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LAYERED COMPOUNDS II. LAYERED CYCLOPHANES CONTAINING HETEROAROMATIC RING

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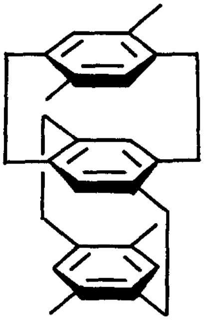
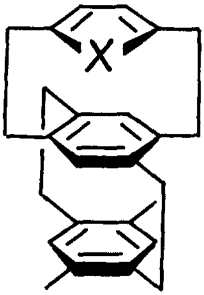
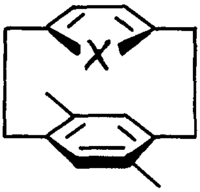
In the preceding communication1) we have reported the synthesis and properties of the triple-layered cyclophane I for the purpose of a study of the transannular interaction between nonbonded aromatic rings. We have been interested in extending this investigation to the layered cyclophanes containing heteroaromatic ring. The present communication will report the synthesis and properties of a few layered cyclophanes (II and III) containing furan and thiophene rings.



I



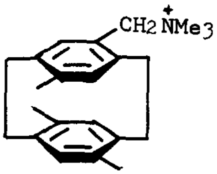
IIa X=O
IIb X=S



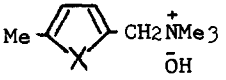
IIIa X=O
IIIb X=S

Pyrolysis of an equimolar mixture of quaternary ammonium hydroxides IV and Va in boiling xylene afforded crude IIa along with VIIa2) and VIII3). The triple-layered compound IIa was separated by means of careful chromatography on silica gel or on 20% silver nitrate coated silica gel. Recrystallization from petroleum ether gave pure colorless prisms (2.2% yield), m.p. 127.0∼128.0°C. The thiophene analogue IIb was obtained together with VIIb2) and VIII by the similar method (1.1% yield), m.p. 149.0∼151.5°C (decomp.). In addition, a double-layered compound IIIa was prepared by the cross-breeding reaction of Va and VI in a 5.9% yield, m.p. 63.0∼64.5°C, and IIIb by the reaction of Vb and VI, 1.5% yield, m.p. 125.0∼126.0°C.

The structure of these cyclophanes was determined on the basis of NMR, IR and MASS spectra and elemental analysis.

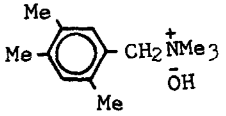


IV

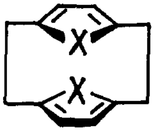


Va X=O

Vb X=S

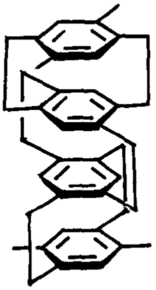


VI

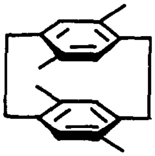


VIIa X=O

VIIb X=S



VIII



IX

The NMR spectral data are assigned as shown in Fig. 1. The methylene protons appear in a range of $6.5\sim8.0\tau$ as a multiplet. All the aromatic protons of triple-layered compounds appear in higher field than the corresponding protons of double-layered ones owing to the anisotropy of the additional aromatic ring. Fixation of the thiophene ring is demonstrated in the spectra of IIb and IIIb and no ring inversion took place in a temperature range up to 150°C. On the other hand, the furan rings in IIa and IIIa undergo the internal inversion at room temperature as illustrated in Fig. 2. The activation free energy of the inversion, $\Delta G_c^{\ddagger}$, is obtained from the spectra at various temperatures (Fig. 3), 10.2 Kcal/mole for IIa (Tc = -62°C in $CDCl_3$-CS_2 of a ratio 2:1) and 11.9 Kcal/mole for IIIa (Tc = -29°C in $CDCl_3$). Easier ring inversion in IIa than in IIIa may be explained in terms of a change in the geometry of the facing benzene ring.

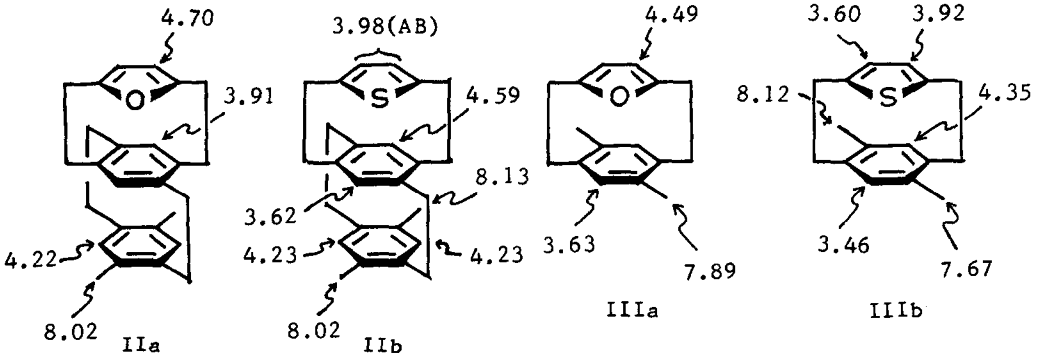


Fig. 1. NMR spectra of II and III in CCl_4 (τ value)

The aromatic protons at pseudo-gem position to the methyl group in cyclophanes I and IX appear in more or less lower field due to the steric compression effect[1,4]. Such the effect is also observed on thiophene protons of the cyclophanes IIb and IIIb, since one of the protons is sterically compressed by pseudo-gem methylene or methyl group. By contrast, furan protons

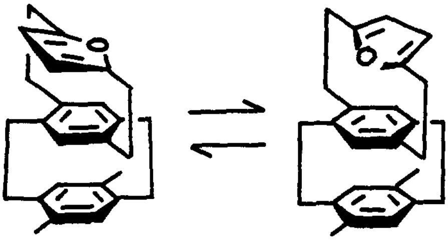


Fig. 2

in IIa and IIIa remain equivalent even below the coalescence temperature, indicating the absence of the effect for the furanophanes. This difference between the furanophane and the thiophenophane is probably due to a difference of the size of oxygen and sulfur atoms.

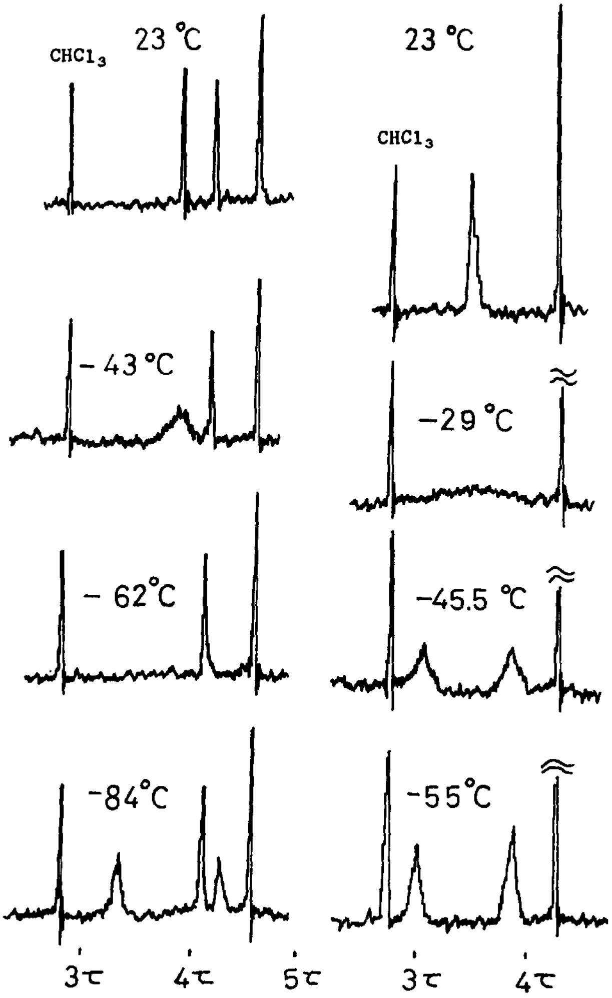


Fig. 3. NMR spectra of the aromatic region of IIa (left) and IIIa (right) as a function of a temperature.

The UV spectra are shown in Fig. 4 and Fig. 5. The spectra of the triple-layered compounds exhibit a remarkable bathochromic shift as compared with those of the double-layered ones, and show an unexpected resemblance to the spectrum of benzenoid analogue I. This similarity may be mainly attributed to the transannular electronic interaction between aromatic rings. The electronic interaction is reflected in the π-basicity of the cyclophanes, which is evaluated from the absorption maxima of TCNE-cyclophane complexes in Table 1. From comparison of π-basicities of layered heterophanes and the corresponding benzenoid analogue, it is suggested that the electronic interaction between heteroaromatic ring and benzene ring is less effective than that between benzene rings.

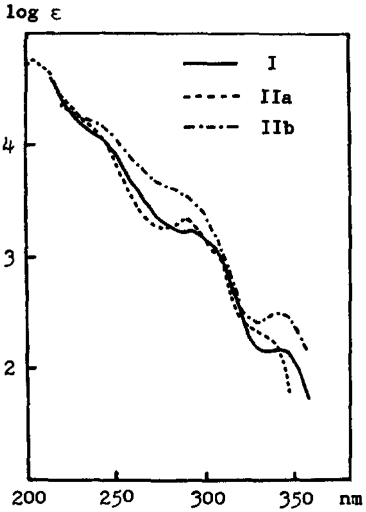


Fig. 4. Electronic spectra of I, IIa and IIb in cyclohexane

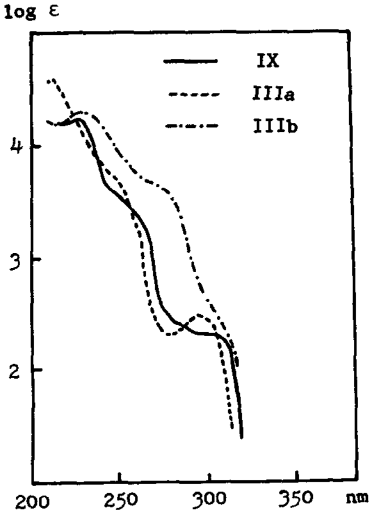


Fig. 5. Electronic spectra of IX, IIIa and IIIb in cyclohexane

Table 1. Absorption maxima of TCNE complexes (in CH_2Cl_2)

Compound	λmax (nm)	Compound	λmax (nm)
durene[a]	480	IIa	622
2,5-dimethylfuran	574	IIb	644
2,5-dimethylthiophene	416, 556	I	655
IIIa	563	VIIa	588
IIIb	572	VIIb	550
IX	584[b]		

a) Reference 5 ; b) 580 in Reference 3.

References

1. Part I; T. Otsubo, S. Mizogami, Y. Sakata and S. Misumi, Chemical Commun., in press.

2. H. E. Winberg, F. S. Fawcett, W. E. Mochel and C. W. Theobald, J. Am. Chem. Soc., 82, 1428 (1960)

3. D. T. Longone and H. S. Chow, ibid., 86, 3898 (1964), 92, 994 (1970)

4. H. J. Reich and D. J. Cram, ibid., 91, 3534 (1969)

5. R. E. Merrifield and W. D. Phillips, ibid., 80, 2778 (1958)