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Communication

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Unraveling the Photoswitching Mechanism in Donor–Acceptor Stenhouse Adducts

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Supporting Information Placeholder

ABSTRACT: Molecular photoswitches have opened up a myriad of opportunities in applications ranging from responsive materialsand control of biological function to molecular logics. Here, we show thatthe photoswitching mechanism of donor–acceptor Stenhouse adducts (DASA), a recently reported class of photoswitches, proceeds by photoinduced*Z–E* isomerization,followed by a thermal,conrotatory 4π-electrocyclization. The photogeneratedintermediate is manifested bya bathochromically shiftedband in the visible absorption spectra of the DASA. The identification of the role of this intermediate reveals a key step in the photoswitching mechanism that is essential tothe rational design of switching properties *via*structural modification.

Molecular switches undergo reversible changes in their structure in response to external stimuli, such aslight or changes in the chemical environment.[1] The use of light as an external stimulus is often preferred over chemical stimuli due to its non-invasive nature,[2–6]and orthogonality to many other processes. Furthermore, light can be applied withprecise spatial and temporal control.[3,4] The photoinducedchangesto molecular structure are manifested in changes to molecular properties, such as dipole moment, conjugation and charge, which can alterthe function of molecules in more complex systems.[7–11]Photoswitchable control elements have been applied successfully in material sciences,[5,12–16]supramolecular chemistry[17–21]and biological systems.[22–27]The range of well-established photoswitches includes azobenzenes, diarylethenes and spiropyrans.[1,15,28–32]The properties of photoswitches can often be tuned easily to provide optimum performance for specific applications, primarily because of the detailed understanding available of the underlying electronic and steric factors that control their photoswitching behavior.

An especially important tunable property is that of switching withvisible light.[26,33–36]Indeed visible light controlled photoswitches are receivingincreasing attention mainly due to photodamage and -degradation observed with short wavelength irradiation in biological and material systems.[26,37–39]Photoswitches that respond to light in the wavelength range650 nm to 900 nmare especially important for biological applications,[40,41]as was recently demonstrated by Woolley and co-workers with the switching of azobenzenes in whole blood.[42]

A new class of visible light photoswitches,the donor–acceptor Stenhouse adducts (DASAs), has been recently introduced by Read de Alaniz, Hawker and co-workers(Figure 1).[43–45] DASAs are stable, synthetically accessible T-type photoswitches.[1,43,44]Initial reports explored the structural scope of DASAsand demonstrated the remarkable control over micelle stability that they can provide and the potential as phase-transfer tags.[43–48]Upon irradiation with visible light (λ= 540 – 580 nm) in aromatic solvents (*e.g.* toluene), the linear triene-form **A**of DASA cyclizes to a zwitter-ionic form**B**(Figure 1 and S1–S6). Form**B**is thermally unstable and reverts to the trieneisomer**A**on the time-scale of seconds to minutes (Figure 1). The triene form**A** is strongly colored ($\varepsilon_{\lambda\text{max}}$ ~10^5 M^{-1} cm^{-1}), whereas**B**is colorless.[43] Although mechanistic studies have, to the best of our knowledge, not been reported to date,[46,49]a 4π-electrocyclizationis anticipated to be crucial, by analogy to the Piancatelli rearrangement.[50–52]

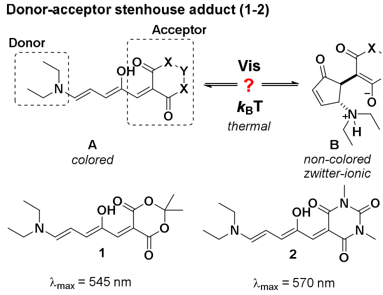


Figure 1. Molecular structure and photoswitching of donor–acceptor Stenhouse adducts (DASAs; **1**-**2**) in toluene.

The understanding of the specific mechanism by which DASAs undergo photoswitching is essential toenable the full potential of these highly promising switches to be realized. It is furthermore important for addressingthe pronounced solvent-dependence of the photoswitching and the ability to tune thermal half-life of **B** and wavelength of excitation for **A**. Insightinto the mechanism is expected to lead to the application of DASAs in more complex functional systems, as was the case withspiropyrans after their switching mechanism was understood well enough to use these photochromic compounds in a highly diverse range of applications.[15,30–32,53–55]

Herein, we show that the photoswitching mechanism of DASAs involves an actinic step which precedesa thermal 4π-electrocyclization. Weidentifya photo-generated intermediate**A'** (proposed *Z–E*isomerization),which then undergoes thermal 4π-electrocyclization to give the closed form**B**. Temperature dependent UV/Vis absorption spectroscopy and NMR measurements (in addition to TD-DFT calculations)provide insight into the mechanism and reaction kinetics.

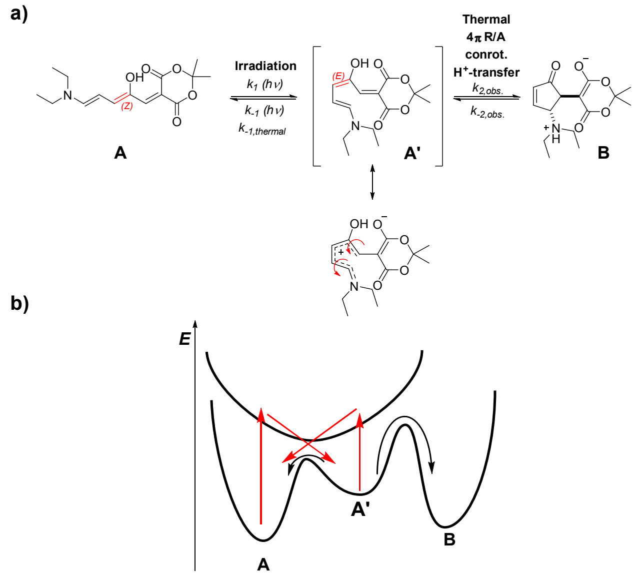


Figure 2. Photoswitching mechanism of DASAs: a) Proposed photoswitching mechanism;b) Representation of the photoswitching pathway in an energy level diagram.

Consideration of possible reaction mechanisms led us to propose initial *Z–E*isomerization (to form **A'**, Figure 2) followed by cyclization to **B** (Figure 2). Considering the stereochemistry of **B** (confirmed by X-ray analysis by the groups of Hawker and Read de Alaniz[43,44]), the cyclization is expected to be a conrotatory, thermally allowed 4π-electrocyclization.[43,44]Hence, we focused on observing the intermediate **A'**. Studyof the photoswitching process in toluene led to the observation of a transient band in the UV/Vis absorption spectrum during photoswitching of **1**(Figure 3, Figure S11–S13). Upon irradiation, the main absorption band of the linear triene (*"open"*) **A** at545 nm diminishes, while a new, red-shifted absorption band at 600 nm transiently appears.

The time-dependent behavior of the visible absorption of **1**at 293 Kis as follows (Figure 3b, Scheme 1a, and Figures S7, S11–S13): a rapid initial increase in absorbance at λ_{max} 600 nm is observed upon irradiation, followed by a slower decay. Cessation of irradiation is followed by a rapid decrease in absorbance at600 nm. Notably, this absorption bandis not observed upon thermal relaxation from state **B** to **A**. The maximum absorption reached at 600 nm was directly dependent on the photon flux and wavelength of irradiation (Figures S18 and S19). At 253 K, the absorption band at 600 nm increases and is then stable during irradiation (Scheme 1b; Figure S17). Upon cessation of irradiation, the absorbance of the band decreases exponentially with an isosbestic point maintained at 566 nm (Figure S17).

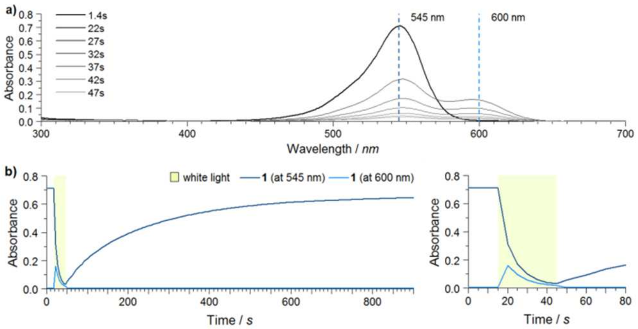
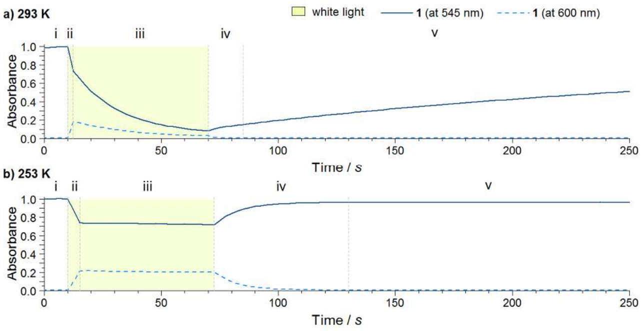


Figure 3. Observation of a transient absorption band: a) Absorption spectra at indicated time-points during photoswitching of **1** (293 K, 4 μM in toluene) under broad band visible irradiation; b) Time-dependent change in absorption of **A** (at 545 nm) and **A'** (at 600 nm) with enlarged irradiation regime.



Scheme 1. Definition of the various phases involved in the photoswitching of compound **1** at 293 K (a) and 253 K (b) on experimental data: Blue solid line = absorption maximum of **A** at 545 nm; and light blue dotted line = absorption maximum of **A'** at 600 nm.

These data indicatethat the formation of isomer **A'**, the absorption of which is red-shifted compared to that of**1** (SI section 5.2.6),is due to photoinduced *Z–E*isomerization. Upon irradiation, **A'** is generated from **A**, with aphotostationary state (PSS) reached rapidly (φ = 0.17; Scheme 1, *phase ii*, Figures S7–S10) and maintained under irradiation. k_1*(hv)* and k_{-1}*(hv)*are both photochemical reaction rates that are dependent on the photokinetic factors (Figure 2a). At low temperature (< 253 K) the absorption (Scheme 1b, *phaseiii*) remains unchanged once the PSS is reached, indicating equilibrium at $k_{1,obs.}$[**A**] = $k_{-1,obs.}$[**A'**] (*vide infra*for kinetic analyses).At higher temperatures, **A'** not only reverts to **A** (k_{-1}*(hv)* and $k_{-1,thermal}$) but can also cyclize to **B** (k_2). This leads to a decrease in absorption during irradiation (Scheme 1a, *phase iii*, 293 K). As $k_{-1,thermal} > k_{2,obs.}$, most of **A'** is switched back to **A** (Scheme 1, *phase iv*). However, **B** also can revert back to **A**thermally (Scheme 1, *phase v*) *via***A'** ($k_{-2,obs.}$ and $k_{-1,thermal}$). **A'** does not reach a significant steady state concentration under these conditions, and hence, the transient absorption in backswitching from **B** to **A** is not observed ($k_{-1,thermal} >> k_{-2,obs.}$; Figures S7–S19). Furthermore, **A'** generated through irradiation at low temperature (<253 K),does not react further to form**B**(FigureS17).Thesedata and the model developed are summarized in the energy level diagram in Figure 2b. The photoswitching behavior of **2** under identical conditions(Figure S4–S6) is similar to the one of compound **1**. Despite the fact that the rate of thermal relaxation is higher for **2**, a transient absorption band is also observed.

The photoswitching of **1** and **2**by photochemical*Z–E*isomerization is followed by a conrotatory, thermal 4π-electrocyclization. The rate limiting step for the overall reaction from **A** to **B**is $k_{2,obs.}$. For reversion of **B** to **A**, the rate limiting step is $k_{-2,obs.}$. Importantly, the proposed mechanism (Figure 2) further involves a late-stage proton-transfer. In the presence of water, these steps are expected to be fast. However, some solvents may favor isomeric distributions (similar to spiropyrans,[31,56] diarylethenes[57] and azobenzenes[58,59])and thus influence the kinetics and thereby the possible observation of the absorption band.Halogenated solvents (e.g. dichloromethane) favor the elongated triene structure **A**.[44] Nevertheless, photoswitching to **A'** is observed (FiguresS47–S49). Polar protic solvents (e.g. methanol and water) result in irreversible photoswitching from**A** to **B**[44] with no observed transient absorption (Figure S43).No decomposition of **B** in water upon prolonged irradiation was observed (Figures S44 and S45). Moreover, under aqueous conditions **A** cyclizes slowly, but spontaneously to **B** in the dark (Figure S46).

To further investigate the nature of intermediate **A'**, and to connect its structure to the observed bathochromic shift of the transient absorption, TD-DFT calculations were performed (SI section 12). The obtained results confirmed that *Z–E*isomerization can cause a bathochromic shift in the absorption spectrum. This finding is further supported by reports on the bathochromic shift of the absorption spectrum upon photoisomerization of analogous cyanine dyes that cannot undergo cyclization.[60,61]Moreover, low-temperature ^{1}H-NMR spectroscopy measurements with *in*-NMR irradiation show the photogeneration of a single unstable intermediate in deuterated dichloromethane that mainly affects chemical shifts in the polyene region (SI section 11).

Finally, the kinetics of photoswitching were studied in more detail. Reaction rates of the different steps were measured directly or indirectly (Table 1) and fitted to a kinetic model based on our mechanistic hypothesis (Figure 2, SI section 13). The time-dependence of the production and consumption of **B**was calculated by making the assumption that **A'** and **B**show negligible absorbance at 545 nm and **A** and **B**show negligible absorbance at 600 nm. Overall, the measured and modelled reaction rates agree qualitatively and are in line the proposed energy level diagram (Figure 2b).

Table 1. Measured rate constants and activation parameters for DASA **1** (given for 293 K).

entry	rate-constant$^{a)}$	k (s^{-1})	ΔG‡ (kJ mol^{-1})	t$_{1/2}$ (s)
1	$k_{-1,\text{thermal}}$	1.62	70.6	0.43
2	k_2	0.17	76.0	4.05
3	k_{-2}	0.0045	84.9	154

a) See Figure 2 for scheme.

In conclusion, we report the observation of a transientabsorption band during the photoswitching of DASA, which we propose manifests *Z–E*isomerization. The *Z–E*isomerization is followed by thermally driven ring-closure. The observed photoswitching behavioris analogous to that of spiropyrans.[15,30–32,62–64]Notably, for spiropyrans the cisoid intermediates are generally not observed and usually only stable enough to be detected at low temperature and in presence of steric bulk in the molecule.[15,62,65–67]The observed intermediate**A'** is responsible for a bathochromically shifted (Δλ = 55 nm)absorptionthat appears transiently during irradiation. **A'** is thermally unstable, but nevertheless it can be studied spectroscopically at low temperature(253 K). Importantly, the present study lays the foundation for a more detailed understanding of this new class of photoswitches. It gives insights into the nature of intermediate **A'** and the relative stabilities of **A'** and **B**. Understanding the role of each species in the overall photoswitching mechanism enables a structured approach to address the thermal stability of the intermediates, spectral properties and solvent dependence. For example, solvatochromism will be mainly governed by the relative stability of **A** and **B**,whereas the wavelength of activation will depend only on the *Z–E*isomerization step. These data will enable the full potential of this remarkable new class of photoswitch to be realized.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures and characterization of compounds, additional UV/Vis absorption spectra, reversible photochromism studies and kinetic modelling. This material is available free of charge via the Internet at http://pubs.acs.org.

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