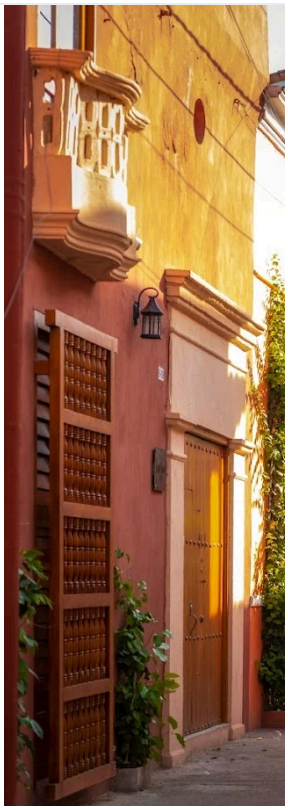

Quitel 2025

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Unveiling the effects of tautomerism on the electronic spectrum of sulfapyridine: a joint theoretical and experimental study

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The molecular structure of sulfonamide antibiotics (SAs) can vary in aqueous solution due to prototropic tautomerism [1], which influences their chemical properties. This study combines theoretical and experimental results to characterize the predominant form of sulfapyridine (SPY) at acidic, neutral and basic pH. Geometry optimizations and vibrational frequency calculations are performed for neutral, protonated, and deprotonated forms using Density Dunctional Theory (DFT) at the PBE-D3(BJ)/cc-pVTZ [2] level with the PCM [3] solvation model. The barrier height description for the reaction between SPY and its tautomeric form (TAUT) is improved via single-point energy calculations done at the CAM-B3LYP-D3(BJ)/def2-QZVPP [4,5] level with the SMD [6] model. Microsolvation effects are considered by using up to two explicit water molecules along with quasi-harmonic thermodynamic corrections at room temperature. These molecules significantly lower the tautomerization barriers (activation Gibbs energy values from 37.0 to 9.6 kcal·mol^{-1} at neutral pH and from 35.3 to 7.9 kcal·mol^{-1} at acidic pH), demonstrating their catalytic effect. There is no tautomerism for the deprotonated form. Microsolvation also turns the TAUT formation from SPY into a spontaneous process with Gibbs energy variations of –1.3 and –3.0 kcal·mol^{-1} for neutral and acidic media, respectively. Ultraviolet/visible (UV/Vis) spectra are calculated using Time-Dependent DFT at the CAM-B3LYP/def2-TZVPD level with C-PCM [7]. The best agreement with experimental UV/Vis spectra is found for the tautomer, with a characteristic band around 300 nm. These results show that the tautomeric form of SPY predominates in aqueous solutions, being produced by a fast interconversion reaction, explaining the features observed in the experimental UV/Vis spectra at different pH conditions. Thus, the tautomeric equilibrium and microsolvation effects should be considered in chemical processes of aqueous solutions containing SPY and, perhaps, other SAs, like biological and photodegradation reactions.

Keywords:

Sulfapyridine, tautomerism, density functional theory, microsolvation, UV/Vis spectrum

Suggested Reading / References:

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