

THE PRIMARY PHOTOCHEMICAL PROCESS OF DIPHENYLACETYLENE

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It has been known that photoirradiation of diphenylacetylene (I) in cyclohexane gives 1,2,3-triphenylnaphthalene (II) and 1,2,3-triphenylazulene (III) as main products.<sup>1)</sup> In the present paper, the mechanism of the primary photochemical process of the above-mentioned photodimerization will be investigated by means of the steady-light irradiation in cyclohexane matrix and the flash spectrophotometry. A 100 W high pressure Hg lamp (Riko Sangyo Co., Ltd., UVL-100P) was used as a light source in the steady-light irradiation in cyclohexane matrix (at -10°C), a pyrex glass being used as a filter. A Ushio UPF-101 flash spectrophotometer was used for the measurements of the transient absorption spectra, in which a flash lamp filled with xenone and a slight amount of hydrogen gas was used. The half width of the flash was 10  $\mu$  seconds with a power of 150 joule/pulse.

As shown in Fig. 1, a compound having a band at 254 nm is produced on a 303 nm light irradiation of I in glycerol. The decreases in optical densities at band maxima of I in various solvents are plotted against the

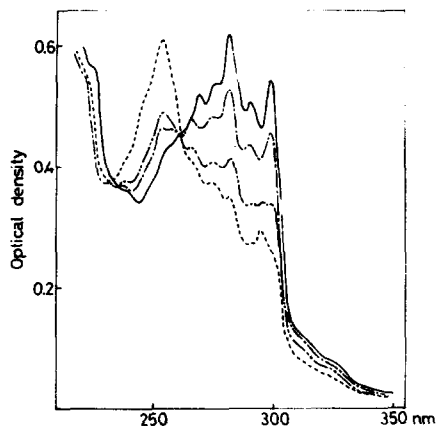


Fig. 1. The progressive spectral change of I in glycerol.  
 — 0 min. irradiation,  
 - - - 4  
 - · - · 10  
 - - - - 30

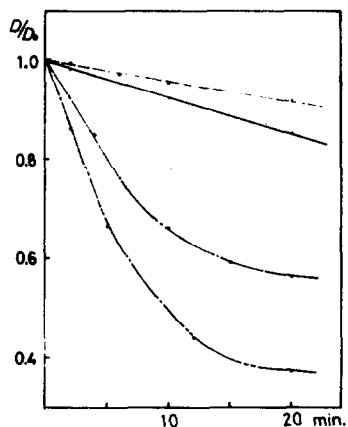


Fig. 2. Decreases in optical densities at band maxima of I in various solvents against the irradiation times.  
 $D_0$ : Optical density before the irradiation.  
 $D$ : Optical density after the irradiation.  
 - - - Cyclohexane  
 — Ethanol  
 - · - · Glycerol  
 - - - - liquid paraffine

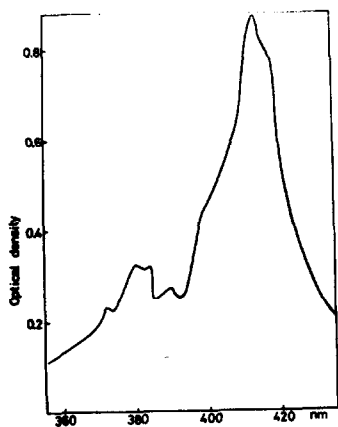


Fig. 3. The transient absorption spectrum of I in glycerol.

irradiation time (Fig. 2). The photochemical reaction of I in a viscous solvent (such as glycerol or liquid paraffine) proceeds rapidly compared

Table I. Half-life times of the triplet states in various solvents.

Solvent	Half-life time
Glycerol	267 ( $\mu$ sec.)
Ethyleneglycol	41
Ethanol	20
Cyclohexane	19

with that in a low viscosity solvent (such as ethanol or cyclohexane). However, even in cyclohexane the photochemical reaction proceeds rapidly in its matrix state around  $-10^{\circ}\text{C}$ . This means that the above photochemical reaction occurs mono molecularly. Thus, the product having the 254 nm band (Fig. 1) is expected to be an isomer of I. In order to confirm this, we carried out a preparative experiment using the cyclohexane matrix and obtained thermally unstable pale green crystals (IV). The mass spectrum of IV at  $0^{\circ}\text{C}$  (probe temperature) has a main peak at 178 (m/e). This may indicate that IV is an isomer of I. When the mass spectrum of IV is measured at  $60^{\circ}\text{C}$ , the intensity of the 178 peak decreases considerably and an intense peak appears at 356 (m/e), indicating that IV dimerizes thermally into II or III. That is, IV is considered to be an intermediate in the dimerization reaction of I to II or III. To know the detailed mechanism of the above reaction, we measured transient absorption spectra of I in various solvents. The spectrum in glycerol, for example, is shown in Fig. 3. The spectrum consists of two bands at 418 and 308 nm. Since

Table II. The calculated and observed transition energies (E) and f-values of IV.

	E(eV)		f
	Calc.	Obs.	Calc.
I	2.40	2.04	0.0657
II	3.58		0.0000
III	4.04		0.0000
IV	4.48	4.09	0.0000
V	4.50	5.02	1.0690
VI	4.93		0.0878
VII	5.29		0.3986
VIII	5.53	} 6.05	0.0000
IX	5.67		0.0000
X	5.80		0.1173
XI	5.96		0.0000
XII	6.10		0.4010
XIII	6.49		0.1948
XIV	6.62		1.1106

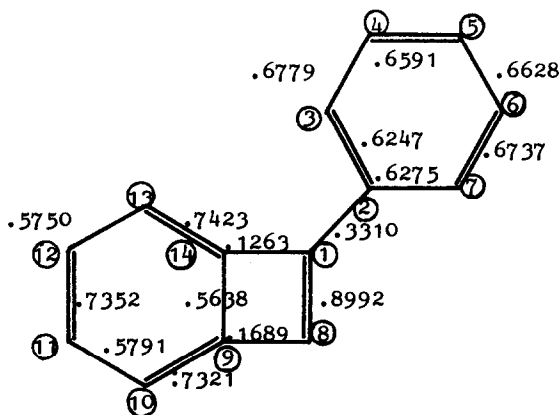
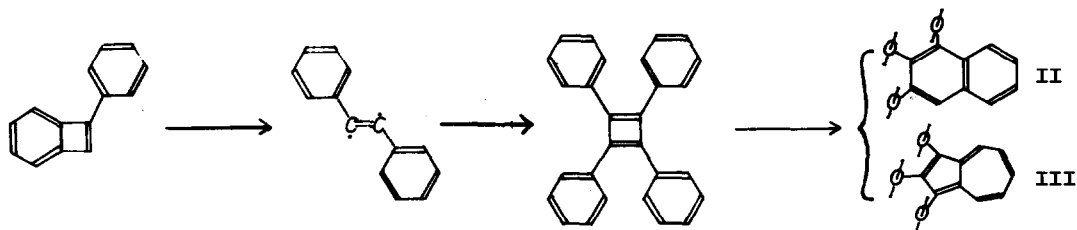


Fig. 4 The chemical structure of IV and  $\pi$ -bond orders.

half-life times measured at these wavelengths are the same, the spectrum shown in Fig. 3 may be due to one transient species. Higuchi et al.<sup>2)</sup> have measured the ESR spectrum of I and confirmed that I exists as a triplet state under the ultraviolet irradiation. Therefore, the spectrum shown in Fig. 3 is attributable to  $T_1-T_n$  transitions. The half-life times of the triplet state measured in various solvents are shown in Table I. The half-life time increases with increasing the viscosity of the solvent. This tendency corresponds well to the viscosity dependence of the rate of the reaction shown in Fig. 2. From this along with the fact that the reaction is quenched by oxygen, the reactive state of the present photochemical reaction is considered to be of a triplet. That the rate of the reaction in the low viscosity solvent is appreciably low may be due to self-quenching. Judging from the results of the PPP calculation (Table II) and of the measurements of UV and mass spectra, at present stage, the chemical structure of IV is supposed to be phenylbenzocyclobutadiene. Since the bond order of the 1-14 bond is relatively small (Fig. 4), the reaction of IV to II or III may be initiated by the 1-14 bond cleavage, and proceeds as follows.



#### References

- 1) G. Büchi, C. W. Perry, and E. W. Robb, J. Org. Chem., **27**, 4106 (1962).
- 2) J. Higuchi, T. Ito, and O. Kanehisa, Chem. Phys. Lett., **23**, 440 (1973).