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Supporting Information

General Methods. UV/Vis spectra were recorded on a Hitachi U-3410 double-beam spectrophotometer using a 1 mm quartz cell. The temperature could be regulated and kept constant between 77 K and 300 K with a precision of 1 degree using a cryostat equipped with a temperature controller. ESR spectra were measured on a ERS-300 spectrometer (X-band microwave unit, 100-kHz field modulation, $f = 9.18$ GHz) equipped with an optical transmission cavity. The azide compound was dissolved in the solvent (10^{-3} mol/L) and placed in a quartz tube (3 mm o.d.). The sample was cooled within the cavity using liquid nitrogen. Samples were irradiated through a water cell (10 cm) and a metal interference filter using a high-pressure mercury lamp (500 W). Irradiation was carried out within the sample chamber of the spectrometer in both UV/vis and ESR spectroscopy. HPLC investigations were carried out using a UV/vis diode array detector (KONTRON 440) and a RP 18 column.

Materials. Unless otherwise described below, all chemicals were used as purchased from Aldrich Chemical Company. 2-Methyltetrahydrofuran was distilled from calcium hydride.

The syntheses were carried out under yellow light.

The purity of products described below was confirmed by HPLC investigations.

trans-4,4'-diazidostilbene (1 A). 20 ml of concentrated HCl and 20 ml of water were added to 2 g of trans-4,4'-diaminostilbene. The mixture was cooled to -10°C and treated dropwise (0.5 h) with a solution of 0.67 g of NaNO_2 in 5 ml of water, and then stirred for another 1.5 h at -10°C . The reaction mixture was filtered at 0°C . A solution of 0.7 g NaN_3 in 10 ml of water was added (0.5 h). The solution was stirred for another 1.5 h at 0°C . The solid was filtered, rinsed with water and dried (yield 75 %). Anal. Calcd: C, 64.1; H, 3.8; N, 32.0. Found: C, 63.7; H, 3.9; N, 31.0. UV/Vis: $\lambda_{\text{max}} = 340$ nm (methanol). IR (KBr; cm^{-1}): 2120.1 (str. $\text{N}=\text{N}=\text{N}$).

trans-4-amino-4'-azidostilbene (2 A). 0.2 g of trans-4,4'-diazidostilbene were dissolved in 20 ml of 85 % ethanol. The mixture was stirred and heated to boiling. Then 0.4 ml of a 1.25 M solution of sodium sulfide, treated for 25 min with hydrogen sulfide, was slowly added. After the solution turned green it was heated to boiling for another 0.5 h and evaporated to dryness at room temperature (without heat, otherwise danger of decomposition). Beside the main product trans-4-amino-4'-azidostilbene, 4,4'-diaminostilbene and 4,4'-diazidostilbene were in the mixture. The solid was recrystallized from ethanol (75 %) several times to obtain a product which contains 92 % of 2 A. It was purified using HPLC (yield about 10 %). Anal. Calcd: C, 71.2; H, 5.1; N, 23.7. Found: C, 71.1; H, 5.0; N, 23.6. UV/vis: $\lambda_{\text{max}} = 344$ nm

(methanol). IR (KBr; cm^{-1}): 2120.3 (str. $\text{N}=\text{N}=\text{N}$).

trans-4-azido-4'-dimethylaminostilbene (3 A). 20 ml of concentrated HCl were added to 1.5 g of trans-4-amino-4'-dimethylaminostilbene. The mixture was cooled in the dark to $-10\text{ }^{\circ}\text{C}$ and treated slowly (1.5 h) dropwise with a solution of 0.48 g of NaNO_2 in 1 ml of water and then stirred for another 5 h at $-10\text{ }^{\circ}\text{C}$. Then the reaction mixture was filtered in the dark at $0\text{ }^{\circ}\text{C}$. A solution of 0.45 g of NaN_3 in 10 ml of water was added and the solution was stirred for another 2 h at $0\text{ }^{\circ}\text{C}$ (dark). The solid was filtered, rinsed with water, and dried (yield 10 %). Anal. Calcd: C, 72.7; H, 6.1; N, 21.2. Found: C, 71.9; H, 5.9; N, 20.8. UV/vis: $\lambda_{\text{max}} = 358\text{ nm}$ (methanol). IR (KBr; cm^{-1}): 2113.7 (str. $\text{N}=\text{N}=\text{N}$).

trans-4-amino-4'-dimethylaminostilbene. 4.2 g of trans-4-dimethylamino-4'-nitrostilbene were suspended in 100 ml of 80 % ethanol. Then a solution of 35 g $\text{FeSO}_4 \cdot 7\text{ H}_2\text{O}$ in 175 ml of water treated with 175 ml of concentrated NH_3 was added. Subsequently the reaction mixture was heated on a steam bath for 2 h and cooled to room temperature. After 12 h the mixture was filtered and the black residue was extracted several times using diethyl ether to isolate the product. After evaporation of the solvent it was recrystallized from ethanol to provide a yield of 68 %. Anal. Calcd: C, 80.6; H, 7.6; N, 11.8. Found: C, 76.9; H, 8.0; N, 11.2. UV/vis: $\lambda_{\text{max}} = 353\text{ nm}$ (methanol).

trans-4-dimethylamino-4'-nitrostilbene. 13.2 g of p-dimethylaminobenzaldehyde, 1.5 ml of distilled piperidine and 16 g of nitrophenyl acetic acid were combined and refluxed for 2 h in an oil bath at $140\text{ }^{\circ}\text{C}$. After cooling down to room temperature the red solid was treated with ethanol filtered and recrystallized from ethanol (yield 85 %). Anal. Calcd: C, 71.6; H, 6.0; N, 10.4; O, 11.9. Found: C, 71.7; H, 6.1; N, 10.4. UV/vis: $\lambda_{\text{max}} = 297, 425\text{ nm}$ (methanol).

trans-4-azido-4'-nitrostilbene (4 A). 20 ml of concentrated HCl were added to 1.56 g of trans-4-amino-4'-nitrostilbene. The mixture was cooled to $-10\text{ }^{\circ}\text{C}$ and treated slowly (1.5 h) dropwise with a solution of 0.46 g of NaNO_2 in 5 ml of water and then stirred for another 6 h at $-10\text{ }^{\circ}\text{C}$. Then the reaction mixture was filtered at $0\text{ }^{\circ}\text{C}$. A solution of 0.46 g of NaN_3 in 10 ml of water was added and the solution was stirred for another 2 h at $0\text{ }^{\circ}\text{C}$. The solid was filtered, rinsed with water, finally with diethyl ether, and dried (yield 70 %). Anal. Calcd: C, 63.2; H, 3.8; N, 21.0; O, 12.0. Found: C, 62.2; H, 3.8; N, 20.6. UV/Vis: $\lambda_{\text{max}} = 283, 364\text{ nm}$ (methanol). IR (KBr; cm^{-1}): 2114.4 (str. $\text{N}=\text{N}=\text{N}$).

trans-4-amino-4'-nitrostilbene. 5 g of trans-4,4'-dinitrostilbene were suspended in 200 ml of 95 % ethanol. The mixture was stirred and heated to boiling. Then 13 ml of a 1.25 M solution of sodium sulfide, treated for 25 min with hydrogen sulfide, were added. After the solution turned dark red it was evaporated to dryness. The residue was extracted with acetone

and recrystallized from acetone (red crystals, yield 52 %). Anal. Calcd: C, 70.0; H, 5.0; N, 11.7; O, 13.3. Found: C, 69.3; H, 5.0; N, 11.5. UV/Vis: $\lambda_{\text{max}} = 287, 403 \text{ nm}$ (methanol). **trans-4,4'-dinitrostilbene.**^{2,3} 10 g of p-nitrobenzyl chloride were dissolved in 30 ml of heated ethanol. Then 3.5 g KOH, solved in a mixture of 3 ml of water and 12 ml of ethanol, were dropwise added at 25°C. The temperature of the reaction mixture rised to about 70°C. It was stirred for 2 h at 70 °C, cooled and filtered. The residue was washed with ethanol (yellow needles, yield 80 %). Anal. Calcd: C, 62.2; H, 3.7; N, 10.4; O, 23.7. Found: C, 62.1; H, 3.7; N, 10.1. UV/Vis: $\lambda_{\text{max}} = 353 \text{ nm}$ (methanol).

References

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- (15) The rate constant of the decomposition of **1C** is raised during irradiation by a factor of about 2. The acceleration of reaction is independent of the irradiation wavelength ($\lambda_{\text{exc}} = 300, 313, 404, 436, 474, \text{ or } 547 \text{ nm}$) and is described by a warming-up of the matrix of about 1.5 K which is ascribed to the energy of vibration caused by the irradiation source.
- (16) The rate constants of the decomposition of **1C** (pseudo first order assumed) are 77 K, $k' = 1.47 \times 10^{-3} \text{ min}^{-1}$; 84 K, $k' = 2.15 \times 10^{-2} \text{ min}^{-1}$, and 87 K, $k' = 2.18 \times 10^{-1} \text{ min}^{-1}$.
- (17) The zfs parameters were determined by calculation of the experimental ESR spectra using the full diagonalization of an appropriate spin-Hamiltonian matrix ($S = 1$).
Empirical correlation: $|D/hc| = 2.87959H_{x,y}^2 - 0.30067$ (D (cm^{-1}), H (tesla), $g = 2.004$, $\nu = 9.18 \text{ GHz}$).
- (18) Between 77 and 83 K there is a thermally-induced, irreversible bathochromic shift of the UV/vis spectra of **1D** and **1B** (**1D**, $\lambda_{\text{max}} = 473, 665, 744 \text{ nm}$, Figure 1b; **2B**, $\lambda_{\text{max}} = 473, 666, 745 \text{ nm}$). **1D** and **1B** react above 85 K¹⁹ to form 4,4'-diaminostilbene and another transient ($\lambda_{\text{max}} = 680 \text{ nm}$), which is both thermally and photochemically reactive. 4,4'-Diaminostilbene was identified by its characteristic UV/vis spectrum at 77 K ($\lambda_{\text{max}} = 339, 363, 383 \text{ nm}$) and by isolation at 300 K using HPLC equipped with a UV/vis diode array detector.
- (19) While the hydrogen abstraction of **1C** starts at 77 K, the hydrogen abstraction of **1D** (**2B**) starts above 85 K,¹⁸ which indicates that N-substitution increases the energy of activation of hydrogen abstraction by the other nitrene nitrogen.
- (20) During photolysis of 4,4'-diazidobiphenyl (**5**) and 2,7-diazidofluorene (**6**) at 77 K we found kinetic behavior similar to that described above for 4,4'-diazidostilbene.

After reaction of the azido nitrenes (4'-nitrene-substituted 4-azidobiphenyl, $H_{xy} = 649.5$ mT, $|D/hc| = 0.914 \text{ cm}^{-1}$; 7-nitrene-substituted 2-azidofluorene, $H_{xy} = 643.6$ mT, $|D/hc| = 0.892 \text{ cm}^{-1}$) and of the dinitrenes, additional mononitrenes are formed during thermal reaction between 77 and 87 K. Both the UV/vis and the ESR spectra of these mononitrenes agree essentially with those of the amino nitrenes (4'-nitrene-substituted 4-aminobiphenyl, $\lambda_{\text{max}} = 388, 607 \text{ nm}$, $H_{xy} = 636$ mT, $|D/hc| = 0.864 \text{ cm}^{-1}$; 7-nitrene-substituted 2-aminofluorene, $\lambda_{\text{max}} = 381, 607 \text{ nm}$, $H_{xy} = 632$ mT, $|D/hc| = 0.849 \text{ cm}^{-1}$)¹⁷ which were generated independently by photolysis of the corresponding amino azides. This proves that the dinitrenes generated from 5 and 6 also react thermally under 2-fold hydrogen abstraction from the solvent. In contrast to 4,4'-dinitrene-substituted biphenyl, 2,7-dinitrene-substituted fluorene cannot twist. The strong similarity of the spectroscopic data of the intermediates generated from 5 and 6 supports our statement that the additional mononitrene signal, which occurs during photolysis of 5,⁵ is caused by an amino nitrene. Furthermore, the results suggest the alternative interpretation that the new mononitrene signal, which occurs during photolysis of 7,⁶ is due to 4'-nitrene-substituted 4-amino-2,2'-dimethylbiphenyl.

Twisted dinitrenes were not found by our work, but their existence is not excluded.

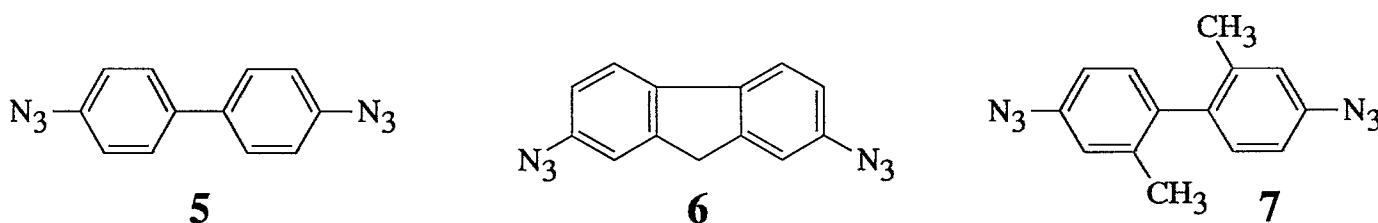


Figure 1. Comparison of the concentration/time dependence of 1 B and 1 D by UV/vis and ESR spectroscopy during photolysis of 4,4'-diazidostilbene (1 A) at 77 K in MTHF using adequate conditions (optical density of 1 A and irradiation equipment). UV/vis spectra were recorded using the very weak absorption bands of 1 B and 1 D between 600 and 750 nm.

Figure 2. Intensity/time behavior of the ESR signals (1 C, 1 D, radical) in the dark at 77 K.

Figure 3. UV/vis irradiation spectra of 4-azido-4'-dimethylaminostilbene (3 A) in MTHF at 77 K ($\lambda_{\text{exc}} = 365 \text{ nm}$) and corresponding ΔE diagram.

Figure 4. UV/vis irradiation spectra of 4-azido-4'-nitrostilbene (4 A) in MTHF at 77 K ($\lambda_{\text{exc}} = 365 \text{ nm}$) and corresponding ΔE diagram.

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