

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

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## 1. Introduction

- 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 design an optimized 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 barrier, it has been related from previous research<sup>1</sup> that for azobenzene the thermal-back isomerization can occur via two different mechanisms: the inversion mechanism and the rotation mechanism.

## 2. Theoretical background

- The inversion mechanism corresponds to the opening of the NNC angle and the rotation mechanism involves rotation around the N=N double bond. (Figure 1)

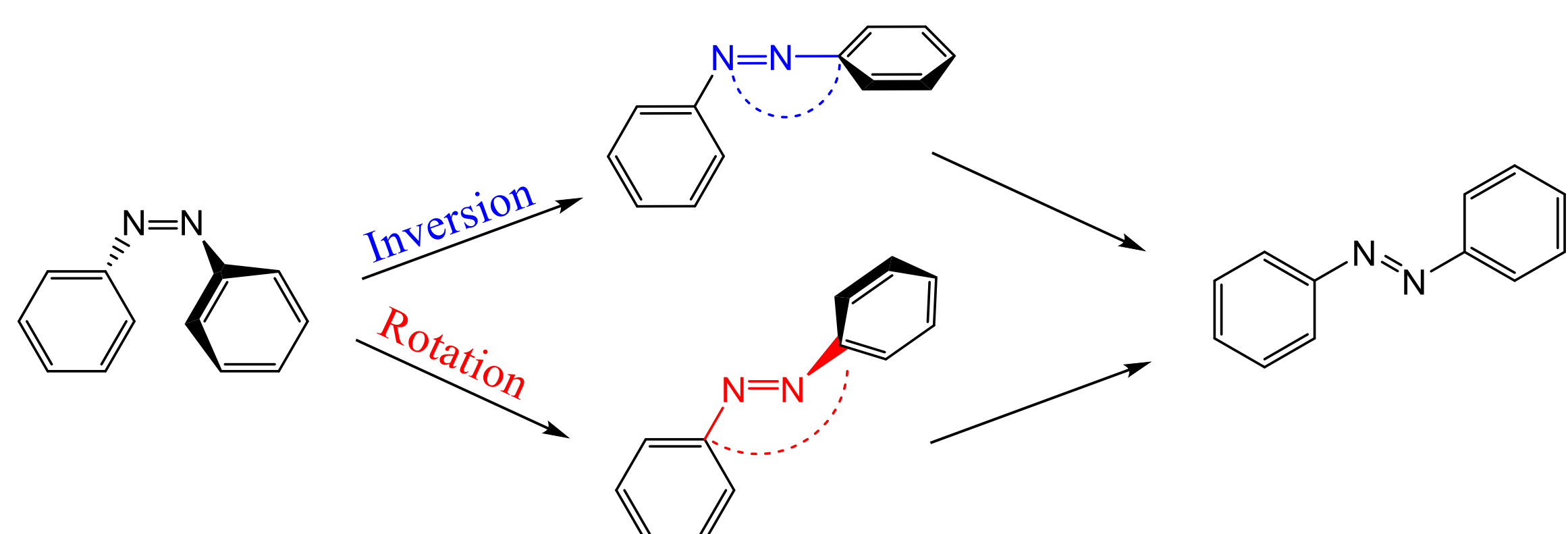


Figure 1. Mechanisms for the thermal-back isomerization

- The Inversion mechanism corresponds to the minimum-energy path from the metastable form to the stable form. Based on DFT calculations
- An inconsistency with DFT is that the activation entropy is largely overestimated. It is not possible to reproduce the correct rate constant with post-HF method such as MP2
- Two studies<sup>2,3</sup> showed that there is a multistate effect involving the  $S_0$  and  $T_1$  state for the rotation mechanism (Figure 2)

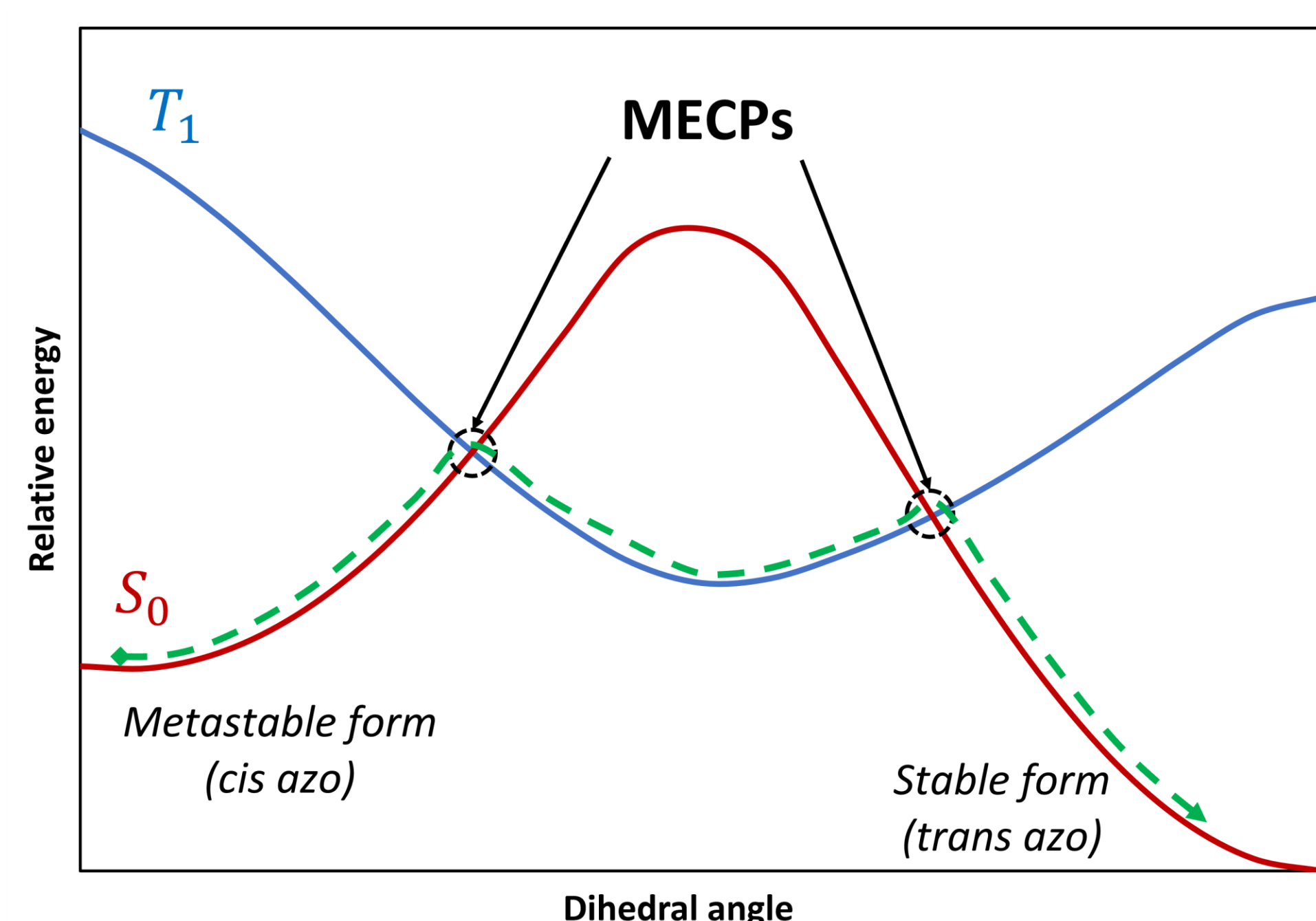
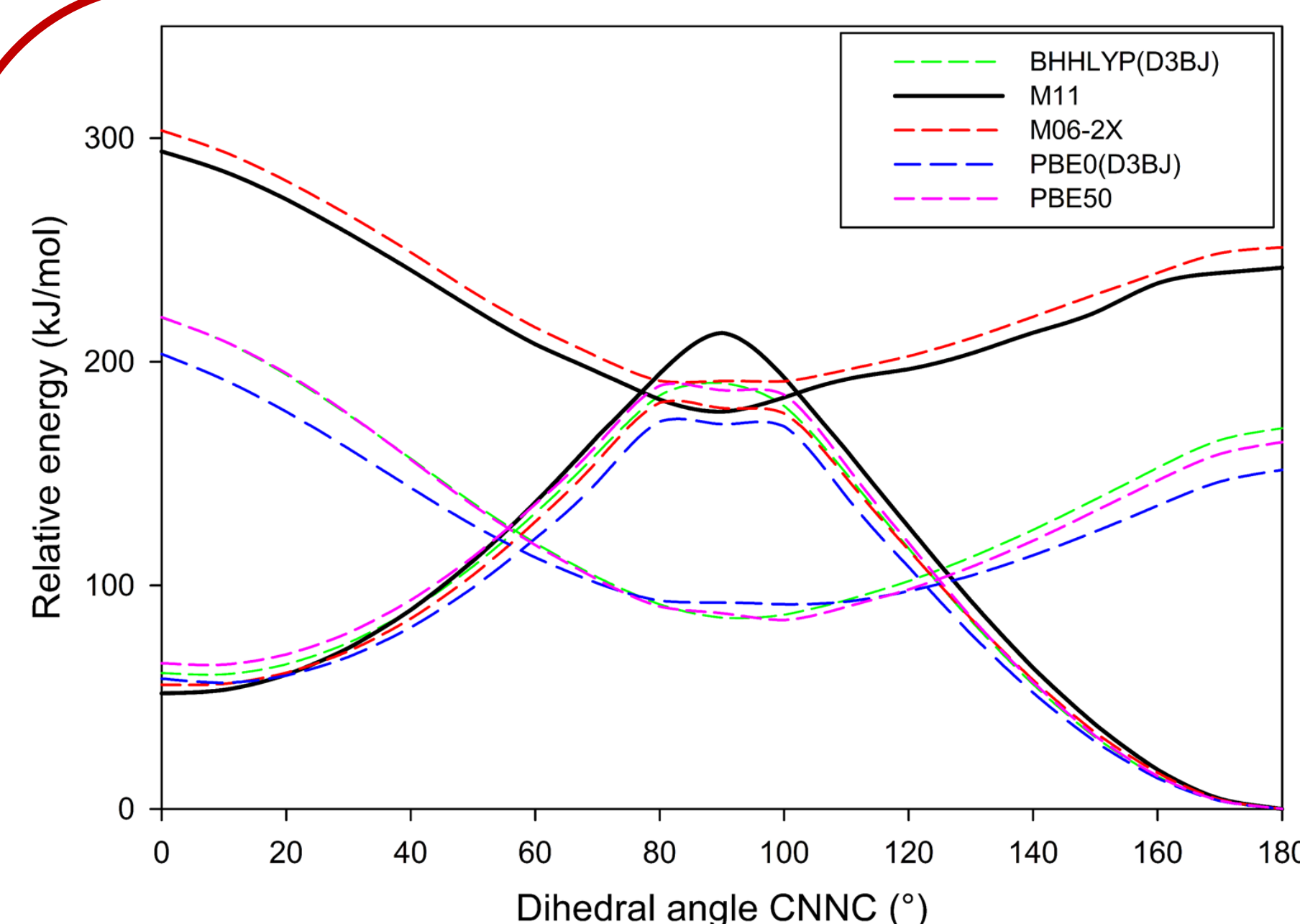


Figure 2. Schematic representation of  $S_0$  and  $T_1$  energy surfaces. These two surfaces cross at the Minimum-Energy Crossing Points (MECPs)

- Reproduce  $S_0$  and  $T_1$  energy curves at the Spin-Flip Time-Dependent DFT (SF-TDDFT) level of theory for azobenzene
- Investigate effects of structural modifications on these two states and how it will affect the thermal-back isomerization

## 3. Results and discussion



- Benchmarking shows that **M11/6-311G\*\*** is the best option for SF-TDDFT on azobenzene

- $\omega(\text{MECP1}) = 73^\circ$  vs  $71^\circ$
- $\omega(\text{MECP2}) = 108^\circ$  vs  $115^\circ$

<sup>2</sup> CASSCF level of theory

Figure 3. Benchmarking of functionals for SF-TDDFT on azobenzene

- Slight overestimation of the cis energy for all functionals in SF-TDDFT
- We can calculate the transmission coefficient  $\gamma$  using Wentzel-Krammer-Brillouin theory (WKB), and activation parameters using Eyring equation :

$$\gamma = \frac{\pi^{3/2} \beta}{2\sqrt{\epsilon_0 k_B T}} \left[ 1 + \frac{1}{2} \cdot \exp\left(\frac{1}{12\beta^2} \cdot \frac{1}{(\epsilon_0 k_B T)^3}\right) \right]$$

$$\beta = \frac{4|V_{SO}|^{3/2}}{\hbar} \cdot \left[ \frac{\mu}{\bar{F}\Delta F} \right]^{1/2}; \quad \epsilon_0 = \frac{\Delta F}{2\bar{F}|V_{SO}|}$$

$$k = \gamma \frac{k_B T}{h} e^{-\frac{\Delta^\ddagger G}{RT}} \quad \text{Eyring equation}$$

- We then found  $\Delta^\ddagger H = 97,3 \text{ kJ} \cdot \text{mol}^{-1}$  and  $\Delta^\ddagger S = -39 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  which is in very good agreement with the CASSCF results<sup>2</sup>

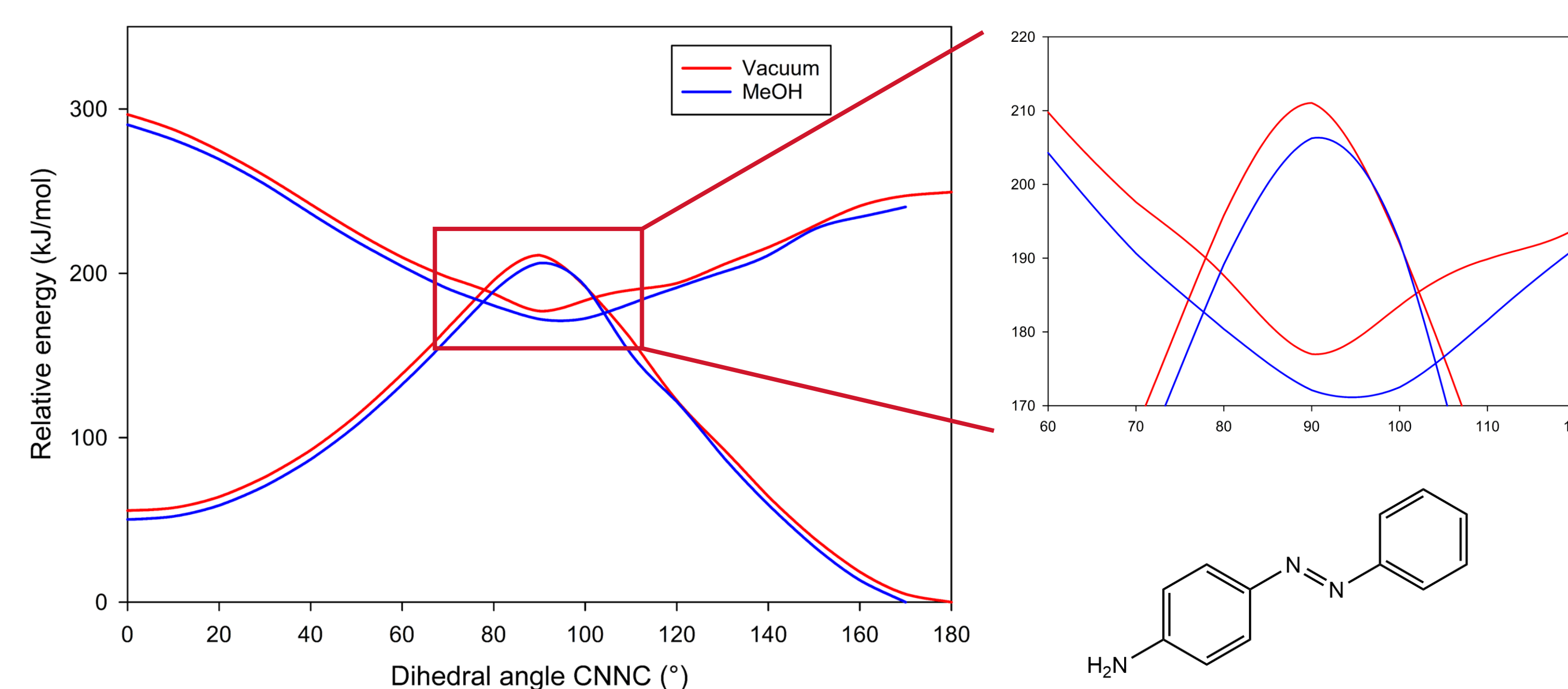


Figure 3. Solvent effect on amino-azobenzene

- Polar solvent (MeOH) tends to reduce the MECP energies !
- Experimentally observed<sup>4</sup>

## 4. Conclusions and outlooks

- M11 functional shows the best performance and reproduces well the theoretical and experimental values from literature
- Spin-Orbit coupling still has to be calculated at CASSCF/CASPT2 level of theory. Overestimation of the constant at (SF)-TDDFT level.
- Solvent affects amino-azobenzene and reduces the MECP energies

### What's next ?

- Determine the rate constant of amino-azobenzene and how solvents impact the spin-orbit coupling
- Study new derivatives

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