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The Photolysis of 4,4'-Diazidobiphenyl in Rigid Matrices at Low-Temperature

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The photolysis of 4,4'-diazidobiphenyl in an organic glassy solvent at low-temperature was investigated by ESR and UV-vis spectroscopies. Two structures of biphenyldinitrene as photoproducts were identified: the twisted biphenyldinitrene and the quinonoid structure. The two nitreno groups of twisted biphenyl were each in the triplet state.

The interaction of triplet centers has been interesting in connection with the synthesis of high-spin organic compounds.1) Since Wasserman and co-workers showed the existence of ground state triplet nitrenes by electron spin resonance (ESR) spectrometry,2) the chemistry of nitrenes has been extensively investigated.3) Trozzolo and co-workers have shown that the dinitrene formed in the low-temperature photolysis of 1,4-diazidobenzene in a rigid matrix has a quinonoid structure, where two unpaired electrons were separated.4) Reiser and co-workers reported the UV-vis spectroscopic studies of a series of symmetrical *p*-dinitrenes in a rigid matrix at 77 K.5) AM1 calculations were carried out for the ground states and low-lying excited states of many dinitrenes by Lahti and Ichimura.6) Moreover, Minato and Lahti showed that the dinitrene generated from the photolysis of 3,4'-diazidobiphenyl in an organic glassy matrix at 77 K was in the quintet ground state.7) In our preceding paper, we confirmed the twisted biphenyl-4,4'-dinitrene as a photoproduct in the photolysis of 4,4'-diazidobiphenyl (**1**), which was investigated by IR and UV-vis spectroscopies in an argon matrix at 20 K.8) In this paper, we wish to report the photolysis of **1** in an organic glassy solvent at low-temperature on the basis of ESR measurements.

ESR measurements were carried out by the photolysis of ca. 10^{-3} - 10^{-4} mol/l of **1** in an ether-isopentane (1/1) glassy matrix at 65-77 K. Figure 1 shows the ESR spectra obtained after short (7 min) and prolonged (31 min) irradiation times.9) Upon the irradiation, three species of magnetic resonance absorptions appeared at

116/205/411, 630, and 642 mT, whose intensities were plotted against the irradiation time (Fig. 2).

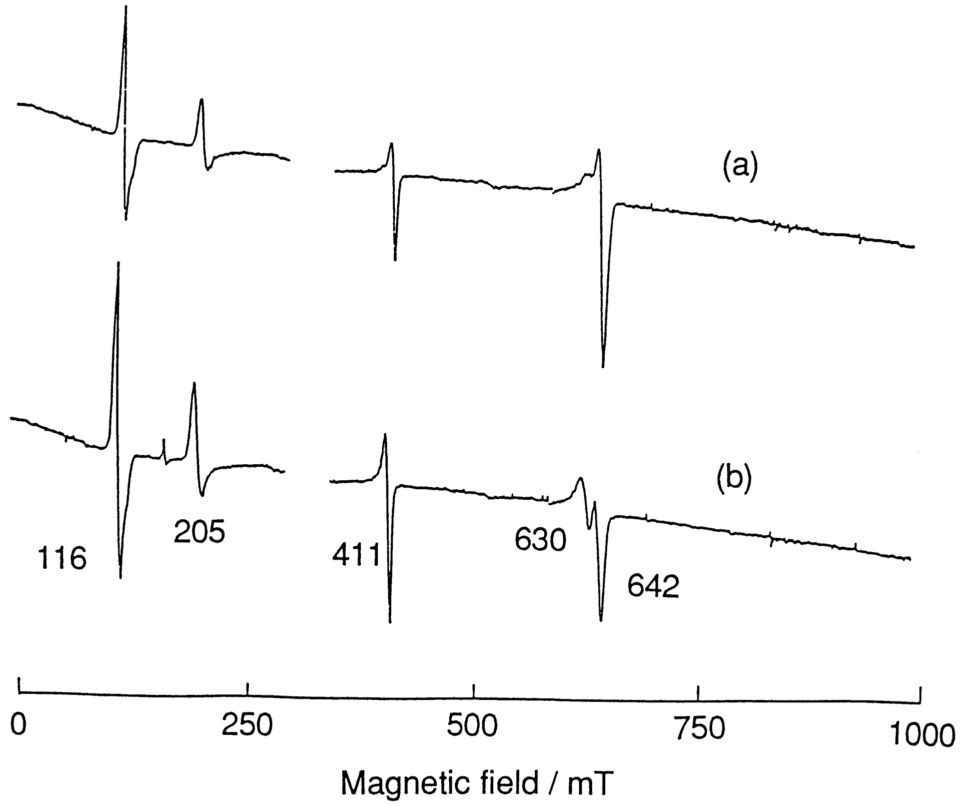


Fig. 1. The ESR spectra after irradiation of **1** in an ether-isopentane matrix at 70 K. Irradiation time: (a) 7 min and (b) 31 min (ν=9.086 GHz).

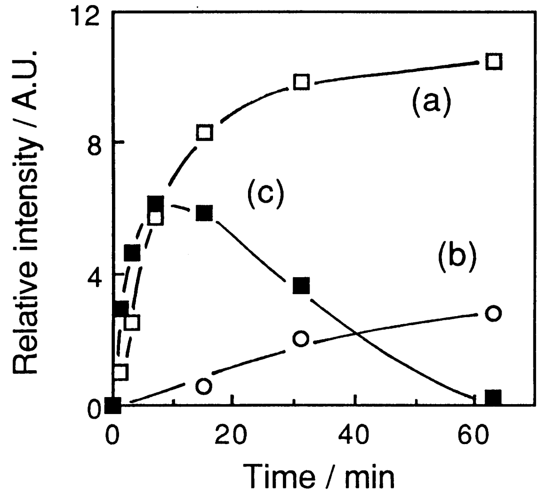


Fig. 2. The intensity of ESR signals at (a) 116, (b) 630, and (c) 642 mT as a function of irradiation time, in an ether-isopentane matrix at 70 K.

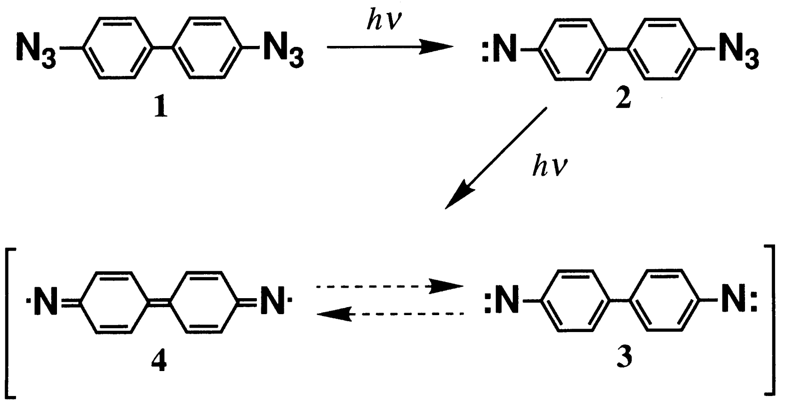
The resonances at 116/205/411 mT were due to typical triplet signals and would be assigned to the intermediate having a quinonoid structure (**4**).[4] The zfs parameters of **4** were estimated to be $D = 0.02\ \mathrm{cm}^{-1}$ and $E \approx 0.0\ \mathrm{cm}^{-1}$, indicating that two unpaired electrons in **4** were separated farther than that in the *p*-phenylenedinitrene having a quinonoid structure. The ESR signal intensities of **4** were increased as the temperature was raised in the range 30-65 K, and these changes were thermally reversible.

This finding indicated that the triplet **4** was not in the ground state but in the thermally excited state. No resonance was detected at higher field than 700 mT, although the resonances in the quintet state were observed by the photolysis of diazido compounds such as *m*-diazidobenzene.1f,7)

On the other hand, the other two adjacent resonances were in the region of typical resonance of triplet nitrenes. From intensity-time profiles as shown in Fig. 2, the resonances at 642 and 630 mT could be tentatively assigned to the mononitrene (**2**)3a) as the initial photoproduct of **1** and the dinitrene (**3**) as the secondary photoproduct, respectively. It was considered that **3** was identical with the twisted biphenyl-4,4'-dinitrene which was previously assigned by IR spectra in an argon matrix at 20 K.8)

The identification above-mentioned was also supported from the results of UV-vis spectra measured simultaneously for the same sample as the ESR spectra. The formation of **3** was confirmed on the UV-vis spectra by the comparison with our previous and Reiser's results.5,8) However, the absorption ascribed to **4** was not apparent. It may be that the amount of **4** produced was too small to be detected and/or the absorption of **4** overlapped with that of **3**. Although the other possible nitrene such as ring-expanded on one side or inserted at one end into the solvent may be produced, we have not observed ESR absorptions ascribable to these species. Thus, the photoproducts of **1** were concluded to be **2**, **3**, and **4** by ESR and UV-vis spectroscopies.

The ESR signal of **3** (630 mT) was very close to that of **2** (642 mT), indicating that the two nitreno groups of **3** were each in the triplet state, and, that is to say, that the interaction between two nitreno groups was negligibly small. No appreciable magnetic interaction between two nitreno groups would be explained by the twisted biphenyl skeleton.10) In the case of the photolysis of 2,2'-dimethyl-4,4'-diazidobiphenyl whose biphenyl skeleton was fairly twisted, the photoproducts generated in an organic glassy solvent at 77 K were the corresponding mononitrene and dinitrene, and the dinitrene having the quinonoid structure was never



Scheme 1.

involved.[11] In the case of **1**, it is of interest that both dinitrenes, which have a strong and no appreciable magnetic interactions through the biphenyl skeleton, are formed coincidentally upon the irradiation and the resonance intensities were saturated upon further irradiation as shown in Fig. 2.

Although, the photochemical or thermal interconversion between **3** and **4** is suggested as shown in Scheme 1, we have not yet got the confirmative evidence experimentally.[12] Further studies on the detailed mechanism for the formation of **3** and **4** are now in progress.

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12) In the preliminary experiment, where the temperature of sample was raised, both the dinitrenes were decomposed immediately over 80 K.

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