

Ultrafast dynamics of bis- and trisazobenzenes

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Azobenzenes (AB) are photochromic switches extensively employed for the development of photoswitchable nanostructures. Their photochromism is relatively well-characterized and is based on the ultrafast $E \leftrightarrow Z$ isomerization of the central N=N bond.^[1] However, the properties of connected ABs are not well understood. The interactions between individual photoswitch units result in higher level of complexity along with a variety of new properties important for the development of advanced photoresponsive systems. We present here a combined femtosecond transient absorption (TA) and quantum chemical calculation study on the photoinduced dynamics of *o*-, *m*-, *p*-bis(AB)s, cyclo-bis(AB) (CBA), and cyclo-tris(AB) (CTA) (Fig. 1) - elementary examples for multiazobenzene constructs.

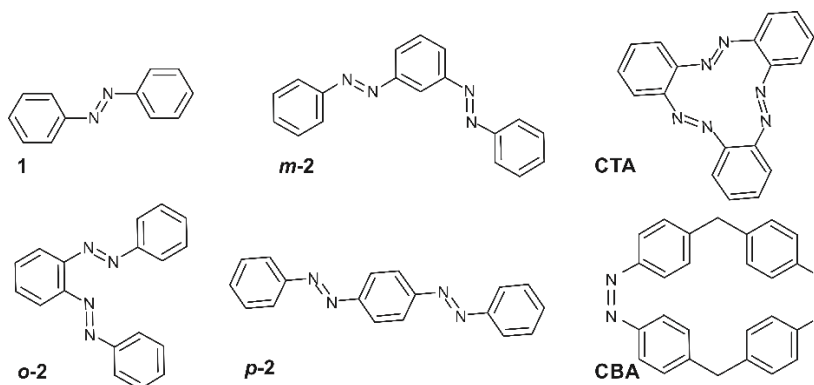


Figure 1. Structures of the studied compounds. **1** - AB; **o-2** - *o*-bis(AB); **m-2** - *m*-bis(AB); **p-2** - *p*-bis(AB); **CTA** - cyclo-tris(AB); **CBA** - cyclo-bis(AB)

The TA measurements^[2] were performed using 100-120 fs pulses tuned either to the $\pi\pi^*$ or the $n\pi^*$ band of the *E*- or *Z*-isomers of the investigated compounds. The resulting data were transformed into the lifetime space and presented as lifetime density maps (LDM)^[3]. Quantum chemical calculations were performed to understand the molecular origin of the spectral properties and the dynamics of the investigated compounds.

We find that the connectivity pattern between the individual switches in **o-2**, **m-2** and **p-2** plays a key role in their spectral characteristics, ultrafast dynamics and general photochromic properties.^[4] The individual AB moieties within **m-2** are largely decoupled and thus, behave as independent photoswitches. Therefore, the dynamics of **m-2** is comparable to that of single

AB. The AB units of **o-2** are not conjugated, but their $\pi\pi^*$ transition dipole moments interact, which results in intramolecular excitonic coupling. We show that **o-2** undergoes $E \rightarrow Z$ isomerization, but due to the very high thermal relaxation rate, no accumulation of the Z-isomer is possible. In contrast, **p-2** has a strongly conjugated π -system that extends over the complete molecule. This decreases the energy of the $\pi\pi^*$ transition and keeps the molecule planar, resulting in a reduced excited state lifetime and a low isomerization quantum yield.

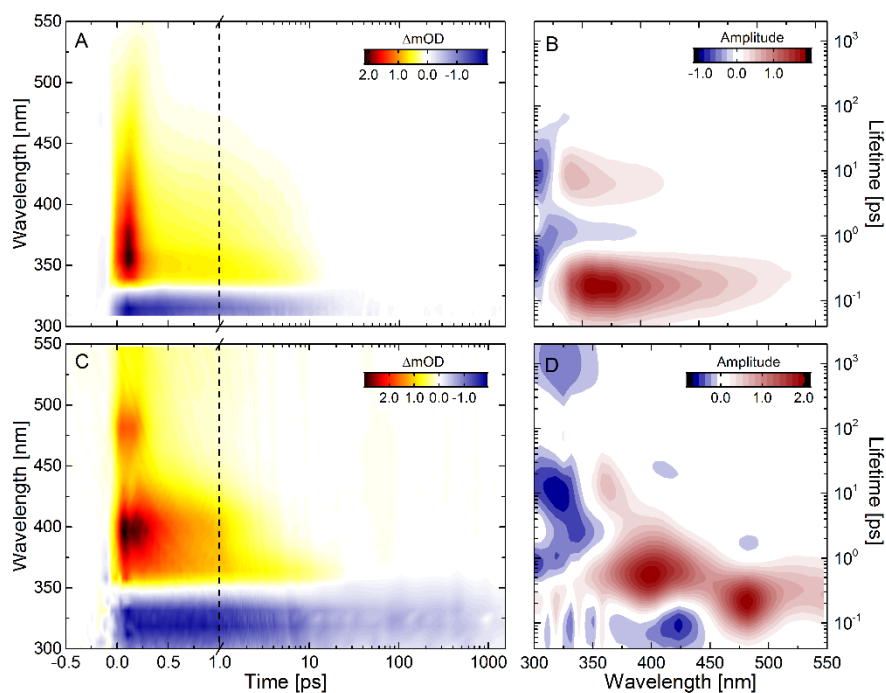


Figure 2. Comparison of the ultrafast dynamics of the E-isomers of AB and CTA after excitation in the $\pi\pi^*$ band. TA data and LDMs of CTA (A,B) and AB (C,D) correspondingly.

Structural constraints can alter the photoisomerization of AB, but it has not been shown that they can block it. CBA and CTA have strongly constrained structure and under stationary illumination do not show any photochromism. Our studies demonstrate that the isomerization of CTA is completely blocked and the excitation energy is dissipated on the ultrafast timescale without any photoproduct formation (Fig. 2). In contrast, photoisomerization is possible in CBA, but high thermal relaxation rate prevents photoproduct accumulation. Based on the theoretical calculations we develop a molecular picture for the observed dynamics.

In conclusion, the azobenzene photochromism shows a strong dependence on the structural constraints and on the connectivity pattern between the individual photoswitch units in multiazobenzene constructs. Understanding these properties opens the way to a rational design of new structures with versatile applications.

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References:

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