

LAYERED COMPOUNDS. XIV¹⁾. MULTICYCLOADDITION REACTION OF [3.3]PARACYCLOPHADIENE

AND A RELATED COMPOUND WITH TETRACYANOETHYLENE

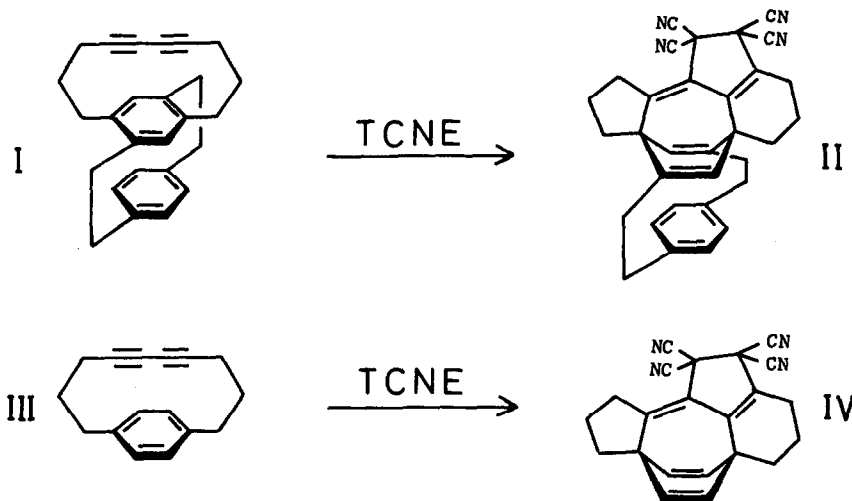
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In the previous papers of this series, we have reported the synthesis and properties of [m.n]paracyclophadiynes.²⁾ We have synthesized a layered paracyclophadiyne I via nine steps from 4,7-dimethyl[2.2]paracyclophane³⁾ for comparison of transannular electronic interaction with [m.n]paracyclophadiynes. When mixed with tetracyanoethylene (TCNE) for the purpose of charge-transfer complex formation, the compound I yielded a 1:1 TCNE-addition product at room temperature. This communication will report on the structure of the adduct as well as a 1:1 TCNE-adduct formed from more simple system, [3.3]paracyclophadiyne or [10]paracycloph-4,6-diyne (III).²⁾



A mixture of I and TCNE in methylene chloride, immediately after preparing the solution, shows an absorption maximum at 572 nm. During standing for 40 min. at room temperature, however

this solution of the complex had a color varying from originally purple to reddish brown at the end. Thinlayer chromatography of the resulting solution gave colorless prisms [m.p. 238~239°C dec; IR (KBr disc) ν_{max} 2248, 2215 and 721 cm^{-1} ; MS m/e 466(M^+), 440, 414, 362, 104; NMR (CDCl_3) Fig. 1]. These spectral data indicate that the reaction of I with TCNE yielded a new product corresponding to a 1:1 adduct of two components.

On the other hand, an equimolar mixture of III and TCNE in sym-tetrachloroethane was heated at 136°C for 30 min. followed by recrystallization from n-hexane-benzene to give colorless

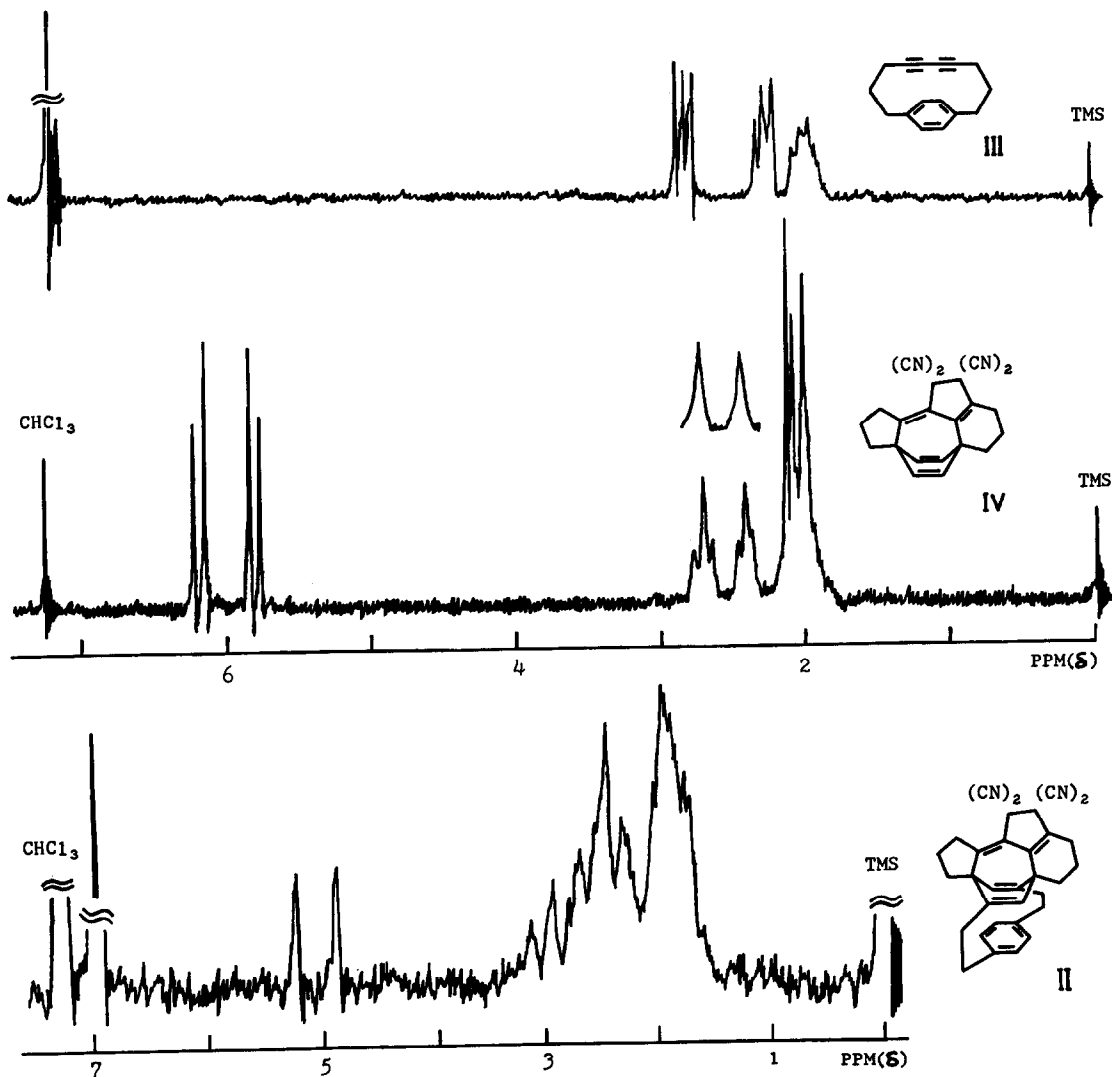


Fig. 1. NMR spectra of II (60 MHz) and III and IV (100 MHz) in deuteriochloroform.

needles in a 73% yield, m.p. 211~212°C; UV (in THF) λ_{\max} ($\log \epsilon$) 250 (3.98) and 281 nm (3.88). Elemental analysis and mass spectrum reveal that the product has a composition $C_{22}H_{16}N_4$ corresponding to a 1:1 addition product of III and TCNE. This adduct shows a new AB pattern centered at 5.99 ppm with disappearance of a singlet of aromatic protons in III on NMR spectra (Fig. 1) and also new peaks at 2253 ($\nu_{C\equiv N}$), 1665, 1638 and 1596 ($\nu_{C=C}$), and 706 cm^{-1} ($\delta_{=CH}$ cis) in the place of $\nu_{C\equiv C}$ bands (2247 and 2153 cm^{-1}) in III on IR spectra. These spectral data clearly indicate the participation of two π -electron systems, benzene nucleus and diacetylenic bond, in the addition reaction.

On the basis of X-ray crystallographic data^{2c)} and molecular model examination, three structural formulae in Fig. 2 remain to be the most reasonable ones of a number of structures presumed for the adduct. As seen in the figure, 1,3-mode formula (IV) which involves cycloaddition of TCNE to 1,3-positions of diacetylenic bond has C_s symmetry, whereas both 1,4- and 2,3-mode formulae possess C_{2v} symmetry. Of these three formulae, only 1,3-mode IV is able to interpret the observed spectral data of the adduct. Thus, the NMR spectrum is best accounted

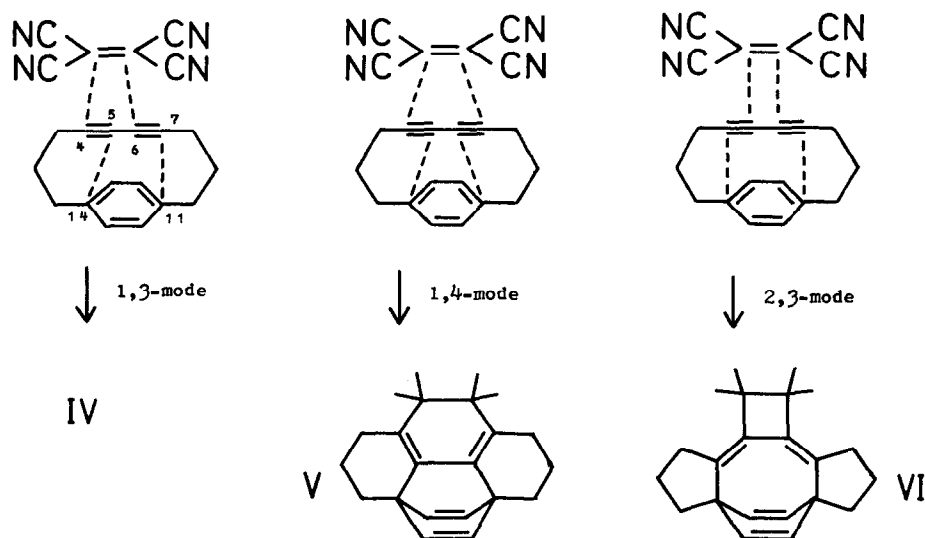


Fig. 2. Cycloaddition modes of TCNE to [3.3]paracyclopentadiene.

for as follows; δ 6.17 and 5.80 (AB, $\sqrt{A_B} = 0.37$ ppm, $J_{AB} = 8$ Hz, 4H, vinyl), 2.72 (t, $J = 7$ Hz, 2H, allylic methylene), 2.42 (b.t, 2H, allylic methylene), and 2.2~2.0 ppm (m, 8H, the rest methy-

lenes). On irradiating at 2.05 ppm, either of two allylic methylene signals become singlet as shown in Fig. 1. Downfield shift of all the protons in IV may be mainly caused by the diamagnetic anisotropy of four cyano groups.

In a similar manner as above, it is anticipated that the layered compound I containing [3.3]paracyclopadiyne function is also subjected to 1,3-addition reaction of TCNE. The NMR spectrum of the adduct is satisfactorily explained with the structure II; δ 6.92 (s, 4H, aromatic), 5.20 (s, 1H, vinyl), 4.83 (s, 1H, vinyl), and 3.2~1.5 ppm (m, 20H, methylene). Upfield shift of both vinyl protons in II compared to the corresponding ones in IV is possibly due to the anisotropy of remaining benzene ring, and it is interesting that a difference in chemical shifts of the two vinyl protons in II, 0.37 ppm, is the same as in the case of IV.

The fact that the unexpected 1,3-mode addition of TCNE proceeds in preference to the other modes can be explained by means of the strain in the presumed structures, V and VI, of the adduct and bond lengths and interatomic distances^{2c)}, e.g., C_4-C_{14} , C_5-C_{14} , etc., in the reactants. Both addition reactions have been established to take place even in the dark, and greater facility of I than III in the reaction may mainly be attributed to dissolution of higher strain in the former system.

These reactions are, to our knowledge, the first examples of thermally symmetry-allowed $(\pi 4s + \pi 2a + \pi 2s + \pi 2a)$ multicycloaddition reaction, providing that they proceed in a concerted manner. Further discussion of this multicycloaddition will be reported as well as the reactions of several [m.n]paracyclopadiynes in future paper.

References

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