

## Photophysical study of Tröger's base molecular scaffolds

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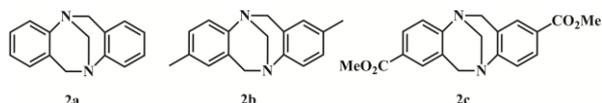
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Keywords: DFT, Photophysical, Tröger's base.

### INTRODUCTION

Tröger's base (TB) is a chiral amine first synthesized by Julius Tröger in 1877. Its intrinsic concavity provides a rigid structure and its chirality results from the very high energy barrier for the inversion of the nitrogen atoms. Due to these characteristic, Tröger's base analogues have countless potential applications, such as molecular recognition, catalysis, medicinal chemistry, supramolecular chemistry and new materials.<sup>1</sup> Although there have been several reports of new Tröger's base analogues, there are few reports in the literature studying the electronic structure of these analogues.<sup>2</sup> In this work, we dedicate our efforts to the understand of the photophysical of Tröger's base structures shown in Figure 1 by comparing experimental and theoretical properties predicted with TD-DFT.



**Figure 1.** Structure of the studied Tröger's bases (2a-c).

### METHODS

Time-dependent Density Functional Theory (TD-DFT) was used to study the photophysical behavior of Tröger's base structures. Geometry optimization and vibrational analysis of the ground ( $S_0$ ) and first excited state ( $S_1$ ) were done at PBE1PBE/cc-pVDZ level of theory and vertical transitions were calculated at PBE1PBE/aug-cc-pVDZ level. Solvent effects are included by IEF-PCM formalism using 1,4-dioxane (DIOX), ethyl acetate (AcOEt), dichloromethane (DCM), ethanol (EtOH) and acetonitrile (MeCN) as solvent. All calculations were carried out using Gaussian 09 Package.

### RESULTS AND DISCUSSION

The theoretical results are very close to the experimental. Tröger's bases 2a-b present absorption maxima ( $\lambda_{abs}$ ) located around 280 nm and emission maxima ( $\lambda_{em}$ ) near to 350nm, while 2c presents a  $\lambda_{abs}$  around 315nm and  $\lambda_{em}$  around 425nm. A larger red-shift observed in 2c could be associated with the increase of  $\pi$  system length, due to the presence of C=O group. A small solvatochromic effect was observed in 2a-c absorption wavelength indicating an almost absence charge transfer in  $S_0$ . However, 2c structure shows a higher solvatochromic effect in emission wavelength. In addition, a larger change in dipole moment from  $S_0$  to  $S_1$  in 2c (around 4 times) indicates an intramolecular charge transfer mechanism in  $S_1$ , corroborates by Lippert-Mataga plot. The vertical transitions from  $S_0$  to  $S_1$  are  $\pi \rightarrow \pi^*$  type, from HOMO to LUMO molecular orbitals.

### CONCLUSIONS

The photophysical study show that i) TB 2a-c present a main absorption in UV region and emission at a violet-blue region; ii) the vertical transitions are ascribed to  $\pi\pi^*$  electronic transitions; iii) the presence of substituents in 2-8 positions causes a bathochromic effect; iv) a small solvatochromic effect in  $S_0$  points to an almost charge transfer, but in 2c a intramolecular charge transfer in excited state is expected.

### ACKNOWLEDGMENTS

The authors are grateful for the support given from the CAPES and CNPq.

<sup>1</sup> D.M.P. Aroche, J.M. Toldo, R.R. Descalzo, P.F.B. Gonçalves and F. Rodembusch. *New J. Chem.*, (2015). DOI: 10.1039/c5nj01166c.

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