Quantum Chemical Studies of a Hemithioindigo-based Photodriven Molecular Motor

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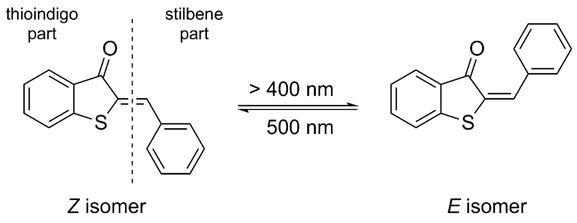
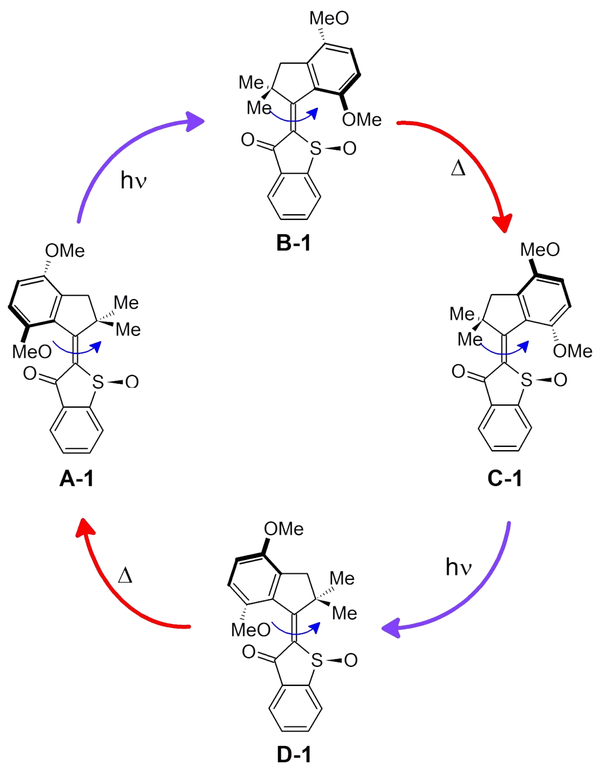
The HTI-based Molecular Motor

The molecular motor is based on the photoswitch hemithioindigo (HTI)

- HTI undergoes efficient and reversible *Z*/*E* isomerisation at the central double bond upon irradiation with visible light (see [1] for a complete overview of the photochemistry)



- Dube and coworkers implemented additional stereochemical elements into the HTI framework to achieve unidirectional rotation around the central double bond



- Low temperature ^{1}H-NMR spectroscopy uncovered a four step process for the rotation, consisting of two thermal and two photoinduced steps [2]
- Excitation for both photoinduced steps is performed at 460 nm
- So far the mechanism of the photoinduced steps is unclear and the unidirectionality is not fully proofen.

Quantum Chemical Studies

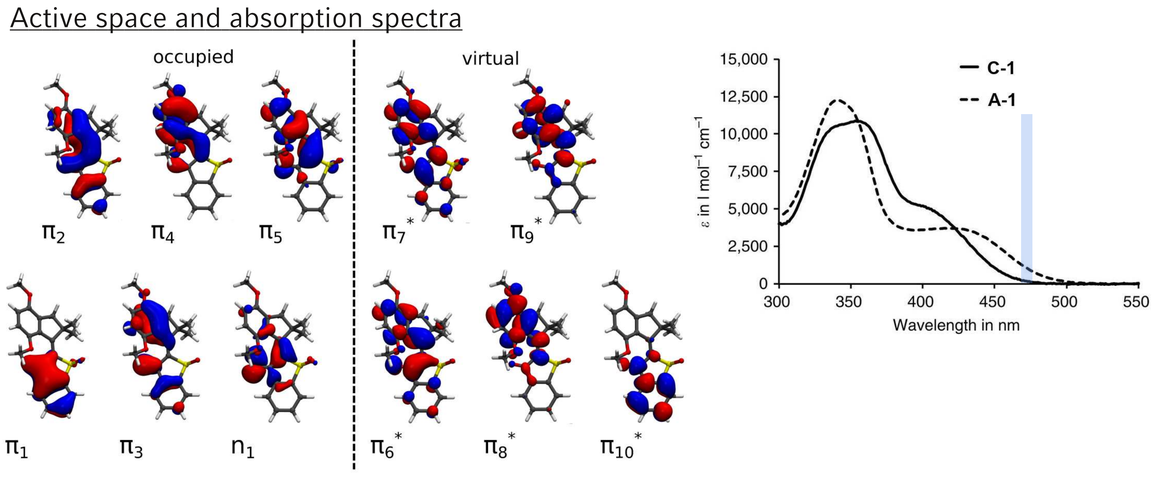
What do we want?

Elucidate the pathways for both photoinduced steps and identify the important points necessary for the rotation

What do we use?

All calculations were done at CASSCF level of theory utilizing a (12/11) active space and the 6-31G* basis set. (powered by MOLPRO 2015)

Active space and absorption spectra



Vertical excitations and oscillator strengths

	Char.	CAS [eV]	RS2C [eV]	CCSD [eV]	TDDFT [eV]	Exp. [eV]
S1	nπ*	3.83	3.53	3.50	3.37	2.88
S2	ππ*	5.40	4.19	3.85	3.64	3.64
S3	ππ*	5.94	4.46	4.33	4.07	
T1	nπ*	3.16	3.04		2.39	
T2	ππ*	3.66	3.40		3.05	

	CAS [a.u.]	CCSD [a.u.]	TDDFT [a.u.]
S1	0.001	0.029	0.056
S2	0.148	0.114	0.093
S3	0.507	0.147	0.159

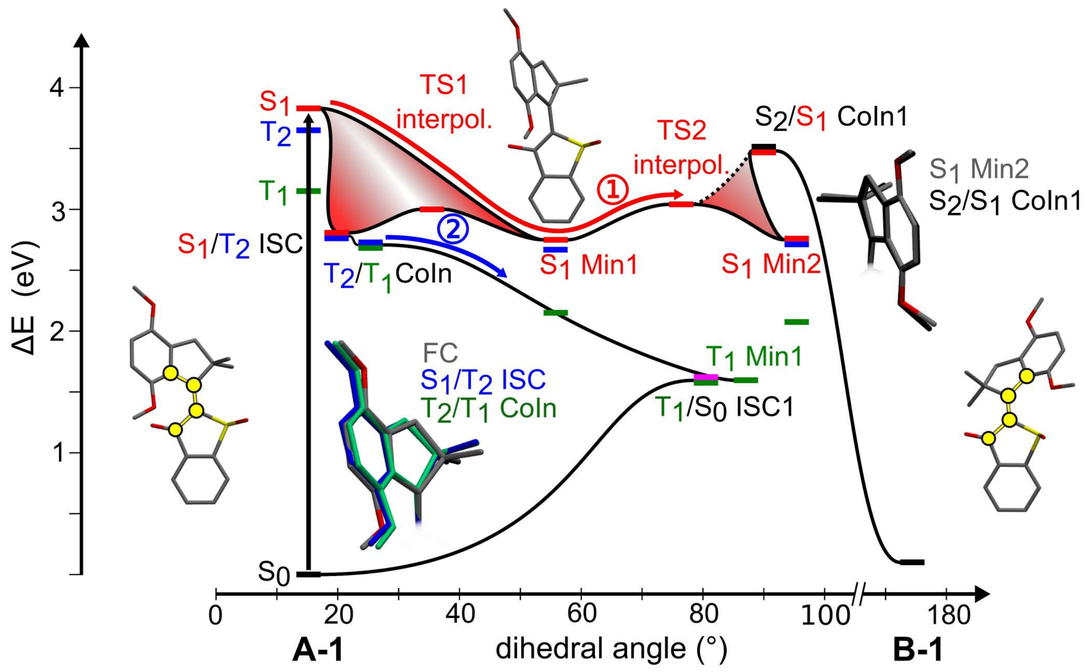
Conclusion

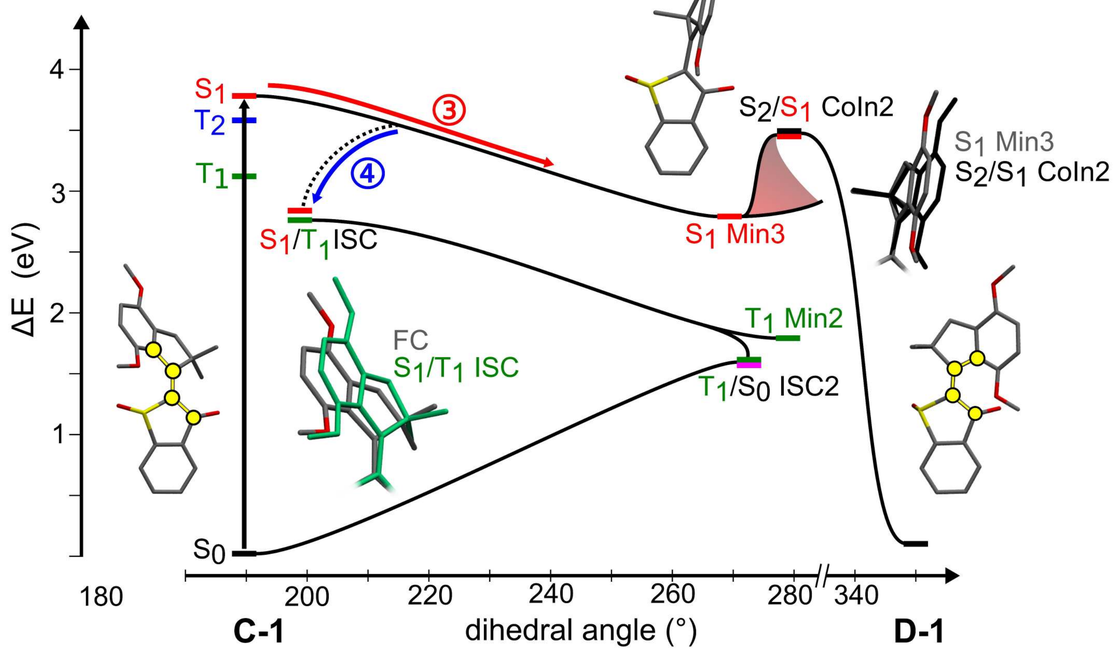
- Upon excitation at 460 nm the S1 state (nπ*) is populated
- In both steps, A-1/B-1 and C-1/D-1, the 180° rotation is completed via a conical intersection, which leads to the groundstate
- A competing channel via ISC to the groundstate is possible for A-1/B-1
- Theoretical pathways compare very well to the time-resolved pump-probe experiments performed in the Riedle Group

References

[1] A. Nenov, T. Cordes, T. T. Herzog, W. Zinth, R. de Vivie-Riedle, J. Phys. Chem. A 114 (2010), 13016-13030
[2] M. Guentner, M. Schildhauer, S. Thumser, P. Mayer, D. Stephenson, P. J. Mayer, H. Dube, Nat. Commun 6 (2015), 8406
[3] R. Wilcken, M. Schildhauer, F. Rott, L. A. Huber, M. Guentner, S. Thumser, K. Hoffmann, S. Oesterling, R. de Vivie-Riedle, E. Riedle, H. Dube, J. Am. Chem. Soc. 140 (2018), 5311–5318.

Reaction Path for Motor 1





The Saga Continues...

- As the rate of the rotation is limited by the barrier height of the thermal step, Dube and coworkes synthesized an improved HTI-based motor
- ^{1}H-NMR spectroscopy uncoverd only a three step process: Two photoinduced and one thermal
- First theoretical results show a similar picture to motor 1