

Role of tautomerism and solvatochromism in UV–VIS spectra of arylhydrazones of β -diketones

Abstract

New arylhydrazones of β -diketones, 5-chloro-3-(2-(1-ethoxy-1,3-dioxobutan-2-ylidene)hydrazinyl)-2-hydroxybenzenesulfonic acid (**1**), 3-(2-(1-ethoxy-1,3-dioxobutan-2-ylidene)hydrazinyl)-2-hydroxy-5-nitrobenzenesulfonic acid (**2**), and 3-(2-(4,4-dimethyl-2,6-dioxocyclohexylidene)hydrazinyl)-2-hydroxy-5-nitrobenzenesulfonic acid (**3**), have been synthesized and characterized by IR, ^1H and ^{13}C NMR spectroscopies and elemental analysis. **3** and known 5-(2-(4,4-dimethyl-2,6-dioxocyclohexylidene)hydrazinyl)-4-hydroxybenzene-1,3-disulfonic acid (**4**) exist in DMSO solution exclusively in the hydrazone form, while **1** and **2** exist in DMSO and H_2O solutions as a mixture of enol-azo and hydrazone tautomeric forms, in ratios dependent on the solvent polarity and inductive effect of the substituents. DFT and TDDFT approaches were applied for simulations of experimental UV–VIS absorption spectra of the studied compounds, taking into account solvatochromic as well as tautomeric effect. The performed simulations have established a correlation of substantial experimental 120 nm red shift of the enol-azo form with respect to hydrazone with HOMO and LUMO orbitals' delocalization.