Photochemistry of the *N*-Nitrosoaniline Having a Diazo Function in an Ar Matrix at 10 K: *EZ*-Isomerization, Liberation of Nitric Oxide, and Its Recombination

Mitsuhiro Takeda and Shigeru Murata*
Department of Basic Science, Graduate School of Arts and Sciences, The University of Tokyo,
Meguro-ku, Tokyo 153-8902

(Received March 3, 2006; CL-060257; E-mail: cmura@mail.ecc.u-tokyo.ac.jp)

On irradiation of *p*-(*N*-methyl-*N*-nitrosoamino)phenyldiazomethane (**1**) in an Ar matrix at 10 K, the liberation of nitric oxide (NO) to afford the quinoidal radical **2** was directly observed by means of IR spectroscopy. The photoisomerization of (*E*)-**1** to its *Z*-isomer preceded the NO liberation. Warming the matrix containing NO and **2** caused their disappearance to give an *EZ*-mixture of the quinoidal imine **3** by the recombination of NO with a radical center of **2**. The photoisomerization of (*Z*)-**3** to (*E*)-**3** was also observed.

Nitric oxide (NO) has known to be involved in various biological processes, such as immune modulation, regulation of blood pressure, and neurological response.[1] In recent years, there has been a continuing interest in photoinduced NO-releasing materials, which may make it possible to liberate NO at the desired time and space. Since NO is a gaseous free radical, its liberation is usually monitored in indirect manners, that is, using absorption, fluorescence, or ESR spectrum after the conversion of NO into stable compounds by the reaction with trapping reagents.[2] In this paper, we report the first direct observation of photochemical NO liberation, as well as the identification of the remaining counterpart radical, by the use of IR spectroscopy and a low-temperature matrix isolation technique. The thermal recombination of NO with the counterpart radical to give a non-radical species is also observed in the matrix.

It is known that irradiation of *N*-nitrosoaniline derivatives causes the homolytic cleavage of the N–N bond, so that these compounds are potential candidates for the photoinduced NO-releasing materials. However, the quantum yields of NO formation in the photolysis of *N*-nitrosoanilines are very poor because of the rapid recombination of radical pairs generated through the N–N bond cleavage.[3] In order to solve this problem, Fujimori and his co-workers synthesized *N*-nitrosoanilines having another *N*-nitrosoamino group at their *para* position, which were designed so that the homolysis of one N–N bond could induce homolysis of the second N–N bond.[4] Unfortunately, our attempts at direct observation of photoinduced NO liberation from *N*,*N*′-dimethyl-*N*,*N*′-dinitroso-*p*-phenylenediamine using a low-temperature matrix isolation technique gave unsatisfactory results, which were due to the rapid recombination between NO and the counterpart radical generated by the first N–N cleavage in rigid low-temperature matrices.

Thus, in order to produce *N*-nitrosoaniline derivatives which can release NO more efficiently, we have designed *p*-(*N*-methyl-*N*-nitrosoamino)phenyldiazomethane (**1**). It is expected that an efficient photodecomposition of the diazo function of **1** can trigger the decomposition of *p*-(*N*-nitrosoamino) group effectively. The diazo compound **1**[5] was synthesized by the thermolysis (100 °C, 3 mmHg) of the sodium salt of *p*-(*N*-methyl-*N*-nitrosoamino)benzaldehyde tosylhydrazone.[6] The compound **1** matrix-isolated in Ar showed an intense diazo stretching band at 2063 $\mathrm{cm^{-1}}$ and bands having a medium intensity at 1077 and 929 $\mathrm{cm^{-1}}$ assigned to the stretching of the *N*-nitrosoamino moiety. The conformation around the N–N partial double bond was definitely assigned to *E* by excellent agreement with the IR spectrum obtained by the density functional theory (DFT) calculation (B3LYP/6-31G(d)).[7] Upon irradiation of (*E*)-**1**[8] in an Ar matrix at 10 K from an extra-high-pressure mercury lamp (310 ± 50 nm), the IR bands at 1277 and 971 $\mathrm{cm^{-1}}$ appeared with a decrease in the intensity of the peaks due to (*E*)-**1**. The photoproduct was identified as the (*Z*)-isomer of **1**[8] by agreement with the calculated spectrum (Figure 1). A photostationary state was attained between these geometrical isomers. It should be noted that the IR band assigned to a stretching vibration of NO molecule, which is expected to appear around 1870 $\mathrm{cm^{-1}}$,[9] was not

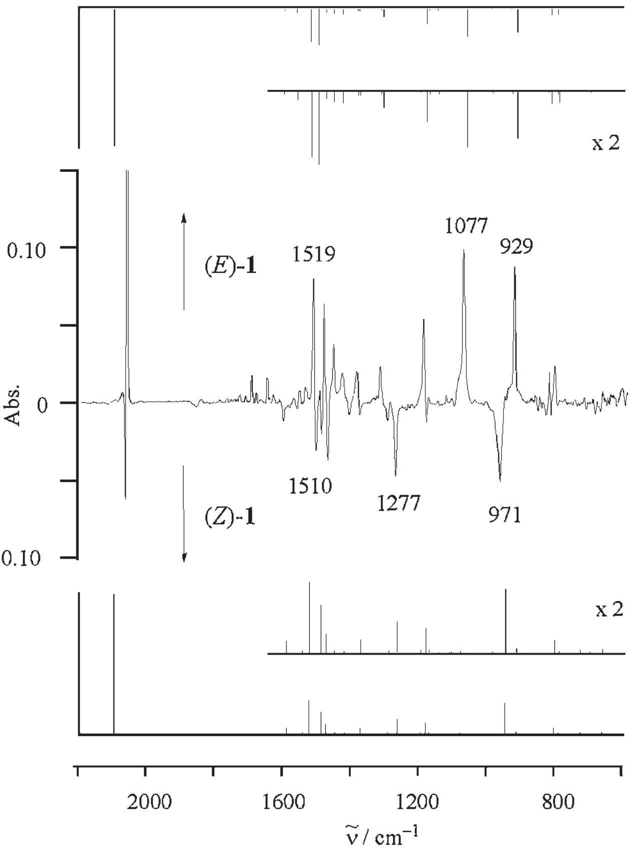


Figure 1. Difference IR spectrum recorded after irradiation of **1** in Ar at 10 K with 310 ± 50 nm light for 3 min (middle); IR spectra calculated for (*E*)-**1** (top) and (*Z*)-**1** (bottom).

observed at this stage. This observation suggests that the *EZ*-isomerization of the N–N=O group, which probably proceeds through the photochemical cleavage and recombination of the N–N bond of **1**, precedes the photodecomposition of its diazo group under these irradiation conditions. Continued irradiation resulted in the total disappearance of the IR bands of both isomers of **1** and produced NO (1872 cm^{-1}) along with the species having weak IR peak at 1624, 1393, 835, and 634 cm^{-1}. After the calculations of vibrational frequencies for several possible photoproducts of **1**, we found that the observed IR spectrum was in fair agreement with that calculated for the quinoidal radical **2**[8] (Figure 2). Thus, the direct observation of the photoinduced NO liberation, as well as the characterization of the remaining radical, is successfully achieved by the use of a low-temperature matrix isolation technique.

Further evidence in support of the structure of the radical **2** was obtained by subsequent reactions in the Ar matrix. Warming the matrix containing NO and **2** to 40 K caused a complete disappearance of their IR bands and the generation of new species having IR bands at 1415, 1364, 1059, and 983 cm^{-1}. Subsequently, irradiation of the resulting matrix at 10 K caused a disappearance of the species having IR bands at 1364 and 983 cm^{-1} (designated as species **A**) and a simultaneous increase in the bands at 1415 and 1059 cm^{-1} (due to species **B**). It appeared that both **A** and **B** were the products derived from the recombination of NO and **2**, and with this in mind, the vibrational frequencies of possible products were calculated. Thus, the agreement between the observed and calculated IR spectra leads us to propose that the species **A** and **B** are assigned to the (*Z*)- and (*E*)-isomers of the quinoidal imine **3**,[8] respectively (Figure 2). The formation of **3** is reasonably explained in terms of the covalent bond formation of the radical **2** at the site having the largest spin density with NO.

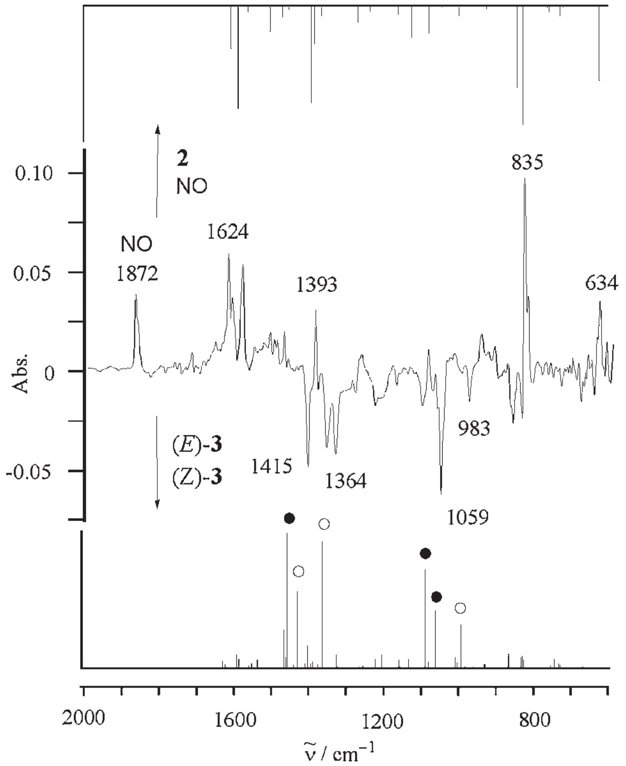
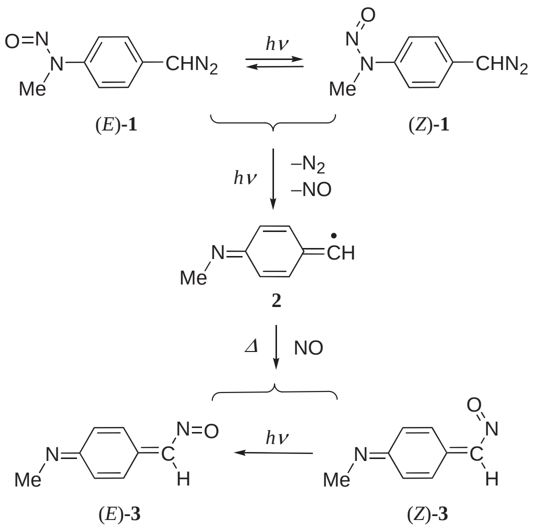


Figure 2. Difference IR spectrum recorded after warming the Ar matrix containing NO and **2** to 40 K (middle); IR spectrum calculated for **2** (top) and superposition of IR spectra calculated for (*E*)- and (*Z*)-**3** (bottom). The peaks characteristic of (*E*)- and (*Z*)-**3** are marked with full and open circles, respectively.



Scheme 1. Total scheme of the reaction of (*E*)-**1** in an Ar matrix.

The total scheme of the photoreaction of **1** in an Ar matrix is summarized in Scheme 1. Since species other than (*Z*)-**1** and **2**, such as the triplet carbene having an intact *N*-nitrosoamino group, could not be identified in the IR spectrum recorded during the course of the photoreaction of (*E*)-**1**, it appears that the photodecomposition of the diazo function can induce the N–N bond cleavage of the *N*-nitrosoamino group substituted at its *para* position as expected. Work to elucidate the photoreactivity of **1** in fluid solutions is ongoing in our laboratory.

References and Notes

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5 Orange granules: mp 72 °C dec; ^{1}H NMR (CDCl$_3$) δ 3.45 (3H, s), 5.02 (1H, s), 7.01 (2H, d, $J = 9.0$ Hz), 7.47 (2H, d, $J = 9.0$ Hz); MS m/z (relative intensity) 176 (M$^+$, 18), 146 (M$^+$ – NO, 100), 118 (M$^+$ – NO – N$_2$, 57).

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7 The DFT calculations were carried out by the Gaussian 03 program package. The calculated vibrational frequencies are scaled by a factor of 0.9614.

8 Although there exist geometrical isomers with respect to the relative geometry of two substituents at the 1- and 4-positions, the IR spectra calculated for these isomers were almost identical.

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