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LAYERED COMPOUNDS. XX.[1] SOME HETEROPHANES LAYERED WITH CONDENSED AROMATIC NUCLEI

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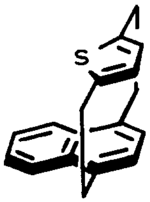
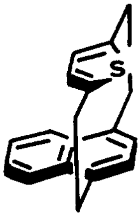
In the previous communication,[2] we have reported the synthesis and properties of some multilayered cyclophanes containing heteroaromatic nuclei, furan and thiophene, for the investigation of transannular electronic interaction between benzene ring and heteroaromatic ring. A few heterophanes stratified with condensed aromatic nuclei have been reported so far.[3,4,5] We wish report the synthesis and properties of several naphthaleno- and anthraceno-heterophanes, I ~ V. They were synthesized by cross-breeding Hofmann degradation method of the corresponding quaternary ammonium hydroxides.

We reported the constrained internal inversion of the thiophene ring which was stratified on paracyclophane rings. In the case of [2.2](1,4)naphthaleno-(2,5)thiophenophane, accordingly, two isomers, anti-form (I) and syn-form (II),



I anti-form



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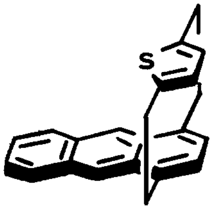

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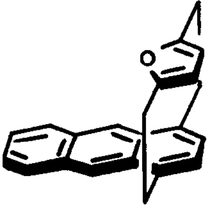

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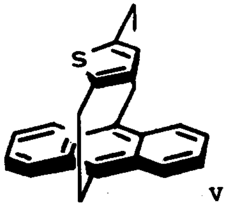
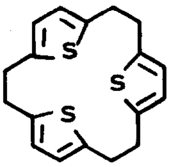


V

can be anticipated to exist, and the latter isomer may be a less stable conformer due to π-π repulsion between both nuclei. When a mixture of two quaternary ammonium hydroxides, VII and IX, in a 2:1 molar ratio was pyrolyzed in boiling xylene with catalytic amount of phenothiazine, a small amount of unstable conformer, syn-[2.2](1,4)naphthaleno(2,5)thiophenophane (II), was actually obtained together with anti-form (I), [2.2](1,4)naphthalenophane, [2.2]-(2,5)thiophenophane, [2.2.2](2,5)thiophenophane (VI), and polymers. I and II, the first of layered thiophenophanes to be separated into conformational isomers, were purified by careful chromatography on silicagel or neutral alumina; I, 4.1% yield, colorless prisms from n-hexane-benzene (1:1), m.p. 182~183°C; II, 0.3% yield, colorless plates from the same solvent, m.p. 142~143°C. The mass spectra of I and II show an identical pattern, indicating that both are isomeric with each other, but thermal isomerization of II to I could not be detected because of ready decomposition.



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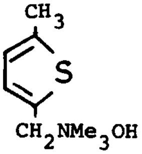
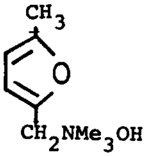
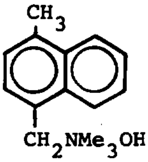


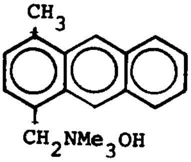
VII



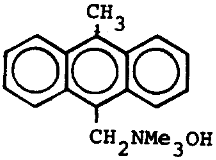
VIII



IX



X



XI

On the other hand, pyrolysis of a mixture of VII and X in a 2:1 molar ratio gave only anti-form (III) of [2.2](1,4)anthraceno(2,5)thiophenophane, 2.8% yield, pale yellow prisms from n-hexane-benzene (1:1), dec. ~195°C. Similarly, a mixture of VIII and X in 2:1 ratio afforded [2.2](1,4)anthraceno(2,5)furanophane IV, whereas a mixture of VII and XI in 2:1 ratio gave [2.2](9,10)anthraceno(2,5)-thiophenophane V; IV, 0.8% yield, pale yellow prisms from n-hexane-benzene (1:1), dec. ~154°C; V, 5.5% yield, greenish yellow needles from n-pentane-dichloromethane, dec. ~100°C. All new heterophanes were characterized by NMR and mass spectra and elemental analysis.

The NMR spectral data of various heterophanes are shown in Fig. 1. It indicates an interesting difference between I and II. Thus, the thiophene ring protons of syn-form II exhibit upfield shift due to diamagnetic shielding effect

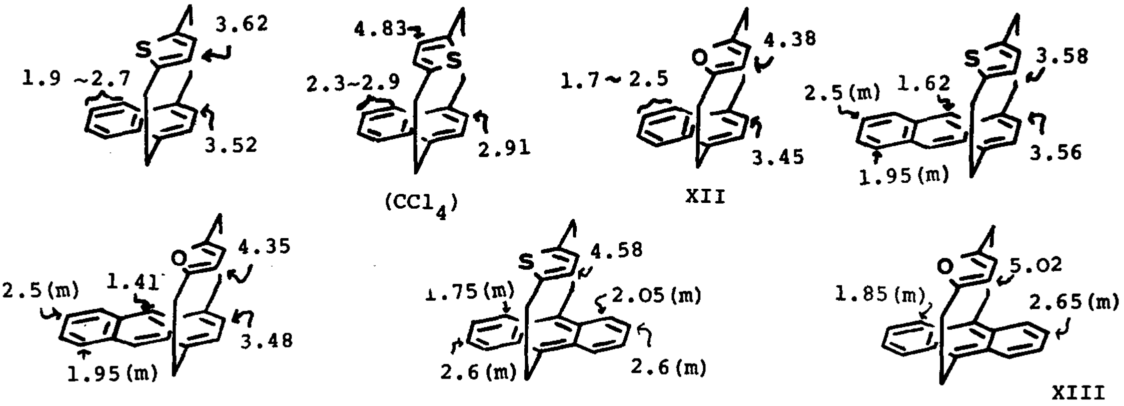


Fig. 1. NMR data (τ value) of naphthaleno- and anthraceno-heterophanes in deuteriochloroform.

of opposed naphthalene ring and the protons at 2 and 3 positions of naphthalene ring downfield shift due to deshielding effect of lone pair electrons of sulfur atom. The chemical shifts of III are rather similar to those of I, and consequently III can be assigned to the anti-conformation without difficulty.

In contrast to thiophene ring, it is well-known that the furan ring stratified on paracyclophane ring rapidly undergoes internal inversion at room temperature, but it is fixed at low temperature. In IV and XII[3], however, the NMR patterns were essentially unchanged even at low temperature and the furan ring protons are not appreciably affected by the diamagnetic shielding due to condensed aromatic nuclei. So these compounds exist exclusively in anti-conformation rather than in syn-conformation.

Figs. 2, 3, and 4 show the electronic spectra of naphthaleno- and anthraceno-heterophanes. It is apparent that all the spectra of thiophenophanes are very similar to those of the corresponding paracyclophanes, suggesting that the transannular electronic interactions between thiophene ring and condensed aromatic rings are comparable to those of the corresponding paracyclophane systems. The marked difference in the short wavelength bands of I and II appears to reflect the difference between the overlappings of sulfur lone pair on naphthalene π-system and of thiophene π-system on naphthalene π-system. In furanophanes XII, XIII,[4] and IV, the transannular electronic interactions between

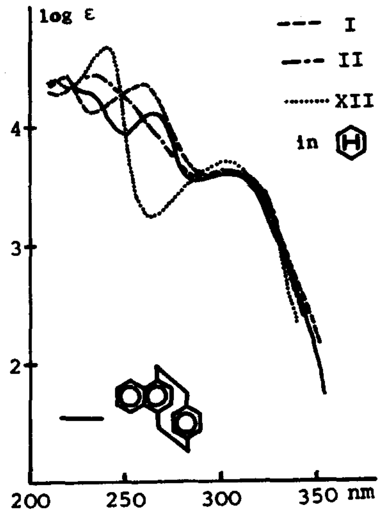


Fig. 2. UV spectra of naphthalenophanes.

furan ring and condensed aromatic nuclei seem to be considerably weak since the spectra exhibit relatively smaller bathochromic shifts compared to those of the corresponding other cyclophanes.

Further studies on the properties of these compounds are under way.

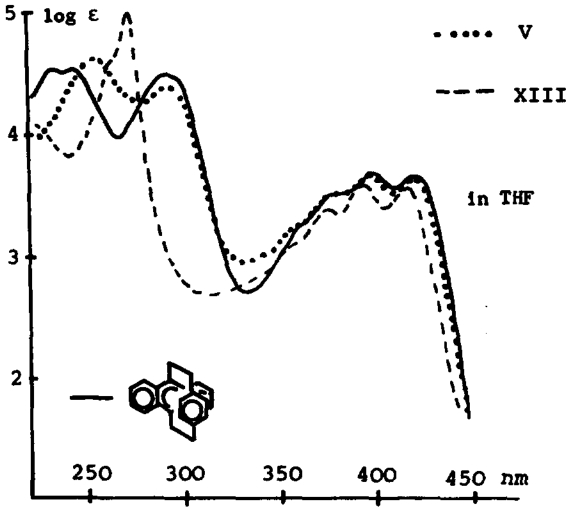


Fig. 3. UV spectra of (9,10)-anthracenophanes.

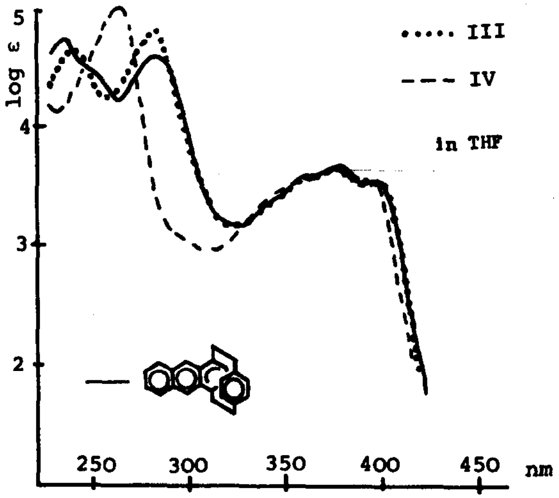


Fig. 4. UV spectra of (1,4)-anthracenophanes.

References

1) Part XIX: H. Horita, N. Kannen, T. Otsubo, and S. Misumi, Tetrahedron Lett., 1974, in press.

2) S. Mizogami, T. Otsubo, Y. Sakata, and S. Misumi, ibid., 2791 (1971).

3) H. H. Wasserman and P. M. Keehn, ibid., 3227 (1969).

4) H. Wynberg and R. Helder, ibid., 4317 (1971).

5) J. F. Haley, Jr. and P. M. Keehn, ibid., 4017 (1973).