

LAYERED COMPOUNDS. XXIII.<sup>1)</sup> NOVEL PHOTOCHEMICAL  
MULTICYCLOADDITIONS OF ANTHRACENOPHADIYNE

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In the previous communication,<sup>2)</sup> we reported intriguing thermal multicycloaddition reactions of [3.3]paracyclophadiyne and a related compound with tetracyanoethylene. For further study of this cyclophane system a related compound, [10](9,10)anthracenopha-4,6-diyne (I), which has a photolabile anthracene nucleus in place of benzene one, has been synthesized by way of bisethynylation of 9,10-bis(3-bromopropyl)anthracene<sup>3)</sup> followed by intramolecular oxidative coupling of the bisethynyl compound. In this communication, we wish to report on photo-induced multicycloaddition reactions of the anthracenophadiyne I to give a dimer II and related cycloaddition compounds, III and IV.

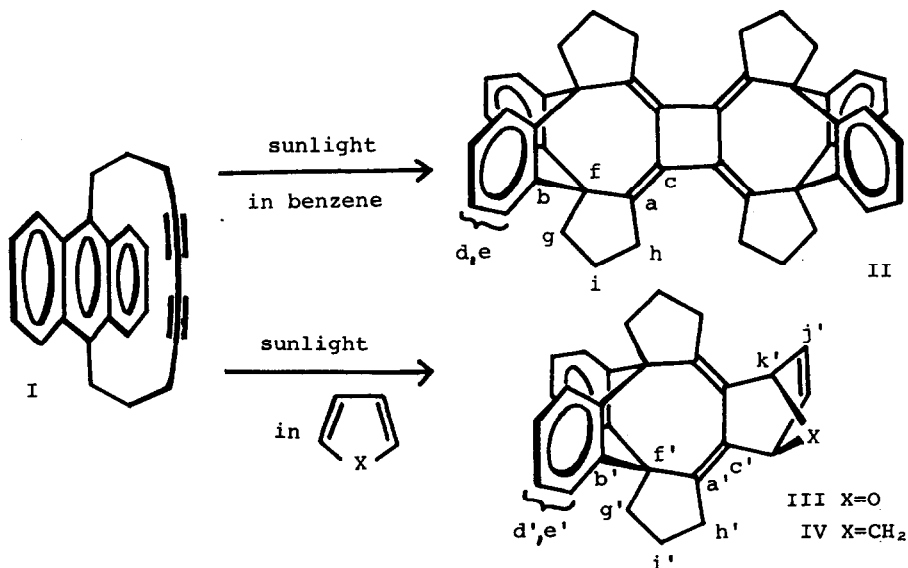


Fig. 1. Photochemical reactions of anthracenophadiyne I.

An exposure of a benzene solution of the anthracenophadiene I (light yellow prisms, 196~199°C dec.) to sunlight for 10 mins. afforded colorless photodimer II (leaflets, 270~280°C dec.) in a quantitative yield. When I in a large excess of furan or cyclopentadiene was exposed to sunlight for 30 mins., a 1:1 addition compound III (colorless plates, m.p. 207~212°C with dec.) or IV (colorless plates, m.p. 151~153°C with dec.) was obtained in a quantitative yield (Fig. 1). The cyclic compounds, II, III, and IV, were confirmed to be formulae,  $C_{18}H_{10}$ ,  $C_{28}H_{24}O$ , and  $C_{29}H_{26}$ , respectively, by elemental analyses and mass spec-

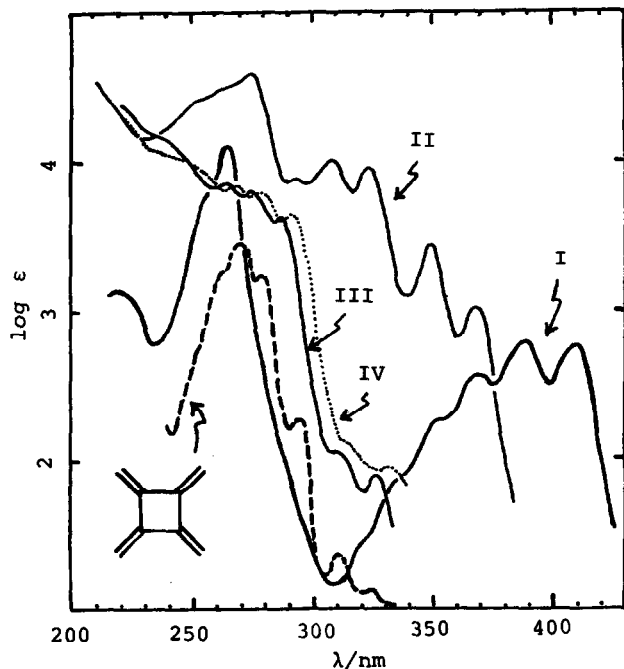


Fig. 2. Electronic spectra of I~IV in THF and of tetramethylenecyclobutane (-----, the ordinate is absorbance since exact concentration is unknown) in hexane.<sup>5)</sup>

The structure V involves a dimerization at C<sub>9</sub> and C<sub>10</sub> positions of anthracene nucleus and the structures II and VI involve dimerizations at 2,3- and 1,4-positions, respectively, of the diacetylene group with intramolecular cycloaddition.

The structure V, however, is eliminated by the lack of  $\nu_{C=C}$  due to the

tra. Their electronic spectra are shown in Fig. 2.

On the basis of the lack of anthracene chromophore in the electronic spectrum as well as the fact that the photodimer shows a simple pattern in pmr spectrum and nine separate signals in the completely decoupled <sup>13</sup>C-nmr spectrum, three structural formulae shown in Fig. 3 remain to be most reasonable ones of a number of possible structures for the photodimer. Thus, they are para-anthracene structure<sup>4)</sup> V (by path A), tetramethylenecyclobutane structure II (by path B), and cyclooctatetraene structure VI (by path C).

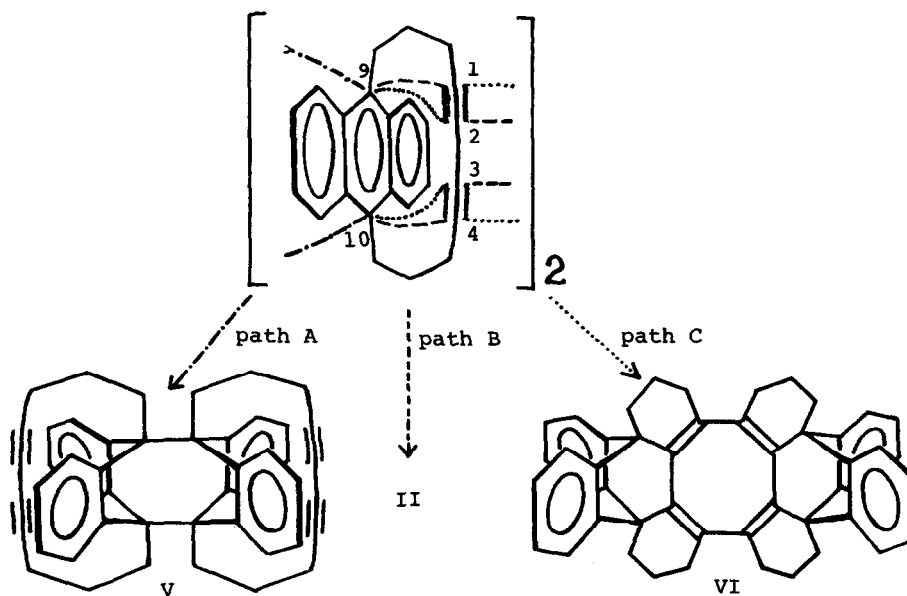


Fig. 3. Dimerization modes of anthracenophadiyne I.

diacetylene bond in the ir spectrum of the photodimer. Since the electronic spectrum of the dimer is similar to that of tetramethylenecyclobutane<sup>5)</sup> in respects of strong intensity and fine structures except red shifts of the bands and is quite different with those of cyclooctatetraene and its octamethyl derivative,<sup>6)</sup> the structure II, in the result, remains to be the most reasonable one. On the other hand, the <sup>13</sup>C-nmr spectral data also support this structure. Thus, comparing with methylene <sup>13</sup>C-chemical shifts of methylenecyclopentane ( $\alpha$  33.3 and  $\beta$  27.1 ppm)<sup>7)</sup> and cyclohexene ( $\alpha$  25.7 and  $\beta$  23.3 ppm)<sup>7)</sup>, the observed values of the corresponding methylenes (36.0 and 28.1 ppm) and the others in the photodimer are best accounted for by the structure II bearing four methylenecyclopentane moieties. [II: pmr (CDCl<sub>3</sub>, 100 MHz)  $\delta$  7.40 and 7.11 (A<sub>2</sub>B<sub>2</sub>, 16H, ArH), 2.76 (t, 8H, [CH<sub>2</sub>]<sub>g</sub>), 2.48 (t, 8H, [CH<sub>2</sub>]<sub>h</sub>), 2.10 ppm (quint., J=7 Hz, 8H, [CH<sub>2</sub>]<sub>i</sub>); <sup>13</sup>C-nmr (CDCl<sub>3</sub>, TMS) a 145.7, b 139.7, c 133.0, d 125.8, e 123.1, f 51.7, g 38.4, h 36.0, i 28.1 ppm].

The structural information of cycloaddition products III and IV was easily obtained from their pmr and <sup>13</sup>C-nmr spectra. Thus, both of these adducts show two equivalent vinyl and methine protons, respectively, in the pmr spectra,

indicating that both furan and cyclopentadiene participate as  $4\pi$ -system in the photocycloadditions. In the  $^{13}\text{C}$ -nmr spectrum of the furan adduct, the signals other than carbons a', c', j', and k' well correspond to those of the photodimer II, and the chemical shifts of a', h', and i' (150.8, 33.9, and 26.9 ppm) are comparable to the shieldings of the corresponding carbons in methylenecyclopentane (152.8, 33.3, and 27.1 ppm). [pmr ( $\text{CDCl}_3$ ) III:  $\delta$  6.18 (s, 2H, vinyl  $\text{H}_j$ ), 4.97 ppm (s, 2H, methine  $\text{H}_k$ ); IV:  $\delta$  5.95 (t,  $J=2$  Hz, 2H, vinyl  $\text{H}_j$ ), 3.18 ppm (quint.,  $J=2$  Hz, 2H, methine  $\text{H}_k$ ).  $^{13}\text{C}$ -nmr ( $\text{CDCl}_3$ , TMS) III: a' 150.8, b' 139.2, 139.5, c'd' 125.7, 125.9, 126.1 ( $J_{\text{C-H}}=160$  Hz), e' 123.0, 123.3 (150), f' 51.0, g' 38.6 (130), h' 33.9 (130), i' 26.9 (130), j' 134.9 (180), k' 82.9 ppm (170)]. From these results, the formula III is assigned to the furan adduct, and then the formula IV to the cyclopentadiene adduct which shows very similar electronic spectrum to that of the former adduct with a few nm red shift.

The formations of II and III or IV above-stated can be represented as photochemically symmetry-allowed [ $\pi 4s + \pi 2a + \pi 2a + \pi 4s + \pi 2a + \pi 2a$ ]<sup>6)</sup> and [ $\pi 4s + \pi 2a + \pi 4s + \pi 2a$ ]<sup>8)</sup> multicycloaddition reactions, respectively, providing that they proceed in concerted manner. In particular, the former is the first example of six  $\pi$ -components cycloaddition. Further studies on multicycloaddition of I with various  $\pi$ -systems are under way.

#### References

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- 8) This denotation was represented according to a notation with the following priority order: 1) largest number of electrons, 2)  $\pi > \sigma$ , 3) supra  $>$  antara.