

Ultrafast photoisomerization dynamics of heterodiazocines upon $S_1(n\pi^*)$ photoexcitation by femtosecond electronic absorption spectroscopy

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Diazocines are bridged azobenzenes which exhibit much higher switching efficiencies and quantum yields than normal azobenzenes.^[1,2] Chemical substitution of the chain enables a high

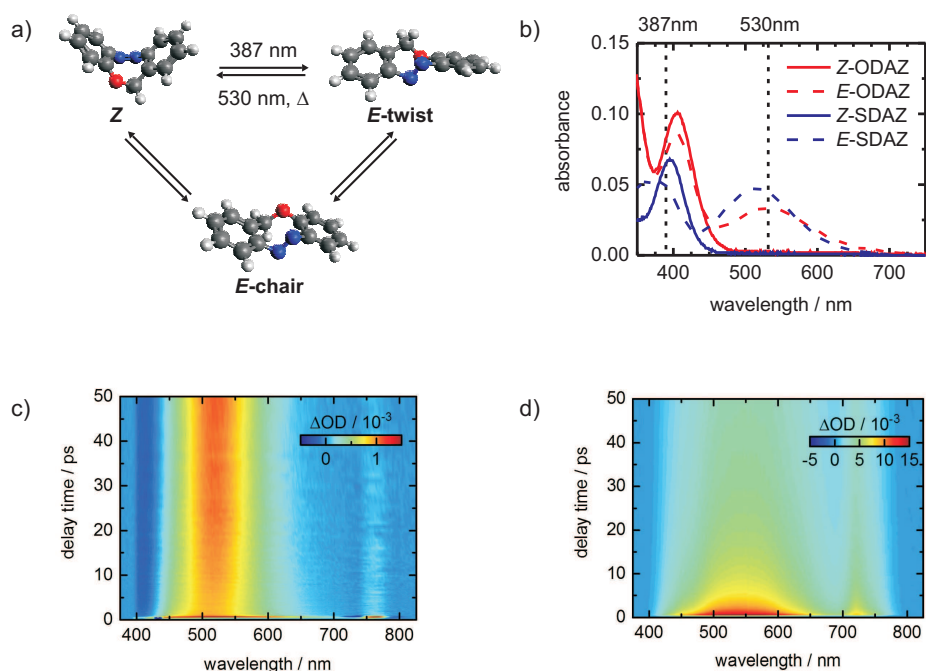


Figure 1: a) Photoisomerization scheme of ODAZ. The thermodynamically stable *E*-form and the two possible *Z*-isomers after photoexcitation are shown. b) Static UV/vis spectra of the *E*-isomers and *Z*-isomers of ODAZ and SDAZ. Two-dimensional spectro-temporal absorption maps of c) ODAZ and d) SDAZ after $S_1(n\pi^*)$ excitation at 387 nm.

variation potential. Depending on the heteroatom incorporated in the bridge moiety, the photochemical behavior changes dramatically.

We investigated 12*H*-dibenzo[*b,f*][1,4,5]oxadiazocine (ODAZ)^[3] and 12*H*-dibenzo[*b,f*][1,4,5]thiadiazocine (SDAZ)^[3] using femtosecond time-resolved electronic absorption spectroscopy. The *Z* → *E* isomerization of both components was studied after excitation at $\lambda = 387$ nm and probed at wavelengths from $\lambda = 390 - 750$ nm. The observed transient spectra for ODAZ show an initial intense excited-state absorption (ESA) which decreases within the experimental time resolution ($\tau < 150$ fs). After $\Delta t = 10$ ps a positive contribution grows in which can be assigned to product formation. Additionally, we observed a ground state bleach below $\lambda = 400$ nm. These ultrafast dynamics are confirmed by quantum chemical calculations employing a floating occupation configuration-interaction (FOCI-AM1) method. In contrast, SDAZ shows much slower dynamics. A strong ESA band was observed dominating the spectral signature over the entire time frame of the measurement. This ESA band contains a fast decay component ($\tau_1 = 0.41$ ps) and two slower contributions ($\tau_2 = 5.1$ ps and $\tau_3 = 82$ ps), which end up in a constant offset indicative for product absorption. Moreover, we investigated the *E* → *Z* isomerization for both molecules after $S_1(n\pi^*)$ excitation at $\lambda = 530$ nm.

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