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Photolysis of Organic Azides. IV.[1] Formation of *o*-Xylylene Derivatives from 2,3-Diazidonaphthalenes. Direct Observation by Low-temperature and Flash Photolysis

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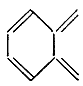
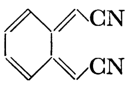
The photolysis of 2,3-diazidonaphthalene (**3a**) in a rigid matrix at 77 K gave the product having absorption bands in the 400—500 nm region, which has been assigned as α,ω-dicyano-*o*-xylylene (**2a**) by use of another precursor 1,2-dicyano-1,2-dihydrobenzocyclobutene. **2a** has been also observed by the flash photolysis of **3a** in fluid solution at room temperature, and the lifetime in methanol at 20 °C was 62 s. The dominating factor in the lability of **2a** was the rigidity of the medium rather than the temperature. The reaction mechanism for the formation of **2a** from **3a** has been proposed as a monophotonic process involving the attack of the nitreno group on the azido group at the *ortho* position. Similarly, direct observations of α,ω-dimethoxy- and α,ω-diacetoxy-α,ω-dicyano-*o*-xylylenes have been given from 1,4-dimethoxy- and 1,4-diacetoxy-2,3-diazidonaphthalenes respectively.

o-Xylylene (*o*-quinodimethane, **1**) and the wide variety of derivatives have evoked theoretical and experimental interest.[2–13] The reactive species have been proposed as intermediates in a number of reactions. In the thermal decomposition of 2,3-diazidonaphthalenes (**3**) to give 1,2-dicyano-1,2-dihydrobenzocyclobutenes (**4**), the α,ω-dicyano-*o*-xylylenes (**2**) have been considered intermediates. Flash pyrolysis in the vapor phase of **3a** has been reported to yield *trans*-1,2-dicyano-1,2-dihydrobenzocyclobutene in 55% yield,[14] and the thermolysis of **3b** in refluxing *o*-dichlorobenzene has given the *trans*- and *cis*-1,2-diacetoxy-1,2-dicyano-1,2-dihydrobenzocyclobutenes (23% and less than 3% yields, respectively),[15] possibly through the intermediate **2**.



1



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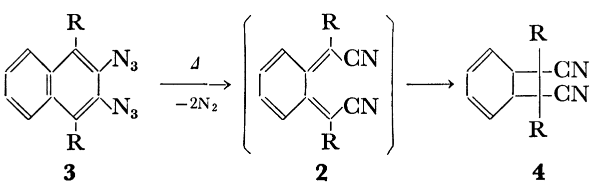


a: R=H
b: R=OCOCH$_3$
c: R=OCH$_3$

The α,ω-dicyano-*o*-xylylene (**2a**), which is a simple derivative of **1**, would itself be of interest since it has not been observed directly and there is the possibility that the dicyano substituents might stabilize the *o*-xylylene system sufficiently to allow isolation. In the course of the work on the low-temperature photochemistry of aromatic diazido compounds, the formation of **2a** was observed in the photolysis of **3a** in rigid matrices at low temperatures. The present paper reports the direct observation of **2a** by matrix isolation and flash photolysis, and the mechanism of the low-temperature photochemical reaction of **3a**, together with two derivatives 1,4-diacetoxy-2,3-diazidonaphthalene (**3b**) and 2,3-diazido-1,4-dimethoxynaphthalene (**3c**).

Results and Discussion

Low-temperature Photolysis. In the thermal reactions of **3** mentioned above, the evidence for dicyano-*o*-xylylene had been indirect, based on speculation from the final products. No study on the photolysis of 2,3-diazidonaphthalenes has been reported. The photolysis of **3a** in methanol or hexane at room temperature did not yield any trace of the expected 1,2-dicyano-1,2-dihydrobenzocyclobutenes, as distinct from the thermolysis. In view of the reactivity of *o*-xylylenes, matrix isolation and flash photolysis techniques appeared appropriate for the direct observation of **2**.

A rigid glassy solution of **3a** in EPA was irradiated at 77 K with a high-pressure mercury lamp with a Toshiba UV-D2 filter (transmission in the 300—400 nm region), and the low-temperature photochemical reaction was followed by absorption spectroscopy. With an increase in irradiation, new absorption bands in the 400—500 nm region were observed as shown in Fig. 1. The melting of the glassy solution containing the photoproduct having the new absorption bands to room temperature resulted in the disappearance of the absorption bands. The photoproduct showed strong fluorescence (λ_{max} 485 and 506 nm) similar to the parent *o*-xylylene and the spectral shape was independent of the excitation wavelength. The excitation spectrum followed the shape of the absorption band and was independent of the monitoring wavelength. Therefore, it has been suggested that all of the absorption curve, at least below 35000 cm^{-1}, belongs to one photoproduct.

On the prolonged irradiation of **3a**, the corresponding 1,2-dihydrobenzocyclobutene derivatives were not obtained, while Flynn and Michl[2] reported that upon strong irradiation the 373 nm band of the photoproduct **1** was replaced by the UV absorption spectrum of 1,2-dihydrobenzocyclobutene. After melting of the glassy solution containing the 400—500 nm bands, no azido group was detected among the reaction products while cyano groups were detected by IR spectroscopy.

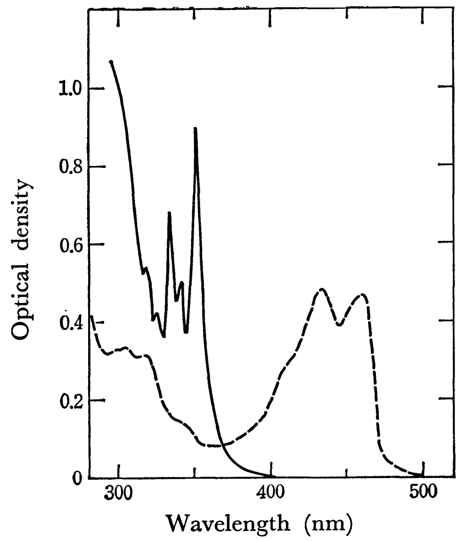


Fig. 1. Absorption spectrum of **3a** in EPA at 77 K before (——) and after (----) irradiation.

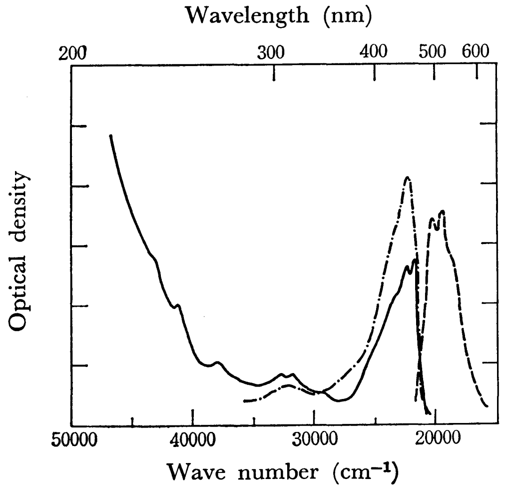
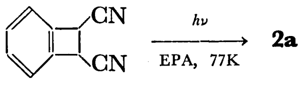


Fig. 2. Absorption (——), excitation (—·—), and emission (----) spectra of **2a** in EPA at 77 K. Excitation and emission spectra are not corrected for instrument response (arbitary scale).

The identity of **2a** for the transient absorption was shown by the photolysis of another precursor. The irradiation of *trans*-1,2-dicyano-1,2-dihydrobenzocyclobutene (**5**) with a low-pressure mercury lamp (253.7 nm) in EPA at 77 K gave a spectrum similar to that obtained in the low-temperature photolysis of **3a**.[16] Moreover, the behavior on warming to room temperature and the fluorescence spectrum were consistent with that observed for **3a**. Thus, the transient absorption has been assigned to the expected **2a**.



5

The conversion of **5** to **2a** was considerable compared with that of 1,2-dihydrobenzocyclobutene to **1**.[17] Upon irradiation of a rigid solution of **5** (10^{-4} M) in EPA at 77 K (15 W low-pressure mercury lamp), the conversion to **2a** was virtually complete after 1 h.

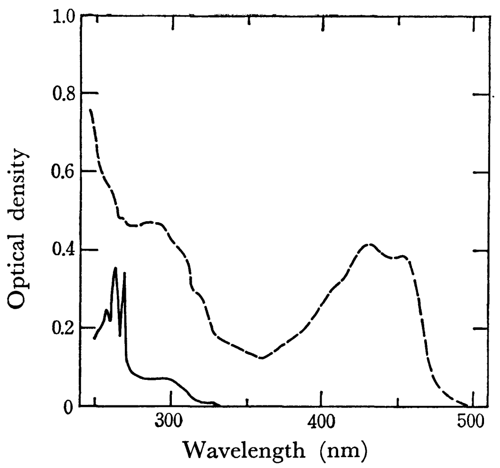
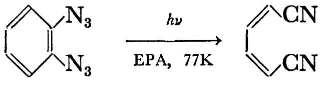


Fig. 3. Absorption spectra of **5** in EPA at 77 K before (——) and after (----) irradiation.

These results which have been attributed to the dicyano substituents are consistent with the fact that **2a** was not converted to **5** in the matrices upon continued irradiation, as mentioned previously.

The spectral shifts compared with **1** can be explained in terms of the substitution of the two cyano groups conjugated with the *o*-xylylene system. The absorption of **2a** is shifted by about 50 nm to a wavelength longer than that of the parent *o*-xylylene, which absorbs at 313—417 nm.[2] In the case of *cis,cis*-1,4-dicyano-1,3-butadiene (λ_{max} 258, 268 nm) and butadiene (λ_{max} 217 nm), a similar shift was observed.

The assignment for **2a** is further supported by the following results. Previously the formation of *cis,cis*-1,4-dicyano-1,3-butadiene (**7**) by the photolysis of 1,2-diazidobenzene (**6**) as well as the results of thermal reactions has been established,[18,19] the photolysis of **6** in a rigid matrix at 77 K being quantitative. In a low-temperature matrix **7** was not converted to cyclobutenes on prolonged irradiation, whereas the cyclization of **7** proceeded readily in fluid solution at room temperature.



6 **7**

In the case of the two derivatives **3b** and **3c**, the appearance of photoproducts could also be observed by the absorption spectra in the 400—500 nm region. Furthermore, the photoproduct from **3c** exhibited strong fluorescence in the 500—600 nm region (λ_{max} 540 nm), such as **2a**. In the low-temperature photolysis of **3b** in a rigid matrix the photolysis differed from the others. After the expected **2b** was generated as a primary photoproduct, some secondary reactions proceeded at considerable rate as shown in Fig. 4. Among the secondary photoproducts the corresponding 1,2-dihydrobenzocyclobutene derivatives (**4b**) were not detected. Details of the secondary reactions will be reported in a separate paper.

Although the stereochemical constitutions of **2** have not been unambigously established, three stereoisomers **2**(*Z*,*Z*), **2**(*E*,*E*), and **2**(*Z*,*E*) of α,ω-dicyano-*o*-xylylenes

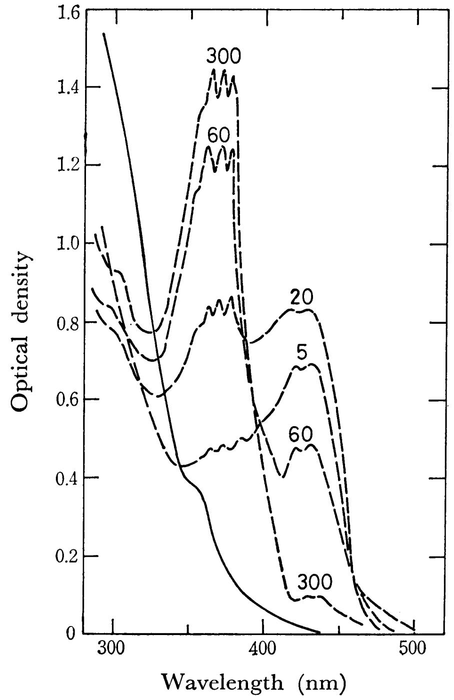


Fig. 4. Absorption spectra of **3b** in EPA at 77 K before (——) and after (----) irradiation. Numbers refer to irradiation time in second.

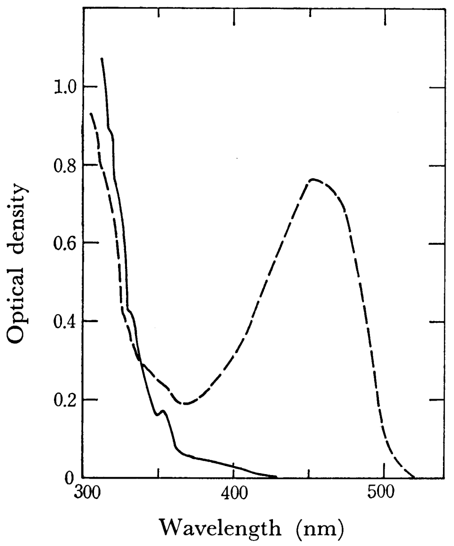
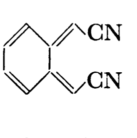
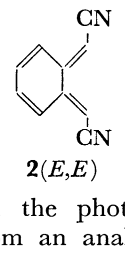


Fig. 5. Absorption spectra of **3c** in 3MP-IP (1 : 4) at 77 K before (——) and after (----) irradiation.

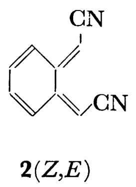
need consideration. One would predict that the



2(*Z*,*Z*)

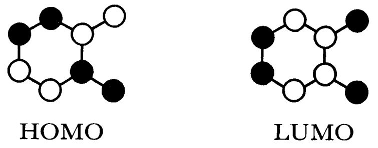


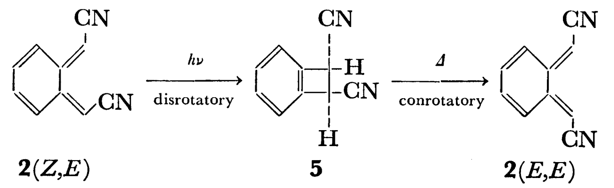
2(*E*,*E*)



2(*Z*,*E*)

isomer generated in the photolysis of **3a** was exclusively **2**(*Z*,*Z*), from an analogy to the photolysis of **6** where the photoproduct **7** was assigned as the *cis*,*cis*-isomer by comparison with an authentic sample. The isomer of **2a** generated in the photolysis of **5** is presumed to be **2**(*Z*,*E*) from a consideration of the orbital symmetry. The whole spectra of **2a** generated from **3a** and **5** are consistent with each other





as shown in Figs. 1 and 3. However, there is a slight difference observed in the longest absorption maxima, *i.e.*, the isomers generated from **3a** and **5** have absorption bands at 458 and 454 nm respectively (Table 1). This spectral shift could be explained in terms of the different configurations, as reported in the case of α,ω-diphenyl-*o*-xylylenes by Quinkert and coworkers.[9e)]

Table 1. Absorption maxima of α,ω-dicyano-*o*-xylylenes by photolysis at 77 K

Reactant	Solvent	Absorption maxima (nm) (>400 nm)
3a	EPA (5:5:2)	432, 458
	3MP-IP (1:4)	427 (broad)
5	EPA (5:5:2)	432, 454
	3MP-IP (1:4)	427 (broad)
3b	EPA (5:5:2)	425, 448
	3MP-IP (1:4)	425
3c	EPA (5:5:2)	452
	3MP-IP (1:4)	450

Temperature and Rigidity Dependence of the Stability of **2**. The dicyano-*o*-xylylenes formed in rigid matrices at 77 K are indefinitely stable under these conditions but as yet have been isolated at room temperature. In order to study the stability and the conditions for the isolation of **2a**, the photolyses of **3** were conducted in media of different viscosities at various temperatures. In the photolysis at 77 K the matrices dependence was not observed in such glassy solvents as ether–isopentane–ethanol (EPA, 5 : 5 : 2), isopentane–3-methylpentane (IP–3MP, 4 : 1, 3 : 1, 1 : 1, 1 : 3, 1 : 4), 3-methylpentane (3MP), or methylcyclohexane–isopentane (MCH–IP, 1 : 3) matrix, which showed a viscosity ranging from 10^2 to 10^{10} Pa s.[20)] Although the shape of the absorption bands in the 400—500 nm region was slightly different, the rates of formation of **2a** were virtually similar.

Figure 6 shows the absorption spectra of **3a** irradiated in 3MP–IP (1 : 4) (8 min, 500 W high-pressure mercury lamp, Toshiba UV-D2 filter, several temperatures). At 100 K, although the spectral shape was considerably different from that generated at 77 K, the concentration of **2a** was deduced to be 60—70% compared with that generated at 77 K. At 170 K, **2a** was no longer detect-

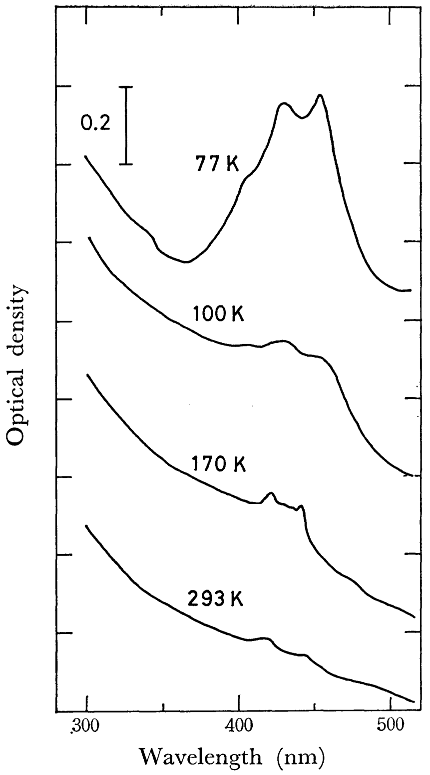


Fig. 6. Absorption spectra of the photoproducts of **3a** in 3MP-IP (1 : 4) by irradiation at several temperatures.

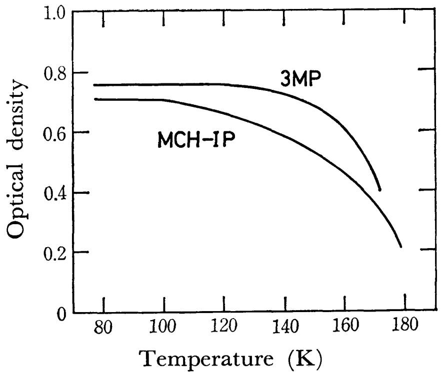


Fig. 7. Change in the absorbance at 432 nm of **2a** with temperature. Temperature-rise time : *ca.* 5 min (77—110 K) and *ca.* 4 min (110—180 K).

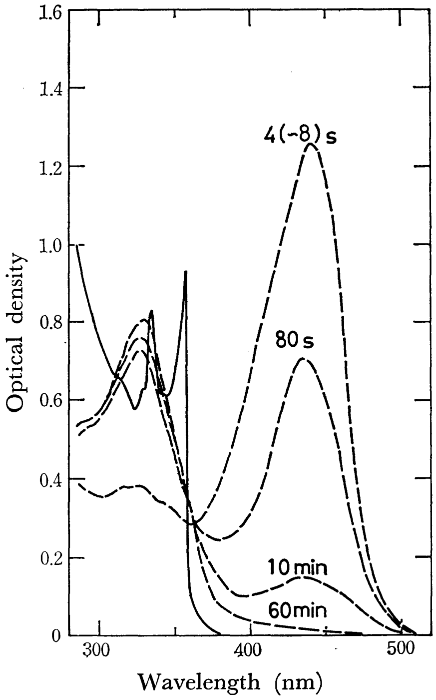


Fig. 8. Absorption spectra of **3a** in methanol at 20 °C before (——) and after (----) flash photolysis.

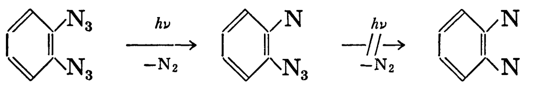
able by fluorescence spectroscopy and therefore the small peaks of the absorption spectra at 170 and 293 K in the 400—500 nm region are not ascribable to **2a**.

The photolysis of **3a** in a glycerol matrix at 180 K (viscosity; 10^{12} Pa s[20]) gave **2a** quantitatively and it was indefinitely stable in this medium. Figure 7 shows the libility of **2a** plotted against the rise in temperature. The change in the absorbance of **2a**, formed by the photolysis in rigid matrices (3MP and MCH–IP) at 77 K, was monitored at 432 nm with an increase in temperature allowing the matrices to grow warmer. The difference in lability of **2a** on 3MP and MCH–IP (1 : 3) matrices may be explained in terms of the rigidity of the medium, since the former had a higher viscosity than the latter (3MP : 9.4×10^{10} Pa s at 77 K, 3.0×10^{9} Pa s at 87 K; MCH–IP : 1×10^{2} Pa s at 89.5 K).[20] The appreciable decrease in absorbance began at 100 K in MCH–IP and at 120 K in 3MP, and the viscosities at these temperatures were estimated to be about 1 Pa s in both media from the literature.[21] Thus, it has been concluded that the rigidity of the medium is a dominating factor for the isolation of **2a**.

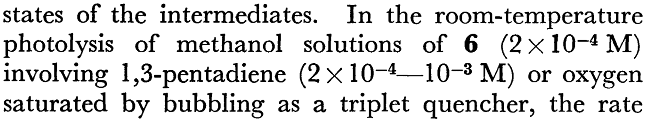
Flash Photolysis. Flash photolysis showed the presence of **2** in fluid solution at room temperature. The absorption spectra of **3a** (4×10^{-5} M) in methanol after flash photolysis at 293 K are shown in Fig. 8. These spectra are consistent with those obtained by low-temperature photolysis although the fine structures have disappeared. The lifetimes of **2a** and **2c** in methanol at 293 K were 62 s (monitored at 432 nm) and 33 s (monitored at 455 nm) respectively. The final photoproducts by room-temperature photolysis were not 1,2-dicyano-1,2-dihydrobenzocyclobutenes as reported above, and the decay of **2a** did not exhibit first-order kinetics. A detailed description of the kinetic study of **2** will be presented in a separate paper together with the reactivity of **2**. The decay of **2b** after the flash photolysis of **3b** was complicated, and the monitoring of the transient (**2b**) was difficult since the absorption bands of the secondary photoproducts interfered with those of **2b**.

Reaction Mechanism. Although the photochemistry of azido compounds has been the subject of considerable interest, little is known about the photochemical reactions of vicinal diazido compounds. In the photolysis of **3** which results in the formation of **2**, it is of interest to examine whether the two neighboring azido groups participate with each other, whether the two azido groups are decomposed by a single quantum or the photolysis proceeds in two separate steps, and whether the mononitrene and/or the dinitrene are included as intermediates. The low-temperature reaction mechanism of **3** has been investigated by a comparison with the preliminary results of 1,2-diazidobenzene.[18]

The photolysis of **6** in a rigid matrix at 77 K yielded 1,4-dicyano-1,3-butadiene (**7**) in one step, *i.e.* no intermediate was observed in the process from **6** to **7** by the absorption spectra. The spectral change by irradiation at low temperature was quite similar to that in the fluid solution at room temperature. Moreover, the dependence of the formation rate of **7** on the incident-light intensity showed a monophotonic process. These results exclude the following reaction mechanism which is a biphotonic process involving the stepwise loss of nitrogen. This is distinct from the mechanism which is a biphotonic process involving the mononitrene and the dinitrene as in the case of 1,4-diazidobenzene.[22,23]



The possibility that the two azido groups were simultaneously decomposed by a single photon was excluded by comparison with the results of 1,4-diazidobenzene[22,23] and 2,2′-diazidobiphenyls.[24] Only one of the two azido groups was decomposed by a single photon. It is well known that nitreno groups located *ortho* to groups with α,β-unsaturation undergo cyclization to give five-membered hetero cyclic rings, as observed in the decompositions of 2-azidonitrobenzene[25] and o,o'-diazidoazobenzene.[26,27] Thus, the intermediate such as **9** appears to be the result of nitreno groups on azido groups. The intermediate **9** would be readily converted to **7** *via* **10** at room temperature or 77 K by the consecutive homolytic cleavage of the nitrogen–nitrogen bonds and the carbon–carbon bond in a nonphotonic process, since the elimination of nitrogen from **9** is exothermic.[28]



An attempt has been made to establish the spin states of the intermediates. In the room-temperature photolysis of methanol solutions of **6** (2×10^{-4} M) involving 1,3-pentadiene (2×10^{-4}—10^{-3} M) or oxygen saturated by bubbling as a triplet quencher, the rate of formation of **7** was not affected. Hence, it may be considered that the azidonitrene **8** is produced in the singlet state from the excited singlet **6**, as reported in the direct photolysis of phenyl azide.[29,30] However, it is still uncertain that the participation of triplet states is excluded, since each process in the formation of **7** from **6** might be much faster than the energy transfer, and since the photochemical reaction from **6** to **7** occurs by triplet sensitization. Moreover, it is possible that the actual precursor of **9** is the triplet **8**, although it may be transferred from the singlet **8** by intersystem crossing. The multiplicity of the diradical (**10**) which was produced by nitrogen elimination would be the singlet state, since the energy required to break the carbon–carbon bond of **10** would be lost if the triplet nitrogen, which is 590 kJ/mol above the ground state, were produced by the decomposition of **9**. That is to say, since the elimination of nitrogen in the singlet ground state is an energetically favored process, **10** must be produced in the singlet state from the spin conservation rule.

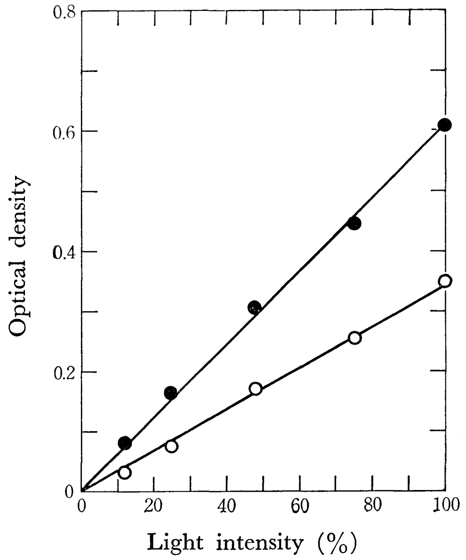
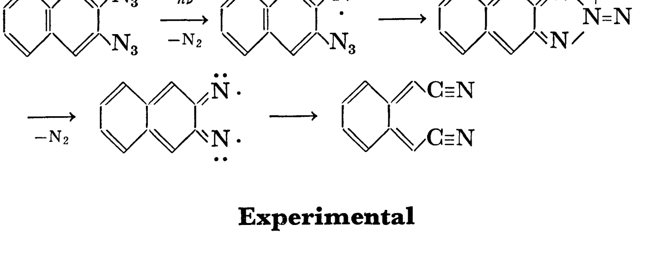


Fig. 9. Dependence of the formation rates of **2a** (○) and **2c** (●) on the light intensity by the photolyses of **3a** and **3c** in 3MP-IP (1 : 4), respectively. The yields of **2a** and **2c** correspond the optical densities at 432 and 452 nm respectively.

The preceding mechanism for 1,2-diazidobenzene may be adapted to the photolysis of **3** in rigid matrices at low-temperature and in fluid solutions at room temperature. In the photolysis of **3** in a rigid matrix at 77 K, no intermediate was observed by absorption spectroscopy. The dependence of the formation rates of **2a** and **2c** on the light intensity is shown in Fig. 9 and as good linearity was obtained in the both cases, it was concluded that the formation of **2** from **3** was a monophotonic process similar to that for **7** from **6**. In an attempt to establish the spin state, the flash photolysis of the solutions of **3** involving 1,3-pentadiene or oxygen were studied. The absorbance belonging to the formed **2**, that is, the yield of **2**, was not affected. Although the spin states of the intermediates were not established by this quenching experiment alone, the pathway from **3** to **2** will be given below.



Experimental

IR and UV absorption spectra were recorded on JASCO IR-S and Shimadzu UV-300 spectrophotometers respectively.

Fluorescence and excitation spectra were recorded on a Hitachi MPF-1 spectrophotometer. In the above measurements, optical densities were uncorrected for volume contraction accompanied by the variation in temperature. NMR spectra were recorded on a Hitachi R-24A spectrometer at 60 MHz using TMS as an internal standard. Mass spectra were recorded on a Shimadzu GCMS-9000 spectrometer. The microanalyses were performed at the Institute of Physical and Chemical Research.

Materials. *2,3-Diazidonaphthalene (**3a**)*,[14] *1,4-diacetoxy-2,3-diazidonaphthalene (**3b**)*,[15] *1,2-diazidobenzene (**6**)*,[19b] and trans-*1,2-dicyano-1,2-dihydrobenzocyclobutene (**5**)*[14] were prepared according to the literature. The crude materials were purified by column chromatography on silica gel and recrystallized.

*2,3-Diazido-1,4-dimethoxynaphthalene (**3c**)* : **3c** was prepared from 2,3-diazido-1,4-naphthoquinone[15] through 2,3-diazido-1,4-naphthalenediol, which was not isolated. A solution of sodium dithionite (12 g; 0.069 mol) in water (20 ml) was added to a well-stirred suspension of the quinone (8 g; 0.033 mol) in ether (200 ml) and methanol (50 ml) at room temperature under an atmosphere of nitrogen. The mixture was vigorously stirred until the color stopped fading after about 30 min. The organic layer containing the 1,4-naphthalenediol was separated and the aqueous layer washed quickly several times with ether. The combined organic layers were then cooled in an ice bath and the cooled solution added dropwise to a cooled ether solution containing diazomethane (about 3 g) prepared from *p*-tolylsulfonylmethylnitrosamide (21.5 g). The reaction mixture was stirred for 1 h in an ice bath and for 1 h at ambient temperature. The solvent was evaporated under vacuum to afford purple crystallites, which were purified by column chromatography on silica gel. Elution with petroleum ether–ether (9 : 1) gave 2.4 g (26.9%) of **3c**: mp 54—55 °C; $\mathrm{UV_{max}}$ (CH_3OH) 300 sh, 260 nm (ε 49000); IR(KBr) 2130 $\mathrm{cm^{-1}}$ (N_3); NMR ($CDCl_3$) δ=8.2—7.3 (m, 4H, aromatic), 3.95 (s, 6H, OCH_3); MS, *m/e* 270 (M^+), 242 ($M-N_2$), 220, 214($M-2N_2$), 199. Found : C, 53.79; H, 3.75; N, 30.03%. Calcd for $C_{12}H_{10}N_6O_2$: C, 53.33; H, 3.73; N, 31.10%.

The solvents used in the spectroscopic study and in the low-temperature photolysis were dried over sodium wire or a molecular sieve and finally passed through a column of alumina.

Irradiation at Low-temperatures. The light sources were an Ushio USH-500D 500 W high-pressure mercury lamp equipped with a Nikon G-250 monochromator and a Toshiba GL-15 15 W low-pressure mercury lamp. The quartz cells of 10 mm path length were immersed in a quartz Dewar vessel equipped with optical windows containing liquid nitrogen and used for absorption and emission spectroscopy at 77 K. Instead of the quartz Dewar vessel, an Oxford Instrument DN-704 liquid nitrogen cryostat was used for spectroscopy at variable low-temperatures. It was equipped with an Oxford Instrument DTC-2 digital temperature controller, and temperatures in the range from 77 K to room temperature could be controlled and measured by a cryogenic linear temperature sensor and carbon resistor.

Flash Photolysis. All flash measurements were made using cylindrical, jacketed quartz cells of 10 cm path length and 25 ml capacity. The flash photolysis system consisted of an Applied Photophysics K-10 flash equipment, a M-300 monochromator, and a Textronix T-912 storage oscilloscope. The two 12 cm length flash lamps fitted in the K-10 equipment are rated at a maximum energy of 1000 J, corresponding to a maximum charged voltage of 22.4 kV. In these experiments, the lamps were discharged at 20 kV and had a half-life of 10 μs. The absorbance and the decay of the transients were followed quantitatively by monitoring the transmittance of the light with the oscilloscope through the monochromator from a tungsten iodine lamp (Osram A 1/125, 12 V/100 W). The absorption spectra of the transient **2a** generated by the flash photolysis of **3a** were recorded on the Shimadzu UV-300 spectrophotometer, after the cell was immediately transferred from the flash cavity to the sample bench of the spectrophotometer (Fig. 8).

References

1) Part III : A. Yabe and K. Honda, *Chem. Lett.*, **1976**, 827.

2) a) C. R. Flynn and J. Michl, *J. Am. Chem. Soc.*, **95**, 5802 (1973); b) C. R. Flynn and J. Michl, *ibid.*, **96**, 3280 (1974), and references cited therein.

3) K. L. Tseng and J. Michl, *J. Am. Chem. Soc.*, **99**, 4840 (1977).

4) N. C. Baird, *J. Am. Chem. Soc.*, **94**, 4941 (1972).

5) E. Migirdicyan and J. Baudet, *J. Am. Chem. Soc.*, **97**, 7400 (1975).

6) J. J. McCullough and A. J. Yarwood, *J. Chem. Soc., Chem. Commun.*, **1975**, 485.

7) R. D. Miller, J. Kolc, and J. Michl, *J. Am. Chem. Soc.*, **98**, 8510 (1976).

8) W. R. Dolbier, Jr., K. Matsui, J. Michl, and D. V. Horák, *J. Am. Chem. Soc.*, **99**, 3876 (1977).

9) a) G. Quinkert, K. Opitz, W.-W. Wiersdorff, and J. Weinlich, *Tetrahedron Lett.*, **1963**, 1863; b) G. Quinkert, K. Opitz, W.-W. Wiersdorff, and M. Finke, *ibid.*, **1965**, 3009; c) G. Quinkert, W.-W. Wiersdorff, M. Finke, K. Opitz, and F.-G. von der Haar, *Chem. Ber.*, **101**, 2302 (1968); d) G. Quinkert, M. Finke, J. Palmowski, and W.-W. Wiersdorff, *Mol. Photochem.*, **1**, 433 (1969); e) K. H. Grellmann, J. Palmowski, and G. Quinkert, *Angew. Chem.*, **83**, 209 (1971); f) G. Quinkert, J. Palmowski, H.-P. Lorenz, W.-W. Wiersdorff, and M. Finke, *ibid.*, **83**, 210 (1971).

10) a) M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **79**, 1701, (1957); b) M. P. Cava and A. A. Deana, *ibid.*, **81**, 4266 (1959); c) M. P. Cava, A. A. Deana, and K. Muth, *ibid.*, **81**, 6458 (1958); d) M. P. Cava, M. J. Mitchell, and A. A. Deana, *J. Org. Chem.*, **25**, 1481 (1960).

11) L. A. Errede, *J. Am. Chem. Soc.*, **83**, 949 (1961).

12) J. R. du Manoir, J. F. King, and R. R. Fraser, *J. Chem. Soc., Chem. Commun.*, **1972**, 541.

13) a) K. K. de Fonseka, J. J. McCullough, and A. J. Yarwood, *J. Chem. Soc., Chem. Commun.*, **1977**, 721; b) K. K. de Fonseka, C. Manning, J. J. McCullough, and A. J. Yarwood, *J. Am. Chem. Soc.*, **99**, 8257 (1977).

14) M. E. Peek, C. W. Rees, and R. C. Storr, *J. Chem. Soc., Chem. Commun.*, **1974**, 1260.

15) D. S. Pearce, M.-S. Lee, and W. Moore, *J. Org. Chem.*, **39**, 1362 (1974).

16) *cis*-1,2-Dicyano-1,2-dihydrobenzocyclobutene was not available by literature method (Ref. 14), although it is an important precursor for the elucidation of the configurational isomers of **2a**.

17) Flynn and Michl (Ref. 2) reported that 2.9×10^{-2} M 1,2-dihydrobenzocyclobutene solution in EPA was converted to **1** in 2% yield after irradiation for 3 h. Quinkert and coworkers (Ref. 9d) reported that the matrix photolysis of 1,2-dihydrobenzocyclobutene proceeded with no reaction.

18) Presented in part at the 32nd National Meeting of the Chemical Society of Japan, Tokyo, April 1975, 3A16.

19) a) J. H. Hall, *J. Am. Chem. Soc.*, **87**, 1147 (1965); b) J. H. Hall and E. Patterson, *ibid.*, **89**, 5856, 1967.

20) W, G. Herkstroeten, "Creation and Detection of

the Excited State," ed by A. A. Lamola, Marcel Dekker, New York, N. Y. (1971), p. 43.

21) H. Geenspan and E. Fischer, *J. Phys. Chem.*, **69**, 2466 (1965).

22) a) A. Reiser, H. M. Wagner, R. Marley, and G. Bowes, *Trans. Faraday Soc.*, **63**, 2403 (1967); b) A. Reiser and R. Marley, *ibid.*, **64**, 1806 (1968).

23) a) B. Singh and J. S. Brinen, *J. Am. Chem. Soc.*, **93**, 540 (1971); b) J. S. Brinen and B. Singh, *ibid.*, **93**, 6623 (1971).

24) a) A. Yabe and K. Honda, *Tetrahedron Lett.*, **1975**, 1079; b) A. Yabe and K. Honda, *Bull. Chem. Soc. Jpn.*, **49**, 2495 (1976).

25) T. F. Fagley, J. R. Sutter, and R. L. Oglukian, *J. Am. Chem. Soc.*, **78**, 5567 (1956).

26) R. A. Carboni and J. E. Castle, *J. Am. Chem. Soc.*, **84**, 2453 (1962).

27) J. H. Hall, J. G. Stephanie, and D. K. Nordstrom, *J. Org. Chem.*, **33**, 2951 (1968).

28) C. D. Campbell and C. W. Rees, *J. Chem. Soc., C*, **1969**, 742.

29) A. Reiser and L. J. Leyshon, *J. Am. Chem. Soc.*, **93**, 4051 (1971).

30) M. Sumitani, S. Nagakura, and K. Yoshihara, *Bull. Chem. Soc. Jpn.*, **49**, 2995 (1976).