

Quantum chemical modeling of physico-chemical properties and reactivity of amphiphilic heterocyclic spiro compounds and imidazoles

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Today organic heterocyclic compounds are widely used in various fields of science, industry, medicine, and healthcare. The most important classes of heterocycles are spirocompounds and imidazole derivatives, which attract particular interest due to their use as working elements in photostitchers, optical logic devices, as well as key components of antitumor drugs and anticorrosion agents. At the same time, as the miniaturization of devices and the use of ultrathin coatings in are current industry trends, new synthesized compounds must meet specific requirements such as the ability to form ordered structures, retaining of functional characteristics at the level of individual molecules, and possessing of target properties in the materials being created.

One of the ways to form ultrathin ordered molecular structures on solid substrates is the Langmuir-Blodgett technique, which allows to obtain mono- and multilayer films with specified characteristics and high mechanical and thermal stability at various surfaces. Functionalization of heterocyclic molecules with long aliphatic chains enables the formation of stable Langmuir monolayers that can be preorganized and transferred onto solid substrates. However, often upon modification of these compounds with various substituents, the functional characteristics of the molecules may become passivated or degrade. In this regard, the current tasks are predicting the behavior of heterocyclic molecules based on their structure and constructing chemoinformatic models that allow forecasting the physicochemical, photophysical, optical properties, and reactivity of synthesized compounds. The most promising methods for predicting the influence of substituents on the properties of organic compounds are based on the use of quantum chemical methods. However, until now, prognostication the spectral characteristics of organic

photochromes using TD-DFT has not always been relevant, and examples of quantum-chemical modeling of physicochemical properties of amphiphilic spironaphthoxazines and reaction mechanisms of N-oxides of imidazoles are absent in the literature.

Thus, this work is devoted to aspects of quantum-chemical modeling of structural, physicochemical, optical properties, and reactivity of spiroheterocyclic compounds and imidazoles. The results of modeling structural parameters of a number of amphiphilic spiropyrans and spironaphthoxazines are presented, as well the influence of long aliphatic chains on their chemical and electronic structure is considered. Energy levels of various conformations of these photochromes have been calculated, the relative stability of their cyclic and merocyanine forms has been determined, and the fundamental possibility of theoretical foundation of negative photochromism in some spiropyran compounds has been demonstrated. The new scaling regressions have been proposed based on revealed correlations between calculated and experimental data, thus allowing prediction of optical properties of new amphiphilic spirocompounds. For the first time, a quantum-chemical base has been provided for the selective reactivity of N-oxides of imidazoles with electron-deficient olefins. Using Density Functional Theory possible reaction pathways have been fully calculated taking into account various combinations of two types of electron-withdrawing substituents – nitriles and ketones. Based on these calculations the dependence of selectivity of the mechanism on substituents has been explained.