

## Theoretical and Experimental Study of Structural and Electronic Effects in DHMC.HCl

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Keywords: Density Functional Theory, Molecular Electronic Spectroscopy, Photophysical Properties,

### INTRODUCTION

Recently [1] 51 natural and synthetic coumarins have been tested to inhibit the mutagenicity of 2-amino-3-methylimidazo [4,5-f] quinoline (IQ), activated in *Salmonella typhimurium* TA98. Only six coumarins were inactive, one of them was 3-(diethylamine)ethyl]-7-hydroxy-4-methyl-1,2-coumarin.HCl (DHMC.HCl), which exists in the form of a monocation, with protonation at N of the tertiary amine. The inactivity of (DHMC.HCl) was explained relating the molecular and electronic structures to the biological activity, and considering the geometrical conformations, the solvent effects ethanol and water, the protonation/deprotonation dynamics, the photophysical properties and solubilization in micelles solutions neutral and charged.

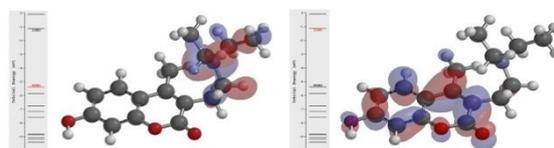
### METHODS

Spectroscopic techniques: emission at 77K, were obtained in Lin Electronic Spectroscopic System (LESS), using the selected band 313 nm. The spectra: UV-Visible were recorded in Perkin-Elmer Lambda 19 UV-Visible and the infrared spectrum was made with the sample in KBr wafers and obtained in ATI Mattson Genesis FTIR spectrometer. The interpretation of the results was done with the aid, the Hartree-Fock method with base function 6-31G\*. the excitation energies were calculated using the Time Dependent Density Functional Theory (TD-DFT) using functional B3LYP and base function 6-31G\* and the theoretical absorption spectra.

### RESULTS AND DISCUSSION

Most known coumarins [2] show a strong phosphorescence emission from emitting state <sup>3</sup>( $\pi,\pi^*$ ), with vibronic progression and it is more intense than the fluorescence emission and partially located on the (C<sub>3</sub> = C<sub>4</sub>) bond of the pyrone ring. The DHMC.HCl dissolved in ethanol and water emits fluorescence but no

phosphorescence. The calculation of the electronic transition HOMO → LUMO to the free base and hydrogen bonded complex species, is assigned as a intramolecular charge-transfer character, originating from a non-bonding electron in the N tertiary amine group to the  $\pi^*$  orbital of benzene ring. This electronic transition is only possible, if the DHMC species, exist in an appropriate geometric conformation, in which the group tertiary amine of DHMC.HC is within close distance to the chromophore benzene, Figure 1. For monocation species, this transition is assigned as ( $\pi,\pi^*$ ), indicating that charge-transfer was interrupted by protonation in the N tertiary amine group, changing the absorptive and emitter chromophores. Their absorption and emission spectra show a dramatic change, compared to the spectra of the hydrogen bonded complex species.



**Figure 1.** On the left, the molecular orbital HOMO, and on the right, the molecular orbital LUMO of free base DHMC. Calculated using Hartree-Fock method with base function 6-31G\*.

### CONCLUSIONS

The results show that inactivity of DHMC.HCl against IQ has several reasons, among which we highlight: (i) their photophysical properties are different from those of most coumarins, (ii) its non-planar molecular structure.

### ACKNOWLEDGMENTS

We would like to thank CNPQ for its support.

<sup>1</sup>R. Edenharder, C. Speth, M. Decker, H. Kolodziej, O. Kayser, K. L. Platt, Mutation Research 345, 57, (1995).

<sup>2</sup> A. D. S. Marques, C. T. Lin, J. Photochem. and Photobiol. B, Biology, 74, 63,(2004).