Computational chemistry to the aid of elucidating photoreaction mechanisms: the case of photoisomerization of azobenzene.

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To elucidate the mechanism of chemical reactions is not an easy task, but the difficulty increases enormously when the reactions are pohotochemical. In these particular cases, photophysical and photochemical processes must be considered, and several excited states of different nature and their interactions have to be taken into account. The short time scale of the phenomena involved only adds difficulties to these kind of studies. Nevertheless, the development of new experimental procedures helps in a notorious measure to the understanding of these interesting and complicated reactions. Computational chemistry, that was considered years ago just a small assistance to these advances, is nowadays considered another tool in photochemical studies, given the amount and specific information that it can provide, and which experimental chemistry cannot always give.

In this talk we present the study of the mechanism of a well-known and long-studied photochemical reaction, as an illustrative example of the application of computational chemistry: the photoisomerization of azobenzene.

Azobenzene is an organic compound that has a singular behaviour due to the possibility of switching between *cis* and *trans* isomers using particular wavelengths of light. The high rate of these forward and back reactions, the fatigue resistance of the system, the stability of both *trans* and *cis* isomers and the possibility of tuning the properties of azo-derivatives by substitution, all give azo compounds a wide range of potential applications.[1,2]

In the absorption spectrum of azobenzene, two major bands are found in the UV-visible region corresponding to a transition to the S_1 state, of n-π* character, and to the S_2 state of π-π* character. For systems with free rotation, a different quantum yield for isomerisation is observed for each state when they are irradiated separately, [3,4] what suggests that two different isomerization mechanisms operate on excitation into these two electronic excited states. For a long time, it was established that the two mechanisms in play for the photoisomerization of azobenzene were in-plane inversion at one of the two nitrogen atoms when the reaction takes place by excitation to the first singlet excited state and twisting around the N=N double bond when excited to the second one (Fig. 1).
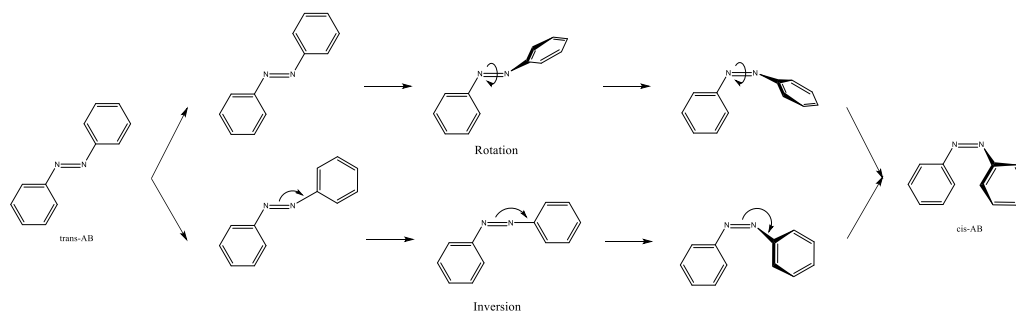
Figure 1. Classical mechanisms proposed for the isomerization of azobenzene

The study presented here revisits the mechanism of photoisomerization of azobenzene on its S_1 (n-π*) and S_2 (π-π*) excited states from the computational point of view. We have determined the topography of the potential energy surfaces (PES) of these low-energy states of the system by means of an ab initio methodology that includes dynamic electron correlation. Specifically, we have used in general the CASSCF/CASPT2 (Complete Active Space Self Consistent Field/CAS second-order multiconfigurational perturbation) combined methodology. We have found that the state populated by the initial excitation is the S_2 (π-π*) state, which decays very efficiently to the S_1 (n-π*) state at a pedal-like non-rotated geometry. On the S_1 state, relaxation leads to a rotated geometry where the system decays to the ground state, in which further relaxation can lead to either the *trans* or *cis* geometries. However, the S_1/S_0 conical intersection seam, where internal conversion can take place, also extends to planar geometries, so this reaction path is also accessible for rotation-constrained systems.[5]

We have also performed a dynamical study that confirms the mechanistic hypothesis suggested by the stationary study.

References:

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