

Electronic properties of hydrazones: planning new complexes for spectrophotometric analysis

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Abstract – Hydrazone complexes were used to develop a highly sensitive spectrophotometric methods. Aiming to propose new complexes, we carried out DFT calculations (SVWN5 and B3LYP functionals) for DPKBH and DPKSH, in both enolic and cetic conformations. We optimized the geometry of each tautomeric conformation in vacuum and in solution (simulated by the integral equation formulation of the polarizable continuum model). In a second step, we have performed calculations of quantities relevant for the formation of complexes, such as the dipole moment and the charge distribution.

Hydrazones are azomethine compounds characterized by the C=N-N group. Some of them may play an important role in the treatment of several diseases such as tuberculosis, by the formation of stable chelates with transition metals that catalyze the corresponding physiological process. Such compounds are also widely used in analytical chemistry, as colorimetric or fluorimetric reagents or in liquid-liquid extraction methods for the determination of metallic ions. In these chelates the aroylhydrazones may behave as a bidentate, tridentate or tetradentate ligand. [1,2]

Recently, complexes of zinc (II) with DPKSH (di-2-pyridil ketone benzoylhydrazone) and complexes of nickel (II) with DPKBH (di-2-pyridil ketone salicyloylhydrazone) were used to develop a highly sensitive spectrophotometric method [1,2]. In aqueous/ethanolic solutions, these hydrazones show tautomeric structures whose can be coordinated to the metallic ion, probably through the nitrogen atoms either alone or in combination with an oxygen atom, of the enolic or phenolic group.[2].

Aiming to propose new complexes, here, we report on a theoretical study of the following hydrazones: DPKBH and DPKSH (Fig. 1). We optimized the geometry of each tautomeric conformation, and calculated the resulting electronic structure, by means of density functional theory. To eliminate possible artifacts of specific density functionals and basis sets in the calculations, we employed both the local spin density approximation in the SVWN5 parametrization, and the B3LYP hybrid functional, each in the 6-31G and in the DGDZVP basis, in vacuum and in solution (simulated by the integral equation formulation of the polarizable continuum model). In a second step, we have performed calculations of quantities relevant for the formation of complexes, such as the dipole moment, the charge distribution and the electrostatic potential surface. Currently, we are performing calculations for zinc, nickel and iron complexes.

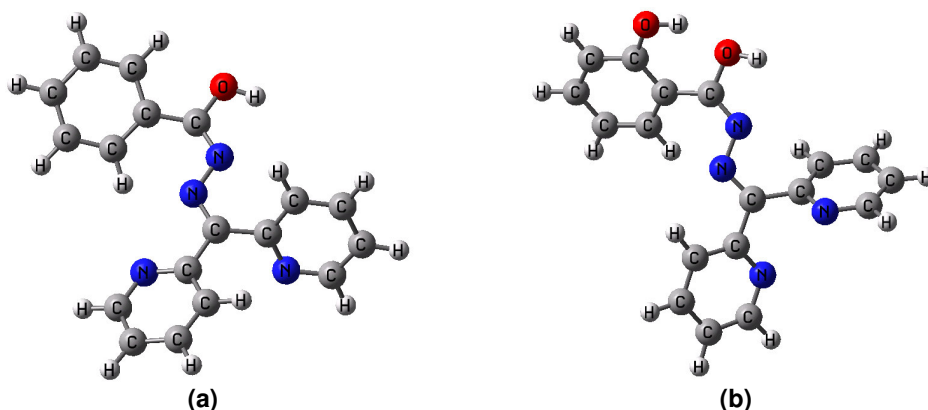


Figure 1 - Enolic structures of (a) DPKBH and (b) DPKSH.

References

- [1] I. Gaubeur *et al.* Spectrosc. Lett. 35 (2002) 455.
[2] I. Gaubeur *et al.* Polyhedron. 23 (2004) 2095