

# 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.<sup>[1,2]</sup> Chemical substitution of the chain enables a high

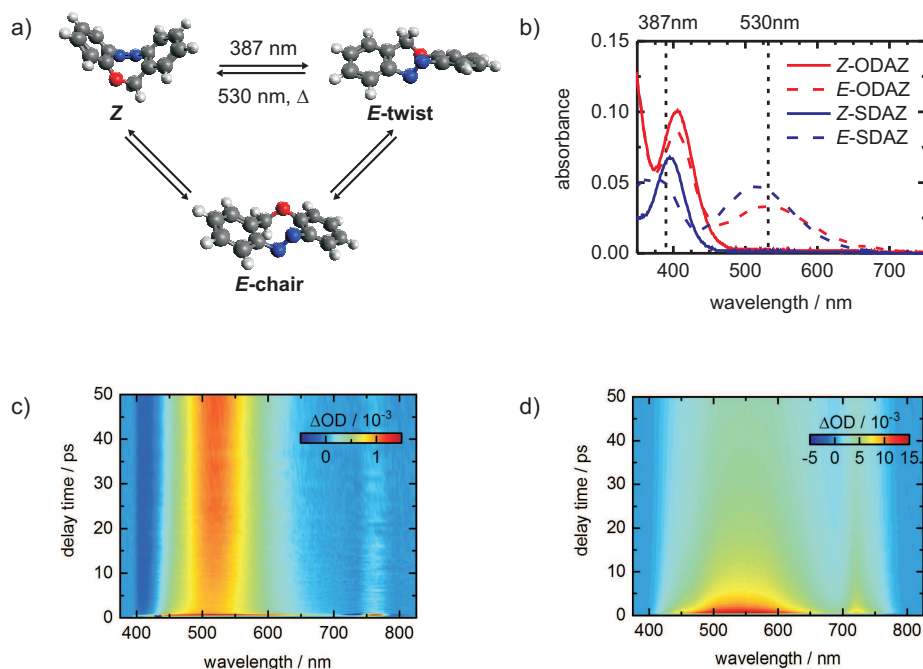


Figure 1: a) Photoisomerization scheme of ODAZ. The thermodynamically stable E-form and the two possible Z-isomers after photoexcitation are shown. b) Static UV/vis spectra of the E-isomers and Z-isomers of ODAZ and SDAZ. Two-dimensional spectro-temporal absorption maps of c) ODAZ and d) SDAZ after  $S_1(n\pi^*)$  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)<sup>[3]</sup> and 12*H*-dibenzo[*b,f*][1,4,5]thiadiazocine (SDAZ)<sup>[3]</sup> using femtosecond time-resolved electronic absorption spectroscopy. The *Z*  $\rightarrow$  *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*  $\rightarrow$  *Z* isomerization for both molecules after  $S_1(n\pi^*)$  excitation at  $\lambda = 530$  nm.

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### References:

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