Photoisomerization of azobenzene. Elucidating the mechanism through molecular dynamics calculations

Marc Alias[1], Coen de Graaf [1,2], Mar Reguero[1]

[1] Universitat Rovira i Virgili, Dpt. of Physical and Inorganic Chemistry, 43007 Tarragona,
Spain
[2]ICREA, 08010 Barcelona, Spain

E-mail: marc.alias@estudiants.urv.cat

Computational chemistry has emerged as an important tool to explain experimental observations and develop theories and intuitive concept to predict helping in the design of new chemical systems to save reactants and time. In the field of photochemistry the role of computational chemistry is of great interest, but especially difficult because in photochemical processes different excited states are involved and a good description of them and their interactions require accurate and expensive computational methodologies.

In the work presented here we study the photoisomerization mechanism of azobenzene. This mechanism has been widely studied, but some questions still remain unanswered. Azobenzene shows two stable isomers (*trans* and *cis*) that can be switched through different pathways. *Cis* to *trans* isomerization can be carried out both thermally and photochemically, while the *trans* to *cis* isomerization only takes place photochemically due to the higher stability of the trans isomer. Photoswitching is not exclusive for azobenzene, it is characteristic for all azo compounds. This property gives them a wide range of potential applications.[1,2]

The mechanism for the isomerization from *trans-* to *cis*-azobenzene has been studied for a long time, and several proposed mechanisms can be found in the literature (Fig. 1), but the dominant pathway is still matter of debate.[3,4]
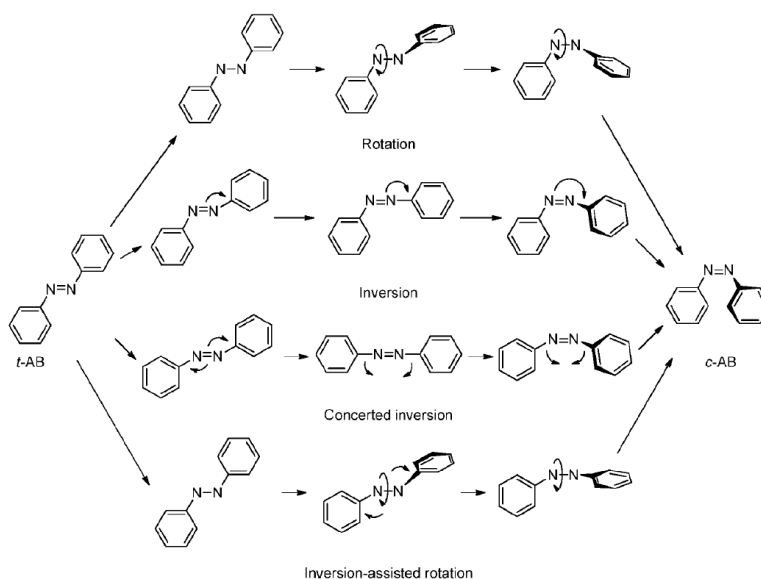

Figure 1. Mechanisms proposed for the isomerization of azobenzene

In this work we have performed an ab initio dynamic study of the azobenzene photoisomerization mechanism using CASSCF (Complete Active Space Self Consistent Field) methodology, which takes into account electron correlation. We have used an active space of 10 electrons in 8 molecular orbitals and Tully's algorithm for surface hopping.

Our methodology starts computing the transition dipole moment for the five lowest excited states of *trans*-azobenzene in a large number of different geometries. We start the dynamic calculations in excited states most probably populated by the initial excitation. After that, the system can hop to other states through the Tully's algorithm until it arrives again to the ground state, evolving on it towards *trans* or *cis* configurations. After computing a large number of trajectories, it is possible to determine accurately excited states lifetimes and to propose a reasonable mechanism for the isomerization process.

References:

[1] Z. Mahimwalla, K. G. Yager, J. Mamiya, A. Shishido, A. Priimagi, C. J. Barrett, *Polym. Bull.* **2012**, 69, 967–1006.

[2] J. García-Amorós, D. Velasco, *Beilstein J. Org. Chem.* **2012,** 8*,* 1003–1017.

[3] H. Bandara, S. Burdette, *Chem. Soc. Rev.* **2012***,* 41, 1809–1825.

[4] J. Casellas, M. J. Bearpark, M. Reguero, *ChemPhysChem* **2016**, 17, 3068-3079