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The effects of pH and hydrogen bonds on photophysical properties of N-(4-bromobenzyl) substituted hydroxystilbazolium hemicyanine and merocyanine

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ABSTRACT

Photophysical properties of (E)-1-(4-bromobenzyl)-4-(4-hydroxy-3-methoxystyryl) pyridinium bromide existing in equilibrium of its protonated (BSHB) and deprotonated (BS) forms at different pH were characterized by UV–Vis spectroscopy, and steady-state, and time-resolved fluorescence techniques.

Absorption, steady-state, and time-resolved emission spectra, and synchronous scanning spectra were used to explain the observed phenomena. The pK_a of BSHB in the ground state was determined. We also found that the deprotonated form – BS, being a weak base, is protonated upon addition of water. The pK_a* of BSHB in the excited state was determined in two different ways giving different results. This inspires the discussion on the applicability of the use of the thermodynamic Förster cycle for calculation of the excited-state pK_a* for hydroxystilbazolium dyes.

Solvatochromism of both BSHB and BS in polar aprotic and protic solvents was analyzed using the four-parameter Catalán solvent scale and the Δf scale. This analysis indicates that both compounds in their emissive states have benzenoid-like (or zwitterionic for BS) structure in protic solvents. However, in aprotic polar solvents the contribution of the zwitterionic structure to their emissive state is reduced in favor of the quinoid structure.

Importantly, the Catalán scale shows a strong influence of solvent basicity (hydrogen-bond accepting ability) on the absorption properties of BSHB, indicating strong stabilization of its ground and vertical excited state by hydrogen-bonded complexes. Contrary to BSHB, the absorption spectra of BS are affected by solvent acidity. Hydrogen – bonded complexes stabilize the ground state of this compound, although their energy decreases strongly upon excitation. The hydrogen-bonded complexes influenced the structures of both compounds in their excited states.

1. Introduction

(E)-1-(4-bromobenzyl)-4-(4-hydroxy-3-methoxystyryl)pyridinium bromide (BSHB) belongs to the class of hemicyanine dyes. This compound is also a member of the family of “push–pull” stilbenes [1–3] which have long attracted attention due to postulated charge-transfer character of their excited states [4,5] and to the large optical nonlinearities in these molecules and their dehydrohalogenated forms [6–10].

Molecules that can have intramolecular charge transfer (ICT) excited states usually exhibit strong solvatochromism and dependence of their fluorescence properties [1] on the environment, including its pH and/or polarity. This implies a wide range of applications for hemicyanines in many fields [11–20]. The problems requiring most attention include the applicability of the Förster cycle for determination of the pK_a* of those compounds in the excited state, and the nature of their protonated and deprotonated forms in the ground and excited states, which may either be zwitterionic or quinoid. Indeed, the pK_a of the Brooker's merocyanine in the ground state has been reported as 8.5 [21–23]. Similar pK_a values have been reported for 1-ethyl-2-(4-hydroxystyryl)pyridinium, 1-ethyl-2-(2-

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hydroxystyryl)pyridinium, and 1-ethyl-2-(4-hyroxystyryl)quinolinium, 1-ethyl-2-(4-hyroxystyryl)quinolinium halides, measured in water and in mixtures of organic solvents and water, and pK_a values of those salts in water are 8.32, 8.17 and 8.04, and 7.96, respectively [21,24]. Gruda and Balduc reported pK_a value from 9.30 to 9.98 for bulky substituted 4-(4-hydroxystyryl)pyridinium salts [25]. The pK_a values for N-benzyl derivatives of hydroxystyrylpyridinium halides were also determined. Namely, Gibson and Bailey [26] reported that the pK_a of (p-substituted) benzyl-2′-hydroxy-4-stilbazolium bromides is about 8.4.

It is widely known that the excited-state pK_a^* can be estimated by means of the Förster cycle [27–30], the fluorescence titration curve [31], and the triplet–triplet absorbance titration curve [32]. Kuder and Wychick [22] and others [23,33,34] applied the Förster cycle for determining the excited-state dissociation constant of 1-methyl-4-(4-hydroxystyryl)pyridinium dye. They estimated that its pK_a^* value is 1.85. The pK_a^* value in the lowest singlet excited state was also determined for 1-methyl-2-(4-hydroxystyryl)pyridinium dye: Abdel-Halim and co-worker estimated this value as 2.74 from the Förster cycle [33]. Therefore, these compounds are expected to be more acidic in the excited as compared to the ground state. Recently, using fluorescence titration experiment, we have determined p$K_a^* = 8.1$ for hydroxystilbazolium dyes, namely (E)-1-(4-chlorobenzyl)-4-(4-hydroxystyryl)pyridinium chloride [35]. Our result was in contradiction to the value obtained in Förster-cycle calculations that yielded p$K_a^* = 1.15$ [35]. The explanation for such discrepancy based on very short fluorescence lifetimes in both acidic and basic environments, resulting in the lack of equilibrium in the excited state. However, the Förster formula may not be used in absence of the equilibrium.

Fig. 1 shows acid–base equilibria of (E)-1-(4-bromobenzyl)-4-(4-hydroxy-3-methoxystyryl)pyridinium bromide and the structures of its protonated and deprotonated forms with their names used in the present work.

Hemicyanines always assume benzenoid structure in acidic and neutral solutions, while in basic solutions, where the deprotonated form of hemicyanines (merocyanines) is present, both zwitterionic and quinoid structures are a possibility. Note that the deprotonated form BS (in fact, it is the dehydrohalogenated form, see Fig. 1) can be separated as an individual compound by extraction with non-polar solvents like CH_2Cl_2 or $CHCl_3$ from basic aqueous solutions.

BS belongs to the class of stilbazolium merocyanines that show one of the largest negative solvatochromic shifts ever reported. For example, the Brooker's merocyanine shows a negative solvatochromic shift exceeding 6500 cm^{-1} between chloroform and water [36].

The zwitterionic form of merocyanines appears in polar solvents such as water or alcohols, while the quinoid one appears in non-polar environments such as chloroform or dichloromethane [37,38]. The zwitterionic and quinoid forms of merocyanine differ from each other in positions of the lowest-energy absorption band, which is bathochromically shifted for the latter form. The zwitterionic structure for hydroxystilbazolium merocyanines in polar environments is also supported by their large dipole moment in the ground state. Indeed, according to Momicchioli and co-workers [39], the dipole moment of N-methyl substituted hydroxystilbazolium betaine (merocyanine) in the gas phase is 17.92 D, indicating its zwitterionic structure. Additionally, this dipole moment grows with increasing solvent-induced polarization. Momicchioli and co-workers [39] suggested that the $S_0 \rightarrow S_1$ transition causes an enrichment of the resonance hybrid in the quinoid form, as supported by the reduced value of the dipole moment of that molecule in the Franck–Condon S_1 state. The shift of N-substituted hydroxystilbazolium betaines towards quinoid structure upon excitation is also supported by other authors [40].

Recently Haas and coworkers described the wavefunction in the ground state (Ψ_g) of stilbazolium betaine (merocyanine) as an in-phase combination of the two (zwitterionic and quinoid) forms, and the wave function in the excited state (Ψ_e) are an out-of-phase combination of the same two forms. It is referred to as the twin state [41]. The same authors suggested that the fluorescence arises from the same state that is populated directly by absorption from the ground state because the absorption and emission spectra of the studied hydroxystilbazolium dyes are the mirror image of each other [42]. They also stated that the contribution of the zwitterionic structure in the ground state of such merocyanine increases in polar solvents, and consequently, its contribution to the twin state (Ψ_e) is reduced; that is why the increment of the dipole moment is smaller for this state than for the ground state, when the polarity of the solvent is increased [41,42]. They additionally stated that in non-polar solvents the structure of merocyanine is mainly covalent (quinoid), while in polar solvents it is mostly zwitterionic, similar to S_1, the excited zwitterionic twin state [42].

Fig. 2 shows the canonical structures of BSHB and BS in the ground and excited states based on the already mentioned information.

Hydroxystilbazolium hemicyanines are also believed to change to the quinoid structure upon excitation [39,40]. We show such

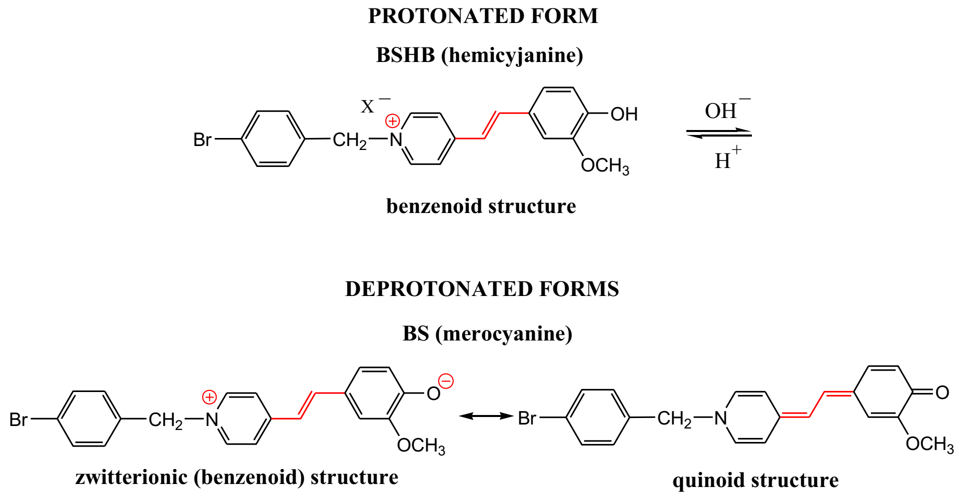

Fig. 1. Acid–base equilibria of BSHB and the structures of its protonated and deprotonated forms with their names used in present work.