

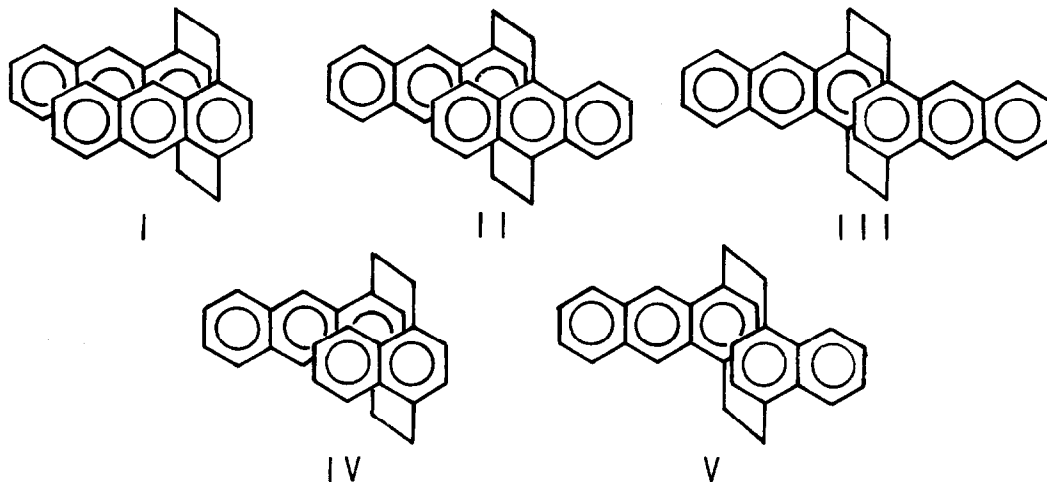
LAYERED COMPOUNDS. XI<sup>1)</sup>. SOME LAYERED ANTHRACENOPHANES

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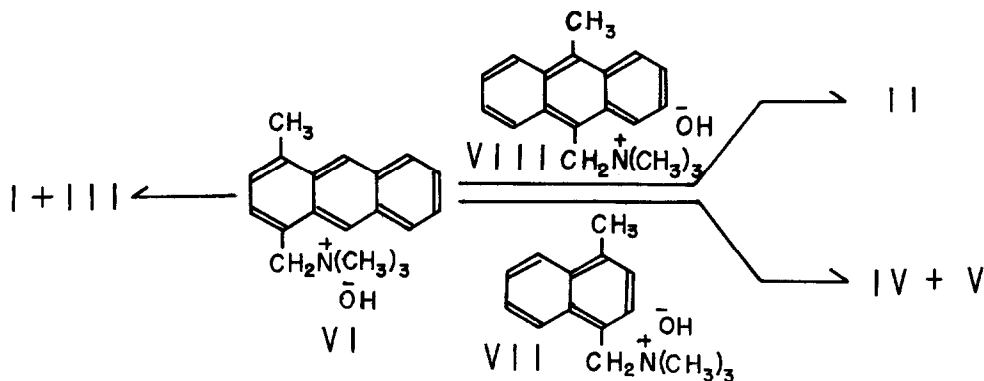
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Layered anthracenophanes in which an anthracene ring is closely fixed together with another benzenoid ring by methylene bridges have been interested in studying the transannular electronic interaction with relation to overlapping of the  $\pi$ -electron clouds. In the previous communication of this series<sup>2)</sup>, we have reported the synthesis of syn- and anti-[2.2](1,4)-anthracenophanes (I and III) for the purpose. The present communication will report the synthesis and properties of [2.2](1,4)(9,10)anthracenophane (II), in which two anthracene nuclei are middlingly overlapped as compared with the other two anthracenophanes, and of syn- and anti-[2.2](1,4)naphthaleno(1,4)anthracenophanes (IV and V) in this regard.



All of new anthracenophanes were synthesized by cross-breeding Hofmann degradation of

quaternary ammonium hydroxides. Pyrolysis of a mixture of two quaternary ammonium hydroxides (1:1 molar ratio of VI and VII) with a small amount of phenothiazine in boiling xylene and



filtration of the warm reaction mixture to remove sparingly soluble material afforded crystals of almost pure anthracenophane II in 22% yield, yellow needles from benzene, m.p. 262.0~264.0°C (partly decomp.). Similarly, syn- and anti-[2.2](1,4)naphthaleno(1,4)anthracenophanes (IV and V) were obtained by cross-breeding pyrolysis of quaternary bases (VI:VIII, 1:1). Fractional recrystallization from toluene and column chromatography on alumina afforded a 1.6% yield of

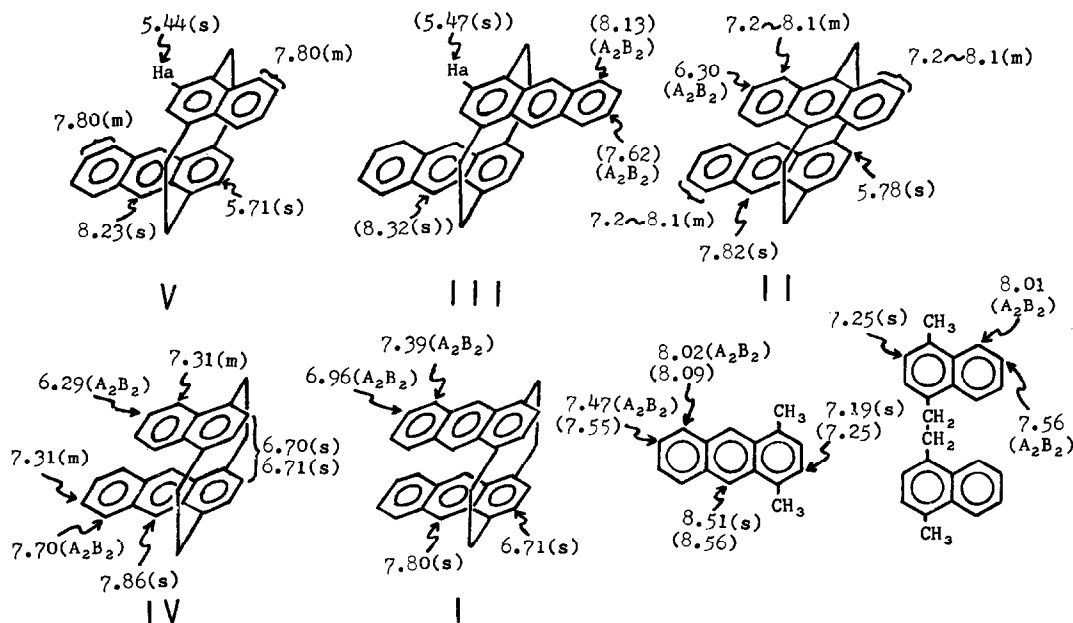


Fig. 1. NMR spectra ( $\delta$  value) of some anthracenophanes and related compounds in  $\text{CDCl}_3$ . Values in parentheses are in  $\text{AsCl}_3$ .

syn-form IV, yellow needles from n-hexane-benzene (9:1), m.p. 221.0~222.0°C and a 29% yield of anti-form V, pale yellow needles from toluene, m.p. 246.5~247.5°C. The mass spectra of IV and V show identical pattern containing a molecular ion peak  $m/e$  358, indicating that both are isomeric with each other. All new cyclophanes were characterized by NMR, IR, and MS spectra and elemental analysis.

NMR spectral data of various anthracenophanes and reference compounds are shown in Fig. 1. In all of the anthracenophanes, the protons situated just above faced nuclei show upfield shifts compared with the corresponding protons in reference compounds due to diamagnetic shielding effect, e.g. ca. 1.8 ppm for Ha protons in V and III.

The electronic spectra of three [2.2]anthracenophanes (I~III) and a reference compound, 4,4'-dimethyldianthrylethane (IX) are shown in Fig. 2 and those of naphthaleno-anthracenophanes IV and V in Fig. 3. It is noted from Fig. 2 that the longest wavelength bands ( $\lambda_a$ ) of these anthracenophanes show unambiguous broadening and red shift compared with that of dianthrylethane

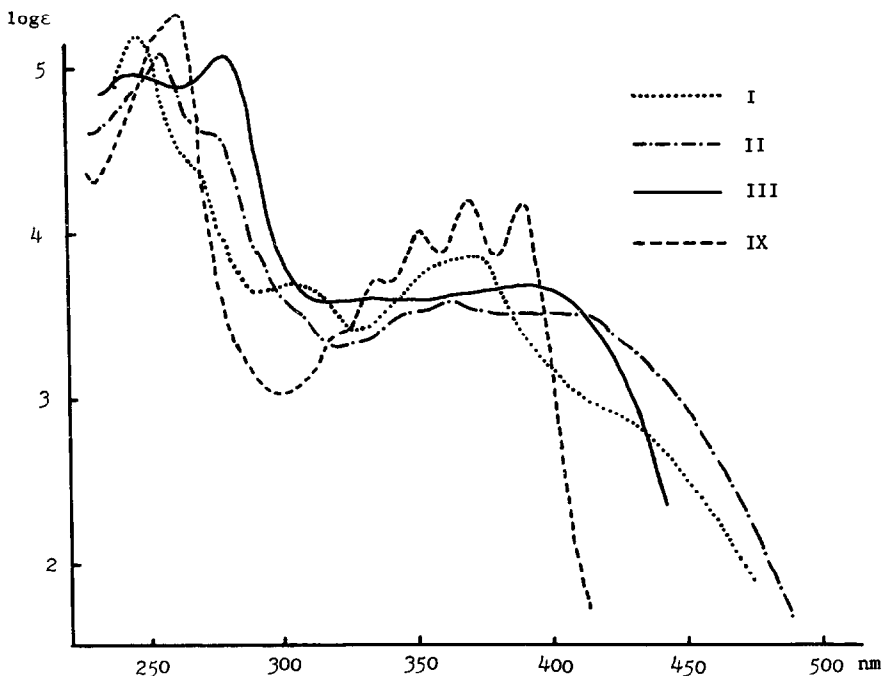


Fig. 2. The electronic spectra of three anthracenophanes (I~III) and 4,4'-dimethyldianthrylethane (IX) in tetrahydrofuran

IX, and that the shorter wavelength bands with high intensity are split into two maxima (in III) or one maximum and one shoulder (in I and II) on either side of Bb band position of IX. The splitting of Bb bands and relative intensities of the split bands are explainable mainly on the basis of exciton interaction of two anthracene chromophores, i.e., by a side-by-side interaction and an end-to-end interaction of two transition dipoles. The exciton theory is also applicable to explain the absorption spectra of syn- and anti-[2.2](1,4)naphthalenophanes<sup>3</sup>. However, the difference in La bands of I~III is suggestive of charge-transfer configuration interactions to contribute appreciably to the spectra of the anthracenophanes as well as those of naphthaleno-

phanes. On the other hand, the absorption spectra of naphthaleno-anthracenophanes (IV and V) are too complicated to interpret consistently owing to the interactions between two different, distorted chromophores.

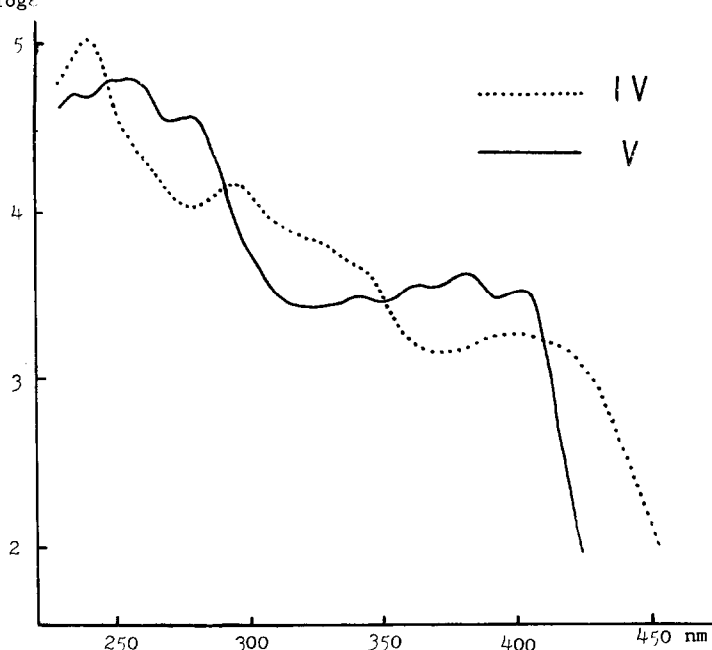


Fig. 3. The electronic spectra of two naphthaleno-anthracenophanes (IV and V) in tetrahydrofuran

#### References

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