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Combined NMR Spectroscopy and Quantum-Chemical Calculations in Fluorescent 1,2,3-Triazole-4-carboxylic Acids Fine Structures Analysis

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Abstract: The peculiarities of the optical properties of 2-aryl-1,2,3-triazole acids and their sodium salts were investigated in different solvents (1,4-dioxane, dimethyl sulfoxide DMSO, methanol MeOH) and in mixtures with water. The results were discussed in terms of the molecular structure formed by inter- and intramolecular noncovalent interactions (NCIs) and their ability to ionize in anions. Theoretical calculations using the Time-Dependent Density Functional Theory (TDDFT) were carried out in different solvents to support the results. In polar and nonpolar solvents (DMSO, 1,4-dioxane), fluorescence was provided by strong neutral associates. Protic MeOH can weaken the acid molecules' association, forming other fluorescent species. The fluorescent species in water exhibited similar optical characteristics to those of triazole salts; therefore, their anionic character can be assumed. Experimental ¹H and ¹³C-NMR spectra were compared to their corresponding calculated spectra using the Gauge-Independent Atomic Orbital (GIAO) method and several relationships were established. All these findings showed that the obtained photophysical properties of the 2-aryl-1,2,3-triazole acids noticeably depend on the environment and, therefore, are good candidates as sensors for the identification of analytes with labile protons.

Keywords: 1,2,3-triazoles; carboxylic acid; fluorescence; TDDFT; dimer; pK_a



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1. Introduction

The 1,2,3-triazole cycle is an important fragment in the molecules of various drugs [1–3], biologically active compounds [4–11], and polymers [12]. Its good accessibility, ease of modification, and specific structural properties, such as a high-dipole moment, molecular rigidity, and the ability to bind by weak intermolecular interactions (hydrogen bonds, dipole–dipole, and π -stacking) with a molecule target, as well as its promising photochemical properties, are attractive properties of triazoles. This has made them a focus of attention in multiple areas of science: chemistry, biology, medicine, physics, and material chemistry [2,13–19]. However, the functional groups and substituents surrounding the heterocyclic core are also very important, since they are effective tools for the design of new fluorophores and biologically active compounds [1,2,20–23]. Therefore, the issues in designing new 1,2,3-triazoles in accordance with the requirements of a specific direction of their use are acute and relevant at present.

Traditional approaches to the design of new fluorophores include many factors that have long been studied and are well-known. Among them, the most significant and widely used are the change in the nature of substituents and their localization with the formation of the A- π -D system, which is more sensitive to the microenvironment and analytes [24]. These factors are undoubtedly important and provide answers to many essential questions concerning the manifestation of photophysical effects and some other effects. However, in

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