

Tuning of isomerization rates in indigo-based photoswitches

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Abstract: Ultrafast excited-state dynamics in indigo-based photochromic compounds was studied with the transient absorption spectroscopy and *ab initio* calculations. We demonstrated an approach of adjusting excited state relaxation routes and photoisomerization rates for applications where fast photoswitching is needed.

OCIS codes: (000.0000) General; (000.0000) General [8-pt. type. For codes, see www.opticsinfobase.org/submit/ocis.]

Introduction

Manipulation of chemical reactions in molecules not only represents a challenging task in chemistry, but also is an important aspect for applications. Different classes of photochromic molecules were proposed for various applications in chemistry, biology, material science [1,2]. However, to be suited for a particular application, a photochromic molecule should fulfill necessary requirements, such as separated absorption spectra for both photochromic isomers, fast isomerization reactions, high thermo- and photostability as well as good fatigued resistance for both isomers. Therefore, adjustment of photochemical and photophysical properties of the molecules of interest should be done. Commonly, those properties can be tuned by changing external (e.g., solvent polarity) or internal (e.g., chemical substitutions) conditions. Recently we have studied a wide range of indigo-based photoswitches focusing our interest on the photoswitching rates [3,4].

An example of isomerization in the hemithioindigo (HTI) photoswitch is shown in fig. 1. The photoisomerization reaction takes place at the central double bond, where the stilbene part and the hemithioindigo parts form a donor-acceptor system, respectively. By attaching chemical groups with different electron-donating strength on the stilbene part and carrying out time-resolved experiments we demonstrated that the rates of the photoisomerization reaction can be successfully tuned. With the help of quantum chemical calculations a detailed understanding of the isomerization processes at the excited state was obtained.

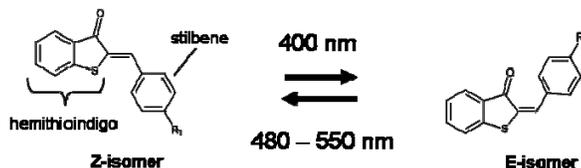


Fig. 1. Chemical structure of the Z- and E-isomers of HTI. The photoreaction between the two isomers is driven with visible light. The R_1 indicates the attachment position for chemical substituents.

Experimental

The time-resolved experiments were carried out on the Ti:Sapphire-based laser amplifier system (Spectra Physics) that delivers pulses at a central wavelength of 800 nm, with a repetition rate of 1 kHz and a pulse duration of 130 fs. The pump pulse is frequency doubled ($\lambda = 400$ nm) and/or converted using a home-built two-stage non-collinear optical parametric amplifier (NOPA). For the excitation of the HTI-derivatives presented here, the excitation (pump) wavelengths of 400 nm, 480 nm, 500 nm, 530 nm were used with duration down to 60 fs. The white-light pulses ($\lambda = 350-700$ nm), used as the probe, are generated by continuum generation from the 800 nm light in a CaF_2 plate. The sample solved in dichloromethane is circulated with a peristaltic pump.

Results and Discussions

The hemithioindigo molecules, as a new class of photoswitchable compounds, are attractive for fundamental and applied studies due to their good isomerization efficiencies and absorption bands located in the visible spectral range for both isomers. The dynamics of the excited states was studied in a pump-probe experiment where changes in absorption were monitored in a time interval up to 3 ns with a time resolution of appr. 50 fs. Examples of transient absorption spectra for the Z- and E-isomers are shown in figure 2.

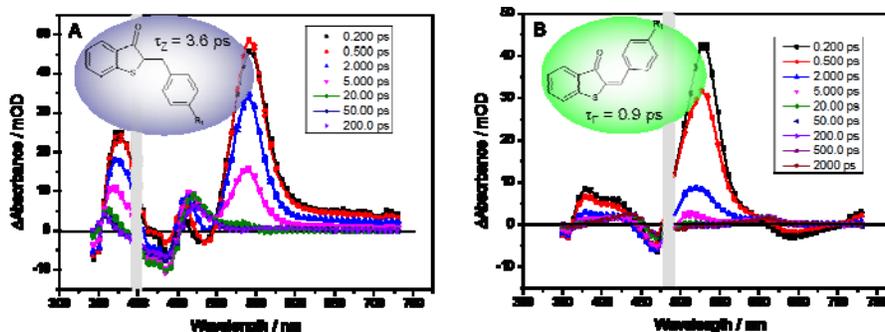


Fig. 2. Transient absorption changes as a function of the time delay in Z-isomer (a) and E-isomer (b) of the methoxy-substituted HTI in dichloromethane. The structure of the corresponding isomers and their isomerization life times extracted from the fit are given in the top left. Gray areas indicate the excitation wavelengths.

The positive signal in both sets of spectra is due to excited-state absorption (ESA) whereas the negative signal observed near 400 nm for the Z-isomer (figure 2a) and near 480 nm for the E-isomer (figure 2b) is a result of ground-state bleaching (GSB). The fast evolution of the absorption signals are observed within the first 2-10 picoseconds for both isomers and assigned to the relaxation of the excited states. The excited-state decay is followed by a slower process assigned to vibrational cooling in the hot ground state. The reaction is complete with a building of a positive absorption signal that remains constant within the studied time interval. Those signals are attributed to formation of the opposite photochromic isomer.

Comparison of the dynamics for all the derivatives, bearing single and multiple substitutions, showed that the increase in the donating strength of a substituent leads to acceleration of the reaction rates as can be seen in the table 1 (from 38 ps to 4.8 ps). The electron-donating strength is described by the Hammett parameter, σ^+ , which is more negative for stronger electron-donating groups.

Table 1. Isomerisation rates for the Z/E-reaction in selected HTI-derivatives with a single substitution.

Isomerisation time, Z/E reaction	$R_1 = \text{H}$ ($\sigma^+ = 0$)	$R_1 = \text{CH}_3$ ($\sigma^+ = -0.31$)	$R_1 = \text{SCH}_3$ ($\sigma^+ = -0.6$)	$R_1 = \text{N}(\text{CH}_3)_2$ ($\sigma^+ = -1.7$)	$R_1 = \text{C}_6\text{H}_{12}\text{N}$ ($\sigma^+ = -2.2$)
τ_Z	38 ps	13 ps	4.8 ps	10 ps	29 ps

However, in the presence of very strong donors, the rates for the Z/E reaction slow down again (10 ps and 29 ps). This phenomenon is attributed to a change in the energies of the excited states involved in the relaxation. It was established for HTI that the isomerisation proceeds via a barrier formed by a forbidden crossing between the locally-excited S_1 state and a charge-transfer S_2 state. Acceleration of the reaction is assigned to decreasing of the reaction barrier due to energetic lowering of the S_2 state solely. For very strong donors however both, the energies of the S_1 and the S_2 states are lowered, leading to an increase of the barrier and therefore to the reduction of the reaction rates.

From the experimental results supported by high-level *ab initio* calculations we conclude that the reaction rates can be tuned via the donor-acceptor character of the HTI molecule. We have shown that electron donating substituents may accelerate the reaction significantly. However, when the single, electron donating group becomes very strong, the potential energy surface is changed significantly and the original trend is inverted. Further acceleration of the isomerisation reaction can be achieved by multiple substituents on the stilbene part of the molecule.

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