Substituent effects on the ESIPT process in 2-Hydroxy-1,4-Naphthoquinones

Henrique A. Rodrigues (IC), Eduardo P. Rocha (PG), Lívia C. T. Lacerda (PG), Mateus A. Gonçalves (PG), Maíra S. Pires (PG), Telles C. Silva (PG), Teodorico C. Ramalho (PQ)

ChemistryDepartament, Federal Universityof Lavras, Lavras, Minas Gerais, Brazil.
teodorico.ramalho@gmail.com
Keywords: ESIPT, Fluorescence, DFT, TD-DFT, Naphthoquinone.

INTRODUCTION

Despite recent technological advances, cancer is still one of the most serious problems of humanity [1,2]. In this line, the use of fluorescent probes for preoperative and postoperative cancer diagnoses is crucial to detect early tumors and increase the changes of treatment. The Excited State Intramolecular Proton Transfer (ESIPT) is usually the main mechanism for fluorescent probes used for the cancer diagnoses (Fig. 1).[2]

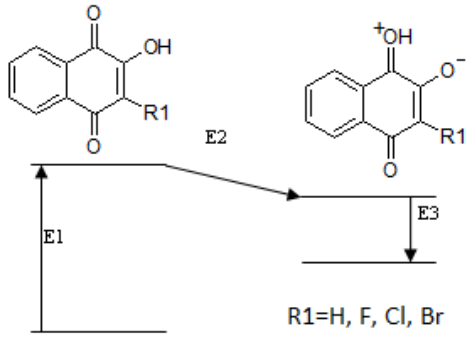

Fig. 1 - ESIPT process for the HNQ.

In spite of great importance associated to substituent effects on the ESIPT process, surprisingly little detailed computational work on this subject has appeared.[3]Thus, the goal of the current work, is evaluate the substituent effects on the ESIPT process of 2-Hydroxy-1,4-Naphthoquinones.

METHODS

Firstly, molecules were optimized by DFT/DGTZVP calculations. The electronic proprieties were calculated at the DFT/B3LYP/DGTZVP level for ground state and TD-DFT/CAM-B3LYP/DGTZVP for excided state. The solvent effect (Water) was evaluated by means of the IEFPCM model.[4]

RESULTS AND DISCUSSION

2-hydroxy-1,4-Naphthoquinone (HNQ) showed ESIPT process and the its derivatives too (Fig. 1). The energy values for the absorption (E1) and emission (E3) were evaluated by means of DFT/B3LYP/DGTZVP and TD-DFT/CAM-B3LYP/DGTZVP techniques. For the HNQ analogues, E1 values are of 3.32, 3.60, 3.66 and 4.69 eV for Br, Cl, F and CN derivatives, respectively. The substituent CN is not favorable for the ESIPT process, because the absorption energy is higher. However, the Br derivative is the more favorable for the ESIPT process.

Table 1 – Energy values (eV) for 2-Hydroxy-1,4-Naphthoquinone derivatives for the ESIPT process.

R1	E1	E2	E3
Br	3.32	3.23	1.20
Cl	3.60	3.52	1.20
F	3.66	2.66	1.14
CN	4.69	5.30	1.22

The E2 values for the Br, Cl, F and CN derivatives were 3.2; 3.52; 2.66 and 5.30 eV, respectively. It should be kept in mind, however, that all compounds showed similar emission values, then, the E3 values are not modulated by the substituent effect.

CONCLUSIONS

The investigation of the ESIPT process for HNQ derivatives by DFT and TD-DFT calculations was satisfactory; however the CN derivative was less favorable in water solution.

ACKNOWLEDGMENTS

The authors are grateful for the support given from the FAPEMIG, CAPES, CNPQ and UFLA.

1. Jali, B. R.; Baruah, J. B. Dye. Pigment. 2014, 110, 56–66.
2. Zhao, J.; Ji, S.; Chen, Y.; Guo, H.; Yang, P. Phys. Chem. Chem. Phys. 2012, 14, 8803.
3. Il'ichev, Y. V; Kühnle, W.; Zachariasse, K. a J. Phys. Chem. A 1998, 102, 5670–5680.
4. Arumugam, K.; Becker, U. Computational Redox Potential Predictions: Applications to Inorganic and Organic Aqueous Complexes, and Complexes Adsorbed to Mineral Surfaces; 2014; Vol. 4.