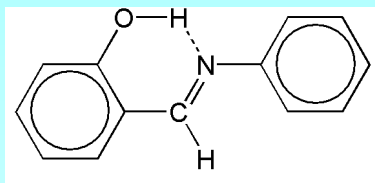


Project KBN: Molecular aspects of photochromism. Study of the photoinduced process of proton transfer in selected Schiff bases using ultrafast optical spectroscopy; 2003-2005

The project concerns molecular aspects of photochromism in some aromatic Schiff bases with the special focus on the processes leading to the formation of long-living photochromic transient taking place on the time scale of tens of fs to hundreds of ps. The mechanism and dynamics of the deactivation of two groups of Schiff bases were investigated: the salicylideneaniline family (SA, SAA, BSP) and the benzoxazole derivatives (BPH, BPHMe). One of the most important results was the observation of the ultrafast decay (<50 fs) of the excited primary enol tautomer due to the intramolecular proton transfer, which initializes the structural changes of the molecules. The existence of the ultrafast internal conversion within the enol form as a competitive channel of deactivation was also revealed. The results obtained indicate that in the BPHMe molecule there is an additional route of photochromic cycle via exceptionally slow excited state intramolecular proton transfer, connected with the nonplanar conformers. The ground state equilibrium between the enol and keto tautomers is found to depend mainly not on polarity but on the proton donating ability of the solvent. Upon selective excitation of each of these tautomers, the same excited state of keto tautomer is created (which is the precursor of the photochromic form). For the molecules from salicylideneaniline family the creation of photochromic transient takes place within 7-35 ps (with the efficiency of 10-30%), while for benzoxazole derivatives this time is at least an order of magnitude longer.



Structure of
salicylideneaniline
(SA)

Figure: Examples of the kinetic curves of the transient absorption signals for SA in ACN, and the fits convoluted with the instrumental function (rise of keto tautomer signals <50 fs).

