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IDENTIFICATION OF TAUTOMERIC INTERMEDIATES OF A NOVEL THIAZOLYLAZONAPHTHOL DYE – A DENSITY FUNCTIONAL THEORY STUDY

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Abstract

The recently synthesized thiazolylazo dye, 1-[5-benzyl-1,3-thiazol-2-yl)diazenyl]naphthalene-2-ol called shortly **BnTAN**, is studied by density functional theory (DFT) in three tautomeric forms in order to explain the available ^{1}H NMR, UV-Vis and FTIR spectra. An experimentally observed IR band at 1678 cm^{-1}, assigned to the C=O bond stretching vibration, supports the notion that **BnTAN** retains in the less stable keto-form even in the solid state due to an ultrafast single-coordinate intramolecular proton transfer. This finding is also in a good agreement with an X-ray crystallography analysis which indicates an intermediate position of the proton between the –OH and –N=N– groups. Calculations also show that some experimentally observed ^{1}H NMR signals could be considered as being averaged values between theoretically calculated chemical shifts for the corresponding protons in keto- and enol-tautomers. At the same time the UV-Vis spectra are almost insensitive to the tautomerization processes as the main single band absorption at 500 nm is presented in all tautomers according to our TD DFT simulations. The minor differences in spectral features of the long-wavelength visible region are also noted and discussed in respect to manifestation of the less stable tautomer form.

Keywords: tautomers, FTIR spectra, UV–vis spectra, NMR spectra, DFT calculations