

# Proton transfer reaction and photochromism of the new family of Schiff bases

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The aromatic hydrogen bonded Schiff bases represent a special group of molecular systems in which two interesting phenomena occur: excited state intramolecular proton transfer and photochromism. After the excitation of the primary enol form the ultrafast proton transfer reaction takes place and at least two transient species are observed: the keto tautomer exhibiting largely Stokes shifted fluorescence, and the long living (in the ground state) photochromic transient, created from the keto form after the structural changes. Previously we have studied the photophysics of salicylideneaniline, the best known photochromic Schiff base (SA),<sup>1</sup> and a much larger molecule, bis(salicylidene)-p-phenylenediamine (BSP).<sup>2</sup> Both molecules were shown to undergo an extremely fast proton transfer reaction, with characteristic times within 50 fs. In the present work we focus our attention on the new Schiff base, a particular structure, isomeric to BSP – the bis(phenyliminomethyl)hydroquinone (BPH), together with its monomethoxy-derivative (BPHMe) shown in Fig.1.<sup>3</sup>

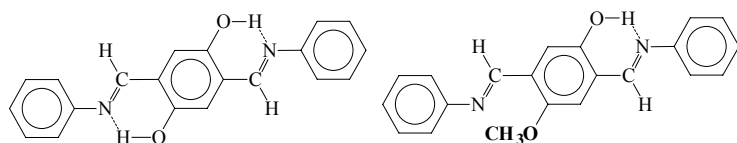


Fig.1. Formulae of studied molecules: **BPH** and **BPHMe**

BPH is structurally similar to the widely studied system, BBHQ, also possessing in its framework a hydroquinone fragment.<sup>4</sup> Here, we study both molecules of Fig.1 combining the data of transient absorption in fs time range with the picosecond time-resolved fluorescence. We have shown, how the elimination of one internal hydrogen bond in the symmetric BPH molecule deeply changes its photophysics. BPHMe molecule is strongly fluorescent with the quantum yield higher by one order of magnitude than BPH. Moreover, the lack of one internal H-bond makes the BPHMe molecule comparatively flexible and its photophysics is accounted for by at least two different conformers. The most important results obtained in acetonitrile as a polar, aprotic solvent, are the following: the two products of excited state proton transfer reaction – two different conformers of the keto tautomer are created, one within 50 fs, and the second one with the time constant about 10 ps. This last value must be regarded as exceptionally low, resembling the slow proton transfer reaction in BBHQ molecule mentioned above. The deep differences in photophysics of both molecules under present study are illustrated by the lifetimes of the corresponding products of proton transfer reaction. Thus the major part of the transient absorption of BPH decays with the time constant of about 0.7 ps what is to be compared with the decay of the excited keto form of BPHMe equal 450 ps. The reasons of these differences will be discussed in terms of different deactivation channels in both studied structures.

The work has been done with the financial support of the KBN project 2 P03B 015 24.

<sup>1</sup> M.Ziolek, J.Kubicki, A.Maciejewski, R.Naskrecki, A.Grabowska, *Phys.Chem.Chem.Phys.*, **2004**, *6*, 4682-4689

<sup>2</sup> M. Ziólek, J. Kubicki, A. Maciejewski, R. Naskrecki, A. Grabowska, *Chem. Phys. Lett.*, **2003**, *369*, 80-89

<sup>3</sup> A. Grabowska, K. Kownacki, J. Karpiuk, S. Dobrin, L. Kaczmarek, *Chem. Phys. Lett.*, **1997**, *267*, 132-140

<sup>4</sup> N.P.Ernsting, S.A.Kovalenko, T. Senyushkina, J.Saam, V.Farzdinov, *J. Phys. Chem. A*, **2001**, *105*, 3443-3453