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Quantum-chemical investigation of structure and reactivity of pyrazol-5-ones and their thio- and seleno-analogs: X. Solvent effect on the chemical shifts of nuclei in the molecules of 3-methylpyrazol-5-ones and 1-phenyl-3-methylchalcogenopyrazol-5-ones and characteristics of tautomeric equilibrium in these compounds

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Abstract

By quantum-chemical DFT/GIAO method chemical shifts of all nuclei in the NMR spectra of 3-methylpyrazol-5-one and 1-phenyl-3-methylchalcogenopyrazol-5-ones in chloroform and dimethyl sulfoxide were calculated and analyzed using various solvation models. Low sensitivity to solvent of the chemical shifts of ^{13}C and ^1H nuclei (except for "acidic" protons) calculated in the framework of various continuum models is revealed. Discrete and discrete-continuum models reflect well deshielding of the active centers of H-complexation and chemical shifts of "acidic" protons of the studied pyrazolones in solutions. Optimization of geometry of pyrazolones in solutions only slightly improves the agreement between the theoretically calculated and the experimental values. Shielding of nitrogen, oxygen, sulfur, and selenium atoms is more sensitive to the nature of solvent and to the nature of tautomeric forms. The methods of NMR spectroscopy allow to identify reliably the dominating tautomeric form but they are insufficient for the quantitative characterization of tautomeric equilibria. © 2009 Pleiades Publishing, Ltd.

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