

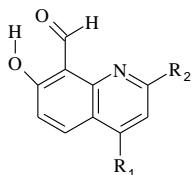
Volha Vetokhina

Ph.D. Thesis

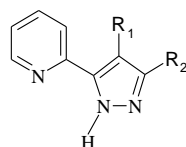
Spectroscopy, photophysics, conformational equilibria, and photoinduced tautomerization in selected bifunctional proton donor-acceptor azaaromatic molecules

ABSTRACT

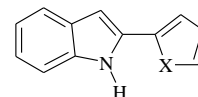
This work is devoted to a study of spectroscopic properties, photophysical processes and photochemical reactions in three series of trifunctional or bifunctional molecular systems having both a proton donor and acceptor centers. The aim of the work, *i.e.*, the qualitative and quantitative characterization of: (i) the photophysical parameters, (ii) the solvent-dependent rotamerization, and (iii) the ground and excited state tautomerization, was successfully realized with the use of steady-state and nanosecond and picosecond time-resolved UV-Vis spectroscopic methods, ^1H NMR spectrometry, and quantum chemical computations. In order to study the solvent effects, the investigations have been performed in solutions and under supersonic jet isolation conditions.



7-HQCs



2-PPs



indole derivatives

The first family of compounds, 7-hydroxyquinoline-8-carbaldehydes (**7-HQCs**), can exist in two tautomeric forms: **OH** (7-quinolinol) and **NH** (7(1*H*)-quinolinone). The compounds are composed of two moieties: a molecular “frame” (7-hydroxyquinolines, **7-HQs**) and a proton “crane” (carbaldehyde group), and have been proposed to serve as models of a reversible optically driven molecular switch. The comparative studies of the spectroscopy and photophysics of the series of **7-HQCs** and **7-HQs** and their prototropic reactions in a wide range of solvents allow us to explain the solvent-dependent mechanism of the ground and excited state long-range tautomerization.

The next two series of the studied compounds: (i) 2-(1*H*-pyrazol-5-yl)pyridines (**2-PPs**) and (ii) **indole derivatives** have the hydrogen bond donor and acceptor centers which are located in separate moieties, covalently linked by a single bond. The compounds can form *syn* (with the donor and the acceptor on the same side) and *anti* (with the two centers on the opposite sides) conformers *via* internal rotation around a single bond.

It is shown that **2-PPs** are a rare example of molecules that exhibit three types of excited state proton transfer (ESPT) reactions: (i) intramolecular (ESIPT) in the *syn* form; (ii) intermolecular (ESDPT) in the dimers in nonpolar media, and (iii) solvent-assisted ESDPT in H-bonded 1:1 complexes with protic partners. The excited state processes are manifested by the appearance of dual luminescence and a bimodal irreversible kinetic coupling of the two fluorescence bands. Ground state *syn-anti* equilibria are detected and discussed. The fraction of the higher energy *anti* form varies for different derivatives and is strongly dependent on solvent polarity and hydrogen bond donor or acceptor ability.

On the contrary, spectroscopy and photophysics of selected bifunctional **indole derivatives** containing thiophene, thiazole, and furan, do not depend on solvent properties – independent of solvent polarity and hydrogen bond donor ability the compounds show strongly allowed and very efficient fluorescence. Due to the fact that the *syn* rotamers of these compounds are able to form cyclic, doubly hydrogen bonded complexes with protic partners which upon excitation can be efficiently deactivated in S_1 *via* internal conversion and/or proton transfer, such finding was not expected. On the other hand, the luminescence of 3-pyridin-4-yl-1*H*-indole (**3-PI**) is strongly quenched in alcohols and water. The mechanism of the excited-state deactivation leading to fluorescence quenching is proposed.