

CIS-TRANS PHOTOISOMERIZATION OF PHENYLAZOPYRIDINE. ROTATION OR INVERSION? A NEVER ENDING DISCUSSION.

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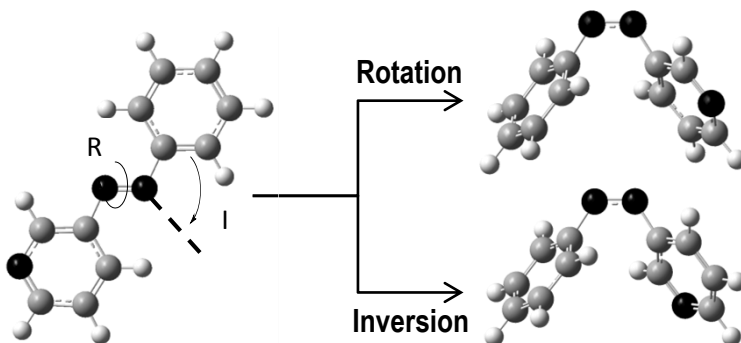
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Phenylazopyridine (PAPy) has been found to be fundamental within the context of big complexes to cause spin-crossover under irradiation by a trans-to-cis conformational change of the PAPy moiety. To understand this reaction is vital to know in detail the mechanism of the isomerization. Photoisomerization has been in vogue recently, mainly relative to azobenzene. Two mechanisms have been proposed in the literature: rotation around the C-N-N-C dihedral angle and N-N-C angle inversion on the azo group. Unlike azobenzene, the presence of an N-atom in the pyridine moiety of the PAPy gives place to several low-energy excited states of n-p* character that have to be taken into account. These states can be more or less involved in the reaction mechanism depending on the position of the N-atom^[1].

In the present work, two isomerization mechanisms proposed in the literature are studied, shedding light on its reaction paths through the lowest excited states. Moreover, the differences between azobenzene and PAPy are evaluated to observe if the added lone pair has some relevant effect on the photochemistry. In order to develop this work, a DFT/CASSCF/CASPT2 study had been performed exploring all minima, transition states and crossing points on the lowest potential energy surfaces to elucidate the reaction path. A theoretical description of the absorption spectra was also made using MD calculations with AMBER99 forcefield with discrete methanol solvent and vertical MS-CASPT2 energies.



References

- 1) L. Wang, C. Yi, H. Zou, J. Xu, W. Xu, *J. Phys. Org. Chem.* **2009**, *22*, 888