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DOI
10.1002/ange.201803058
10.1002/anie.201803058

Publication date
2018

Document Version
Final published version

Published in
Angewandte Chemie

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Citation for published version (APA):
Solvent Effects on the Actinic Step of Donor–Acceptor Stenhouse Adduct Photoswitching

Michael M. Lerch*, Mariangela Di Donato, Adèle D. Laurent, Miroslav Medved†, Alessandro Iagatti, Laura Bussotti, Andrea Lapini, Wybren Jan Buma, Paolo Foggi, Wiktor Zymański,* and Ben L. Feringa*

Abstract: Donor-acceptor Stenhouse adducts (DASAs) are negative photochromes that switch with visible light and are highly promising for applications ranging from smart materials to biological systems. However, the strong solvent dependence of the photoswitching kinetics limits their application. The nature of the photoswitching mechanism in different solvents is key for addressing the solvatochromism of DASAs, but as yet has remained elusive. Here, we employ spectroscopic analyses and TD-DFT calculations to reveal changing solvatochromic shifts and energies of the species involved in DASA photoswitching. Time-resolved visible pump-probe spectroscopy suggests that the primary photochemical step remains the same, irrespective of the polarity and protic nature of the solvent. Disentangling the different factors determining the solvent-dependence of DASA photoswitching, presented here, is crucial for the rational development of applications in a wide range of different media.

Molecular photoswitches change structure and properties reversibly upon light-irradiation,[1] enabling successful applications in the dynamic control of functions in material sciences,[2–4] supramolecular chemistry,[5,6] and in the biological context.[7–12] Applications differ markedly in the environment the photoswitch is exposed to, be it different solvents,[13,14] matrices or surfaces, and understanding how a given photoswitch behaves in various environments is crucial for its success in any applications.

Donor–acceptor Stenhouse adducts (DASAs, Figure 1a) were introduced in 2014[17,18] and feature important advantages as compared to traditional photoswitches, including visible light responsiveness[11,19,20] and negative photochromism.[21] Moreover, their modular architecture[22] allows for a fine-tuning of properties.[23] First-generation DASAs (1 and 2, Figure 1a)[17,18] are based on dialkylamine donors, whereas second-generation DASAs (3)[24,25] employ secondary anilines leading to bathochromically shifted spectra. Upon irradiation in toluene, the strongly colored elongated DASA (A) cyclizes to a colorless form (B) that then thermally opens back to the triene form (A). First-generation DASAs switch reversibly only in aromatic solvents such as toluene. In water and methanol, in contrast, irreversible cyclization takes place. In chlorinated solvents, photo-isomerization (to form A’, Figure 1b) is observed, but it is not followed by cyclization.[15,16,18] Second-generation DASAs, however, do cyclize in chlorinated solvents.

A clear understanding of the photoswitching mechanism is key to disentangle the influence of solvents on the observed photoswitching behavior (Figure 1b). Our current mechanistic hypothesis suggests an initial photoisomerization around C2–C3, followed by a rotation around C3–C4, to facilitate

[1] M. M. Lerch, Dr. W. Szymański, Prof. Dr. B. L. Feringa Centre for Systems Chemistry, Stratingh Institute for Chemistry University of Groningen Nijenborgh 4, 9747 AG, Groningen (The Netherlands) E-mail: w.c.szymanski@rug.nl b.feringa@rug.nl

Dr. W. Szymański
Department of Radiology, University of Groningen
University Medical Center Groningen
Hanzeplein 1, 9713 GZ, Groningen (The Netherlands)
E-mail: w.c.szymanski@umcg.nl

Dr. M. D. Donato, Dr. A. Iagatti, Dr. L. Bussotti, Dr. A. Lapini, Prof. Dr. P. Foggi
European Laboratory for Non Linear Spectroscopy (LENS) via N. Carrara 1, 50019 Sesto Fiorentino (Italy)

Dr. M. D. Donato, Dr. A. Iagatti, Dr. A. Lapini, Prof. Dr. P. Foggi
Istituto Nazionale di Ottica
Largo Fermi 6, 50125 Firenze (Italy)

Prof. Dr. P. Foggi
Dipartimento di Chimica, Università di Perugia
via Elce di Sotto 8, 06100 Perugia (Italy)

Dr. A. D. Laurent
CEISAM, UMR CNRS 6230, BP 92208
2 Rue de la Houssinière, 44322 Nantes, Cedex 3 (France)

Dr. M. Medved’
Regional Centre of Advanced Technologies and Materials, Department of Physical Chemistry, Faculty of Science
Palacký University in Olomouc
17. listopadu 1192/12, CZ-771 46 Olomouc (Czech Republic)

Dr. M. Medved’
Department of Chemistry, Faculty of Natural Sciences
Matej Bel University
Tajovského 40, SK-97400 Banská Bystrica (Slovak Republic)

Prof. Dr. W. J. Buma
Van’t Hoff Institute for Molecular Sciences, University of Amsterdam
Science Park 904, 1098XH Amsterdam (The Netherlands)

† These authors contributed equally.

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under: [3]

https://doi.org/10.1002/ange.201803058.

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a subsequent thermal cyclization accompanied with proton transfer (Figure 1b). Bieske and co-workers recently showed the possibility to drive the thermal steps in the gas phase by additional light-absorption. Earlier observation of a transient absorption band in toluene under steady-state conditions for first-generation DASAs was attributed to the product of the actinic step $A'$ (Figure 1b and 2c). Importantly however, such a transient absorption band cannot be detected in polar protic solvents (e.g., methanol and water, Figure 2c) under steady-state conditions where photoswitching is slowed down by at least two orders of magnitude (Figure 2; Supporting Information (SI) section 5 and 6) and proceeds, albeit slowly, even without irradiation (SI section 3). These observations raise questions about the nature of the photoswitching mechanism in various solvents.

We set out to study the actinic step of 1–3 using ultrafast time-resolved spectroscopy across a range of solvents, in order to verify if the nature of the intermediate species formed upon light absorption remains the same. We further tried to understand why photoswitching is reversible only in selected solvents and which factors determine the observed large differences in photoswitching kinetics. Here, we provide evidence that DASAs undergo the same actinic step irrespective of the solvent used. DFT calculations unveil the overall kinetics and thermodynamics governing the reversibility of photoswitching (Figure 1c). Furthermore, solvents influence the band-overlap of $A$ and $A'$, potentially influencing the photostationary states reached and thus affecting overall cyclization kinetics.
The behavior of second-generation DASA 3 in different solvents follows closely the previously described behavior in chloroform \cite{16} (Table 1, Figure S7.7–S7.9). The major difference with first-generation DASAs is that the excited state of the elongated form lives long enough to allow cooling to occur in the excited state before isomerization. As a result, the red shift of the positive band rising on the ps timescale is not observed when the hot ground state of \(A\) is not involved in the relaxation process. Solvent effects on the isomerization kinetics are generally minor, except in dimethyl sulfoxide (DMSO), where the photoisomerization rates decrease for all the analyzed compounds and more markedly for compound 3. Notably, this is also the case when the viscosity of the solvent is increased (as for instance can be achieved with a 60/40 wt \% glycerol/methanol mixture, SI section 7). Figure 4 shows that increasing the viscosity leads to a slower in-growth of the positive absorption band attributed to the intermediate (see raw data reported in SI section 7). As a result, the absorption band of the intermediate appears in dimethyl sulfoxide (Figure 4b) as a structuring of the bleaching feature instead of a positive absorption band as observed in methanol (Figure 4a).

Analysis of time-resolved infrared (TRIR) spectra (Figure 5) and comparison of experimental and computed difference spectra of the possible photogenerated isomers (Figure 6) provides additional information on the structure of the intermediate \(A\) in different solvents. The comparison of
the long-lived spectral component of 1 and 3 in different solvents (Figure 5c and 5d, respectively), which represents the \( A' - A \) difference spectrum, shows that the IR spectrum of compound 3 is barely influenced by the solvent, while a few differences can be noticed for compound 1, particularly in the C–C stretching and C–H rocking region (1100–1200 cm\(^{-1}\)). This is also noticeable for their corresponding FTIR spectra (Figure S2.1 and S2.2, SI section 2). Nevertheless, the comparison between experimental and computed difference IR spectra (see below) suggests that the light induced photoisomerization remains the same in all investigated solvents, and that small changes in the EADS shapes are caused by solvatochromic shifts of the IR absorption bands.

To better understand the effects of substitution and solvent on the kinetics and thermodynamics of the photoswitching process, key steps of the proposed mechanism were studied by (TD-)DFT in combination with the implicit solvent model (SMD) (see SI section 8 for computational details). The results for 1–3 in selected solvents are summarized in Table S8.1 and illustrated in Figures 1c and S8.5. In line with experimental observations, the calculations show that the nature of the solvent strongly affects both the kinetics and thermodynamics of the photoswitching reaction. In particular, the activation barrier for the C\(_3\)–C\(_4\) bond rotation and the product stability are significantly affected, inducing different DASA behavior after photoactivation. The irreversibility of the whole process for 1 and 2 in polar protic solvents, such as water and methanol, can be rationalized in terms of a higher thermodynamic stability of the zwitterionic form B compared to A and also by a relatively high barrier for the backward \( B \rightarrow A'' \) transition. The formation of B through intermolecular proton transfer could further be mediated by the protic solvent. On the other hand, in aprotic solvents the cyclization step stops at the formation of a neutral form B whose stability (taking the energy of A as zero) decreases with increasing solvent polarity. This can explain the observed reversible photoswitching in toluene, whereas in more polar, non-protic, chlorinated solvents the cyclization does not occur. Importantly, it also should be noticed that the transition barriers (for both \( A' \rightarrow A'' \) and \( A'' \rightarrow B/B' \)) are the lowest for toluene, which again supports the reversibility and relatively fast kinetics of the photoswitching in this solvent. On the contrary, the barrier for the C\(_3\)–C\(_4\) bond rotation is the highest for methanol (due to a smaller dipole moment of TS (5.0 D) compared to \( A' \) (11.3 D) as revealed by DFT computations), which explains the observed slow dynamics in this solvent.

**Figure 6.** Comparison of experimental and calculated ground state IR spectra (a, b) and the long-lived component of TRIR EADS (c, d) of compounds 1 and 3 in deuterated chloroform (CHL), deuterated dichloromethane (DCM), and (deuterated) dimethyl sulfoxide (DMSO).
In conclusion, although solvents strongly influence the overall photoswitching of DASAs, the kinetics of the actinic step is only slightly perturbed. Time-resolved spectroscopy suggests that the same key intermediate \( \text{A}' \) is produced across all solvents studied, giving credibility to the proposed photoswitching mechanism.\(^{[15,16,30]}\) and showing that in the presented cases the thermal steps are likely rate-limiting. With a full understanding of the actinic step that has now been obtained, it is clear that the focus of future studies will need to shift toward the thermal part of the reaction mechanism to further improve photoswitching and reduce detrimental solvent effects. We foresee immediate application of the lessons learned that make use of the peculiarities of DASAs, not seen in other photoswitches, to inspire the rapidly developing field of visible light molecular photoswitches and beyond.

**Acknowledgements**

The authors gratefully acknowledge financial support from Laserlab-Europe (LENS002289, grant no. 654148), the Ministry of Education, Culture and Science (Gravitation program 024.001.035), The Netherlands Organization for Scientific Research (NWO-CW, Top grant to B.L.F., VIDI grant no. 723.014.001 for W.S.), the European Research Council (Advanced Investigator Grant, no. 227897 to B.L.F.) and the Royal Netherlands Academy of Arts and Sciences Science Foundation (KNAW). M.M. acknowledges the Czech Science Foundation (project no. 16-01618S), the Ministry of Education, Youth and Sports of the Czech Republic (grant NPU I, LO1305), the Grant Agency of the Slovak Republic (VEGA project No. 1/0737/17) and CMST COST Action CM1405 MOLIM: MOlecules In Motion. This research used computational resources of 1) the GENCI-CINES/IDRIS, 2) CCIPL (Centre de Calcul Intensif des Pays de Loire), 3) a local Troy cluster, and 4) the HPCC of the Matej Bel University in Banska Bystrica by using the infrastructure acquired in projects ITMS 2623012002 and 2621012002 supported by the Research and Development Operational Programme funded by the ERDF. The Swiss Study Foundation is acknowledged for a fellowship to M.M.L. We would like to thank Prof. Dr. Wesley R. Browne (University of Groningen, The Netherlands) for fruitful discussions.

**Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** donor–acceptor Stenhouse adducts · photoswitches · solvent effects · spectroscopy · visible light

**How to cite:** Angew. Chem. Int. Ed. 2018, 57, 8063–8068

**Angew. Chem. 2018, 130, 8195–8200**

\[1\] Molecular Switches (Eds.: B. L. Feringa, W. R. Browne), Wiley-VCH, Weinheim, 2011.
