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Intermediates from Low-Temperature Photolysis of 4,4'-Diazidobiphenyl in Rigid Matrices

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The photolysis of 4,4'-diazidobiphenyl (**1**) in an Ar matrix at low-temperatures (15-20 K) was investigated by UV-vis and IR spectroscopies. The dinitrene was identified as an intermediate by using ^{15}N-labeled **1** and by trapping of the nitrene with CO. The presence of didehydroazepine and quinonoid structures was excluded.

The photochemistry of aryl azides has been extensively investigated because of its important applications to syntheses, photoaffinity labeling, and photoimaging.1) Despite many reports on their low-temperature photolyses, however, it seems that details of intermediates have not been completely elucidated. In 1962 the first direct observation of intermediates produced by photolysis of aryl azides was made by Wasserman and co-workers who observed triplet nitrenes by ESR spectroscopy at 77 K.2) Subsequently Reiser and co-workers assigned triplet nitrenes by UV-vis spectra under the similar conditions.3) Chapman and co-workers identified didehydroazepine as the major product produced on photolysis of phenyl azide in an Ar matrix at 8 K by IR spectroscopy.4) In addition, Dunkin and co-workers detected the IR absorption band assigned to the azirine structure produced on photolysis of 1-naphthyl and 2-naphthyl azides in Ar and N_2 matrices at 8 K.5) In these studies, the assignments of the observed intermediates have varied with the different experiments. Recently, Hayes and Sheridan have reported that the distinctive absorptions of triplet phenylnitrene appeared in the UV-vis spectrum of the matrix simultaneously with the IR spectrum.6) In this paper, we report the identification of transient intermediates in the photolysis of 4,4'-diazidobiphenyl (**1**), on the basis of UV-vis and IR spectroscopies in low-temperature matrices.

The UV-vis spectral changes produced upon irradiation of **1** was followed at 20 K in an Ar matrix.7) With increased radiation, new absorption maxima appeared at 388, 368, and 351 nm with the decrease of the azide absorption maximum at 290 nm. The spectrum obtained was similar to that of 4,4'-dinitrenobiphenyl (**2**) measured at 77 K by Reiser and co-workers.8) This was stable even if stored overnight in an Ar matrix at 20 K and was not changed upon further irradiation. IR absorption spectrum of the mixture produced upon photolysis of **1** was measured under the same conditions used to obtain the UV-vis spectra, although the sample was accumulated by repetition of deposition and irradiation in order to increase sensitivity. As shown in Fig. 1, many new peaks appeared upon photolysis of **1**. To assign this spectrum, ^{15}N,^{15}N-labeled (α, α'-positions) diazide (**1a**) was prepared 9) and photolyzed under the same conditions as previously described. Among the many peaks in IR spectra, a clear ^{15}N-isotope shift was observed for the peak at 1175 cm^{-1}, which was shifted to 1156 cm^{-1} by ^{15}N-labeling as shown in the inset of Fig. 1. The shift of 19 cm^{-1} would be reasonable to assign its band to the C-N stretching of nitrene structure from the calculation by the simple equation of diatomic harmonic oscillator. Moreover, the formation of the dinitrene (**2**) was confirmed by the

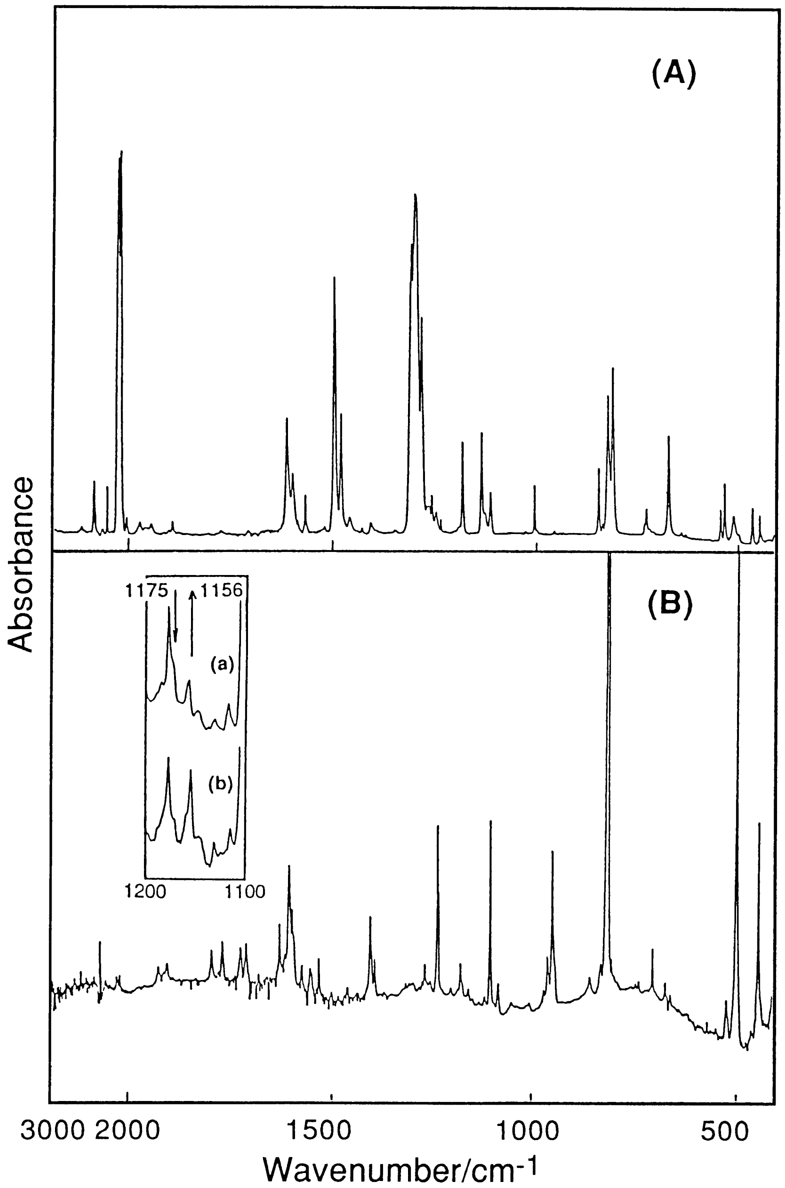
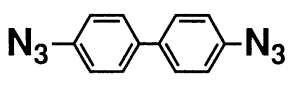
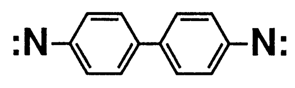


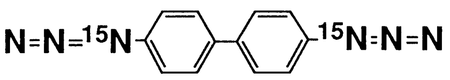
Fig. 1. The IR spectra of 4,4'-diazidobiphenyl before irradiation (A) and after irradiation (B) in an Ar matrix at 20 K. The inset shows the extended IR spectra of the photoproduct of **1** (a) and that of **1a** (b).



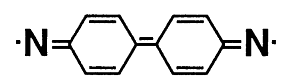
1



2



1a



3

photolysis of **1** in CO/Ar (1/1) matrix at 15 K (Fig. 2).[10] Upon the irradiation, the dinitrene formed was trapped with carbon monoxide and gave the isocyanate having the absorption band at 2264 cm^{-1}. This peak showed also a ^{15}N-isotope effect, shifted to 2256 cm^{-1} by the photolysis of **1a**. Thus, the presence of **2** was recognized as an intermediate in an Ar matrix at low-temperatures . By the way, 4-azido-4'-nitrenobiphenyl, which is postulated as an intermediate into **2**, was not observed, because the decomposition of two azido groups proceeded at one step by one photon. [11]

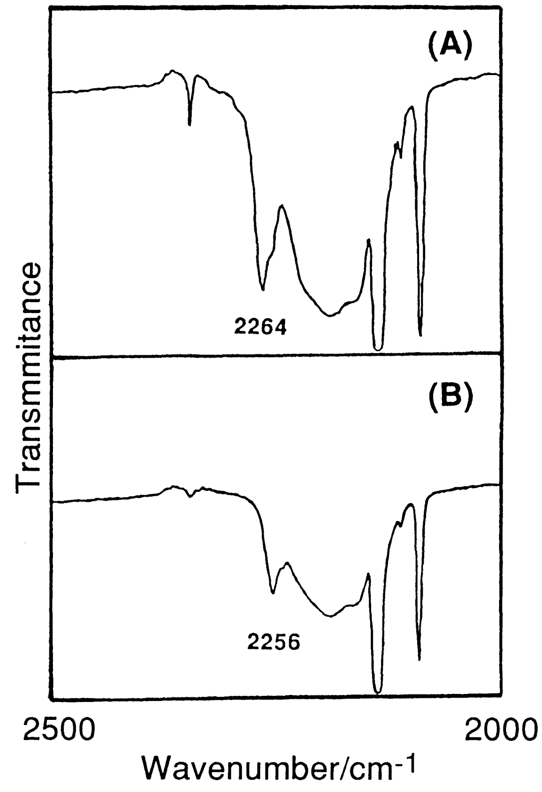
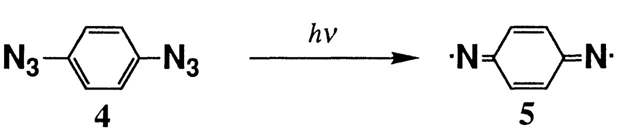


Fig.2. The IR spectra of the photoproduct of **1** (A) and that of **1a** (B) in a CO/Ar (1/1) matrix at 15 K.

Finally, other possible intermediates such as didehydroazepine, azirine, and quinonoid structures were searched. We have previously found that the absorption bands at 1759 and 1775 cm^{-1} can be assigned to C=N stretching of the quinonoid structure (**5**) produced by the photolysis of 1,4-diazidobenzene (**4**) in an Ar matrix at 20 K (Scheme 1).[12] In addition, it has been reported that absorption bands at 1895 and 1708-1736 cm^{-1} were assigned to didehydroazepine and azirine structure, respectively.[4,5] In the case of the photolysis of **1**, weak absorption bands were observed at 1926, 1904, 1793, 1767, 1722, and 1708 cm^{-1} in the region corresponding to those bands. However, these peaks did not show a ^{15}N-isotope effect in the IR spectrum observed in the photolysis of **1a**. Therefore, the presence of didehydroazepine, azirine, and quinonoid structures was excluded.



Scheme 1.

By analogy to **5**, we had assumed, from the preliminary consideration, that **3** would be the most probable photoproduct of **1** in a cryogenic matrix. Interestingly, our results showed that the intermediate was not **3** but **2**. These results mean that the interaction between two nitreno groups would be severed by the twisted biphenyl skeleton.13) Another interesting finding is that the didehydroazepine structure is not formed, as opposed to results of phenylazide.4) The conversion of **2** into didehydroazepine structure, which is observed in phenylazide, would be suppressed by the substituent effect of another phenyl group. The facile interconversion between intermediates is well known in the photochemistry of aryl azide.14) In the case of **1**, it is suggested that the biphenyl skeleton has a definitive effect on nitreno groups.

Further investigations to confirm the formation mechanism and structure of intermediates in the photolysis of **1** are carried out by using ESR spectroscopy in our laboratory.

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7) Experiments in an Ar matrix were carried out with a closed cycle cryostat system (Air Products, Displex CS-202). Plate crystals of **1** was sublimed at 320-330 K with Ar gas and deposited on a sapphire plate for UV-vis spectral measurements or a CsI plate for IR spectral measurements at 20 K *in vacuo* (ca. 10^{-6} Torr). The irradiation of matrix-isolated azide (**1**) was performed using a high pressure mercury lamp (500 W) through a cut-off filter ($\lambda > 290$ nm).

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11) Details on these will be reported in the near future.

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