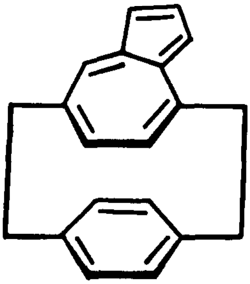
Tetrahedron Letters No. 12, pp 1063 - 1066, 1978. Pergamon Press. Printed in Great Britain.

SYNTHESES OF [2.2]PARACYCLOAZULENOPHANES1)

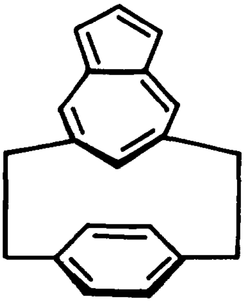
Toshihide KAWASHIMA, Tetsuo OTSUBO, Yoshiteru SAKATA and Soichi MISUMI
The Institute of Scientific and Industrial Research, Osaka University
Suita, Osaka 565, Japan

(Received in Japan 17 January 1978; received in UK for publication 2 February 1978)

In connection with benzenoid phane chemistry developed conspicuously, much attention has recently been paid to the transannular electronic interaction in some cyclophanes incorporating nonbenzenoid aromatic ring, e.g., tropyliophane,2) azulenophane,3) and annulenophane.4) A strong transannular interaction in tropylioparacyclophane led us to scrutinize the interaction in paracycloazulenophanes where π-donating benzene ring is stacked on the seven-membered positive moiety of dipolar azulene ring. We now wish to report on the syntheses of two types of [2.2]paracycloazulenophane for this purpose.



1



2

The two paracycloazulenophanes 1 and 2 were synthesized by intramolecular carbene insertion5) to [2.2]cyclophane as shown in the scheme. [2.2]Paracyclophanylpropionic acid 5, prepared via 4-bromomethyl[2.2]paracyclophane 46) from [2.2]paracyclophane 3 in 30% yield, was converted to diazoketone 6. Treatment of 6 with Cu-powder in decaline at 160°C gave two cyclic ketones 7 (21.8% yield based on 5) and 8 (10.1% based on 5) which were purified by column chromatography on silica gel [7: colorless prisms from ethyl acetate, mp 161.0-161.5°C. 8: colorless scales from benzene-hexane, mp 118.0-119.5°C]. The ketones 7 and

8 were treated with tosylhydrazine followed by butyllithium to afford the corresponding olefins 9 and 10. Dehydrogenation of each of the two olefins with 5% Pd-C in naphthalene at 220°C gave the desired [2.2]paracyclo(4,7)azulenophane 1 (8.0% yield based on 7 and 8, respectively) [1: deep blue crystals from hexane, mp 107-109°C, M^+ obs. 258.14023, calcd. for $C_{20}H_{18}$ 258.14084]. [2.2]Paracyclo(5,7)azulenophane 2 was synthesized from 5-methyl[2.2]metaparacyclophane 11 7) in a similar manner [2: violet columns from hexane, mp 145-146°C with partial decomposition, M^+ obs. 258.14228, calcd. for $C_{20}H_{18}$ 258.14084].

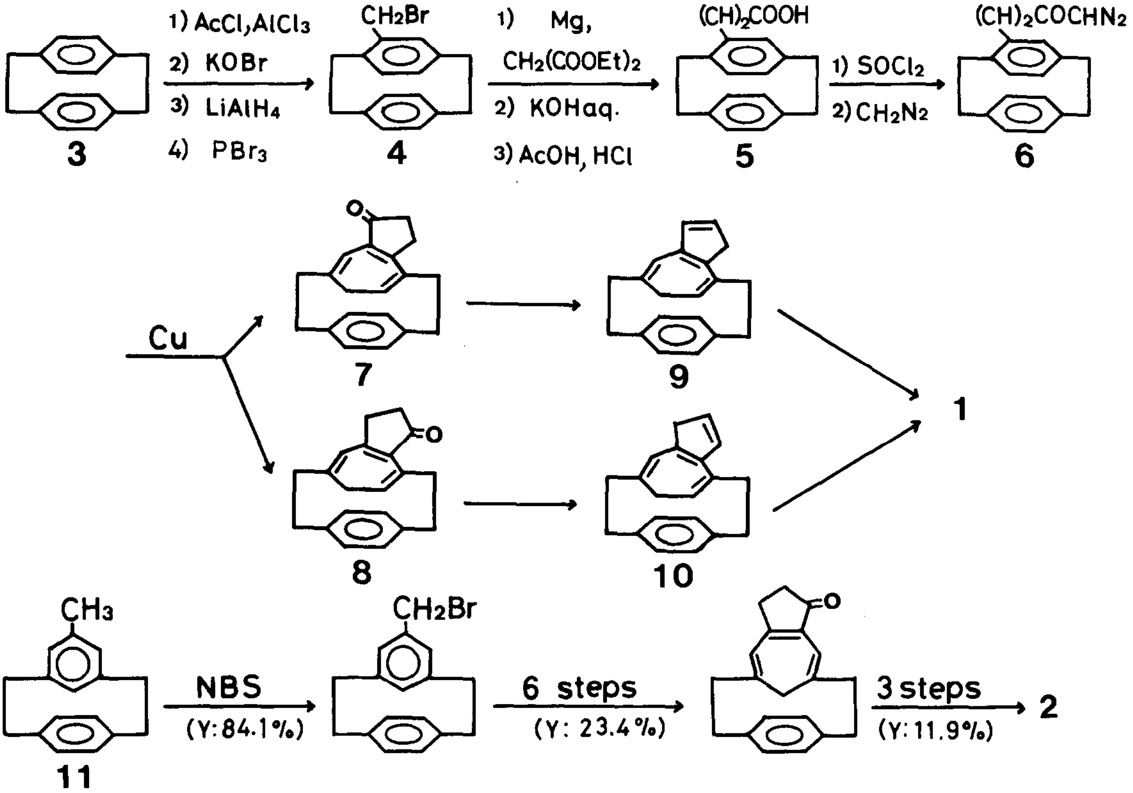


Figure 1 shows the ^{1}H-nmr data consistent with the present structures 1 and 2. All the aromatic proton signals of 1 are shifted to upfield compared with those of *p*-xylene and 4,7-dimethylazulene, due to the magnetic anisotropy of the faced aromatic ring. Marked upfield shifts of Hd and He of all the azulene protons indicate that they are placed over the benzene ring. On the other hand, the spectral feature of 2 is quite similar to that of [2.2]metaparacyclophane.8) Thus, the inner proton Hd appears in an extraordinarily high field and the protons He and Hf, which are significantly different in chemical shift, become

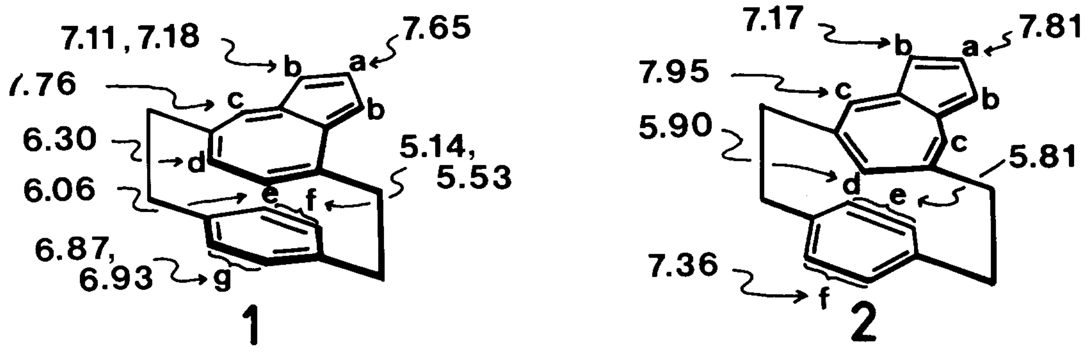


Fig. 1. ^{1}H-nmr data of 1 and 2 (δ values in $CDCl_3$, 100 MHz at 23°C).

equivalent at high temperature (Tc = 70°C) owing to a conformational flipping.9) These spectra suggest that in stacking mode of the two aromatic rings the azulenophane 2 resembles [2.2]metaparacyclophane.

The electronic spectra of 1 and 2 are shown in Fig. 2. The spectrum of 1 exhibits general broadening and bathochromic shifts of all the absorption bands. And it shows a red shift of the structureless longest wavelength band (^1L_b) by 17 nm relative to 4,7-dimethylazulene,10) indicating that there is a relatively strong transannular electronic interaction between the two aromatic rings. On the other hand, 2 demonstrates no noticeable shift of the longest wavelength band, remaining fine structure, from a value of absorption maximum calculated for 5,7-dialkylazulene according to the Plattner rule.11) This spectrum

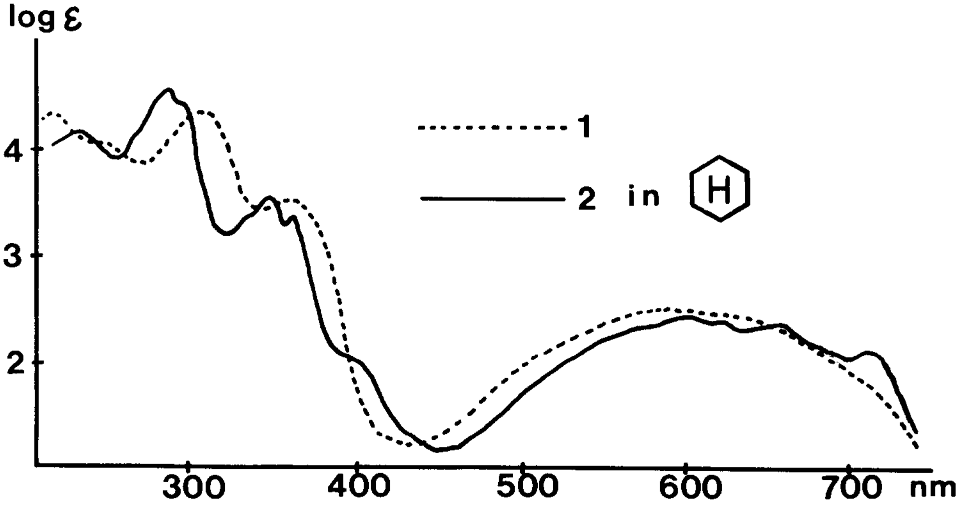


Fig. 2. Electronic spectra of 1 and 2 in cyclohexane.

suggests the two aromatic rings in 2 to weakly interacted due to their partial overlapping. Very recently Itô et al. have reported that there is no appreciable interaction between the two aromatic rings of [2.2]paracyclo(1,3)azulenophane, in which the benzene ring is stacked on the five-membered moiety of azulene ring.12) These results are indicative of that the seven-membered moiety of azulene ring interacts more definitely with a faced donor molecule than the five-membered moiety.

References and Notes

1) Layered Compounds XLIX. Part XLVIII: H. Machida, H. Tatemitsu, Y. Sakata and S. Misumi, to be submitted.
2) 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, 8446 (1976).
3) R. Luhowy and P. M. Keehn, *Tetrahedron Lett.*, 1043 (1976); *J. Am. Chem. Soc.*, 99, 3797 (1977); N. Kato, Y. Fukazawa and S. Itô, *Tetrahedron Lett.*, 2045 (1976).
4) M. Matsumoto, T. Otsubo, Y. Sakata and S. Misumi, *Tetrahedron Lett.*, 4425 (1977).
5) A. Contantio, G. Linstrumelle and S. Julia, *Bull. Soc. Chim. France*, 1970, 907, 912.
6) D. J. Cram and N. L. Allinger, *J. Am. Chem. Soc.*, 77, 6289 (1955); D. J. Cram and L. A. Singer, *ibid.*, 85, 1075 (1963).
7) 5-Methyl[2.2]metaparacyclophane 11 was prepared in a good yield by pyrolysis of the disulfone of 6-methyl-2,11-dithia[3.3]metaparacyclophane, colorless plates from ethanol, mp 59.5-60.0°C.
8) D. T. Hefelfinger and D. J. Cram, *J. Am. Chem. Soc.*, 92, 1073 (1970); F. Vögtle, *Chem. Ber.*, 102, 3077 (1969); S. Akabori, S. Hayashi, M. Nawa and K. Shiomi, *Tetrahedron Lett.*, 3227 (1969).
9) The activation energy of the conformational process corresponds to 16.2 Kcal/mol.
10) H. Pommer, *Ann.*, 579, 47 (1953).
11) E. Heilbronner, Non-Benzenoid Aromatic Compounds, edit. by D. Ginsburg, Interscience (1959), p. 225 and references cited therein.
12) M. Aoyagi, Y. Fukazawa and S. Itô, Abstracts of 10th Symposium on Structural Organic Chemistry, Matsuyama, Japan (1977), p. 220 and to be submitted.