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LAYERED COMPOUNDS. VI[1]. ANTI- AND SYN-[2.2](1,4)ANTHRACENOPHANES

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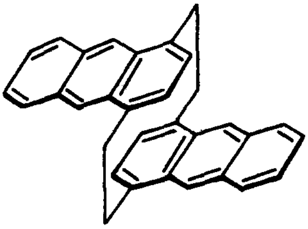
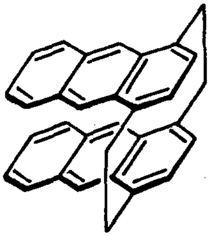
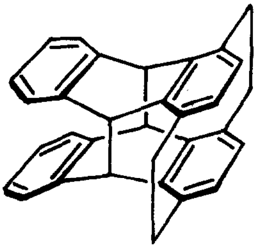
IN previous papers[2], we have reported the syntheses and properties of multilayered compounds containing benzene nuclei for an investigation of transannular electronic interaction and steric effect. The cyclophanes containing condensed aromatic nuclei are of special interest for studying those effects. Up to date, there have been a few cyclophanes[3,4,5], each of which contains anthracene nucleus with methylene bridges at its 9,10-carbons, not any with 1,4-bridges. As in the case of [2.2](1,4)naphthalenophanes[5,6], both anti- and syn-forms should also be present for [2.2](1,4)anthracenophane which may exhibit spectral evidence on the transannular electronic interaction between the two anthracene nuclei. We now wish to report the isolation, spectral properties, and the interconversion of both the isomers.

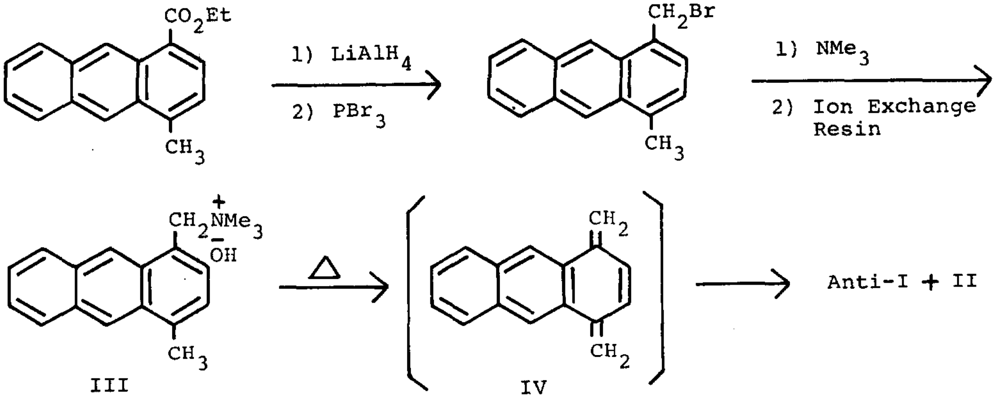

Anti-I


Syn-I

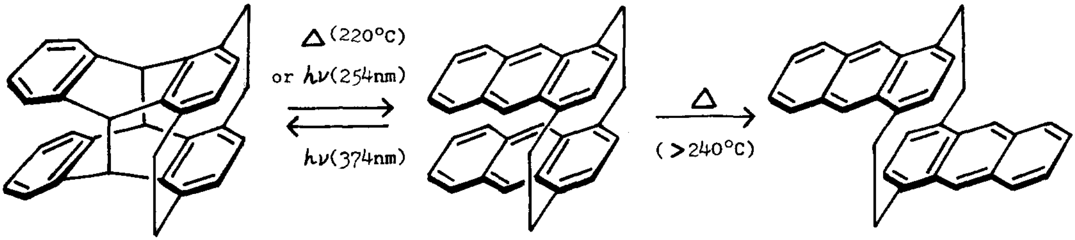

II

Pyrolysis of a quaternary ammonium hydroxide (III) in boiling xylene, which was prepared from 4-methylanthracene-1-carboxylic acid[7] through the following reaction scheme, afforded crude anti-I and a small amount of the compound anticipated as a photoisomer of syn-I along with some polymer, but syn-I was not obtained. It is reasonable from the results described below that an intermediate[5,6], 1,4-anthraquinodimethane (IV), can be dimerized to lead to anti-I and syn-I, but the latter may be converted into the photoisomer II. The separation and purification of both compounds are shown as follows. Anti-I was extracted with xylene from the precipitate containing the polymer. Recrystallization from the same solvent gave pure, yellow lustrous granules (14% yield), m.p. > 300°C (decomp.). This isomer is quite stable to light and prolonged heating.

From the mother liquor of the reaction mixture, on the other hand, the photoisomer II was isolated by careful chromatography on silica gel and on neutral alumina. Recrystallization from ethyl acetate-alcohol afforded colorless plates (0.46% yield). II, a derivative of quadruple-bridged [2.2.2.2](1,2,3,4)cyclophane, became yellow at ca 205°C and decomposed at 242°C. The structure of these compounds was determined on the basis of PMR, IR, and mass spectra and elemental analysis.



Particularly interesting is the conversion of the photoisomer II to the syn-isomer. When the crystals of II were heated at ca 220°C under a stream of nitrogen in the dark, development of yellow color was observed. This yellow substance was recrystallized from benzene to give yellow needles. The UV and PMR spectra of the crystals thus obtained indicate that II was converted to syn-I on heating. Furthermore, the interconversion of II and syn-I was found to take place in the photochemical process. Thus, irradiation of II in tetrahydrofuran at 254 nm afforded syn-I, whereas the latter was reversed by irradiation at 374 nm to the former colorless material. However, when syn-I was heated above 240°C as solid state, it was converted into the anti-form without melting, probably through a biradical intermediate[6a,8].



II Syn-I Anti-I

The mass spectra of anti-I and syn-I show the same pattern containing a molecular ion peak m/e 408 and a base peak m/e 204. This fact confirms that both are isomeric with each other.

The PMR spectra of anti-I, syn-I, and a reference compound, 1,4-dimethylanthracene, represent significant variation as shown in FIG. 1. The Ha of anti-I are strikingly shifted to

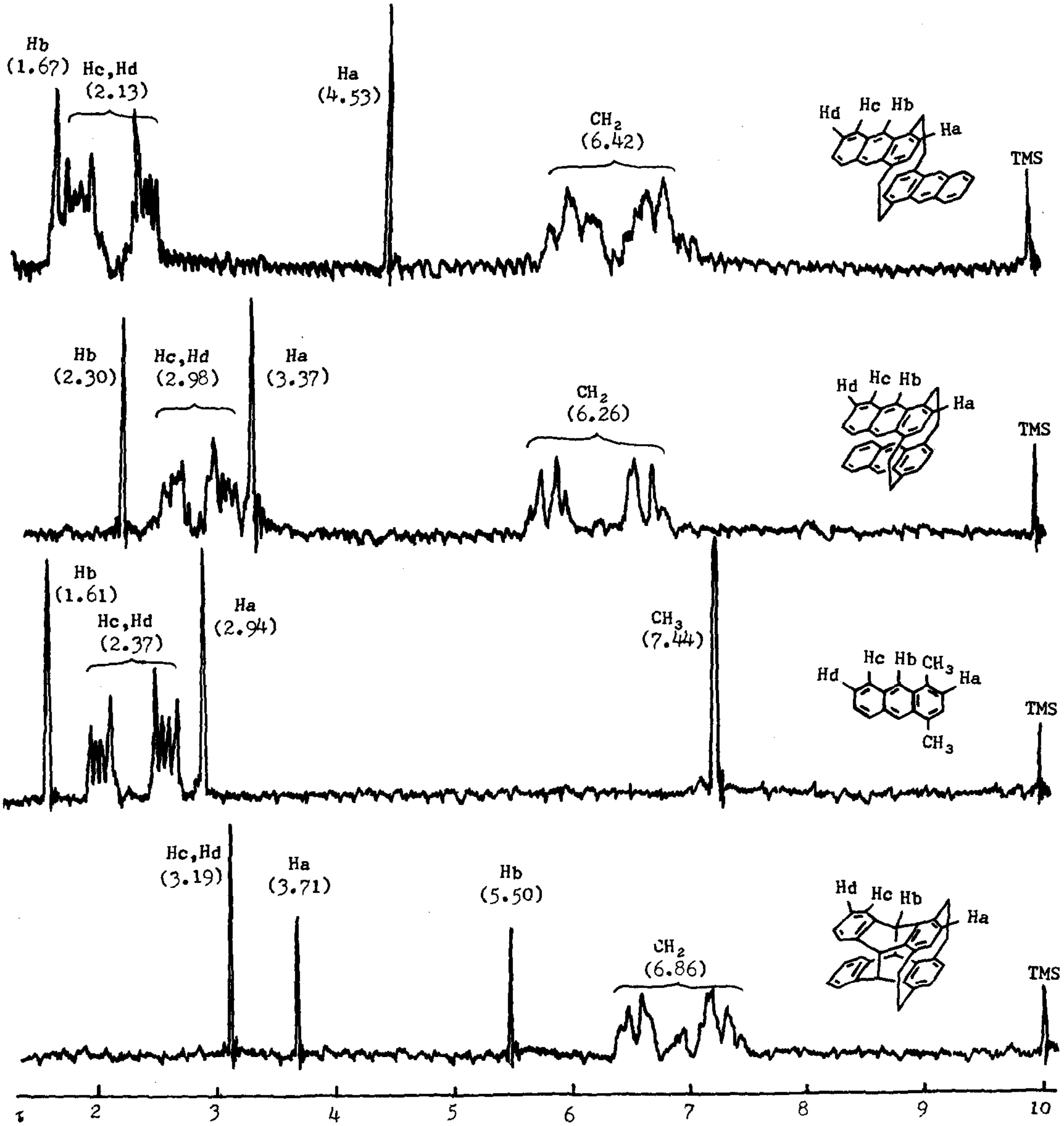


FIG. 1. The NMR spectra of anti-I in $AsCl_3$ and syn-I, photoisomer II, and 1,4-dimethylanthracene in carbon tetrachloride.

higher fields than the corresponding protons of the other compounds because the former are situated just above the other anthracene nucleus. On the other hand, as expected, the aromatic protons other than Ha of syn-I appear at higher fields than the corresponding protons of anti-I and 1,4-dimethylanthracene. The Hb~d signals of anti-I were observed at the nearly same positions as those of 1,4-dimethylanthracene, indicating less shielding of the transannular anthracene nucleus to them in anti-I.

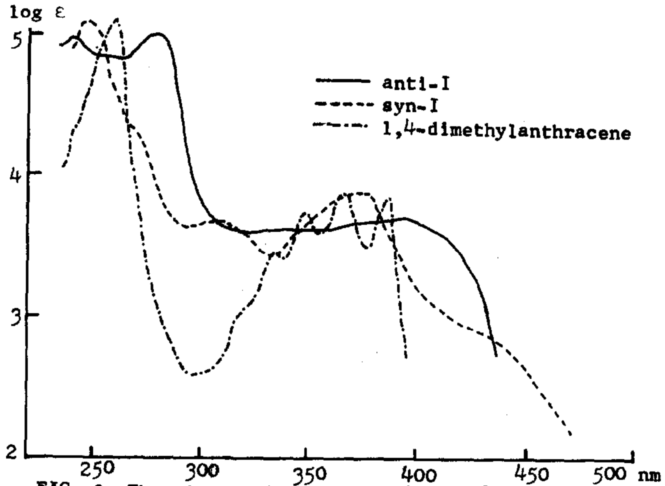


FIG. 2. The electronic spectra of anti-I, syn-I, and 1,4-dimethylanthracene in tetrahydrofuran.

The UV spectrum of anti-I exhibits a remarkable bathochromic shift compared to that of 1,4-dimethylanthracene, while the spectrum of syn-I is somewhat similar to the latter (see FIG. 2). This phenomenon was also observed in the spectra of isomeric [2.2](1,4)naphthalenophanes[6,9]. The problem in what manner it is correlated to the distortion and the difference in overlapping of both π-systems is to be on further studies of electronic absorption and emission spectroscopies.

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