

Ultrafast photo-induced Z-E and E-Z isomerizations of a severely constrained azobenzene with improved photochromic properties

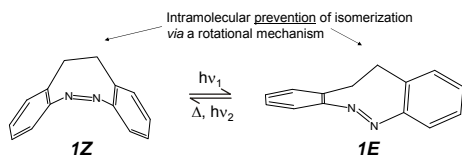
R. Siewertsen^a, F. Renth^a, B. Buchheim-Stehn^b, R. Herges^b, F. Temps^a

^a Institut für Physikalische Chemie, ^b Otto-Diels-Institut für Organische Chemie
Christian-Albrechts-Universität zu Kiel, D-24098 Kiel, Germany



Introduction

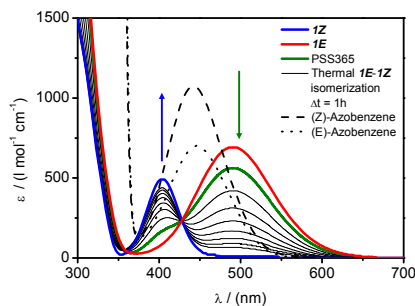
The photo-induced isomerization of azobenzene (**AB**) and its derivatives forms the basis of numerous applications as molecular optical switches and light-driven molecular machines. [1]



Isomerization scheme of the bridged azobenzene derivative 5,6-dihydro-dibenzo[c,g][1,2]diazozin (**1**).

- To design new functional optical devices, a detailed knowledge of the influence of affecting factors such as steric hindrance on molecular dynamics is required.
- The ethylene bridge in **1** strongly impedes the rotation about the central NN-bond and restricts the simultaneous opening of the NNC bond angles.
- The photoinduced isomerization of **AB** and its derivatives proceed on an ultrafast timescale [2,3,4]. Femtosecond time-resolved spectroscopy is indispensable to obtain detailed information of the molecular dynamics of **1**.

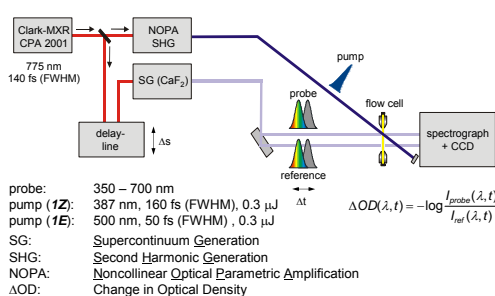
Static UV/Vis Spectra and Photokinetics



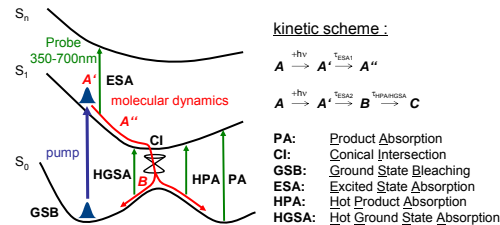
UV/Vis-spectra of **1Z** and **1E** in *n*-hexane and thermal **1E-1Z** isomerization after irradiating at $\lambda = 365$ nm (PSS365). The spectrum of **1E** was derived from the photostationary state at $\lambda = 365$ nm (PSS365) with a least-squares fit of the PSS365 curve.

- Clearly separated absorption maxima at $\lambda = 404$ nm for **1Z** and $\lambda = 490$ nm for **1E** attributed to a $S_1 \leftarrow S_0$ ($n\pi^*$) transition.
- Improved photochromic properties compared to unbridged azobenzene (**AB**), where the corresponding maxima of the $S_1 \leftarrow S_0$ ($n\pi^*$) transitions are between 430 and 440 nm.
- Contrary to other **AB** the (Z)-isomer of **1** is the thermodynamically stable form. Kinetic measurements yielded an thermal E-Z-isomerization half-time of $\tau_{1/2} = 3.7$ h.

Transient Absorption Setup

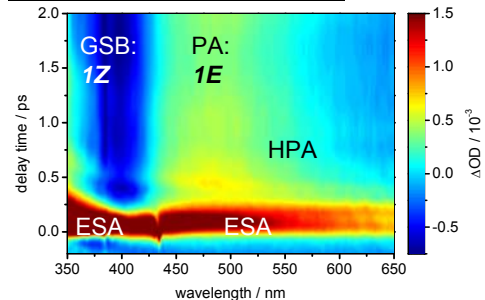


Molecular Contributions



Dynamics of 1Z after photoexcitation

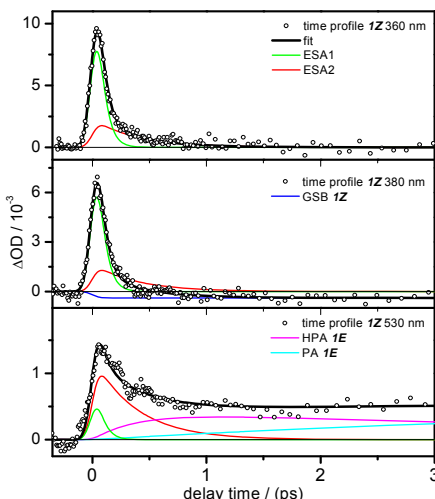
a) Spectrotemporal evolution $\Delta OD(\lambda, t)$



Spectrotemporal evolution ($\Delta OD(\lambda, t)$) of the transient absorption following excitation of **1Z** at $\lambda_{pump} = 387$ nm.

- GSB of **1Z** (350 - 450 nm) and ESA (350 - 650 nm) rise instantaneously after excitation.
- ESA decays rapidly within the first few hundred fs.
- HPA of **1E** rises on the time scale of the ESA-decay and subsequently decays on a ps-time-scale (500 - 650 nm).
- A positive offset due to PA of **1E** remains.

b) Time Profiles $\Delta OD(t)$ of 1Z



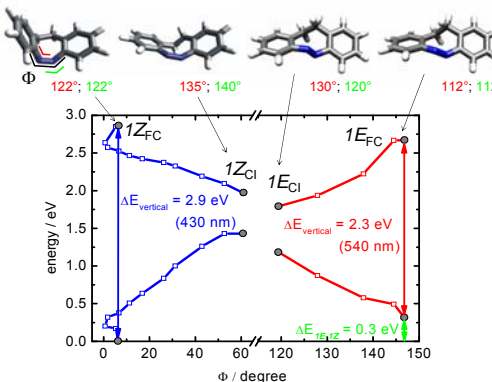
Time profiles $\Delta OD(t)$ at selected wavelengths fitted according to the kinetic scheme with exponential functions convoluted with a gaussian.

- Time constants obtained from a global fit:

λ / nm	τ_{ESA1} / ps	τ_{ESA2} / ps	τ_{HPA} / ps
350 - 500	0.10 (4)	0.28 (7)	—
500 - 650	0.10 (4)	0.28 (7)	6 (7)

- τ_{ESA1} describes the initial dynamics out of the Franck-Condon region.
- τ_{ESA2} corresponds to the isomerization time scale.
- τ_{HPA} is the time scale of vibrational cooling of **1E** in the electronic ground state.

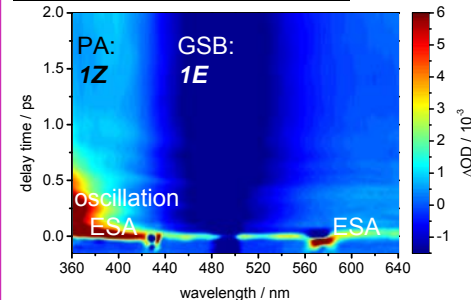
Excited State Geometry Optimizations



TDDFT/B3LYP/def2-TZVP excited state geometry optimizations show complex reaction coordinates for both isomerization directions.

Dynamics of 1E after photoexcitation

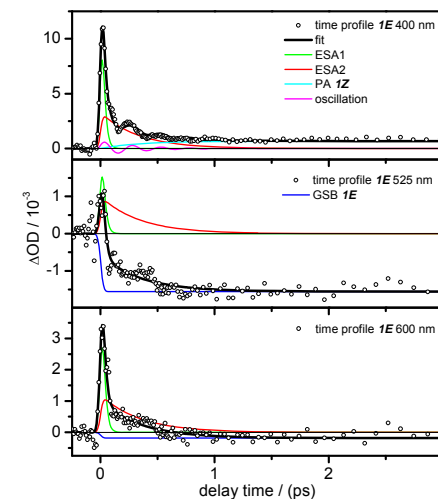
a) Spectrotemporal evolution $\Delta OD(\lambda, t)$



Spectrotemporal evolution ($\Delta OD(\lambda, t)$) of the transient absorption following excitation of **1E** at $\lambda_{pump} = 490$ nm.

- GSB of **1E** (400 - 600 nm) and ESA (350 - 650 nm) instantaneously after excitation.
- Distinct oscillatory behaviour attend to the change in optical density at shorter wavelength (350 - 450 nm).
- ESA and oscillation decay within the first few hundred fs
- A positive offset due to PA of **1Z** remains.

b) Time Profiles $\Delta OD(t)$ of 1E



Time profiles $\Delta OD(t)$ at selected wavelengths fitted according to the kinetic scheme with exponential functions convoluted with a gaussian.

- Time constants obtained from a global fit:

λ / nm	τ_{ESA1} / ps	τ_{ESA2} / ps	ν_{osc} / cm^{-1}
350 - 450	> 0.05	0.35 (6)	133 (18)
500 - 650	> 0.05	0.35 (6)	—

- τ_{ESA1} describes the initial dynamics out of the Franck-Condon region.
- τ_{ESA2} corresponds to the isomerization time scale.
- Observed oscillations are interpreted as excited-state vibrations perpendicular to the E-Z reaction path.

Conclusions

- The photo-induced isomerization of azobenzenes excluding a rotational reaction pathway is possible.
- The ultrafast time scales of both isomerization directions suggests barrierless excited state reaction pathways including a CI to the electronic ground state as found for unbridged azobenzenes. [2,3]
- 1** has an high application potential because of the photochromic behavior and the large geometric differences of the two isomers.

References

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