

Crystalline-State Photoreaction of 1-Azido-2-nitrobenzene – Direct Observation of Heterocycle Formation by X-Ray Crystallography

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Dedicated to Professor *Jack D. Dunitz* on the occasion of his 80th birthday

The crystalline-state photoreaction of 1-azido-2-nitrobenzene (**1**) was investigated by a combination of X-ray crystallography, IR spectroscopy, electron-spin resonance (ESR), and by means of theoretical calculations. Upon low-temperature (80 K) photolysis of **1**, the formation of benzofuroxan (**2**) was directly observed by X-ray single-crystal analysis. ESR Measurements at 5 K suggested the presence of a *triplet* nitrene as an intermediate in the formation of the heterocycle. Temperature-dependent IR spectroscopy also revealed that another intermediate, *trans,trans*-1,2-dinitrosobenzene, was produced at temperatures below 80 K.

Introduction. – Azidobenzene derivatives with an unsaturated *ortho* substituent are useful starting materials for heterocyclic-ring syntheses *via* pyrolysis. Thereby, anchoring assistance of the *ortho* substituent plays an important role in decreasing the activation energy [1]. *Dyall* proposed that such substituents, *e.g.*, NO₂ groups, participate in a pericyclic process with little nitrene character [2]. 1-Azido-2-nitrobenzene (**1**) is a well-studied precursor for heterocyclic-ring syntheses *via* photolysis and pyrolysis in both liquid and gas phases [3]. The final cyclization product, benzofuroxan (**2**; 2,1,3-benzoxadiazole 1-oxide), shows an intriguing tautomeric reaction on which recent experimental and theoretical studies performed in solution and inert matrices have provided solid evidence for the existence of 1,2-dinitrosobenzene as an intermediate [4].

Recently, we succeeded in observing reactive intermediates, such as photo-induced radicals from hexaaryldiimidazolyl derivatives, *triplet* diphenylcarbenes, and *triplet* phenylnitrenes in crystals by X-ray analysis as well as spectroscopy [5]. Here, we present crystallographic and spectroscopic studies on the crystalline-state photoreaction of **1**.

Results and Discussion. – *Crystallographic Studies.* X-Ray-diffraction analyses of **1** were performed at 80 K before and after photo-irradiation ($\lambda = 436$ nm). The crystallographic data are summarized in the *Table*. *Fig. 1* shows the molecular structure, packing diagram, and reaction cavity (2.35 Å³) [6] of **1**, the reactive groups being N(2) and N(3). The intramolecular distance (2.710(1) Å) between N(1) and O(2)

Table. Crystallographic Data for 1-Azido-2-nitrobenzene (**1**)

	Before irradiation	After irradiation ($\lambda = 436$ nm)
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Temp. [K]	80(2)	80(2)
a [Å]	7.2552(3)	7.2746(4)
b [Å]	7.5737(2)	7.5857(4)
c [Å]	7.9331(4)	7.8993(5)
α [°]	70.896(2)	72.294(2)
β [°]	62.804(1)	63.282(2)
γ [°]	66.748(1)	67.106(2)
V [Å ³]	350.43(2)	354.24(4)
Z	2	2
D_{calc} [g/cm ³]	1.555	1.539
μ [mm ⁻¹]	0.123	0.121
Crystal size [mm]	0.20 × 0.15 × 0.05	0.20 × 0.15 × 0.05
No. of reflections measured	5624	5662
No. of unique reflections	2038	2053
$2\theta_{\text{max}}$	60	60
Merging $R(I)$, $R(\text{sigm})$	0.0368, 0.0453	0.0542, 0.0705
No. of reflections ($I > 2\sigma(I)$)	1500	1263
Conversion	0	0.103(3)
No. of variables	125	64
No. of restraints	0	0
$R_1(F)$ ($I > 2\sigma(I)$)	0.0400	0.0590
$wR_2(F^2)^a$ (all data)	0.1064	0.1581
Goodness-of-fit	0.943	0.912

$$^a) w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP], P = [2F_c^2 + \text{Max}(F_o^2, 0)]/3$$

is significantly shorter than the sum of *Van der Waals* radii (3.07 Å). The dihedral angle between the NO₂ and phenyl groups is not zero, but 37.6(1)° to avoid steric repulsion.

After X-ray data collection of **1**, the crystal was irradiated with light of 436 nm wavelength at 80 K for 30 min. Then, X-ray data were recollected under the same conditions. The space group ($P\bar{1}$) was retained after the irradiation. The difference electron-density maps of **1** *before* and *after* irradiation are shown in *Fig. 2*. The formation of a five-membered ring lying in the molecular plane is evident from *Fig. 2, b*. Including the five-membered ring, the least-squares refinement was performed where the initial structure was treated as a rigid group, permitting only translation and rotation. No chemical restraints were applied to the geometrical parameters of the photoproducts. The refined structure revealed that the photoproducts are benzofuroxan (**2**) and dinitrogen molecules. The isotropic temperature factors of the atoms of the photoproducts are reasonable, as shown in *Fig. 3*, even though the population of benzofuroxan is only *ca.* 10%. A final difference electron-density map showed no significantly large residual peaks corresponding to any other product, such as 1,2-dinitrobenzene or nitrene compounds. The dinitrogen molecule fits well into the reaction cavity, as shown in *Fig. 1, c*. Such a fitting is one of the essential conditions to prevent deterioration of the crystal form upon photolysis. The intermolecular distances of N(1A) \cdots N(2A) (3.22(3) Å) and N(1A) \cdots N(3A) (3.24(3) Å) are larger than the

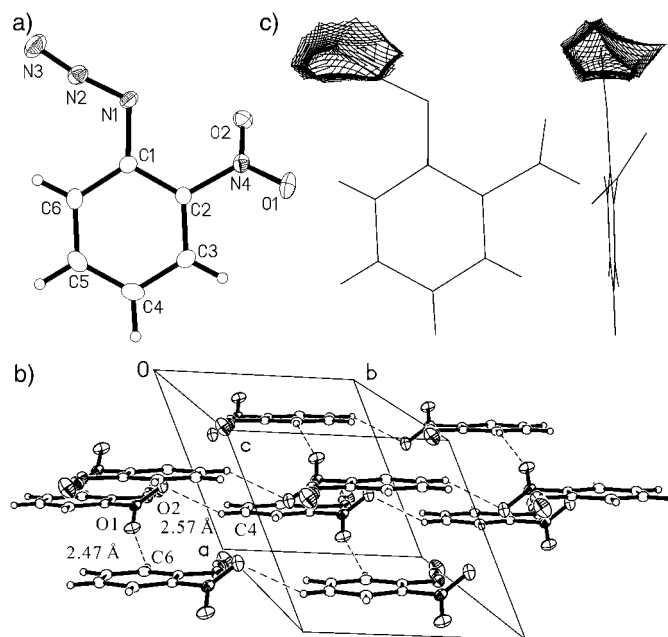


Fig. 1. *Thermal-ellipsoid plots* (probability level 50%). *a*) Molecular structure. *b*) Packing diagram of **1** (short intermolecular distances: C(4)–H \cdots O(2), 2.47 Å; C(6)–H \cdots O(1), 2.57 Å; C–H bond length fixed at 0.915 Å. *c*) Reaction cavity for the N(2)–N(3) group (contour level, 0.1 Å³) seen from the top (left) and from the side (right).

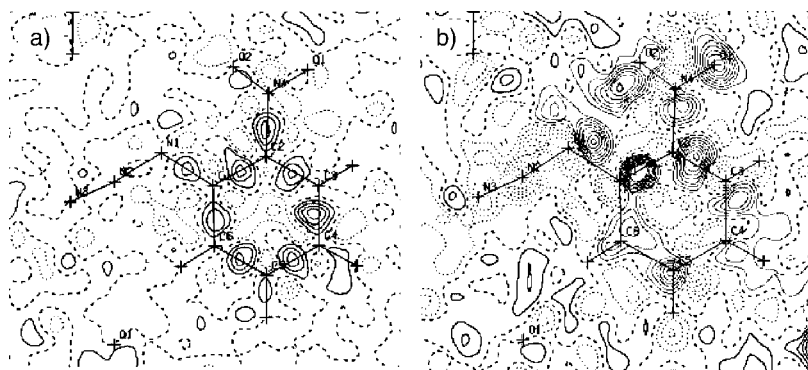


Fig. 2. *Difference electron-density maps*. The section is the plane of benzene. The contours are at 0.1 e Å⁻³. Broken lines indicate negative contours. *a*) Before irradiation. *b*) After irradiation at 436 nm (initial molecule treated as a rigid group with an occupancy factor of 1.0).

sum of *Van der Waals* radii (3.1 Å). Although most bond lengths in **2** reasonably agree with those reported previously [7], C(2A)–C(3A) (1.30(3) Å) and C(3A)–C(4A) (1.26(3) Å) significantly differ from the reported values (1.416(4) and 1.330(5) Å, respectively). This can be explained by the fact that C(2A) and C(3A) occupy the

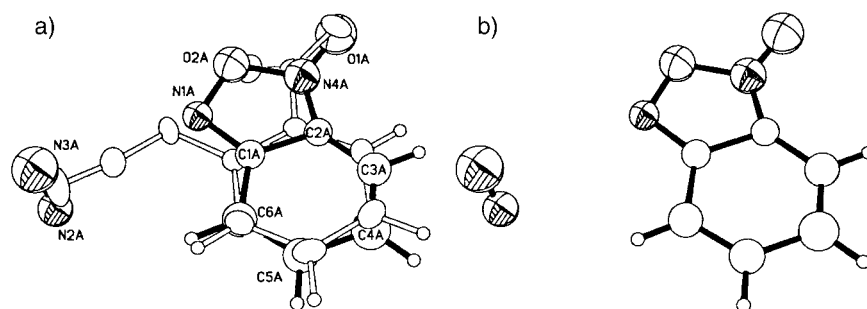


Fig. 3. Thermal-ellipsoid plots (probability level 50%) of **1** after photo-irradiation. a) Disordered structure of **1** and **2**. b) Benzofuroxan (**2**) and dinitrogen molecules (the initial molecule **1** is omitted). Selected bond lengths and intramolecular distances [Å]: C(1A)–N(A), 1.35(2); C(1A)–C(6A), 1.39(3); C(1A)–C(2A), 1.40(3); C(2A)–C(3A), 1.30(3); C(2A)–N(4A), 1.35(3); C(3A)–C(4A), 1.26(3); C(4A)–C(5A), 1.42(3); C(5A)–C(6A), 1.31(3); N(1A)–O(2A), 1.38(2); N(4A)–O(1A), 1.21(3); N(4A)–O(2A), 1.43(3); N(2A)–N(3A), 0.96(3); N(1A) ⋯ N(2A), 3.22(3); N(1A) ⋯ N(3A), 3.24(4).

positions in the neighborhood of the bonding electrons between C(2) and C(3) and between C(3) and C(4), respectively.

ESR Studies. To investigate intermediate species produced during the solid-state photoreaction of **1**, the ESR spectra of the powdered microcrystal were measured between 5.4 and 300 K. Fig. 4 shows the ESR spectra of **1** after photo-irradiation at 5.4 K, which indicates the presence of a triplet nitrene. When the sample was warmed to 300 K, the ESR signal became considerably smaller at 20–40 K, and silent at 80 K, which suggested that the triplet nitrene had disappeared. This was consistent with the X-ray analysis performed at 80 K, in which no nitrene was observed (*cf.* above).

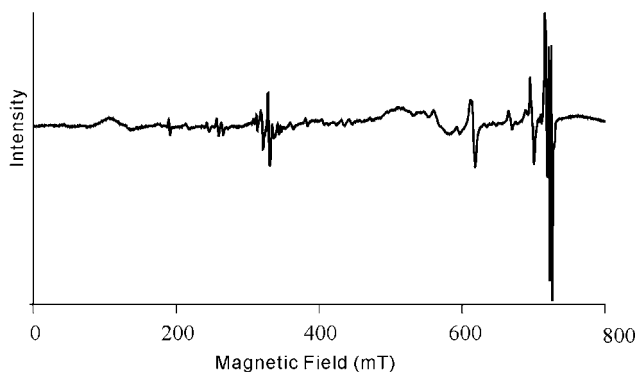


Fig. 4. ESR Spectrum of **1** after irradiation at 5.4 K by using microcrystals

Vibrational Studies. Recently, we demonstrated that IR-spectroscopic analysis in combination with vibrational calculation by the DFT method well explained the generation of diphenylcarbenes and radicals in the crystalline state [5a,b,e]. The solid-state photoreaction of **1** was, thus, also observed by IR spectroscopy at temperatures of 7–300 K. Photolysis of **1** at 7 K produced benzofuroxan (**2**) as a major product, as

shown in Fig. 5, where negative peaks were assigned to **1** (Fig. 5, a) and positive peaks to **2** (Fig. 5, b). When the sample was warmed to 80 K, several negative peaks (1505, 1419, 1249, 1162, 1112, 1077, 808, 773 cm^{-1}) disappeared (Fig. 6, a), while those of benzofuroxan (positive ones) appeared. The negative peaks show a pattern similar to that of the IR spectra recorded by Hacker at 14 K in a Xe matrix [4b]. These spectra were assigned to 1,2-dinitrosobenzene. Later, Rauhut *et al.* proposed that the obtained 1,2-dinitrosobenzene has the *trans,trans*-conformation according to density-function-based vibrational analysis (Fig. 6, b) [4g]. Our experimental spectra in a KBr matrix also showed excellent agreement with the calculated spectra of the *trans,trans*-conformer. To confirm whether any peaks assignable to the *triplet* nitrene correspond to those in our experimental spectra, the vibrational analysis of 2-nitrophenylnitrene was performed at the DFT UB3LYP/6-31G* level of theory. The experimental spectra shown in Figs. 5 and 6 include no signals around 1338 cm^{-1} , which is characteristic for *triplet* nitrenes, probably because the amount of the *triplet* nitrene is too low to be observed by IR. Therefore, it is clear that the photolysis of **1** at 7 K in the crystalline state produces benzofuroxan as the major product, *trans,trans*-1,2-dinitrosobenzene as a minor product, and a trace of *triplet* 2-nitrophenylnitrene.

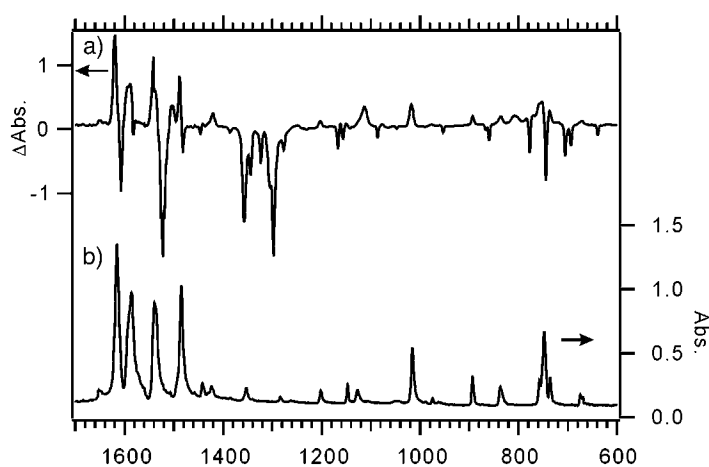


Fig. 5. IR Spectra recorded in a KBr matrix. a) Difference IR Spectra of **1** between those after and before irradiation at 7 K. b) IR spectra of benzofuroxan (**2**) at 300 K.

Crystalline-State Photoreaction Mechanism. Heterocyclic ring formation of benzofuroxan from **1** is generally believed to occur *via* an intermediate showing little *triplet*-nitrene character, probably because the distance between the reaction centers, N(1) and O(2) (2.710(1) Å), is very short so that the cyclization can smoothly proceed *via* *singlet* nitrene (small activation energy). Therefore, trapping *triplet* nitrenes as main products at low temperatures seems to be impossible. In the crystalline-state photoreaction of 2-azido-1,1'-biphenyl at 80 K [8], we, nevertheless, succeeded in observing a *triplet* nitrene by X-ray crystallography, probably because the distance between the reaction centers forming the corresponding carbazole ring is 3.091(1) Å, *i.e.*, considerably longer than in **1**. Although further investigation is necessary to

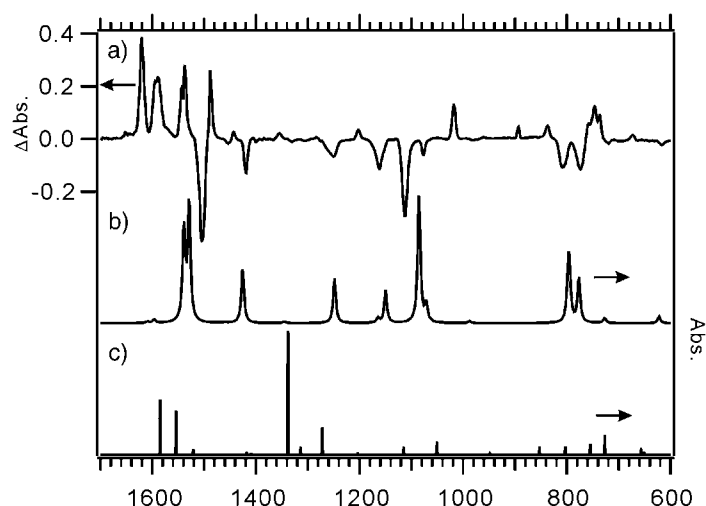


Fig. 6. IR Spectra (KBr matrix) and vibrational analyses. a) Difference IR spectra of **1** (80 K vs. 7 K) after irradiation. b) Calculated spectra for *trans,trans*-1,2-dinitrosobenzene (by Dr. R. Rauhut). c) Simulated spectra for triplet 2-nitrophenylnitrene generated by the DFT UB3LYP/6-31G* level of theory (scale factor 0.97).

understand the behavior of 1,2-dinitrosobenzene in crystals, this compound is clearly formed *via* nitrene and/or benzofuroxan, judging from previous work [4].

Conclusions. – The formation of 1,2-dinitrosobenzene and benzofuroxan (**2**) from **1** on photolysis at low temperatures was confirmed by X-ray crystallography. Combined results obtained from X-ray crystallography, IR spectroscopy, ESR, and theoretical calculations suggest that ring formation proceeds *via* the nitrene with a small activation energy because of the considerably short distance (2.710(1) Å) between the reaction centers. In addition, we detected another intermediate at 7 K by IR spectroscopy in the crystalline state (KBr matrix), *trans,trans*-1,2-dinitrosobenzene, which tautomerizes to benzofuroxan (**2**) on warming to 80 K.

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Experimental Part

General. 1-Azido-2-nitrobenzene (**1**) was prepared by the modified method given in [9]. A transparent crystal suitable for X-ray analysis was obtained from a saturated MeOH soln. at 279 K. Samples were irradiated with a high-pressure Hg lamp (SAN-EI UVF-352S) in combination with a band-path filter (LA2 TOSHIBA; $\lambda = 436$ nm). ESR Spectra were measured on a JEOL JES-TE300 spectrometer equipped with a liquid-He low-temperature device. Fourier-transform IR spectra were recorded on a JASCO FT/IR-5300 instrument. A sample dispersed in a KBr pellet was attached to the cold finger of a He cryogenic refrigerator system (DAIKIN PS24SS) equipped with KBr windows.

Single-Crystal X-Ray-Diffraction Analysis. A crystal was mounted on a tip of a glass fiber with Paratone oil and was cooled to 80 K with a Rigaku cryostat system. The X-ray data were collected on a Siemens SMART CCD X-ray diffractometer before and after photo-irradiation. The crystal was slowly rotated around the ϕ -axis on the goniometer and was irradiated with a high-pressure Hg lamp ($\lambda = 436$ nm) at 80 K for 30 min. The

structures have been deposited at the *Cambridge Crystallographic Data Centre* as CCDC numbers 203791 and 203792.

Refinement of Disordered Structures. Compound **1** was treated as a rigid group based on the initial structure analysis where the rotation around the C(2)–N(4) bond and the bond length were allowed to refine. The rigid group was allowed to translate and rotate and the occupancy factor was adjusted to $1 - x$, where x is the occupancy factor of the produced benzofuroxan. The anisotropic temp. factors obtained from the initial structure analysis were scaled with a unique value (refined scale factor, 1.44074). The temp. factors of O(1A) and O(2A) were refined without a scale factor, because the NO₂ group slightly shifted from its initial position after photolysis. On the other hand, no restraints were applied to either the bond lengths or the isotropic temperature factors of benzofuroxane. The occupancy factor became 0.103(3).

Computational Studies. DFT Calculations were carried out with the GAUSSIAN98 program [10]. An optimized geometry of *triplet* 2-nitrophenylnitrene was obtained at the (U)B3LYP/6-31G* level of theory [11]. Vibrational frequencies obtained at the (U)B3LYP level of theory were scaled by a factor of 0.97.

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