

Original Heteroaryl Azobenzene derivatives As Solar Thermal Fuel Candidates : a Mass Spectrometry and UV-vis Spectrophotometry Investigation

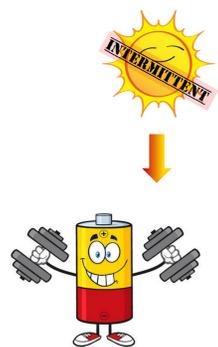
Gwendal Henrard^{1,2}, Thomas Robert¹, Benjamin Tassignon^{1,2}, Ari Serez², Julien De Winter¹, Jérôme Cornil², Pascal Gerbaux¹

Organic Synthesis and Mass Spectrometry laboratory¹ (S²MOs) & Laboratory for Chemistry of Novel Materials² (CMN)
University of Mons, 23 Place du Parc, B-7000 Mons – Belgium

Energy challenges: a matter of storage?

Sun as renewable energy source 

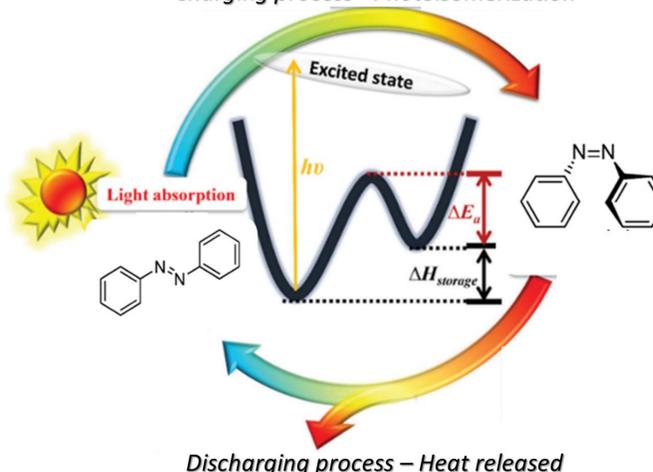
Sun energy potential / years > 1000 X World consumption



Storage

MOlecular Solar Thermal systems (MOST)

Charging process - Photoisomerization



To store solar energy, chemical storage appears to be a promising approach with systems known as MOST [1]. The working principle of those systems is based on iterative closed cycles of photoisomerization and back-isomerization between a parent compound and its metastable isomer which possesses a certain half-life time and thermal energy is released during the thermal back-isomerization process [2] [3]. Azobenzenes with their E→Z photoisomerization are among the most widely studied molecular photoswitches and appear as good candidates. However, properties such as the storage enthalpy, spectroscopic properties and the half-life time need to be improved. To do so at UMONS We imagine different strategies to enhance those properties.

Figure 2. Working principle of a MOST system: the azobenzene case [3].

Improving azobenzene MOST properties: two strategies

Two important properties are targeted in the present study; (i) matching the absorption spectrum of the E-isomer with the solar emission and (ii) extending the half-life time of the Z-isomer. These two properties are among the most important. (i) the transition $\pi-\pi^*$ which is the principal transition of the E-isomer must be in the visible range. Ideally the Z-isomer should not absorb in this wavelength range. (ii) The half-life time is also important, but it is much more dependent on the intended application. In each case, the MOST properties are all determined to identify the molecule with the best compromise in all the properties.

Spectroscopic property improvement

The first strategy consists to induce a bathochromic shift of the $\pi-\pi^*$ transition to the visible wavelength. To do so, heteroatoms need to be incorporated into the molecules, they are known for inducing a $\pi-\pi^*$ shift to higher wavelengths. We decide to substitute one phenyl group by a thiazolyl moiety to red shift the absorption of the chromophore in the visible region [4]. The photoisomerization of this heteroaryl azobenzene is shown in Figure 3.

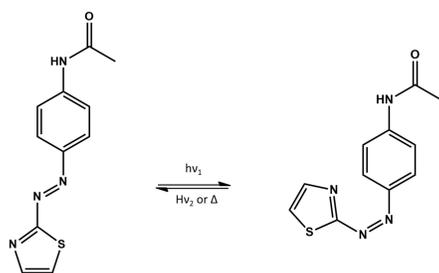


Figure 3. Photoisomerization of N-(4-(thiazol-2-yl)diazenyl)phenylacetamide.

Half-life time improvement

The second strategy consists of the use of a five-membered aromatic rings with an hydrogen atom in the ortho position relative to the N=N bond. The Z-isomer configuration is characterized by a stabilizing C-H... π interaction inducing longer half-life time [5]. In this case we decide to synthesize azobenzene from 3-amino-5-methylisoxazole. The photoisomerization of this five-membered azobenzene is shown in Figure 4.

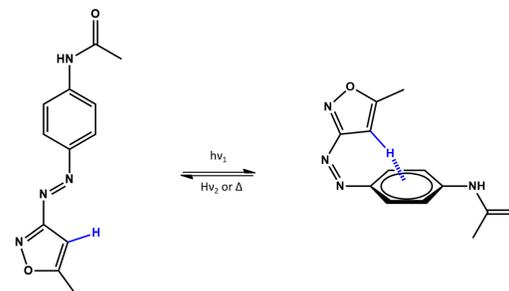


Figure 4. Photoisomerization of N-(4-((5-methylisoxazol-3-yl)diazenyl)phenyl)acetamide

Spectroscopic analyses : UV-Visible

UV-Vis spectra were recorded on a Perkin Elmer Lambda 35 UV/Vis spectrophotometer. Solutions (C = 5.10⁻⁵ M) were prepared in the dark in MeOH HPLC grade.

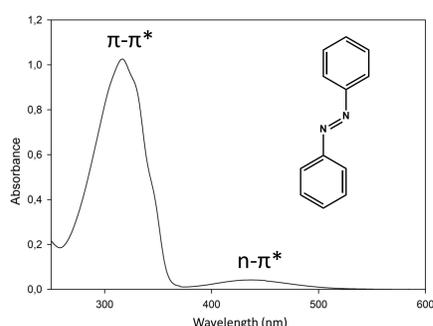


Figure 5. UV-Vis spectrum of azobenzene

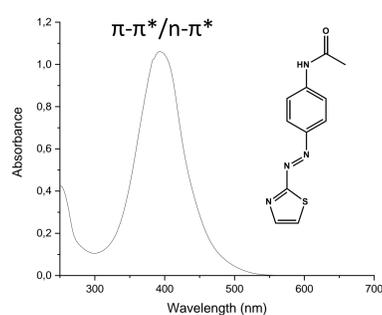


Figure 6. UV-Vis spectrum of N-(4-(thiazol-2-yl)diazenyl)phenylacetamide.

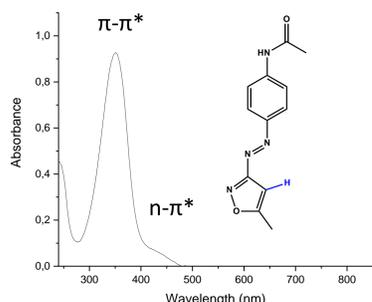


Figure 7. UV-Vis spectrum of N-(4-((5-methylisoxazol-3-yl)diazenyl)phenyl)acetamide

	$\pi-\pi^*$ (nm)	$n-\pi^*$ (nm)
Azo	315	440
Azo-thiazole	394	/
Azo-isoxazole	350	430

Bathochromic shift 

Visible reach 

Photoisomerization : LC-MS analyses

Azobenzene solutions were irradiated with a lightningcure LC8 L9588-02A UV lamp (ca. 220 - 400 nm) to induce azobenzene isomerization. After different irradiation times, solutions were analyzed by liquid chromatography (Waters Alliance 2695) coupled to mass spectrometry (Waters QToF Premier, ESI (+)) in order to discriminate stereoisomers and to quantify the photostationary state distribution (PSD).

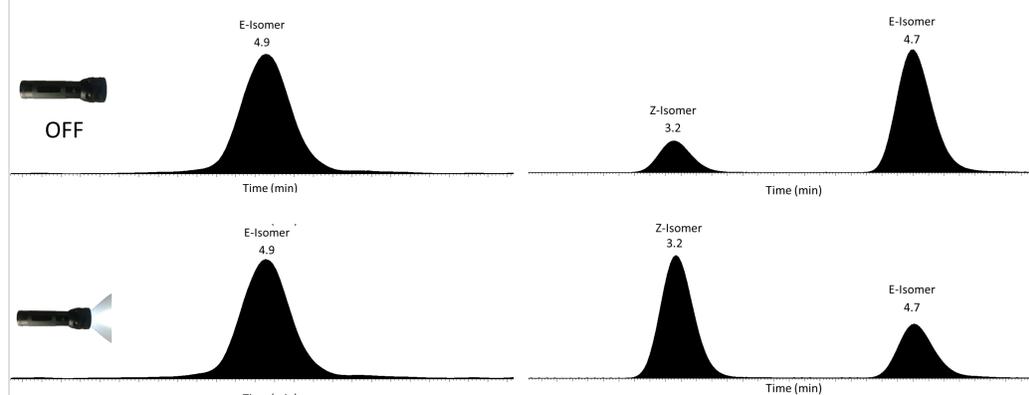
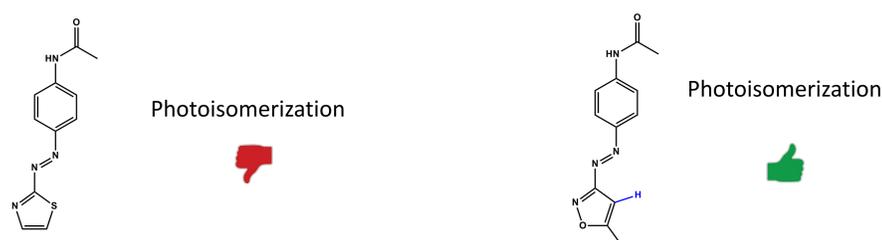


Figure 8. HPLC-MS analysis of N-(4-((5-methylisoxazol-3-yl)diazenyl)phenyl)acetamide

Figure 9. HPLC-MS analysis of N-(4-((5-methylisoxazol-3-yl)diazenyl)phenyl)acetamide



Conclusions

With this work combining synthesis and photochemical characterization, we successfully prepared two different molecules and analysed their principal MOST properties. For the spectroscopic properties, both molecules undergo a bathochromic shift but not enough to reach visible wavelengths. For the photoisomerization process, the conclusion is completely different, since, for the thiazolyl moiety, no photoisomerization was observed. On the other hand, for the isoxazole moiety, the photoisomerization was detected. In perspective of this work, we can imagine associating both these azo-derivatives within a single macromolecule to maybe trigger cooperative effects inducing therefore better properties.

Acknowledgments

The S²MOs lab thanks the FRS-FNRS for the financial support in the frame of the PDR project T.0095.22. G.H. thanks the FRS-FNRS for his PhD grant.

References

- [1] T.J. Kucharski, Y. Tian, S. Akbulatov, R. Boulatov, *Energy Environ. Sci.* **2011**, *4*, 4449–4472.
- [2] A. Lennartson, A. Roffey, K. Moth-Poulsen, *Tetrahedron Lett.* **2015**, *56*, 1457–1465.
- [3] L. Dong, Y. Feng, L. Wang, W. Feng, *Chem. Soc. Rev.* **2018**, *47*, 7339–7368.
- [4] Abdallah Abomelha H. *Text. Res. J.* **2020**, *90* (11-12), 1396-1403
- [5] Claire E. Weston, Robert D. Richardson, *J. Am. Chem. Soc.* **2014**, *136*, 11878–11881