

Theoretical study of the thermal-back isomerization of azobenzene and its derivatives

^{a,b}A. Serez, ^{a,b}E. Piplart, ^aV. Lemaur, ^cM. Frère, ^bP. Gerbaux, ^aJ. Cornil

^aLaboratory for Chemistry of Novels Materials, Center of Innovation and Research in Materials and Polymers, University of Mons – UMONS, 23 Place du Parc, B-7000 Mons, Belgium

^bOrganic Synthesis and Mass Spectrometry Laboratory, Interdisciplinary Center for Mass Spectrometry, University of Mons – UMONS 23 Place du Parc, B-7000 Mons, Belgium

^cThermodynamics and Mathematical Physics Unit, University of Mons – UMONS, 31 Boulevard Dolez, B-7000 Mons, Belgium

ari.serez@umons.ac.be

Azobenzene appears to be an interesting candidate for MOST applications. From its stable trans (E) isomer, it can be converted by photoisomerization into its metastable cis (Z) form. The metastable form can be converted-back by a spontaneous reaction, the thermal-back isomerization. To have the best MOST system, we must control the heat release. It implies to control when and how the energy is released; it is directly connected to the thermal-back isomerization. It has been related from previous research¹ that for azobenzene the thermal-back isomerization can occur via two different mechanisms: the inversion mechanism and the rotation mechanism. It was first reported that the inversion mechanism corresponds to the minimum-energy path from the metastable form to the stable form. This result was supported by DFT (Density Functional Theory) calculations. But there are some inconsistencies with DFT: the activation entropy is largely overestimated, and it is not possible to reproduce the correct rate constant with post-HF method such as MP2. More recently, two studies^{2,3} showed that there is a multistate effect involving the S0 and T1 state, and they were able to reproduce the experimental values of entropy and enthalpy for the thermal-back isomerization of the azobenzene. The scope of this study is to reproduce these results for the azobenzene and also investigate the effects of structural modification on these two states and predict how it will affect the thermal-back isomerization. The method that will be used is the SF-TDDFT (Spin-Flip Time-Dependent DFT), this method is a good balance between accuracy and rapidity of calculations.

¹ Bandara, H et al. Chem. Soc. Rev. 2012, 41, 1809

² Reimann, M. et al. J. Phys. Chem. Lett. 2022, 13, 10882

³ Axelrod, S. et al. ACS Cent. Sci. 2023, 9, 166