Title: **Analysis of the electronic structure of amidates derived from simple secondary amides.**

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The amide group is an essential chemical bond formed by the condensation of an amine and a carboxylate group (-NH-CO-) and constitutes the primary covalent linkage of all protein structures, where it is also known as peptide bond, and other polymers. The amide group of primary and secondary primary amides can participate in acid/base equilibrium to produce the corresponding amidate anion by deprotonation. The amidate may have low energy electronic states with complex multireference structure due to the variable weight of the amidate/imidate resonance that may include open shell forms. Quantum Chemistry has powerful theoretical tools to describe in detail the ground and excited electronic states of lower energy of medium sized molecules with different levels of precision. In this project, wavefunction based methods have been used to investigate the nature of the low energy electronic states of simple secondary amides and the related amidate. Initially, model systems (N-methylacetamide and its phenyl-substituted derivates) are studied to establish the essential elements for the analysis of the ground state and excited low-energy open shell states as well as their stabilization by inclusion of polar groups such as -NO2 or- CN in the phenyl rings.

The most relevant results based on the analysis of the molecular structure of minimum energy structures and the analysis of frontier orbitals (HOMO/LUMO for closed shell electronic states and SOMO orbitals for triplet states), show that the effect of the phenyl groups bonded directly to the nitrogen atoms increases the acidity of the amide hydrogen atoms in line with available pKa values. It is also observed that this effect largely increases when -NO2 group is bonded to the phenyl ring in para position showing that this group contributes to stabilize the amidate form and the first triplet electronic state mostly by resonance effects.

Keywords: Amide bond, amidate, electronic structure, quantum chemistry, excited states.