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Analysis of DFT functionals on determining tetraphenyl (hydroxy) imidazole properties for photochemical studies

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The hydroxyl-substituted tetraphenylimidazole (HPI) has been studied since 2005, due to its notable photochemical and photophysical properties.[1] While experimental studies have advanced, understanding the excited state and the intramolecular proton transfer (ESIPT) mechanism requires support from computational chemistry, which can provide accurate answers to guide further applications in laser dyes, metal sensors, etc[2,3]. However, selecting the most appropriate theory for simulating their properties is challenging due to the numerous options developed over recent decades. For this reason, in this work, we have selected a series of functionals, which includes B3LYP, B3LYP-D3, CAM-B3LYP, M06, M06-2X, wB97X-D3, PB86, PBE, and PBE0, with the 6-311G (d,p) basis set using the ORCA software (5.0.4). Two conformations were evaluated, and an energy difference of 8 kcal.mol^{-1} was observed between the structure with the intramolecular hydrogen bond and the one without it, conferring the first one the most stable. The wavelengths were calculated via TDDFT, comparing the PCM implicit solvent method results in dichloromethane (CH_2Cl_2), and experimental values (λ_{abs} = 279 nm), which some results are presented in Fig. 1. We have found that the inclusion of dispersion interaction correction is vital to obtain a match with the experimental data.

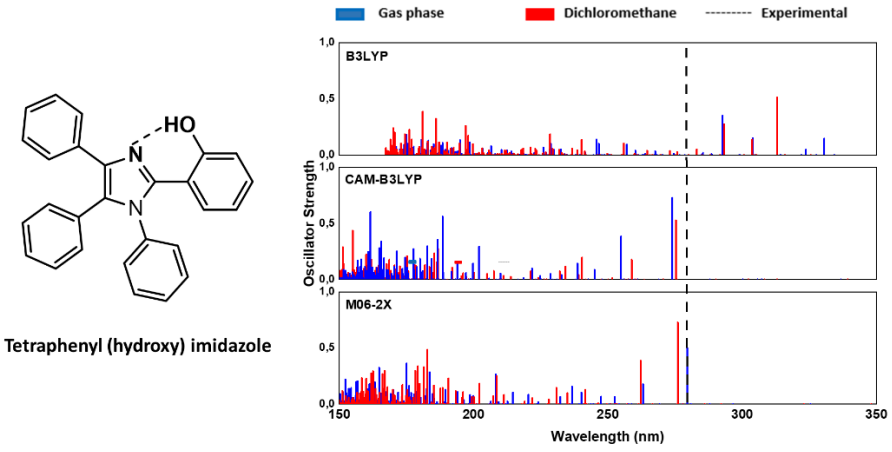

Figure1. Structure and electronic absorption spectra calculated for HPI with different TD-DFT functionals in gas-phase and in dichloromethane.

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