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Photochemistry of 2*H*-Azirine—Formation of Nitrile Ylide Evidenced by Laser Flash Photolysis and Pulse Radiolysis—

Ikuo Naito,* Hideaki Morihara, Akito Ishida,† Setsuo Takamuku,†
Kazuaki Isomura,†† and Hiroshi Taniguchi††
Department of Photography, Kyushu Sangyo University, Matsugadai,
Higashi-ku, Fukuoka 813
† The Institute of Scientific and Industrial Research, Osaka University,
Mihogaoka, Ibaraki, Osaka 567
†† Faculty of Engineering, Kyushu University, Hakozaki,
Higashi-ku, Fukuoka 812
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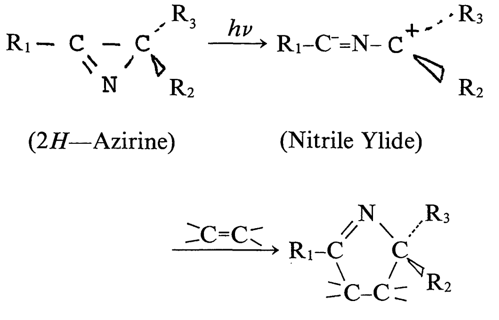
Laser flash photolysis of 3-(4-biphenylyl)-2*H*-azirine (AZ) was carried out in cyclohexane for the direct detection of a nitrile ylide (NY). Two kinds of transient species, triplet AZ (T_1) and NY, have been measured. Decay rates of these species were determined to be $6.7\times10^5\ s^{-1}$ (T_1) and $8\times10\ s^{-1}$ (NY). The rate constants for the reactions of NY toward acetone and acrylonitrile were determined to be $2.5\times10^3\ dm^3\ mol^{-1}\ s^{-1}$ and $2.3\times10^6\ dm^3\ mol^{-1}\ s^{-1}$, respectively. These results were supported by the results of pulse radiolysis of AZ in benzene and stational irradiations of AZ.

Nitrile ylide (NY) is an important reaction intermediate for the synthesis of heterocyclic compounds. This species is one of a group of 1,3-dipoles and is highly reactive toward a wide variety of dipolarophiles such as olefins, ketones, and esters. Various dehydrohalogenation reactions of imidoyl chloride deviatives to yield this species have initially been investigated by Husgen.[1)] Padwa[2)] and Schmid[3)] have independently shown that 2*H*-azirine undergoes facile ring opening on photoirradiation to give NY which reacts with olefins to give 3,4-dihydropyrrole (Eq. 1).



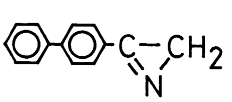
(1)

The NY thus formed was originally detected by the photoirradiation of arylazirine in a rigid matrix at 77 K by Schmid and coworkers.[4)] However, the reaction dynamics of NY were not clarified because of the experimental limitations of stational photoirradiation at low temperature.

Recently, NY produced by the addition reaction of carbenes with nitriles was studied throughly by using a laser flash technique.[5)] Scaiano and co-workers reported that the reaction rate constants of the intermediate, which was produced by the addition reaction of 1-naphtylcarbene and acetonitrile with acrylonitrile and diethylfumalate were similar to the values obtained for the 1,3-dipolar addition of NY.[6)]

Currently the laser flash photolysis of 2*H*-azirine is the most powerful method to study the charactristics and reactivities of NY. Padwa and co-workers carried out the laser flash photolysis of 2,2- and 2,3-diphenyl-2*H*-azirine.[7)] They reported the absorption spectra of NY and the existence of a new complex in the 1,3-dipolar addition reaction. Unfortunately, the profiles of the 2*H*-azirine photoreactions have not been clarified.

Biphenyl compounds are activated by 308 nm irradiation. The transient species formed to excite is expected to be stabilized by the large chromophor and also to be assigned easily. In this study, we carried out the 308 nm laser flash photolysis and a pulse radiolysis of a 2*H*-azirine derivatives substituted at the 3-position with a biphenyl group, 3-(4-biphenylyl)-2*H*-azirine (AZ, R_1=4-biphenylyl, R_2=R_3=H), to elucidate the reaction mechanism for the formation of NY. The stational photoirradiation of AZ was also carried out in order to obtain further experimental support of the mechanism.



[3-(4-Biphenylyl)-2*H*-azirine, AZ]

Results and Discussion

1. Transient Species. Laser flash photolysis of AZ was carried out in argon-saturated cyclohexane ([AZ]=$1.0\times10^{-3}\ mol\ dm^{-3}$). Figure 1 shows the transient absorption spectra recored at various times after the flash and decay traces monitored at 410 nm. The traces indicate the presence of two kinds of transient species with different lifetimes which are indicated as **A** (short-lived) and **B** (long-lived) in Fig. 1 (Eq. 2) in the laser flash photolysis of 2,2-diphenyl-3-methyl-2*H*-azirine reported by Padwa and co-workers.[7)] The decay

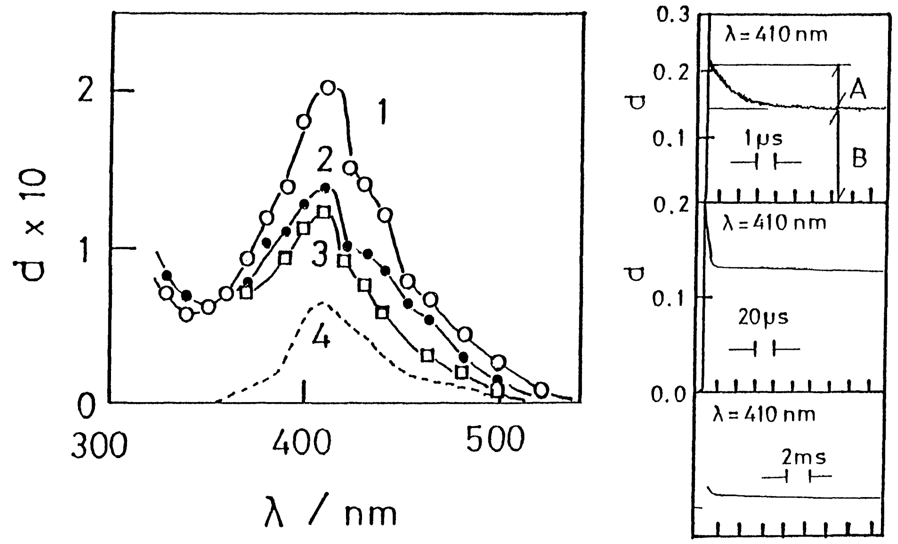


Fig. 1. Transient absorption spectra and the decay traces. Recorded at 0.1 (1), 6 (2), and 160 μs (3) after the flash. Dotted line shows the difference spectrum (1—2). [AZ]=1.0×10^{-3} mol dm^{-3} in cyclohexane.

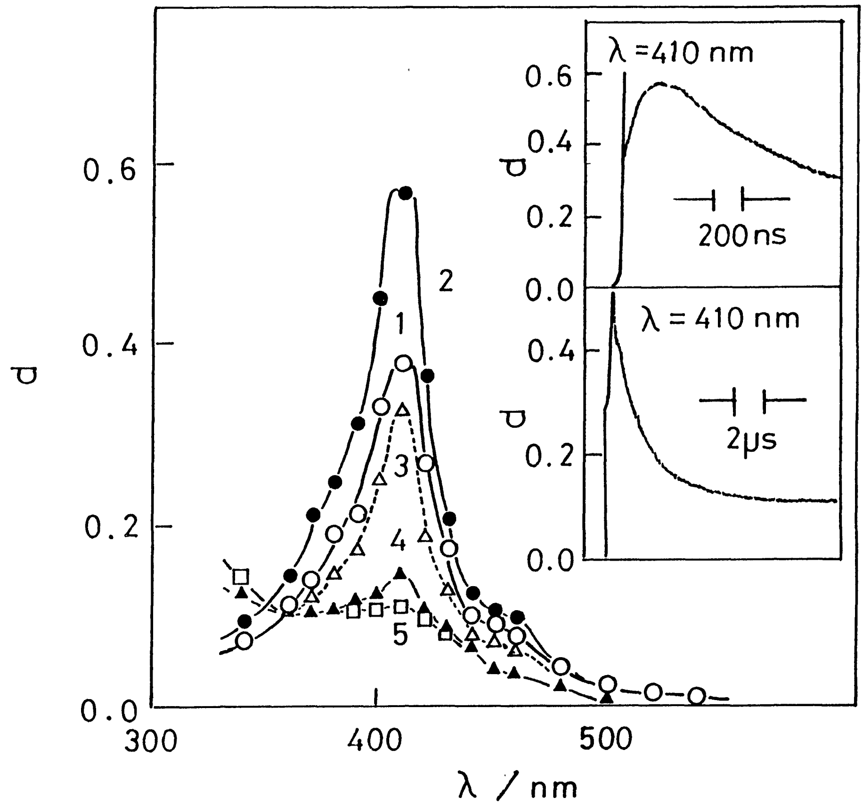


Fig. 2. Transient absorption spectra and digitizer traces measured in the laser flash photolysis of AZ in the presence of acetone. Recorded at 0.1 (1), 0.35 (2), 1.64 (3), and 6 μs (4) after the flash. [AZ]=1.0×10^{-3} mol dm^{-3}, [Acetone]=0.5 mol dm^{-3} in cyclohexane.

of these species follows first-order kinetics and the rate constants for **A** and **B** are 6.7×10^5 s^{-1} and 8×10 s^{-1}, respectively. The absorption spectrum of **A** is exhibited by the difference spectrum as shown by a dotted line in Fig. 1 and is similar to that of **B** (spectra 2 and 3). Both have an absorption maximum around 410 nm. In the presence of oxygen, **A** was quenched whereas **B** was not affected. Thus, it was obvious that **A** was not a precursor of **B** and they were produced simultaneously.

$$\mathrm{AZ}\ \xrightarrow[\text{Ar-saturated cyclohexane}]{h\nu}\ \begin{matrix}\text{Short-lived}\\ \text{Species }(\mathbf{A})\end{matrix} + \begin{matrix}\text{Long-lived}\\ \text{Species }(\mathbf{B})\end{matrix} \qquad (2)$$

2. Effect of Acetone. The laser flash photolysis of AZ was also carried out in the presence of acetone as a triplet sensitizer in cyclohexane. The result are shown in Figs. 2 and 3. Since triplet acetone does not absorb light with wavelengths longer than λ=320 nm,[8] the signals measured are due to the transient species of AZ or the reaction intermediates. The rise of the transient species with a $\lambda_{\max}$ at 410 nm was observed at acetone concentrations higher than 0.2 mol dm^{-3}. The yield of **A** increased with increasing acetone concentration (Fig. 3a). On the other hand, the decay rate of **A** (k=7.3×10^5 s^{-1}) was independent of the acetone concentration and was identical to the value obtained by the direct photolysis of AZ. The decay rate of **B** increased with increasing acetone concentration. Based on the linear plots in Fig. 3b, the rate constant for the reaction between **B** and acetone was calculated to be 2.5×10^3 dm^3 mol^{-1} s^{-1}. Since NY reacts with acetone to give 3-oxazoline,[9] species **B** was believed to be NY (Eq. 3).

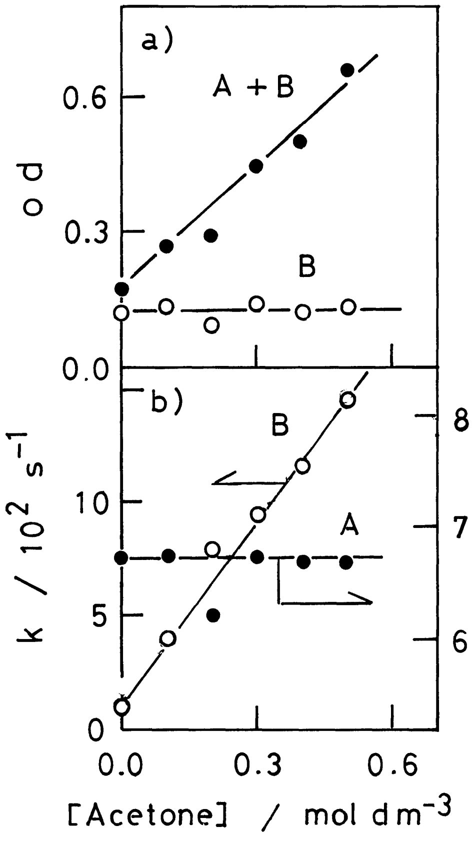


Fig. 3. Effect of acetone on the transient species absorbance (a) and decay rate (b) of the short-lived species (**A**) and the long-lived species (**B**).

$$\mathbf{B} + \text{acetone} \longrightarrow \begin{matrix}\text{Adducts}\\ (\text{3-Oxazoline ?})\end{matrix} \qquad (3)$$

3. Effect of Acrylonitrile. NY was reported to react with an electron-deficient olefin such as acrylonitrile (AN).[10] The laser flash photolysis of AZ was, therefore, carried out in the presence of AN and oxygen. The initial absorbance of **B** was not affected by the AN. The decay rate of **B** increased with increasing AN concentration, as shown in Fig. 4. The rate constant was determined to be 2.3×10^6 dm^3 mol^{-1} s^{-1}. The stational irradiation of AZ in the presence of AN gave 5-(4-biphenylyl)-3-cyano-3,4-dihydro-2*H*-pyrrole quantitatively. As a result, it was concluded that **B** can be assigned to NY.

4. Pulse Radiolysis of AZ. Pulse radiolysis in bensene is an excellent method to give the triplet state of the solute.[11] The pulse radiolysis of AZ was carried out in benzene to study triplet AZ and its reactivity ([AZ]=1.0×10^{-2} mol dm^{-3}). The transient species measured immediately after the pulse had a $\lambda_{\max}$ around 415 nm. This band decayed exponentially to zero with a decay rate constant of 6.7×10^5 s^{-1} which was consistent with that of species **A** in the direct photolysis reaction. This species was quenched by oxygen; k=6×10^9 dm^3 mol^{-1} s^{-1}.[12] From these results, **A** was concluded to be triplet AZ, although there were a few possibilities that other species, e. g. a radical anion, were formed by the electron pulse.

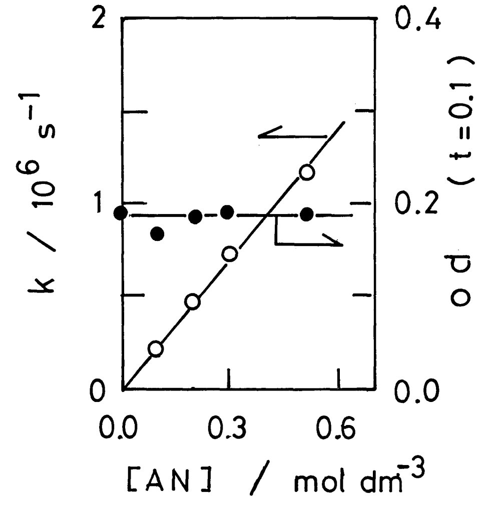


Fig. 4. Effect of AN on the long-lived species [decay rate and absorbance at 0.1 µs after the flash]. The laser flash photolyses were carried out in the presence of oxygen in cyclohexane.

In order to confirm the formation of triplet AZ, the pulse radiolysis of AZ was carried out in the presence of benzophenone (BP) ([AZ]=1.0×10^{-3} mol dm^{-3}, [BP]=2.0×10^{-2} mol dm^{-3} in benzene). Figure 5 shows the time-resolved absorption spectra obtained in this reaction. Immediately after the pulse, an absorption band with a λ_{max} at 530 nm, which was assigned to triplet BP,[13] was measured. The 530 nm band according to pseudo first-order kinetics (3.3×10^6 s^{-1}) with the simultaneous formation of a 420 nm band. The spectra measured at 460 ns after the pulse (spectrum 5 in Fig. 4), is similar to A. The rate of the latter band formation (4×10^6 s^{-1}) agrees well with that of the decay of the 530 nm band. Therefore, it was concluded that species A was the triplet state of AZ and was formed by energy transfer from triplet BP (Eq. 4). An ε_{max} value of triplet AZ was estimated to be 3.8×10^5 dm^2 mol^{-1} by means of the ε_{max} value of triplet BP.[13]

$$^3BP^* + AZ \longrightarrow BP + {}^3AZ^* \qquad (4)$$

5. Stational Photoirradiation. In order to obtain information on the reaction products, the stational photoirradiation of AZ was carried out in cyclohexane. A dimer, 4,5-di(4-biphenylyl)-1,3-diazabicyclo[3,1,0]-hex-3-ene (**C**) was obtained in a good yield (83%, Eq. 5). In the presence of AN (0.5 mol), 5-(4-biphenylyl)-3-cyano-3,4-dihydro-2*H*-pyrrole (**D**) was formed almost quantitatively (89%) along with an AN-polymer (Eq. 6). These compounds were produced by the 1,3-dipolar addition of NY with AZ or AN as reported by Padwa and co-workers.[10]

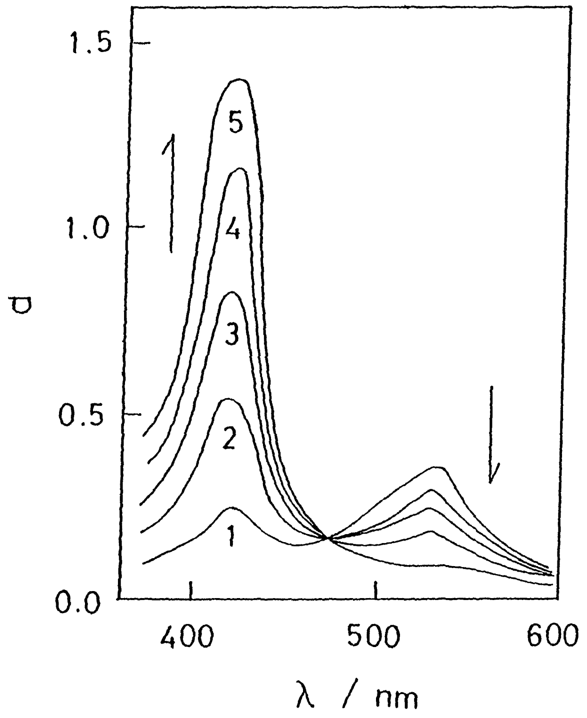
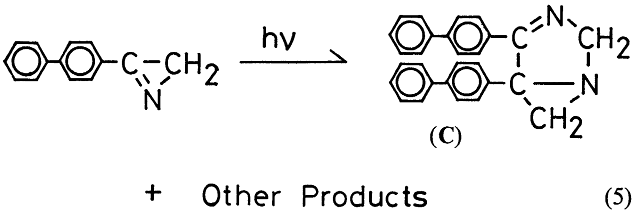


Fig. 5. Time-resolved absorption spectra measured in the pulse radiolysis of AZ in the presence of BP in benzene. Recorded at 10 (1), 50 (2), 100 (3), 200 (4), and 460 ns (5) after the pulse. [AZ]=1.0×10^{-3} mol dm^{-3}, [BP]=2.0×10^{-2} mol dm^{-3} in benzene.



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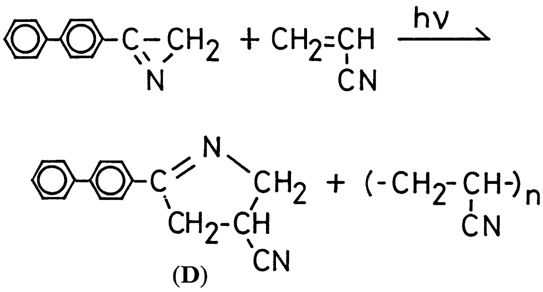

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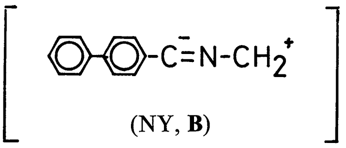
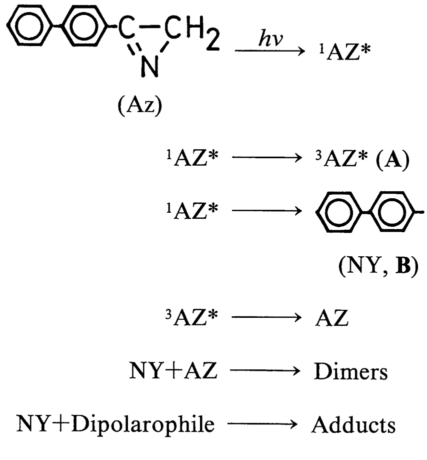


Upon irradiation with 360 nm light in the presence of BP, an adduct such as 3-oxazidine was not obtained and AZ was mainly recovered. BP was activated to the triplet state by the irradiation. The triplet state of AZ must then have been produced by energy transfer from triplet BP, as shown in Eq. 4. Triplet AZ was unreactive and was deactivated to the ground state.

6. Reaction Mechanism. In the laser flash photolysis of AZ, two kinds of transient species, triplet AZ and NY, were detected. It seemed that the excited singlet state



Scheme 1.

decayed very rapidly to triplet AZ and/or NY. The quenching rate constant of oxygen toward triplet AZ (6×10^9 dm^3 mol^{-1} s^{-1}) also supported the above assigment of the transient species. Since the stational photoirradiation of AZ in the presence of BP didn't give any adducts, the structure of triplet AZ was the closed form and decayed to the ground state. NY was assigned by the reactions with acetone and AN. NY was relatively stable in the absence of the dipolarphile, with a decay rate of 8×10 s^{-1}. It seemed that the rate was the value of the dimer (**C**) formation. The present results support the following mechanism (Scheme 1).

Experimental

AZ was synthesized from 4-vinylbiphenyl by way of 4-(1-azidoethyl)-biphenyl as reported by Hortmann and coworkers.[14] AZ was purified by column chromatography (Florisil) and several recrystallizations from hexane. The yield of AZ for starting olefin was 80.8%. Pale yellow crystals; mp 73.5—74.2 °C; *m*/*z* 193 (M$^+$); Elementary analysis, Found: C, 86.87; H, 5.74; N, 7.21%; Calcd for $C_{14}H_{11}N$: C, 87.01; H, 5.84; N, 7.15%. ^{1}H NMR ($CDCl_3$, TMS) δ=1.81 (s, 2H) and 7—8 (m, biphenyl); IR (KBr) $\nu_{C=N}$=1742 cm^{-1}, δ_{CH_2}=1442 cm^{-1}, and ν_{C-N}=986 cm^{-1}; UV (cyclohexane) λ_{max}=268.8 nm (1.99×10^5 dm^2 mol^{-1}).

Spectroscopic grade benzene, cyclohexane, and acetone were used without further purification.

Benzophenone (BP) was purified by two recrystallizations from ethanol.

Acrylonitrile (AN) was washed three times with a 5% NaOH aqueous solution, then three times with distilled water. After drying on sodium carbonate, the monomer was distilled twice under a N_2 stream.

Apparatus. The laser flash photolyses were carried out with the aid of a Lambda Phisik EMG 501 lamp with Xe and Cl_2 gases. This apparatus generates a λ=308 nm light pulse (pulse width: 15 ns, ca. 0.1 J).

The pulse radiolyses were carried out with the aid of the L-band electron beam linear accelator at Osaka University (pulse width: 8 ns, ca. 1 kGy).[15]

Stational Photoirradiations. The photoirradiations were carried out by using a 300 W high-pressure Hg lamp and a pyrex filter (thickness: 2 mm). Since AZ absorbs light of wavelengths shorter than 340 nm, an excitation wavelength of 313 nm was used. AZ (0.300 g) was irradiated in cyclohexane (0.5 dm^3) at room temperature for two hours. After several recrystallizations of the products from hexane, 0.249 g 4,5-di(4-biphenylyl)-1,3-diazabicyclo-[3.1.0]hex-3-ene (**C**) was obtained (yield: 83%). White crystals; mp 214—215.2 °C; *m*/*z*=386 (M$^+$); Elementary analysis, Found: C, 86.78; H, 5.77; N, 7.11%. Calcd for $C_{28}H_{22}N_2$: C, 87.01; H, 5.84; N, 7.15%. ^{1}H NMR ($CDCl_3$, TMS) δ=2.05 (s, -CH_2-N), 3.04 (s, N-CH_2-N=), and 7.3—8.0 (m, biphenyl); IR (KBr) $\nu_{C=N}$=612 cm^{-1} and ν_{C-N}=1332 cm^{-1}.

AZ (0.135 g) was irradiated with 0.50 mol of AN at 4 °C for three hours in cyclohexane (0.5 dm^3). The products were the adduct, 5-(4-biphenylyl)-3-cyano-3,4-dihydro-2*H*-pyrrole (0.154 g, **D**) and polyacrylonitrile (0.84 g). The adduct was isolated from the polymer by reprecipitations. White crystals; mp 170.2—170.6 °C; *m*/*z*=246 (M$^+$); Elementary analysis, Found: C, 82.89; H, 5.80; N, 11.21%. Calcd for $C_{17}H_{14}N_2$: C, 82.90; H, 5.73; N, 11.37%. ^{1}H NMR ($CDCl_3$, TMS) δ=2.05 (m, -CHCN-), 3.43 (dd, -C-CH_2-), 4.43 (dd, -N-CH_2-), and 7.3—8.0 (m, biphenyl); IR (KBr) ν_{CN}=2240 cm^{-1}, $\nu_{C=N}$=1618 cm^{-1}, δ_{CH_2}=1450, 1428 cm^{-1}, and ν_{C-N}=1364 cm^{-1}.

The irradiation of AZ (0.097 g) was carried out in the presence of BP (1.92 g) in cyclohexane (0.1 dm^{-3}) by using a 500 W Xe lamp and an interference filter (λ_{max}=360 nm, T_{max}=21%, $\Delta_{1/2}$=10 nm) for 20 h. AZ was mainly recovered and a small amount of diphenylmethanol was also obtained.

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