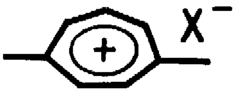
Tetrahedron Letters No. 43, pp 3899 - 3902, 1976. Pergamon Press. Printed in Great Britain.

LAYERED COMPOUNDS. XXXIX.[1] SYNTHESES OF [2.2]CYCLOPHANES CONTAINING A TROPYLIUM CATION MOIETY

Hisanori Horita, Tetsuo Otsubo, Yoshiteru Sakata, and Soichi Misumi*
The Institute of Scientific and Industrial Research, Osaka University
Suita, Osaka, Japan

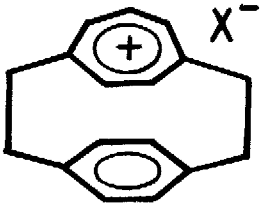
(Received in Japan 9 August 1976; received in UK for publication 9 September 1976)

In recent years, a variety of cyclophanes have been synthesized as models for intermolecular electronic interactions between aromatic nuclei and for examining strain effect on physical and chemical properties of the aromatic nuclei.[2] However, there have been reported few cyclophanes of non-benzenoid aromatic ring.[3] Now we wish to report the syntheses of [2.2]cyclophanes containing a tropylium cation, one of typical non-benzenoid aromatic compounds in connection with the study of transannular electronic interactions in benzenoid cyclophanes.

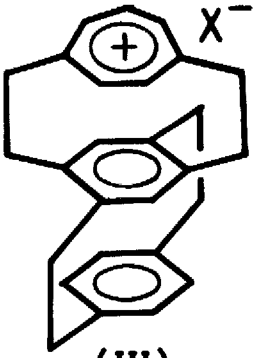


$X^- = BF_4^-$

(I)

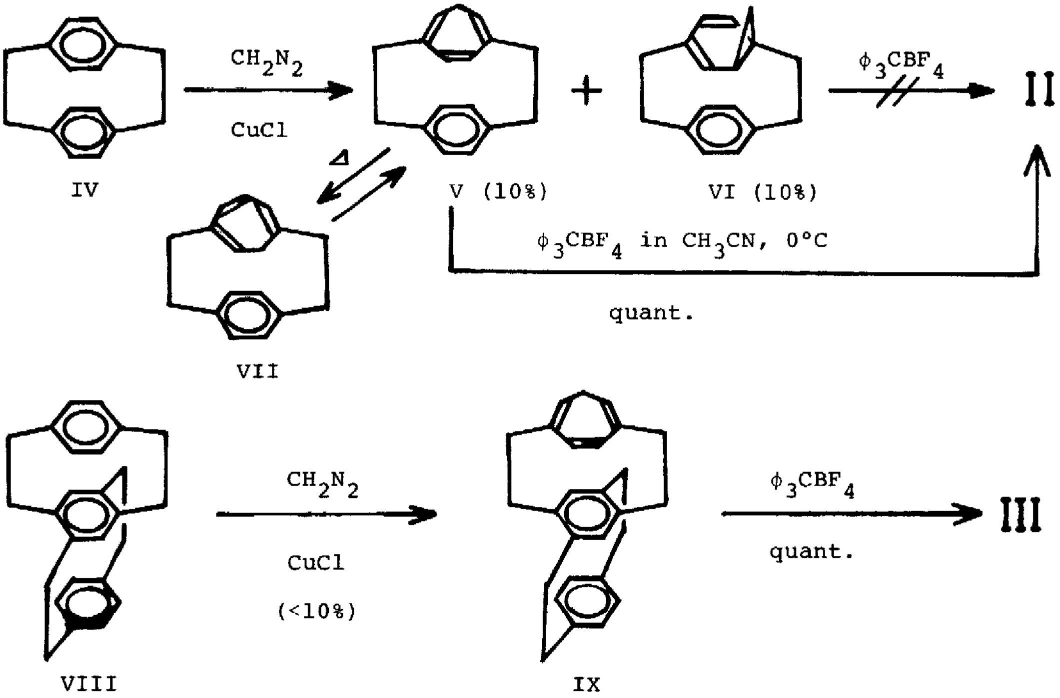


(II)



(III)

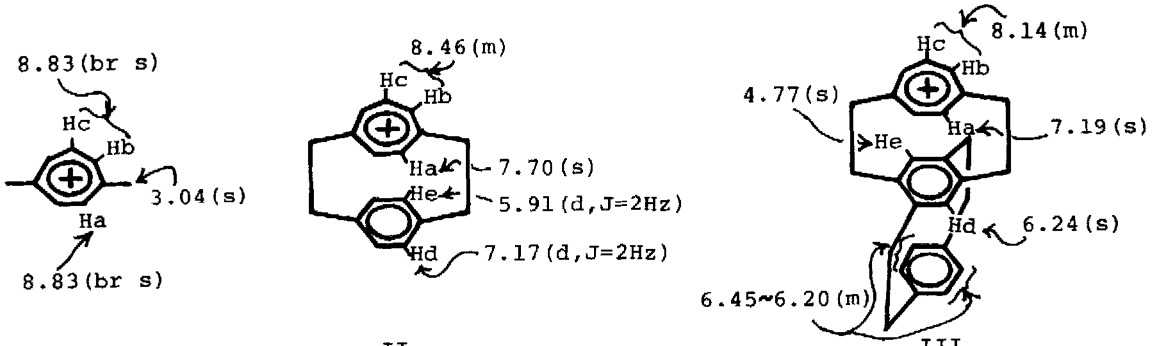
Näder and Meijere obtained recently a mixture of monomethylenated cyclophanes V ~ VII from the reaction of [2.2]paracyclophane IV with diazomethane followed by gas chromatography.[4] We carried out the same reaction and isolated successfully the two isomers, V and VI, by means of column chromato-



graphy on silica gel.[5] It was found that at 150°C the isomer V was isomerized to the third isomer VII which could not be detected in the methylenated reaction mixture. Similarly, the reaction of triple-layered [2.2]paracyclophane VIII with diazomethane gave a tropylidene cyclophane IX.[6]

Treatment of both tropylidene cyclophanes, V and IX, with trityl fluoroborate in acetonitrile followed by addition of ether afforded the desired [2.2]tropylium cyclophanes, II and III, respectively.[7] On the other hand, the norcaradiene type isomer VI was unreactive for hydride abstraction by trityl fluoroborate under the same conditions. As a reference compound, 1,4-dimethyltropylium fluoroborate I was prepared from p-xylene according to the literature.[8]

As seen in Fig. 1, the NMR data of II and III are consistent with the present structures. The chemical shifts of all the aromatic protons shift to upfield with increase of the layer number as in the case of multilayered paracyclophanes.[9] It may be pointed out that Ha of tropylium ring appears at higher field than Hb and Hc in the same ring, while in benzene moiety He appears at higher field than Hd. This is probably attributable to the stacking



I

II

III

Fig. 1. NMR spectra of I ~ III (δ values in CD_2Cl_2 ; 100 MHz).

of tropylium ring on the faced benzene ring at some angle or with a mutual parallel displacement of the two aromatic rings.

The electronic spectra are shown in Fig. 2. The broad absorptions in long wavelength region, λ_{max} 354 nm for II and 434 nm for III, are characterized to be intramolecular charge transfer bands because of lack of the corresponding absorption for I and a solvent-shift of these maxima in polar solvent. The bathochromic shift of the band of III relative to that of II indicates obviously the increase of transannular electronic interaction.

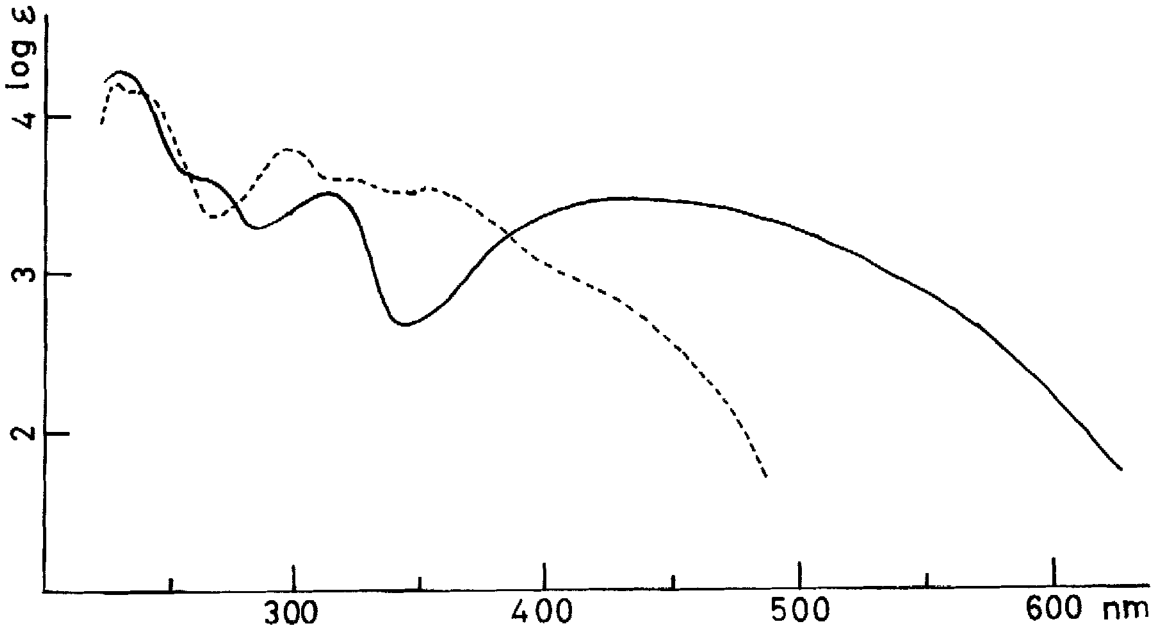


Fig. 2. Electronic spectra of II (-----) and III (——) in dichloromethane.

The authors are greatly indebted to Mrs. Y. Miyaji of Microanalytical Laboratory, Faculty of Technology, Osaka University, for NMR measurements.

References

1) Part XXXVIII, M. Yoshida, H. Tatemitsu, Y. Sakata, and S. Misumi, submitted to Tetrahedron Letters.

2) D. J. Cram and J. M. Cram, Accounts Chem. Res., 4, 204 (1971); T. Sato, Nippon Kagaku Zasshi (Japanese), 92, 277 (1971); F. Vögtle, Chem. Z., 95, 668 (1971); F. Vögtle and P. Neumann, Angew. Chem., 84, 75 (1972); Chimia, 26, 64 (1972); Synthesis, 85 (1973); S. Misumi, Kagaku no Ryoiki (Japanese), 28, 927 (1974); Y. Sakata, ibid., 28, 947 (1974); S. Misumi, Mem. Inst. Sci. Ind. Res., Osaka Univ., 33, 53 (1976).

3) As a representative example, [2.2](2,6)azulenophane was reported very recently; R. Luhowy and P. M. Keehn, Tetrahedron Letters, 1043 (1976); N. Kato, Y. Fukazawa, and S. Itô, ibid., 2045 (1976).

4) R. Näder and A. de Meijere, Angew. Chem., 88, 153 (1976); Angew. Chem. Internat. Edit., 15, 166 (1976).

5) Both the products V and VI gave colorless needles from acetonitrile, which gradually melted at 100-120°C with decomposition or slowly decomposed on standing at room temperature. NMR (CCl_4, δ): V, 6.76 (d, J=2 Hz, 2H), 6.39 (d, J=2 Hz, 2H), 5.43 (s, 2H), 4.77 (t, J=7 Hz, 2H), 3.0-2.0 (m, 9H), 1.31 (dt, J=13.5 and 7 Hz, 1H); VI, 6.98 (d, J=8 Hz, 1H), 6.80 (d, J=8 Hz, 1H), 6.77 (d, J=8 Hz, 1H), 6.58 (d, J=8 Hz, 1H), 5.47 (d, J=12 Hz, 1H), 4.86 (d, J=6 Hz, 1H), 4.69 (dt, J=12 and 4 Hz, 1H), 3.4-1.6 (m, 6H), 1.10 (t, J=10 Hz, 1H), 0.96 (t, J=10 Hz, 1H), 0.71 (m, 1H), 0.33 (m, 1H).

6) NMR of IX (CCl_4, δ): 6.19 (s, 4H), 5.80 (s, 1H), 5.20 (s, 1H), 5.20 (dd, J=7 and 2 Hz, 1H), 5.11 (dd, J=7 and 2 Hz, 1H), 4.55 (t, J=6 Hz, 1H), 4.49 (t, J=6 Hz, 1H), 3.4-1.6 (m, 17H), 1.15 (dt, J=13 and 6 Hz, 1H).

7) II: yellow plates from acetonitrile-ether, decomp.>128°C (with melt); III: red columns from dichloromethane, decomp.>115°C. These compounds gave satisfactory elemental analyses.

8) E. Müller, H. Kessler, H. Fricke, and W. Kiedaisch, Ann. Chem. A 675, 63 (1964).

9) T. Otsubo, S. Mizogami, Y. Sakata, and S. Misumi, Bull. Chem. Soc. Japan, 46. 3831 (1973).

.0) M. Feldman and S. Winstein, J. Amer. Chem. Soc., 83, 3338 (1961), reported that charge transfer band of tropylium-p-xylene intermolecular complex in 1,2-dichloroethane appeared at 340 nm comparable to the present CT band of II.