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Shedding Light on the Photoisomerization Pathway of Donor—Acceptor Stenhouse Adducts

Mariangela Di Donato, Michael M. Lerch, Andrea Lapini, Laura Bussotti, Svante P. Ihrig, Miroslav Medved, Wiktor Szymański, Wybren Jan Buma, Paolo Foggi, and Ben L. Feringa

Department of Radiology, University of Groningen, University Medical Center Groningen, Hanzeplein 1, 9713 GZ Groningen, The Netherlands
Centre for Systems Chemistry, Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands
European Laboratory for Non Linear Spectroscopy (LENS), via N. Carrara 1, 50019 Sesto Fiorentino, Italy
Department of Chemistry, Faculty of Natural Sciences, Matej Bel University, Tajovského 40, 851 07 Bystrica, Slovak Republic
Institute for Molecular Sciences, University of Amsterdam, Science Park 904, 1098XH Amsterdam, The Netherlands

ABSTRACT: Donor—acceptor Stenhouse adducts (DASAs) are negative photochromes that hold great promise for a variety of applications. Key to optimizing their switching properties is a detailed understanding of the photo switching mechanism, which, as yet, is absent. Here we characterize the actinic step of DASA photo switching and its key intermediate, which was studied using a combination of ultrafast visible and IR pump–probe spectroscopies and TD-DFT calculations. Comparison of the time-resolved IR spectra with DFT computations allowed to unambiguously identify the structure of the intermediate, confirming that light absorption induces a sequential reaction pathway in which a Z−E photoisomerization of C4−C3 is followed by a rotation around C3−C4 and a subsequent thermal cyclization step. First and second-generation DASAs share a common photoisomerization mechanism in chlorinated solvents with notable differences in kinetics and lifetimes of the excited states. The photogenerated intermediate of the second-generation DASA was photo-accumulated at low temperature and probed with time-resolved spectroscopy, demonstrating the photoreversibility of the isomerization process. Taken together, these results provide a detailed picture of the DASA isomerization pathway on a molecular level.

Molecular photoswitches allow reversible optical control in a plethora of applications. Each photoswitch has its own favorable and adverse properties that ultimately determine how well it is suited for photo regulation of a particular responsive system. Highly desirable properties include switching with visible light and negative photochromism.

Donor—acceptor Stenhouse adducts (Figure 1a) are an emerging class of photoswitches. They are particularly attractive due to their modular nature and rapid synthesis and undergo a large structural change upon photoswitching with visible light. Theoretical studies have provided a first effort to rationalize their photoswitching characteristics. Structural improvements of these adducts have led to a second generation of DASAs. Successful applications of DASAs have already emerged for smart materials, sensors, catalysis, and drug-carriers. Although such applications are promising and highlight the potential of DASAs, the understanding of their photoswitching behavior is far from complete.

Initial insights into the DASA photoswitching mechanism stem from the observation of an intermediate, presenting a bathochromically shifted transient absorption band in the UV/vis spectrum with respect to the main absorption band upon light irradiation. Time- and temperature-dependent studies revealed a strong dependence on temperature and light intensity, and suggested that this intermediate results from a photoinduced Z−E isomerization followed by a thermal conrotatory 4π-electrocyclization (Figure 1b). This observation suggests the separation of the mechanism into an actinic step and a thermal step. Intermediate A′′ (Figure 1b) is needed for successful cyclization,
Figure 2 reports the evolution-associated difference spectra (EADS) obtained by global analysis\textsuperscript{31} of time-resolved visible data recorded for 1 (a) and 2 (b) in chloroform.

Figure 2. Evolution-associated difference spectra obtained from global analysis\textsuperscript{31} of time-resolved visible data recorded for 1 (a) and 2 (b) in chloroform.

In order to get detailed insight into the conformation of the intermediate, visible-pump/Mid-IR probe spectra were measured for both samples in the 1100–1750 cm\textsuperscript{-1} spectral range. Figure 3 shows the EADS obtained by global analysis\textsuperscript{31} of the
The TRIR spectra confirm the time scale of photoisomerization: the intermediate bands in the 1100–1200 cm\(^{-1}\) fingerprint region appear on a 2 ps time scale for 1 and on a 24 ps time scale for 2. In case of 1 additional positive bands appear in the second EADS, as for instance at 1139 and 1331 cm\(^{-1}\). These signals decay in the following 10 ps evolution, suggesting that they are not attributable to \(A'\) but possibly to the hot ground state of the A species. Target analysis\(^{35}\) of both the visible and IR transient data of 1 assuming a branched decay of A\(^*\) in both A’ and the hot ground state of A successfully disentangles the individual spectra of these two species (SI section 4.4). In contrast, the initial (vibrational) relaxation of 2 occurs on the A\(^*\) excited-state surface. Notably, in the first spectral component of both samples, assigned to the A\(^*\) – A difference spectrum, only a few low intensity positive bands are noticed, indicating much weaker IR absorption in A\(^*\). The most prominent band shifts in the initial EADS are in the 1600 cm\(^{-1}\) region, attributable to carbonyl stretch vibrations according to the DFT calculations.

Besides the analysis of the IR spectra, our calculations of relative energies, electron density differences (EDD) and geometrical changes upon excitation provide additional information supporting the proposed mechanism. The EDD plots (Figure 1c and SI Figure S6.9) show that for both samples the electron density changes upon excitation are localized on the π-conjugated linker. In the excited-state electron density flows toward the carbon atom functionalized by an OH group, resulting in decreased electron density on “double” bonds. Upon excitation, the structure remains planar (SI Figure S6.10), but the bond lengths increase by ca. 0.01–0.02 Å along the chain, except for the central C\(_3\)–C\(_4\) bond, in line with the EDD analysis. The experimental and theoretical red shift of 2 vs 1 in the excitation energy for A → A\(^*\) (Figure 2 and SI Table S6.2) is related to an extension of the π-conjugation to the indoline moiety. The energy level diagram also reveals that the A’ → A”’ barrier is ca. 2 kcal/mol smaller for 2, suggesting faster kinetics for the C\(_3\)–C\(_4\) bond rotation step, which is related to a less distorted TS structure (difference of ca. 5°) for this derivative.

Finally, we photo-accumulated intermediate A’ of compound 2 at 233 K under continuous illumination at 520 nm in deuterated dichloromethane (SI section 5). Irradiation at 660 nm resulted in back-switching to the elongated A species as assessed by TRIR spectra (SI Figure S5.2), suggesting that reversible isomerization can be induced by selectively pumping A or A’, while ring-closure to form B is only possible via thermal pathway. The electrocyclization time scale is several orders of magnitude longer than the actinic step, thus being the rate-determining step as tentatively concluded before.\(^{27}\) Our study identifies key factors for improving switching characteristics, for instance, increasing the photochemical quantum yield by optimizing A’ properties and disfavor the reverse isomerization process. It also suggests that the reason why first-generation DASAs do not cyclize in chloroform or dichloromethane, as opposed to second-generation DASAs, is solely a question of energy levels and barriers involved in the thermally induced 4π-electrocyclization, and is not due to the actinic step. The presented results elucidate the time scale of the actinic step and bode well for implementation of photoswitch improvement.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b09081.
Experimental procedures and characterization of compounds; additional UV/vis absorption spectra and photo-switching studies; ultrafast visible and mid-IR spectroscopy; evolution-associated difference spectra obtained by global analysis; species associated spectra obtained by target analysis and DFT computations (PDF)

■ AUTHOR INFORMATION

Corresponding Author
*b.l.feringa@rug.nl

ORCID
Mariangela Di Donato: 0000-0002-6596-7031
Michael M. Lerch: 0000-0003-1765-0301
Adèle D. Laurent: 0000-0001-9553-9014
Denis Jacquemin: 0000-0002-6596-7031
Ben L. Feringa: 0000-0003-0588-8435

Author Contributions
©M.D.D. and M.M.L. contributed equally.

Notes
The authors declare no competing financial interest.

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