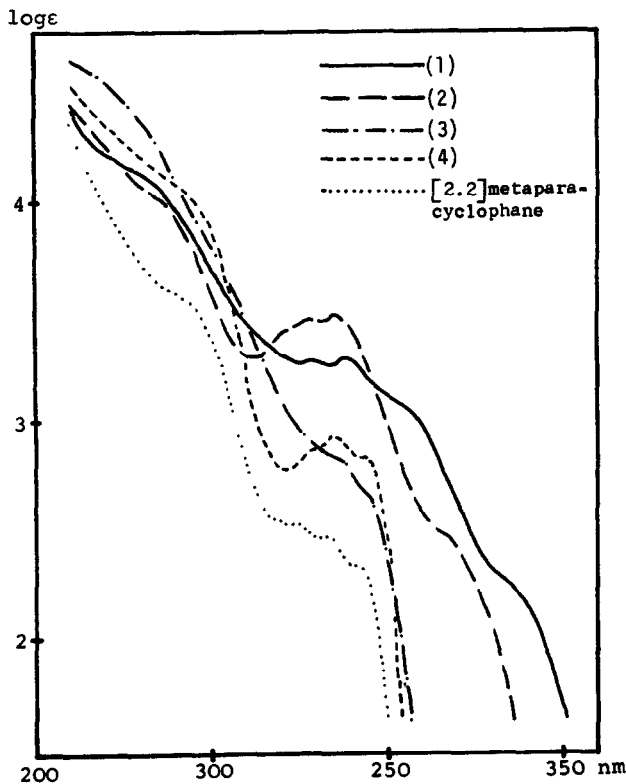


Fig. 2. Electronic spectra of (1)~(4) and [2.2]metaparacyclophane in cyclohexane.

References

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