Tetrahedron Letters No. 50, pp 4425 - 4428, 1977. Pergamon Press. Printed in Great Britain.

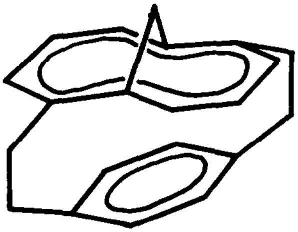
SYNTHESES OF ANNULENOPHANES[1]

Mansuke Matsumoto, Tetsuo Otsubo, Yoshiteru Sakata, and Soichi Misumi*

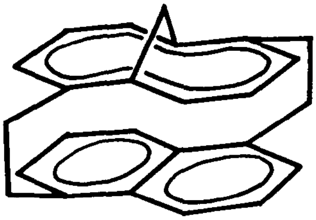
The Institute of Scientific and Industrial Research, Osaka University
Suita, Osaka 565, Japan

(Received in Japan 3 October 1977; received in UK for publication 20 October 1977)

Although recent interest in cyclophane chemistry has been denoted to the cyclophanes of non-benzenoid aromatics such as azulenophane[2] and tropyliophanes[3], no annulenophane has so far been studied. It would be worthwhile to explore how the aromaticity of annulene ring is affected by the transannular interaction in such annulenophanes. In this communication we wish to present the first examples of annulenophanes, i.e., [2]paracyclo[2](2,7)(1,6-methano[10]-annuleno)phane 1 and [2](1,5)naphthaleno[2](2,7)(1,6-methano[10]annuleno)phane 2.

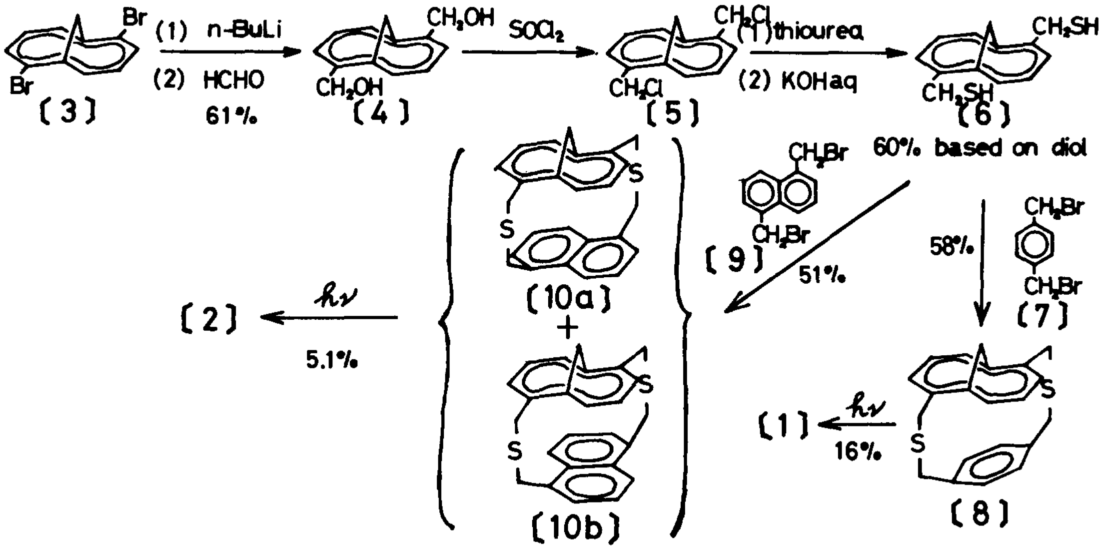


[1]



[2]

2,7-Dibromo-1,6-methano[10]annulene 3, prepared according to the Vogel's procedure,[4] was treated with n-butyl lithium followed by formaldehyde to give diol 4. The reaction of 4 with thionyl chloride in chloroform afforded relatively labile bischloromethyl derivative 5 which was immediately converted to the corresponding dithiol 6 via bis-isothiuronium salt. A coupling reaction between 6 and α,α'-dibromo-p-xylene 7 gave dithiacyclophane 8[5] in good yield. When 8 was irradiated with a low pressure mercury lamp for 30 hrs in a mixed solution of triethylphosphite and benzene under a nitrogen atmosphere, the desired paracycloannulenophane 1 was obtained as slight yellow prisms (from hexane), mp 254.5-256°C (with dec.).[6] A similar coupling reaction between 6 and 1,5-bis(bromomethyl)naphthalene 9 gave a mixture of two isomeric dithiacyclophanes 10a and 10b in a ratio of about 10:1.[7] The mixture was irradiated for 40 hrs under the same conditions to yield naphthalenoannulenophane 2 as slight yellow prisms (from benzene), mp 320-321.5°C.[6] Although two configurational isomers as seen in the case of 10 are possible for this naphthaleno-



phane, only one isomer was formed. Considering that 10a is the major isomer on the formation of dithiacyclophane 10, we suppose the configuration of the naphthalenophane to be of the fully stacking type 2.

The structural features are demonstrated by the NMR spectra (Figs. 1 and 2). All the aromatic protons exhibit considerable upfield shifts characteristic of the cyclophane system. Especially the benzenoid protons of 1 shows dramatic shift (1.30 ppm) as compared to that of p-xylene (δ 6.95), supporting the presence of strong ring current in the opposite [10]annulene ring. The signals of the methano protons appear at significant high field due to the diamagnetic anisotropy of the annulene ring. The marked difference (0.79 or 0.96 ppm) in the chemical shifts of the methano protons between 1,6-methano[10]annulene (δ -0.52) and 1 or 2 is most likely attributed mainly to the magnetic anisotropy of the stacked benzene or naphthalene ring and at least partly to some change of the methano-bridged annulene ring framework caused by constructing the [2.2]cyclophane system.

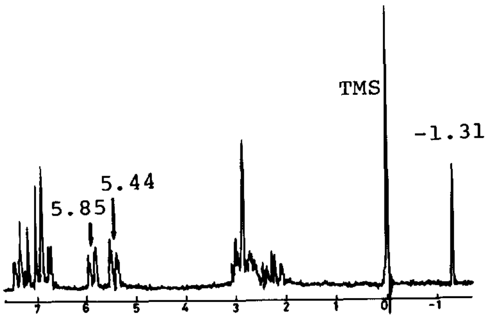


Fig. 1. NMR spectrum of 1 in CCl_4.

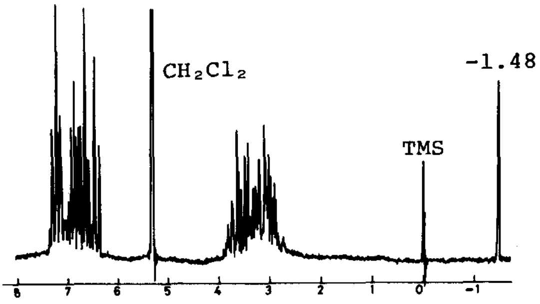


Fig. 2. NMR spectrum of 2 in CD_2Cl_2.

The electronic spectra are shown in Figs. 3 and 4. The spectrum of **1** is very similar to the superposed curve of the spectra of the two component chromophores, 2,7-dimethyl-1,6-methano[10]annulene8) and p,p'-dimethylbibenzyl (instead of p-xylene), indicating that the transannular π-electronic interaction between the two chromophores is, if there is, not so large. On the other hand, the spectrum of **2** shows remarkable bathochromic shift and broadening of the absorption bands due to significant interaction between the two chromophores. The difference in the interaction between the two cyclophanes is accounted for as follows. The ring sizes of the two chromophores in **2** are very suitable to overlap extensively to each other, but the case is not for **1**, and the energy of the transition associated with the longest wavelength band of [10]annulene is relatively closer to that of naphthalene than that of benzene.

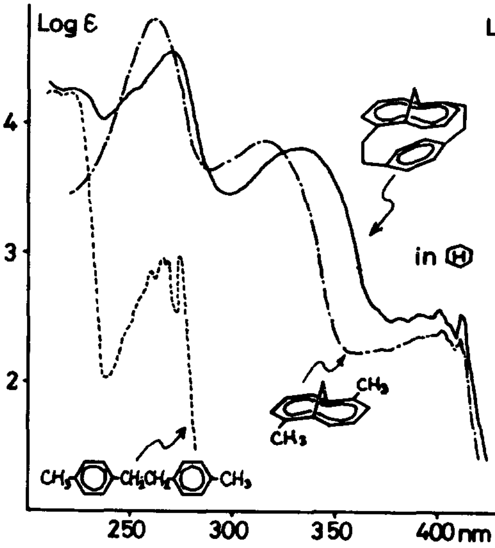


Fig. 3. Electronic spectrum of **1**.

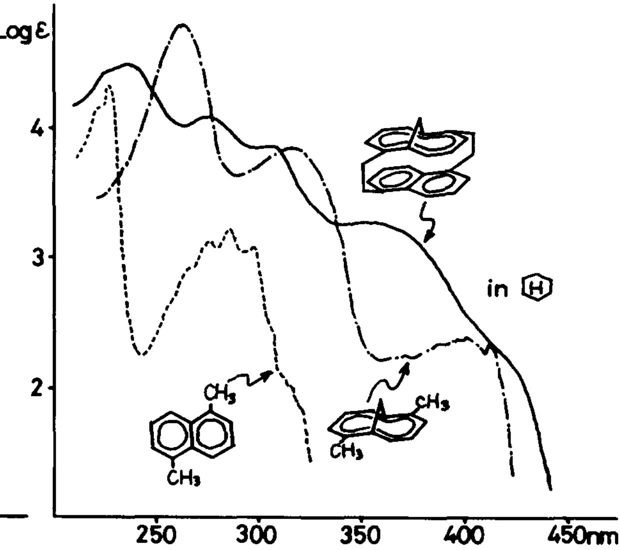


Fig. 4. Electronic spectrum of **2**.

The authors express their hearty thanks to Professor E. Vogel for his helpful discussions and also to Professor V. Boekelheide and Mr. R. Gray for their kind comment on the NMR data of the annulenocyclophanes.

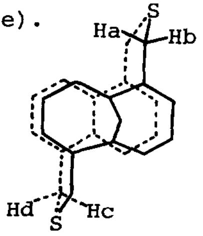
References and Notes

1) Layered Compounds XLVII. Part XLVI: H. Horita, T. Otsubo and S. Misumi, Chem. Lett. (1977) in press.
2) R. Luhowy and P. M. Keehn, Tetrahedron Lett., 1043 (1976); N. Kato, Y. Fukazawa and S. Ito, ibid., 2045 (1976).
3) H. Horita, T. Otsubo, Y. Sakata and S. Misumi, Tetrahedron Lett., 3899 (1976); J. G. O'Connor and P. M. Keehn, J. Am. Chem. Soc., **98**, 8846 (1976).
4) E. Vogel and W. A. Boll, Angew. Chem., **76**, 784 (1964).

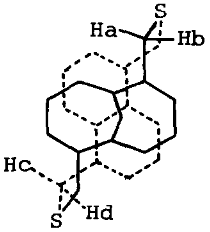
5) NMR data of 8 (δ in CCl_4): singlet at -1.17 (2H, methano), broad singlet at 3.40 (4H, CH_2S), broad singlet at 4.06 (4H, CH_2S), singlet at 6.14 (4H, benzene), multiplet at 6.70-7.47 (6H, annulene).

6) These cyclophanes 1 and 2 gave satisfactory elemental analysis and high resolution MS spectral datum, respectively.

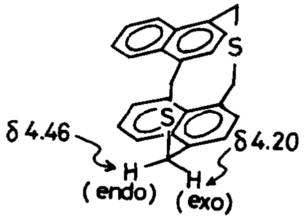
7) The structures of the two isomers were assigned on the basis of NMR analyses. NMR data of the less soluble major isomer 10a (δ in CD_2Cl_2): -1.25 (s, 2H, methano), 3.79 (ABd, 2H, J=15.2Hz, Hb or Hd), 4.13 (ABd, 2H, J=16.4Hz, Hd or Hb), 4.39 (ABd, 2H, J=15.2Hz, Ha or Hc), 4.43 (ABd, 2H, J=16.4Hz, Hc or Ha), 6.54-7.59 (m, 12H, naphthalene and annulene). NMR data of the more soluble minor isomer 10b (δ in CD_2Cl_2): -1.31 (s, 2H, methano), 4.06 (ABq, 4H, Ha,b or Hc,d), 4.09 (s, 4H, Hc,d or Ha,b), 6.54-7.76 (m, 12H, naphthalene and annulene).



10a



10b



11

In the parallel stacked configuration such as syn-2,15-dithia[3.3](1,4)-naphthalenophane 11 [T. Otsubo and V. Boekelheide, J. Org. Chem., 42, 1085 (1977)], the bridged methylene protons, H*endo* and H*exo*, appear as non-equivalent signals because H*endo* is more shifted to downfield than H*exo* due to the additional deshielding effect of the condensed benzene ring. The less soluble isomer shows a similar tendency of spectrum and therefore is assigned to the configuration 10a. On the other hand, the methylene signals of the more soluble isomer appear rather as a singlet and a AB quartet near to singlet. These data are best explained by the crossly stacked configuration 10b, in which the diamagnetic anisotropies of the opposite rings cause the upfield shifts for Hb and Hd in contrast to the behaviors of the corresponding protons in 10a.

8) W. Klug, Dissertation, Universität Köln, 1972.