Fluorescence Calculations and PCA Analysis for investing structural and electronic properties of naphthoquinones in methanol.

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Keywords: *DFT, naphthoquinones, PCA,TD-DFT, ESIPT.*

Introduction

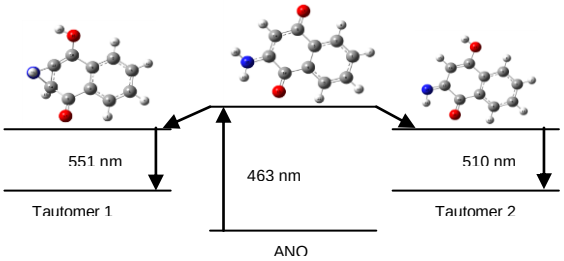
Recently, the use of naphthoquinones, such as 2-amino-1,4-naphthoquinones (ANQ), has provided an economically viable way to develop compounds for disease diagnosis.[1] It is also important to mention that many studies about the anti-tumor, anti-Leishimania and anti-bacterial activity of ANQ have also been reported during the last decade.[2] Actually, naphthoquinones exhibit Excited State Intramolecular Proton Transfer (ESIPT), which is the main mechanism responsible for their use as fluorescent probes.[3] In fact, ANQ shows the Enolic form in the excited state, which is converted to a Keto form through the fluorescence emission from excited state to ground state. [4] The understanding of the ESIPT mechanism for naphthoquinones is an important way of developing more efficient and selective fluorescent probes.[3,4] Thus, the goal of the current work is to evaluate the ESIPT mechanism and to put together TD-DFT calculations and PCA analysis to select the more adequate functional for studying the ESIPT mechanism for ANQ.

Metodology

Firstly, ANQ was optimized at the MP2/ DGTZVP level to ensure the same geometry for the electronic calculation. After the geometry optimization, the electronic proprieties were calculated with the functionals B3LYP, B3PW91, MPW1PW91, PBEPBE, CAM-B3LYP and WB97XD, employing the basis set DGTZVP. The solvent effect was evaluated by means of the IEFPCM model. The absorption energy and the wavelength were compared to the experimental values. The error values were applied to PCA analysis for determining the adequate functional for the electronic proprieties.

Results and Discussion

The Dendogram analysis highlighted three groups formed for the Hybrid (B3LYP, B3PW91, and MPW1PW1), GGA (PBEPBE) and the Long-Range (CAM-B3LYP, WB97XD) Functionals. The PCA analysis showed a correlation of 99% for the Principal Component 1, and the functional CAM-B3LYP showed more significant in the PCA analysis, being chosen for the electronic proprieties calculation. The geometric study for ANQ was then carried out for each functional tested, employing the CAM-B3LYP functional for the calculated error for the wavelength. Those values were then used for selecting the adequate functional for the optimization step from the PCA analysis. B3LYP revealed to be the best functional for the optimization geometry. Thus, the ESIPT mechanism for ANQ was evaluated at the B3LYP/CAM-B3LYP/DGTZVP, according to Scheme 1. It is important to mention that ANQ can form two possible tautomers during the ESIPT process. These tautomers exhibit fluorescence in very nearby regions. Tautomer 1 shows absorption at 2.67 eV (~463 nm) and fluorescence at 2.24 eV (~551 nm), Tautomer 2 shows absorption at 2.80 eV (~445 nm) and fluorescence at 2.45 eV (~510 nm). ANQ shows absorption at ~463 nm (exp. ~471 nm in methanol)[2] and fluorescence in ~535 nm (exp. ~550 nm in methanol).[2] Studies on the process are still being conducted to understand which is the preferred pathway.



Scheme 1. Values of ANQ wavelength absorption and fluorescence and tautomers thereof.

Conclusions

The most adequate DFT functional for the geometric studies was the B3LYP, and for the electronic properties, CAM-B3LYP. ANQ shows fluorescence at 535 nm and Tautomer 1 and 2 show fluorescence at 551 and 510 nm, respectively.

Acknowledgements

Post-Graduation Program as well as the financial agencies CNPq, FAPEMIG and CAPES.

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