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Photochemistry of o-Nitrophenylazide in Matrices. The First Direct Spectroscopic Observation of o-Dinitrosobenzene[1,2)]

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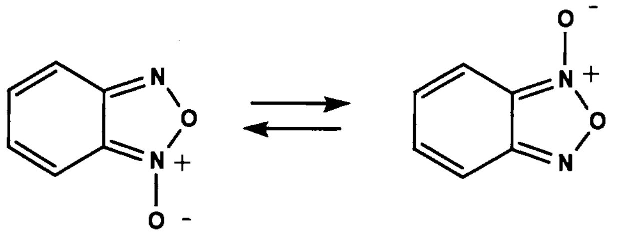
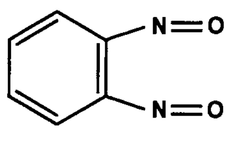
Photolysis of o-nitrophenylazide in an Ar matrix at 12 K produced the mixture of benzofuroxan and a new species, which could be identified as o-dinitrosobenzene on the basis of its IR and UV spectra.

Based on the kinetic studies, it is generally considered that the thermal isomerization of benzofuroxan (benzofurazan-1-oxide, **1a** ⇄ **1b**) involves o-dinitrosobenzene (**2**) as a transient intermediate.3,4) The trapping of **2** has been successful,5) but no direct observation of this intermediate has yet been reported.2) In this paper we wish to report that o-dinitrosobenzene **2** could be formed by the photolysis of o-nitrophenylazide (**3**) and undergo reversible photoisomerization to **1** in an Ar matrix at 12 K.



1a **1b**



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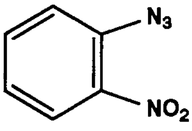

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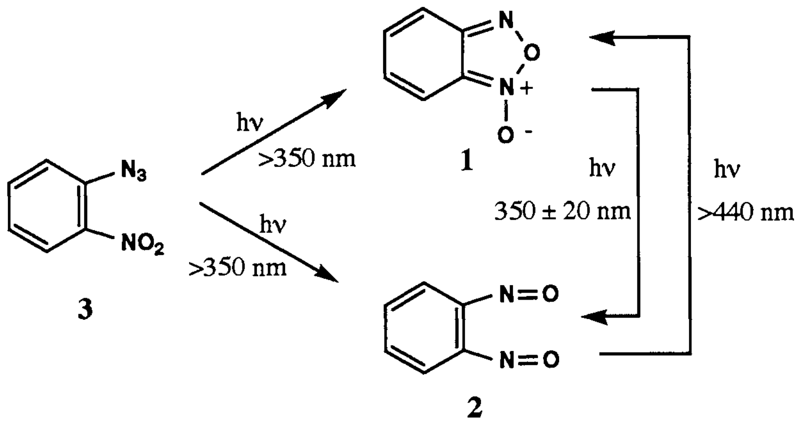
Photolysis6) (>350 nm) of o-nitrophenylazide (**3**)7) matrix-isolated in Ar at 12 K resulted in a disappearance of the IR bands assigned to the nitro stretching vibrations (1609, 1541, and 1296 cm^{-1}), as well as the intense azide stretching peaks (2138, 2122, and 2096 cm^{-1}). New bands appeared at 1622, 1513, 1102 cm^{-1}, and so on. Continued irradiation with long-wavelength light (>390 nm) caused a dramatic change in the IR spectrum. Upon irradiation, the intensities of the strong bands at 1513, 1102, and 767 cm^{-1} decreased significantly, and the intensities of peaks at 1622, 1597, and 1545 cm^{-1} increased. The species which increased on irradiation with long-wavelength light was easily identified as benzofuroxan **1** by direct comparison with the matrix-isolated IR spectrum of an authentic sample.8) Irradiation of the resulting matrix with short-wavelength light (>350 nm) reproduced the species (A) exhibiting IR bands at 1513, 1102, and 767 cm^{-1} with a decrease of **1**. Thus, the photochemical transformation of (A) to **1** was revealed to be



reversible. The proportion of (A) at the photostationary state was estimated to be 85% and 40% under short-wavelength (>350 nm) and long-wavelength irradiation (>390 nm), respectively.[9] All peaks which appeared on the irradiation of **3** were assigned to either **1** or (A).

Though shorter wavelength photolysis (>200 nm) of the matrix obtained after irradiation at >350 nm resulted in a slight decrease of the proportion of (A), longer wavelength light (>440 nm) was much more effective to reduce the fraction of (A), which was estimated to be less than 10% at the photostationary state. On the other hand, irradiation with monochromatic light (350 ± 20 nm) shifted the equilibrium toward (A) to the extent of ca. 90% in the proportion of (A).

The reversible photoisomerization was observed by the irradiation of **1** as well. Photolysis (350 ± 20 nm) of **1** matrix-isolated in Ar at 12 K caused a significant decrease in the intensities of the peaks of **1** and a simultaneous appearance of the bands due to (A) (Fig.1). Irradiation of the resulting matrix with long-wavelength light (>440 nm) resulted in an increase of the proportion of **1**. This photo-isomerization was also examined in the UV spectrum (Fig. 2). On photolysis (350 ± 20 nm) of **1** in Ar at 12K, the intensity of the transition at 358 and 372 nm due to **1** extremely decreased, and a very intense absorption with a maximum at 278 nm and absorptions with vibrational structures in the region 320-380 nm appeared, both of which are assigned to UV absorptions due to (A). Longer wavelength irradiation (>440 nm) caused a decrease in the intensity of the absorption at 278 nm, regenerating the UV absorptions due to **1**. In the course of this reversible photo-isomerization, there was an isosbestic point at 322 nm, and no absorptions were observed in the range above 500 nm.

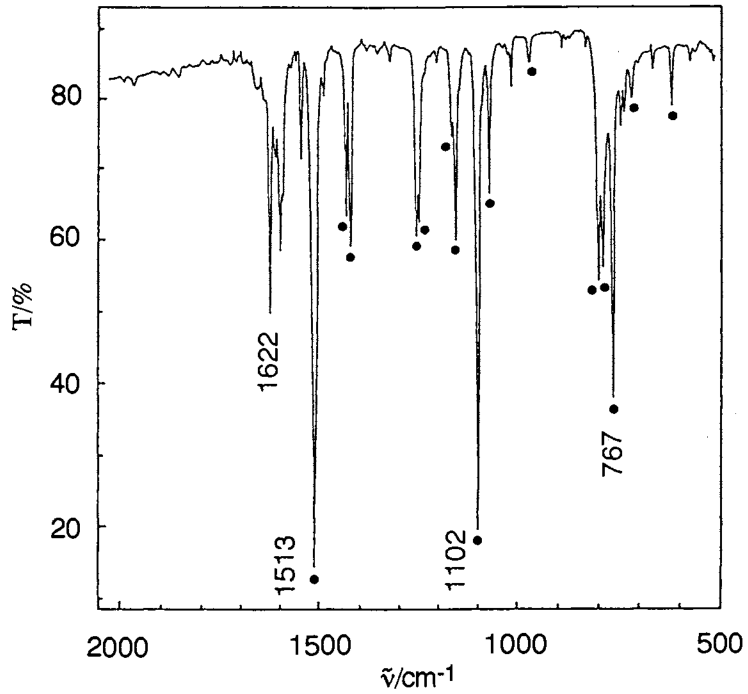
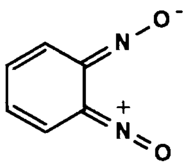


Fig. 1. IR spectrum obtained by irradiation of **1** at 350 ± 20 nm in an Ar matrix at 12 K. The peaks marked with full circles are assigned to the bands due to **2**, and other peaks are assigned to the bands due to **1**.



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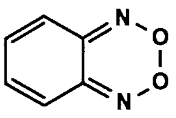

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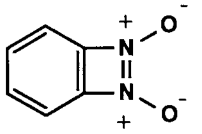

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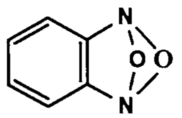

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The new species (A)10) could be identified as o-dinitrosobenzene **2** on the basis of the intense IR band at 1513 cm^{-1}, which is reasonably assigned to N=O stretching vibration.11) Although the other possible structures **4-7** cannot be rigorously excluded at this stage, the spectroscopic data of (A) appear to be different from those expected for these structures. The intense transition at 278 nm in the UV spectrum strongly suggests the presence of aromatic ring in (A), which excludes a linear o-dinitrosobenzene structure **4** and o-quinodiimine peroxide **5**. For **4**, the stretching vibration due to a cumulenic double bond is expected in the region 2000-2100 cm^{-1}, and cis-nitrosodimer structure in **6** should show a strong N-O stretching band around 1400 cm^{-1} in the IR specturm.11) No intense IR bands are observed in these range. The strong IR band at 1513 cm^{-1} would not be expected for benzobicyclo[2.1.1]hexane derivative **7**. Thus, o-dinitrosobenzene **2** could be the most reasonable structure for the species (A).

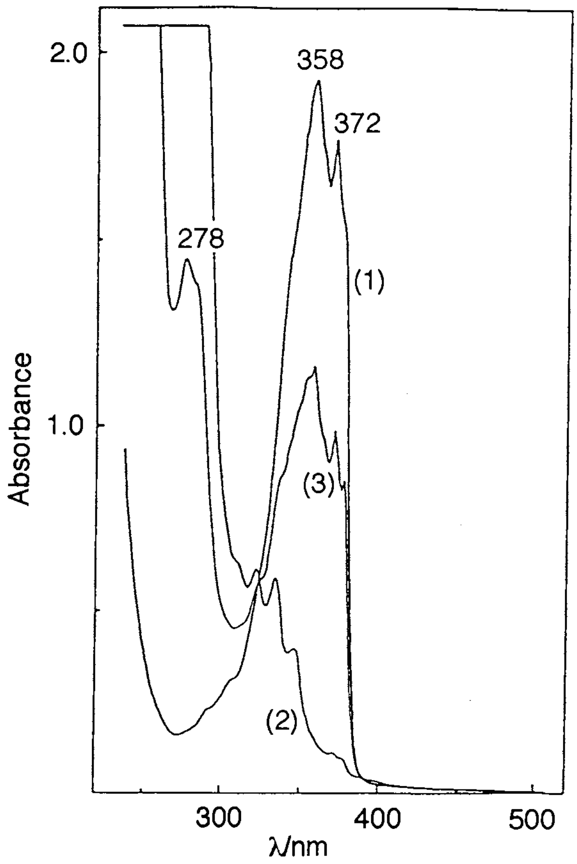

Fig. 2. UV spectrum obtained by irradiation of **1** in an Ar matrix at 12 K. The spectra were recorded (1) before irradiation, (2) after irradiation at 350 ± 20 nm, and (3) after further irradiation at > 440 nm.

In conclusion, we have directly observed o-dinitrosobenzene **2**, which is formed by the irradiation of o-nitrophenylazide **3** and is photochemically equilibrated with benzofuroxan **1** in an Ar matrix at 12 K.12) Further investigations to confirm the structure of the intermediate are in progress in this laboratory.

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References

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of Japan, Matsuyama, October 1989, p. 199.

2) After this manuscript was submitted, Dunkin and his co-workers reported the first characterization of o-dinitrosobenzene **2** yielded by photolysis of **1** in Ar matrices at 14 K: I. R. Dunkin, M. A. Lynch, A. J. Boulton, and N. Henderson, *J. Chem. Soc., Chem. Commun.*, **1991**, 1178.

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8) IR (Ar; 12 K) ν_{max} 1650w, 1622s, 1597s, 1545s, 1489m, 1444w, 1424w, 1354w, 1202w, 1122w, 1017m, 892w, 833w, 746m, 737m, 666w, 574m, 563w cm^{-1}; UV (Ar; 12 K) λ_{max} 290sh, 306sh, 358, 372 nm.

9) The standard IR absorptions of each product which were not saturated or did not overlap with other absorptions were chosen (1017 cm^{-1} for **1** and 1257 cm^{-1} for (A)). The proportion of (A) could be estimated from the ratio of intensities of these two peaks and the ratio of their absorptivities which was determined to be 0.59 by assuming a quantitative photoisomerization.

10) IR (Ar; 12 K) ν_{max} 1513s, 1434m, 1422m, 1257m, 1250m, 1166w, 1157m, 1102s, 1072m, 972w, 804m, 791m, 767s, 719w, 620w cm^{-1}; UV (Ar; 12 K) λ_{max} 278, 320, 332, 344, 370, 376sh nm.

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12) The thermal or IR induced isomerization of **2** to **1** was also observed in matrices. Detailed examinations are in progress.

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