

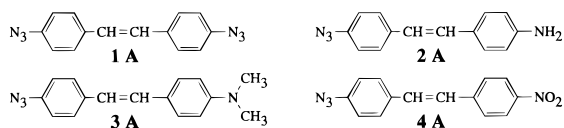
On the Existence of Conjugated Dinitrenes at 77 K

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Both the structure of primary products and the mechanism of reaction in the photolysis of aromatic bisazides have been under contradictory discussion for years. On the basis of the results of different techniques (UV/vis, ESR, IR) authors reported alternately on a biphotonic^{1,2} or a monophotonic^{3,4} process of photolysis of bisazides. Furthermore, some authors reported on the formation of twisted dinitrenes after prolonged photolysis of aromatic bisazides.^{5,6} This could not be confirmed by other scientists who found quinonoid dinitrenes.⁷ In other reports the authors have impressively shown that nitrenes react thermally at 77 K, which makes it difficult to distinguish between primary and secondary products.^{2,8,9} Furthermore, it was shown that a relationship between ESR spectra and molecular structures cannot be established on the basis of simple dipole–dipole models.¹⁰ Independent arguments for the assignment of intermediates are therefore necessary.



We now report mechanistic, chemical, and spectroscopic evidence that resolves earlier discrepancies between various pieces of experimental data. The remaining questions concerning the number of intermediates and their structures, as well as the types of subsequent products at 77 K, are clarified by an exact kinetic analysis of the photochemistry of 4,4'-diazidostilbene (**1A**). The results are compared with those obtained by photolyses of different substituted mononitrene precursors (**2A–4A**). In this way, independent arguments for the assignment of the intermediates that occur upon the photolysis of **1A**, based on their chemical reactions, are obtained for the first time. We utilized studies of UV/vis in combination with ESR studies to characterize the transients.

The UV/vis irradiation spectra of 4,4'-diazidostilbene (**1A**) at 77 K (Figure 1a) are similar to those reported by Reiser¹ but exhibit much better spectral resolution. Irradiation ($\lambda_{\text{exc}} = 313$ or 337 nm) causes a decrease in the absorbance of **1A** ($\lambda_{\text{max}} = 334, 350, 369$ nm), the appearance of an intermediate **1B** ($\lambda_{\text{max}} = 402, 640, 717$ nm), and an increase in the absorbance of **1C** ($\lambda_{\text{max}} = 383, 405, 434$ nm). Given the higher resolution, we are able to discover the formation of an additional product **1D**

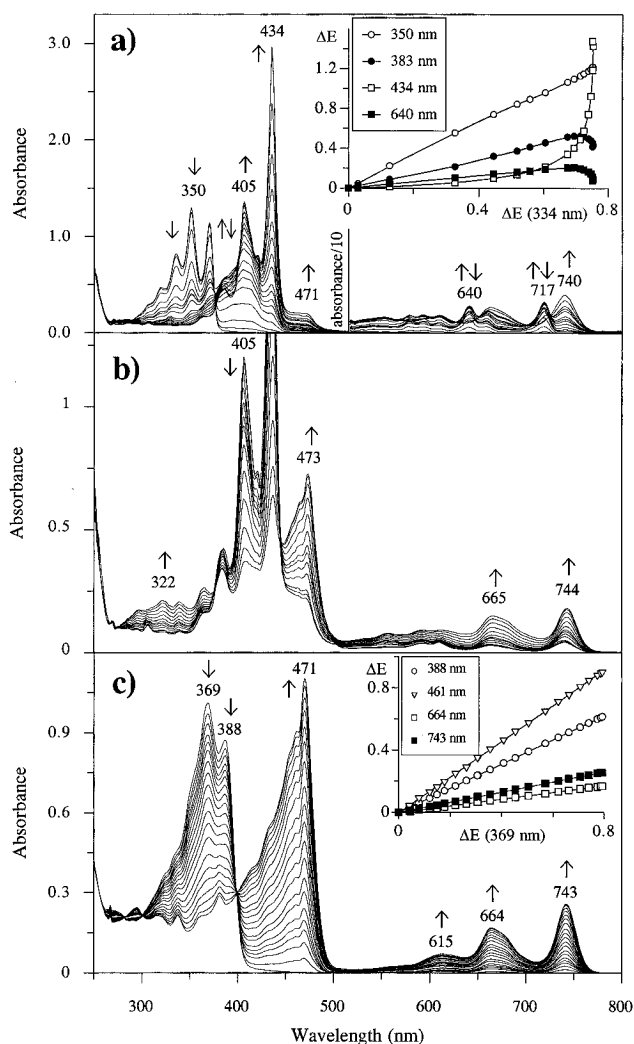


Figure 1. (a) UV/vis irradiation spectra of **1A** in MTHF at 77 K ($c_0 = 1.74 \times 10^{-4}$ mol/L, $\lambda_{\text{exc}} = 337$ nm, nitrogen laser) and corresponding ΔE diagram. Values of absorbance higher than 515 nm are multiplied by 10. (b) UV/vis spectra of the thermal reaction of **1C** between 77 and 87 K in MTHF. (c) UV/vis irradiation spectra of **2A** in MTHF at 77 K ($\lambda_{\text{exc}} = 365$ nm) and corresponding ΔE diagram.

($\lambda_{\text{max}} = 471, 663, 740$ nm; Figure 1a). Continued excitation ($\lambda_{\text{exc}} = 436$ nm, spectral region of strong absorbance of **1C**) shows that **1C** is not photoreactive.¹⁵ The analysis of the dark reaction (Figure 1b) between 77 and 87 K proves **1D** to be the product of the thermal reaction of **1C**.¹⁶ Irradiation with light of 474 nm indicates that **1D** is photochemically stable at 77 K.

Careful kinetic analysis of the irradiation process of **1A** at 77 K using ESR spectroscopy proves the intermediate formation of a triplet mononitrene **1B** ($H_{xy} = 617$ mT, $|D/hc| = 0.796$ cm^{-1}) and the formation of a triplet species **1C** ($H_{\text{res}} = 148, 258, 389$ mT, $|D/hc| = 0.122$ cm^{-1}). Furthermore, a signal in the $g' = 2$ region and the signal of a second triplet mononitrene **1D** ($H_{xy} = 607.5$ mT, $|D/hc| = 0.762$ cm^{-1}) increase in intensity with time (Figure 2).¹⁷ Caused by the thermal reaction at 77 K, the signal of the triplet mononitrene **1D** and the radical signal increase in intensity while that of triplet species **1C** decreases.¹³ It was shown that both the decomposition of **1C** ($k' = 5.1 \times$

(13) See supporting information.

(14) Because of the stronger donor–acceptor interaction in 4'-nitrene-substituted 4-(dimethylamino)stilbene (in comparison to **2B**) a bathochromic shift of its UV/vis spectrum ($\lambda_{\text{max}} = 479, 618, 674, 750$ nm)¹³ and a decrease in its zfs parameter ($H_{xy} = 606$ mT, $|D/hc| = 0.750$ cm^{-1}) are caused. Both the UV/vis and the ESR spectra of 4-nitrene-substituted 4'-nitrostilbene ($\lambda_{\text{max}} = 380, 395, 450$ nm, $H_{xy} = 620.8$ mT, $|D/hc| = 0.801$ cm^{-1}) are completely different from those of **1D**.¹³

(15) See supporting information for footnotes 15–20.

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(1) Reiser, A.; Wagner, H. M.; Marley, R.; Bowes, G. *Trans. Faraday Soc.* **1967**, *63*, 2403.

(2) Brichkin, S. B.; Smirnov, V. A.; Alfimov, M. V.; Naydenova, T. P.; Avramenko, L. F. *J. Photochem.* **1980**, *12*, 25.

(3) Shimizu, S.; Bird, R. J. *Electrochem. Soc.* **1977**, *124*, 1394.

(4) Ohana, T.; Kaise, M.; Yabe, A. *Chem. Lett.* **1992**, 1397.

(5) Ohana, T.; Kaise, M.; Nimura, S.; Kikuchi, O.; Yabe, A. *Chem. Lett.* **1993**, 765.

(6) Ling, C.; Lathi, M. *Chem. Lett.* **1993**, 769.

(7) Minato, M.; Lathi, P. M.; Willigen, H. *J. Am. Chem. Soc.* **1993**, *115*, 4532.

(8) Singh, B.; Brinen, J. S. *J. Am. Chem. Soc.* **1971**, *93*, 540.

(9) Brinen, J. S.; Singh, B. *J. Am. Chem. Soc.* **1971**, *93*, 6623.

(10) Minato, M.; Lathi, P. M. *J. Phys. Org. Chem.* **1993**, *6*, 483.

(11) Platz, M. S.; Leyva, E.; Haider, K. *Org. Photochem.* **1991**, *11*, 367.

(12) (a) Bendig, J.; Mitzner, R.; Dähne, L. *Makromol. Chem. Macromol. Symp.* **1988**, *18*, 145. (b) Dähne, L.; Bendig, J.; Stösser, R. *J. Prakt. Chem.* **1992**, *334*, 707.

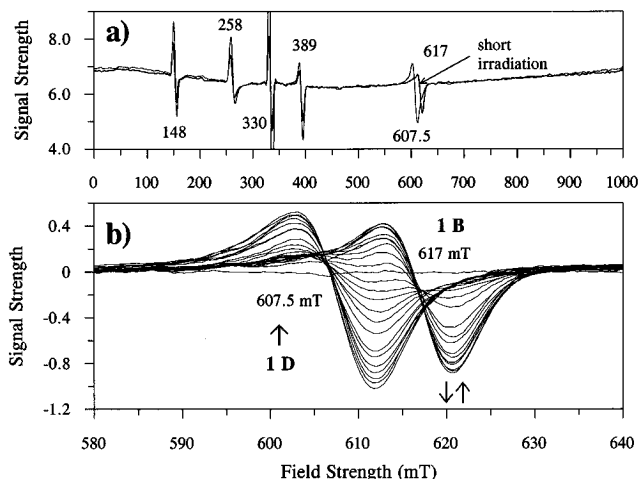


Figure 2. (a) X-band ESR spectra after short and prolonged irradiation of **1A** in MTHF at 77 K ($\lambda_{\text{exc}} = 313$ nm). (b) X-band ESR spectra of **1B** and **1D** obtained upon photolysis ($\lambda_{\text{exc}} = 313$ nm) of **1A** in MTHF at 77 K.

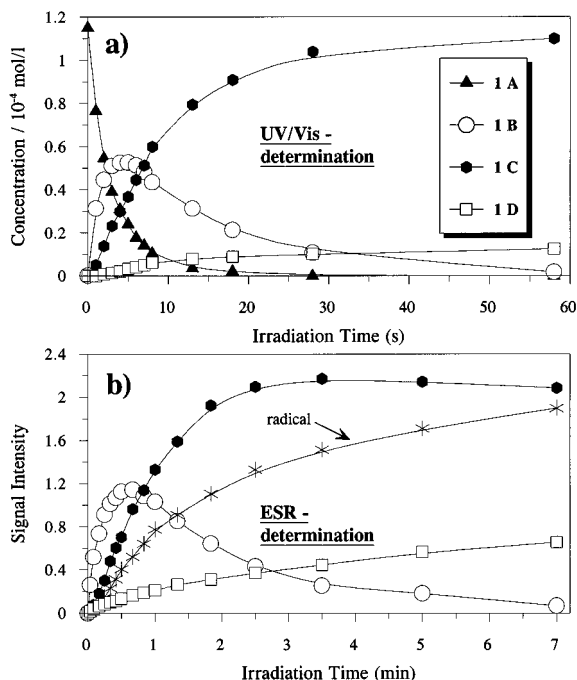


Figure 3. Concentration/time dependence of the transients observed upon photolysis (mercury lamp, $\lambda_{\text{exc}} = 313$ nm) of **1A** in MTHF at 77 K: (a) using UV/vis spectroscopy ($c_0 = 1.15 \times 10^{-4}$ mol/L; **1A**, $\epsilon^{334\text{nm}} = 47\,200$ L/mol·cm; **1B**, $\epsilon^{402\text{nm}} = 61\,304$ L/mol·cm); **1C**, $\epsilon^{434\text{nm}} = 180\,000$ L/mol·cm; **1D**, $\epsilon^{740\text{nm}} = 14\,380$ L/mol·cm); (b) using ESR spectroscopy ($c_0 = 10^{-3}$ mol/L).

10^{-4} min^{-1}) and the formation of **1D** ($k' = 5.4 \times 10^{-4} \text{ min}^{-1}$) run in accordance with the same kinetic law. As observed by UV/vis spectroscopy, **1C** and **1D** are not photoreactive.¹⁵

In Figure 3a,b the UV/vis and ESR results obtained by photolysis of **1A** using the same irradiation equipment but different concentrations (UV/vis, $c = 10^{-4}$ mol/L; ESR, $c = 10^{-3}$ mol/L) are compared. The compatibility of the time scales for the product formation was confirmed by photolyses of samples of equal concentrations (10^{-3} mol/L).¹³

Comparing the results of both techniques, species **1B** is assigned to triplet 4'-nitrene-substituted 4-azidostilbene.

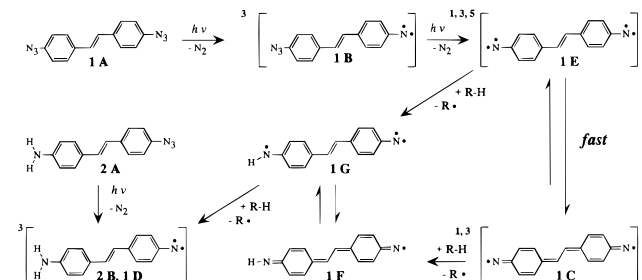
Photolysis of **2A–4A** at 77 K leads each of them to form only one UV/vis active species. The ESR experiments prove these species to be the corresponding triplet nitrenes. In contrast to phenylnitrene derivatives,^{11,12} the triplet stilbene nitrenes generated by photolysis of **2A–4A** are not sensitive to light.

Furthermore, they are thermally stable at 77 K.¹⁹ This makes their assignment by different techniques very reliable.

In a key experiment, both the UV/vis (Figure 1c) and the ESR spectra of 4'-nitrene-substituted 4-aminostilbene (**2B**) ($\lambda_{\text{max}} = 471, 664, 743$ nm; $H_{x,y} = 607.5$ mT, $|D/hc| = 0.762 \text{ cm}^{-1}$), produced independently by photolysis of 4-amino-4'-azidostilbene (**2A**), are essentially the same as those found for **1D**. The small energetic difference in the low-energy part of the UV/vis spectra of **1D** and **2B** at 77 K (**1D**, $\lambda_{\text{max}} = 740$ nm; **2B**, $\lambda_{\text{max}} = 743$ nm) suggests that the effective donor–acceptor interaction in **1D** is somewhat smaller than in **2B**. But the difference in their UV/vis spectra is much less than between **2B** and 4'-nitrene-substituted 4-(dimethylamino)stilbene.¹⁴ The UV/vis spectra shown in Figure 1b are therefore explained by a superimposition of mainly 4'-nitrene-substituted 4-aminostilbene, and by the product of a single hydrogen abstraction (**1F/1G**), in which the donor–acceptor interaction should be somewhat weaker. Since the consecutive thermal and photochemical reactions of **1D** and **2B** between 77 and 300 K are the same,¹⁸ it is certain that **1D** is **2B**.

Since **1D** is the product of the thermal reaction of **1C**, it implies on the basis of chemical arguments that **1C** is the dinitrene. The ESR spectrum of **1C** proves this molecule to have a quinonoid structure (biradical). This statement is the first independent assignment of **1C**.

The reactions of 4,4'-diazidostilbene and its products (in MTHF at 77 K) are summarized in the following scheme. 4,4'-Diazidostilbene (**1A**) reacts biphotonically via the triplet **1B** to the quinonoid species **1C**. **1C** is photochemically stable but reacts thermally under 2-fold hydrogen abstraction from the solvent, thus forming **1D**. The formation of **1D** during thermal reaction proves that the energy of activation for the second hydrogen abstraction by the imine nitrogen is lower than that for the first hydrogen abstraction by the nitrene nitrogen of **1G**.¹⁹ Otherwise, the thermal reaction of **1G/1F** should give the bis-quinimine, for which we have no experimental evidence. The unexpected high yield of **1D** after short irradiation times (Figures 1–3) indicates that the energetic nonequilibrium dinitrene **1E** does not completely relax to form the quinonoid species **1C** but also reacts thermally under hydrogen abstraction from the solvent.



The investigations of 4,4'-diazidobiphenyl (**5**) and 2,7-diazidofluorene (**6**) under equal conditions indicate the existence of the dinitrenes and suggest a similar mechanism of reaction.²⁰

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Supporting Information Available: Experimental procedures for the syntheses of **1A–4A** and their precursors, the UV/vis irradiation spectra of 4-azido-4'-(dimethylamino)stilbene (**3A**) and 4-azido-4'-nitrostilbene (**4A**) at 77 K, the concentration/time behavior during dark reaction of **1C** (ESR determination) at 77 K, and the concentration/irradiation time dependence of **1B** and **1D** under adequate conditions (UV/vis and ESR determination at 77 K) (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.