On the Mechanism of Alcohol-Catalyzed Excited-State Intramolecular Proton Transfer in Cationic Benzimidazoles

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The ground- and excited-state behavior of the monocations of 2-(6′-hydroxy-2′-pyridyl)benzimidazole (**1**) and 1-methyl-2-(6′-hydroxy-2′-pyridyl)benzimidazole (**2**) is discussed. Excited-state proton transfer from the hydroxyl group to the pyridyl nitrogen occurs in compounds **1** and **2** in acidified acetonitrile solutions by the assistance of an alcohol. We propose a model for the mechanism of this proton-transfer process which includes a concerted biprotonic or multiprotonic transfer with one or two alcohol molecules. Essential for the occurrence of the proton transfer is the presence of a quencher with hydrogen-bond donating and accepting properties. Furthermore, it is shown that also the size and geometry of the quencher play a role in the efficiency of the proton-transfer process. Compounds **1** and **2** differ remarkably in the efficiency of this process as a result of the presence of the methyl group on the benzimidazole nitrogen N(1) in compound **2**.

Introduction

Molecules with acidic or basic groups can undergo excited-state proton-transfer processes as a result of the increase of the acidity or basicity experienced by those groups upon excitation. Molecules having both an acidic and a basic site in close proximity and with a suitable geometry may undergo excited-state intramolecular proton transfer (ESIPT), usually ultrafast, from the acidic to the basic group, yielding a phototautomer. These ESIPT processes take place through an intramolecular hydrogen bond which forms usually part of a six- or five-membered ring. ESIPT processes are the object of considerable current interest.[1−4]

If the acidic and basic groups are too far from each other or cannot adopt the needed geometry for an intramolecular hydrogen bond, the excited molecule may undergo proton transfer in the excited state assisted by molecules with hydrogen-bond accepting and donating abilities, usually water or hydroxylic molecules.[4] This kind of excited-state proton-transfer (ESPT) process has been reported, e.g., for 7-azaindole,[4−12] 1-azacarbazole,[13] hydroxyquinolines,[14−20] 2-(2′-pyridyl)benzimidazole,[21−23] and 2-(2′-pyridyl)indoles.[24] A concerted biprotonic transfer is experienced by 7-azaindole, 7-hydroxyquinoline, and 2-(2′-pyridyl)indoles in alcohol solutions, alcohol molecules thereby acting as bridges between the acid and basic sites. A two-step model has been proposed for this process,[7,10,24] in which the first step involves a rearrangement of the solvent around the excited molecule in order to obtain the structure suitable for the occurrence of tautomerization. The second step is a double proton transfer to yield the tautomer. The process is controlled by the solvent rearrangement in the low-temperature region and by the proton transfer in the other extreme. In some cases an appropriate structure of the complex is already present in the ground state. These systems can show very fast intermolecular proton transfer in the excited state, as reported, for example, for the 1:1 hydrogen-bonded ground-state complex between 7-azaindole and carboxylic acids in cyclohexane.[11]

We decided to investigate the monocations of 2-(6′-hydroxy-2′-pyridyl)benzimidazole (**1**) and 1-methyl-2-(6′-hydroxy-2′-pyridyl)benzimidazole (**2**) (see Figure 1). The neutral molecules (Figure 2) have an acidic site (−OH) and two basic groups [the benzimidazole N(3) and the pyridyl N]. In this article we will focus on the ground- and excited-state behavior of both monocations in acetonitrile solution. Investigations carried out in our group on the structurally related molecule 2-(3′-hydroxy-2′-pyridyl)benzimidazole[25,26] showed that this compound protonates in acidic media at the benzimidazole N(3) to afford an enol cation. It was shown that both the acidity of the hydroxyl group and the basicity of the pyridyl nitrogen of HPyBI increased in the first excited state. Furthermore, it was demonstrated that in acidic aqueous solution, upon excitation of the enol cation, a keto cation protonated at the pyridyl nitrogen was formed via two-step processes involving protonation of the pyridyl nitrogen and deprotonation of the hydroxyl group. In compounds **1** and **2** the hydroxyl group occupies the *ortho* position with respect to the pyridyl nitrogen and a priori an ESIPT process, if the distance N···H−O is appropriate, and/or excited-state concerted multiprotonic transfer in the presence of protic species might take place. In this article we will demonstrate that concerted multiprotonic transfer from the hydroxyl group to the pyridyl nitrogen occurs in the excited monocations **1** and **2** in acetonitrile in the presence of small amounts of an alcohol. We will show that the compounds differ remarkably in the efficiency of this process as a result of the presence of the methyl group on the benzimidazole nitrogen N(1) in compound **2**. In compound **3** (see Figure 1) ESPT cannot take place. Furthermore, we will propose a model for the mechanism of the proton-transfer process.

Experimental Section

The compounds **1** and **2** were prepared by high-temperature condensation of 6-hydroxy-2-pyridinecarboxylic acid with 1,2-benzenediamine and *N*-methyl-1,2-benzenediamine following a published procedure for the synthesis of 2-(2′-pyridyl)-benzimidazole.[27] Compound **3** was obtained by refluxing **1** in toluene in the presence of CH_3I and KOH. The compounds were purified by repeated crystallization and identified by NMR

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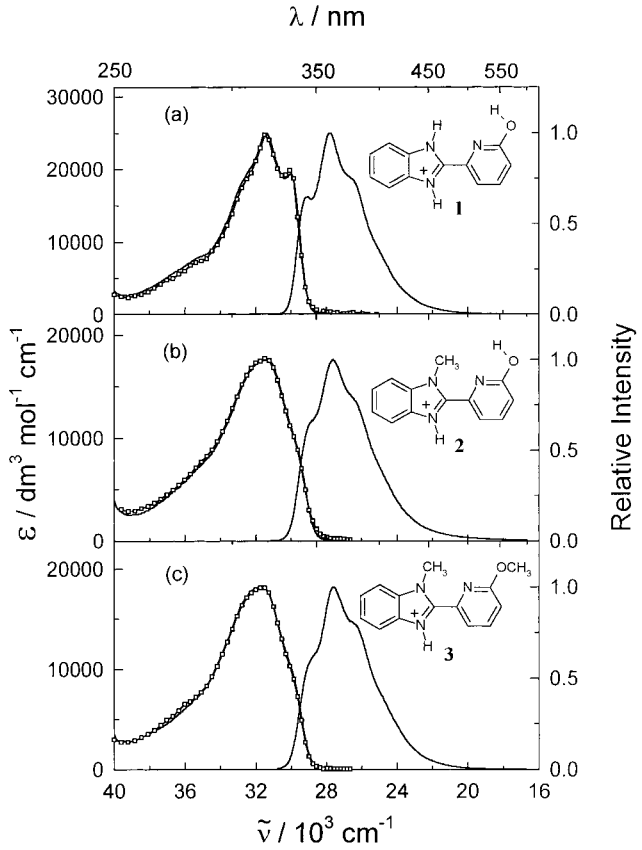


Figure 1. Absorption spectrum (−□−) and normalized fluorescence excitation and emission spectra (—) in acidified acetonitrile of compound **1** (a), compound **2** (b), and compound **3** (c). $[HClO_4] = 5.0 \times 10^{-4}$ mol dm^{-3}. $\tilde{\nu}_{ex} = 31750$ cm^{-1}. $\tilde{\nu}_{em} = 27780$ cm^{-1} (compounds **1** and **2**). $\tilde{\nu}_{em} = 27620$ cm^{-1} (compound **3**). $[\mathbf{1}] = 4 \times 10^{-6}$ mol dm^{-3}, $[\mathbf{2}] = 3 \times 10^{-6}$ mol dm^{-3}, and $[\mathbf{3}] = 5 \times 10^{-6}$ mol dm^{-3} for fluorescence.

spectroscopy and mass spectroscopy. NMR data of these compounds[28] will be published later. Solutions were made up as previously described[25] in spectroscopy grade ethanol (Scharlau) and acetonitrile (Scharlau). Alcohols used were methanol (Scharlau; spectrosol), 1-propanol (Fischer Scientific Company), 1-butanol (Aldrich; 99%), *tert*-butyl alcohol (Merck; p.a.), 1,2-ethanediol (Aldrich; spectrophotometric grade 99+%) and 2,2,2-trifluoroethanol (Aldrich; 99+%). Spectroscopy grade dimethyl sulfoxide (DMSO) (Scharlau) was also employed.

Solutions were not degassed. Acidity was varied with $HClO_4$ (Merck p.a.). To obtain an acidic medium in acetonitrile, $[HClO_4] = 5.0 \times 10^{-4}$ mol dm^{-3} was used. We checked by UV−vis absorption spectroscopy that all ground-state **1**, **2**, and **3** are found as the monocations under these conditions. All experiments were carried out at room temperature. UV−vis absorption spectra were recorded on a Cary 3E Varian spectrophotometer. Fluorescence excitation and emission spectra were recorded on a Spex Fluorolog-2 FL340 E1 T1 spectrofluorometer, with correction for instrumental factors by means of a Rhodamine B quantum counter and correction files supplied by the manufacturer. Fluorescence lifetimes were determined by single-photon timing on an Edinburgh Instruments CD-900 spectrometer equipped with a hydrogen-filled nanosecond flashlamp and the analysis software supplied by the manufacturer.

Theoretical equations were fitted to experimental data by means of a nonlinear weighted least-squares routine based on the Marquardt algorithm.

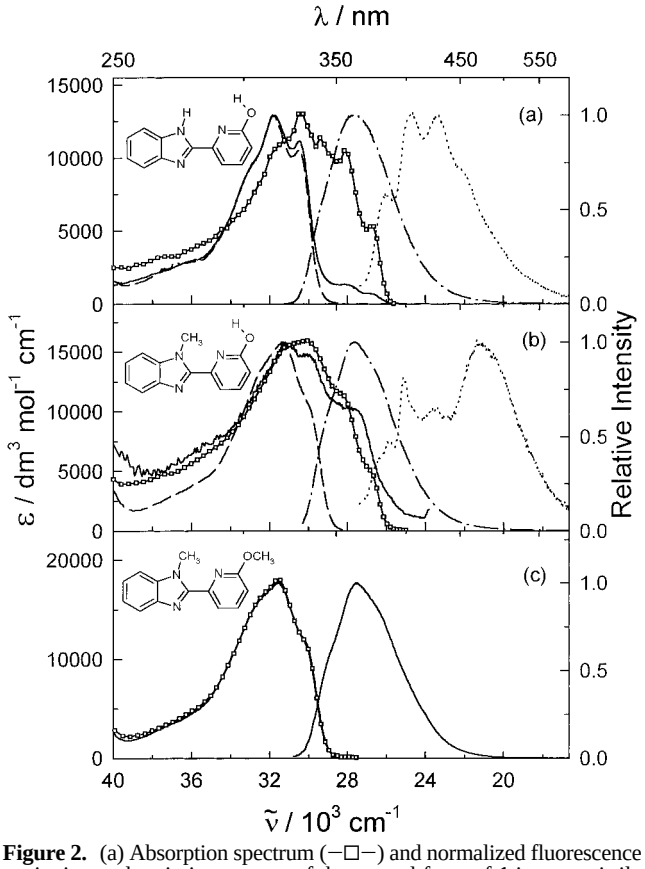


Figure 2. (a) Absorption spectrum (−□−) and normalized fluorescence excitation and emission spectra of the neutral form of **1** in acetonitrile (− − − $\tilde{\nu}_{em} = 27780$ cm^{-1}, —— $\tilde{\nu}_{em} = 24690$ cm^{-1}, − · − · − $\tilde{\nu}_{ex} = 31750$ cm^{-1}, ··· $\tilde{\nu}_{ex} = 28090$ cm^{-1}). (b) Absorption spectrum (−□−) and normalized fluorescence excitation and emission spectra of the neutral form of **2** in acetonitrile (− − − $\tilde{\nu}_{em} = 27780$ cm^{-1}, —— $\tilde{\nu}_{em} = 21050$ cm^{-1}, − · − · − $\tilde{\nu}_{ex} = 32260$ cm^{-1}, ··· $\tilde{\nu}_{ex} = 27780$ cm^{-1}). (c) Absorption spectra (−□−) and normalized fluorescence excitation and emission spectra (——) of the neutral form of **3** in acetonitrile ($\tilde{\nu}_{ex} = 31750$ cm^{-1}, $\tilde{\nu}_{em} = 27780$ cm^{-1}). $[\mathbf{1}] = 4 \times 10^{-6}$ mol dm^{-3}, $[\mathbf{2}] = 3 \times 10^{-6}$ mol dm^{-3}, and $[\mathbf{3}] = 5 \times 10^{-6}$ mol dm^{-3} for fluorescence.

Results

1. Absorption and Fluorescence Spectra in Acetonitrile. The fluorescence excitation spectrum of the neutral form of **3** in acetonitrile shows one band and matches the absorption spectrum (Figure 2c). The emission band overlaps the fluorescence excitation band, showing a normal Stokes shift and a monoexponential decay with a lifetime of 1.63 ns. Both fluorescence excitation and emission spectra are independent of the monitoring emission and excitation wavenumbers. In acidified acetonitrile, the fluorescence excitation band of the monocation **3** shifts slightly to the blue and coincides with the absorption band measured under the same conditions (Figure 1c). The emission band shows vibrational structure with its maximum located at the same position as that of the neutral species. No dependence of the monitoring wavenumber was observed for the fluorescence excitation and emission bands, and the emission decay was monoexponential with a lifetime of 2.0 ns.

The absorption spectrum of the neutral form of **2** in acetonitrile (Figure 2b) is broad and shows vibrational structure. The fluorescence obtained upon excitation at 31750 cm^{-1} shows a monoexponential decay, with a lifetime of 1.69 ns. The fluorescence excitation band overlaps the emission band and is narrower and blue shifted with respect to the absorption band. Excitation within the wavenumber region 26320−28570 cm^{-1} leads to a very weak emission at $\tilde{\nu} < 25000$ cm^{-1}. In acidified

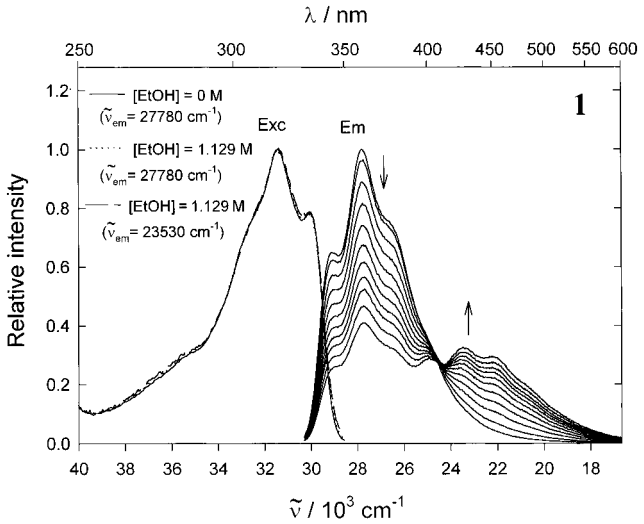


Figure 3. Fluorescence excitation and emission spectra of **1** in acidified acetonitrile ($[HClO_4] = 5 \times 10^{-4}$ mol dm^{-3}) with increasing concentration of ethanol (EtOH) in the range 0−1.129 mol dm^{-3}. [**1**] = 4×10^{-6} mol dm^{-3}. $\tilde{\nu}_{ex} = 31250$ cm^{-1}.

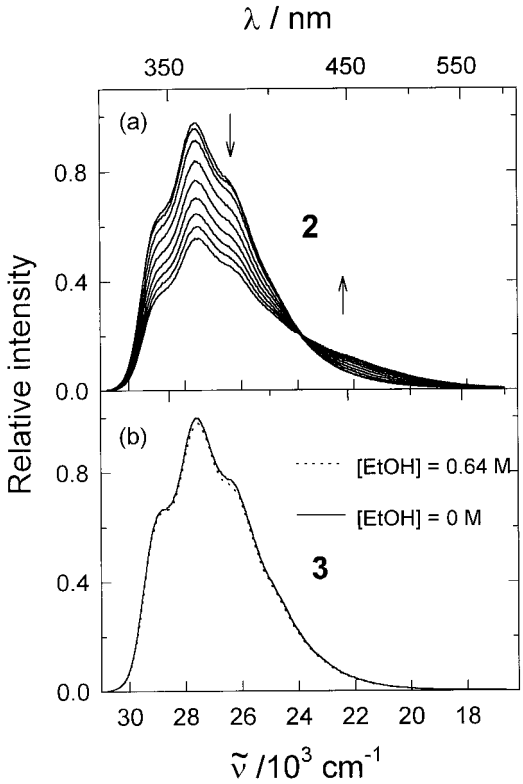


Figure 4. (a) Fluorescence spectra of **2** in acidified acetonitrile ($[HClO_4] = 5 \times 10^{-4}$ mol dm^{-3}; $\tilde{\nu}_{ex} = 31750$ cm^{-1}) with increasing concentration of ethanol (EtOH) in the range 0−1.013 mol dm^{-3}. (b) Fluorescence spectra of **3** in acidified acetonitrile ($[HClO_4] = 2 \times 10^{-4}$ mol dm^{-3}; $\tilde{\nu}_{ex} = 31250$ cm^{-1}) at concentrations [EtOH] = 0 mol dm^{-3} and [EtOH] = 0.640 mol dm^{-3}. [**2**] = 3×10^{-6} mol dm^{-3}, and [**3**] = 5×10^{-6} mol dm^{-3}.

acetonitrile the absorption spectrum narrows, shifts to the blue, and its intensity increases (Figure 1b). The fluorescence excitation spectrum in acidified acetonitrile matches the absorption band obtained under the same conditions. Furthermore, the fluorescence emission spectrum overlaps the fluorescence excitation spectrum and a monoexponential emission decay with a lifetime of 2.05 ns was observed.

Both the neutral form of **1** and the monocation show the same behavior as compound **2** in acetonitrile solutions (Figures 2a and 1a), although the absorption spectrum of **1** in acidified acetonitrile shows more vibrational structure (Figure 1a).

2. Fluorescence Quenching by Alcohols. We recorded the fluorescence spectra of **1** and **2** in acidified acetonitrile with various concentrations of an alcohol. The alcohols used were methanol, ethanol, 1-propanol, 1-butanol, *tert*-butyl alcohol, 1,2-ethanediol, and 2,2,2-trifluoroethanol. In all experiments the excitation wavenumber was 31250 cm^{-1} for **1** and 31750 cm^{-1} for **2** and the alcohol concentration was varied in the range 0−1.2 mol dm^{-3}.

All alcohols used except trifluoroethanol quenched the fluorescence of **1** and **2**. As an illustrative example, Figure 3 depicts the steady-state fluorescence spectra of **1** in acidified acetonitrile with various concentrations of ethanol. A single structured emission band with its maximum at 27780 cm^{-1} is observed in the absence of ethanol. Upon addition of ethanol, the intensity of this emission decreases, and a new structured emission band with maxima at 25000, 23530, and 22220 cm^{-1} appears. As can be seen in Figure 3, the fluorescence excitation spectrum obtained at [EtOH] = 1.129 mol dm^{-3} matches the fluorescence excitation spectrum obtained in the absence of ethanol and is independent of the monitoring wavenumber. Figure 4a displays a series of fluorescence spectra of **2** in acidified acetonitrile with various concentrations of ethanol. The same features are seen as for **1**: a decrease of the fluorescence band at 27780 cm^{-1}, concomitant with an increase of the emission at ∼22000 cm^{-1}, although the increase of the intensity of the latter emission is not so strong as observed for **1**.

We measured the fluorescence lifetimes of acidified acetonitrile solutions of **1** and **2** with various concentrations of alcohol at various detection wavenumbers. The fluorescence detected at 27780 cm^{-1} shows for both compounds a monoexponential decay (1.95 ns for **1** and 2.05 ns for **2** in the absence of alcohol), with decreasing lifetime as the concentration of alcohol increases. At lower wavenumbers, a biexponential decay is observed, the contribution of the longer lifetime becoming larger at higher concentrations of the alcohol. The longer lifetime is independent of the alcohol used, showing a value of 3.0 ± 0.2 ns for **1** and 1.5 ± 0.2 ns for **2**. At relatively low wavenumbers (<24000 cm^{-1}), a third fluorescence component with a weak contribution (<10%) was observed for both compounds (ca. 6 ns for **1** and ca. 4 ns for **2**). As an example, Figure 5 shows the fluorescence decay of **1** in acidified acetonitrile with [EtOH] = 0.855 mol dm^{-3} at different monitoring emission wavenumbers. We analyzed simultaneously (global analysis) the fluorescence decay at six emission wavenumbers (between 20000 and 25000 cm^{-1}) to fit a triexponential decay function with lifetimes $\tau_1 = 1.02 \pm 0.03$ ns, $\tau_2 = 3.05 \pm 0.06$ ns, and $\tau_3 = 5.8 \pm 0.8$ ns. Figure 5 shows the decays at $\tilde{\nu}_{em} = 23810$ cm^{-1} and $\tilde{\nu}_{em} = 21740$ cm^{-1}. Upon going to lower wavenumbers, the amplitude of lifetime τ_1 decreases, while the amplitude of lifetime τ_2 increases. Furthermore, the amplitude of τ_1 is negative in the wavenumber region $\tilde{\nu}_{em} < 23000$ cm^{-1}. At wavenumbers $\tilde{\nu}_{em} > 26000$ cm^{-1}, the fluorescence of **1** decayed monoexponentially with a lifetime of 1.02 ± 0.03 ns at [EtOH] = 0.855 mol dm^{-3}.

Addition of trifluoroethanol to an acidified solution of **1** in acetonitrile does not reduce the quantum yield and lifetime of the fluorescent species. Addition of dimethyl sulfoxide quenches the fluorescence of **1** and **2**, but no new emission is observed.

As can be seen in Figure 4b, the emission spectrum of **3** in acidified acetonitrile remains unchanged upon addition of ethanol. Furthermore, fluorescence lifetime measurements on a solution of **3** in acidified acetonitrile with [EtOH] = 0.622 mol dm^{-3} showed monoexponential decay of the emission independent of the monitoring wavenumber and yielded a

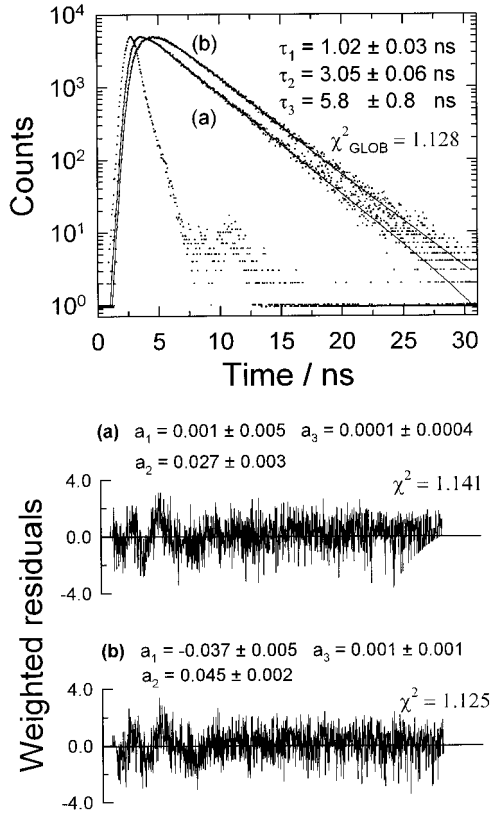


Figure 5. Fluorescence decay of compound **1** in acidified acetonitrile solution ($[HClO_4] = 5 \times 10^{-4}$ mol dm^{-3}) with [EtOH] = 0.855 mol dm^{-3} at $\tilde{\nu}_{em} = 23810$ cm^{-1} (a), $\tilde{\nu}_{em} = 21740$ cm^{-1} (b), and lamp profile ($\tilde{\nu}_{ex} = 31250$ cm^{-1}). The decays at six emission wavenumbers were analyzed simultaneously (global analysis) to fit a triexponential decay function. Fluorescence lifetimes τ_i, associated amplitudes a_i, and weighted residuals for two emission wavenumbers are shown.

lifetime of 2.1 ns, which is the same as that obtained in the absence of ethanol.

Discussion

As can be seen in Figure 2c, the neutral form of compound **3** exhibits in acetonitrile a single absorption and a single emission band, whereas the neutral forms of **1** and **2** show a broad absorption spectrum and — dependent on the excitation wavenumber — two distinct fluorescence bands (Figures 2a and 2b). Moreover, the fluorescence excitation spectra of the neutral forms of **1** and **2** monitored in both emission bands do not coincide with the absorption spectra. This means that for these species there are at least two neutral forms in the ground state and two fluorescent species. A weak fluorescent species located at $\tilde{\nu}_{em} < 25000$ cm^{-1} for both compounds and a stronger fluorescent species with emission maximum at 27930 cm^{-1} for the neutral form of **1** and at 27780 cm^{-1} for the neutral form of **2** are observed. The complex behavior observed in neutral solutions is currently under investigation and will be published later. We only mention here that the fluorescent species in acetonitrile are neutral forms, as expected taking into account the nonprotic character of acetonitrile.

In acidified acetonitrile, the absorption bands of compounds **1** and **2** are almost coincident and very similar to that of compound **3** (Figure 1). Furthermore, no dependence of the monitoring wavenumber was observed for the fluorescence excitation and emission bands. Two protonation sites are possible for the three compounds under study: the benzimidazole N(3) and the pyridyl N. In Figures 1c and 2c, it is clearly observed that the absorption spectrum of compound **3** is very similar to that of its neutral form. Since it is known that protonation at the benzimidazole N(3) in benzimidazole and derivatives does not change the absorption spectrum significantly, whereas protonation at the pyridyl N in pyridylbenzimidazoles[23,26,29] induces a red shift in the absorption and emission spectra, we might conclude that the protonation in **1**, **2**, and **3** takes place at the benzimidazole N(3), giving what we call the enol cations shown in Figure 1. A further argument for this conclusion is that the absorption spectra of **1** and **2** in acidified acetonitrile are very similar to the corresponding bands of the compounds 2-(3′-hydroxy-2′-pyridyl)benzimidazole[26] and 1-methyl-2-(3′-hydroxy-2′-pyridyl)benzimidazole,[30] respectively, which are known to be protonated first at the benzimidazole.

From the facts that in acidified acetonitrile (a) both fluorescence excitation and emission spectra of **1**, **2**, and **3** observed in the absence of a quencher are independent of the monitoring emission and excitation wavenumbers and (b) a monoexponential fluorescence decay is observed, we conclude that in the excited state only one emitting species is present. As the emission band of this species (maximum at 27780 cm^{-1}) overlaps with the fluorescence excitation band, it can only be attributed to the species present in the ground state for all three compounds, i.e., the enol cation. However, in the presence of an alcohol, a second emission band around 22000 cm^{-1} is observed for **1** and **2**. We should consider the possibility of the occurrence of three kinds of processes in the excited state of the enol cations **1** and **2**: (1) protonation at the pyridyl N by the alcohol, (2) deprotonation at the hydroxyl group to give a neutral species (a zwitterion), and (3) transfer of a H from the benzimidazole N to the pyridyl N to yield a cation protonated at the pyridyl N, or proton transfer from the hydroxyl group to the pyridyl N to give a keto cation.

The occurrence of process (1) can be ruled out by taking into account that for compound **3**, in which this process can also take place, no quenching of the fluorescence was observed upon addition of ethanol. Furthermore, no change of the emission spectra of the enol cations **1** and **2** was observed in the presence of trifluoroethanol, which is a stronger acid.

Deprotonation at the hydroxyl group (process 2) gives a zwitterion. This neutral species has been detected for **1** and **2** in acidic aqueous solutions and acidified ethanol solutions,[31] showing a lifetime of ca. 6 ns for **1** and of ca. 5 ns for **2** and showing fluorescence at relatively low wavenumbers ($\tilde{\nu}_{max} \approx$ 22000 cm^{-1} for **1** and **2**). The third fluorescence component with a weak contribution (<10%), which was observed at low wavenumbers (<23500 cm^{-1}) for both compounds (ca. 6 ns for **1** and ca. 4 ns for **2**), might be attributed to this zwitterion species. However, only a small fraction of the excited enol cation molecules experiences process (2).

With respect to process (3), only a proton transfer from the hydroxyl group to the pyridyl N explains the fact that the quenching was not observed for the cation **3**. This proton-transfer cannot be direct, since an alcohol is required to observe the red-shifted fluorescence band for **1** and **2**. Furthermore, species with only hydrogen-bond donating capacity (trifluoroethanol) do not quench the fluorescence, while species with only hydrogen-bond acceptor character (dimethyl sulfoxide) quench the fluorescence, but no red-shifted emission is observed. Species with both hydrogen-bond donating and accepting capacity are required to observe the fluorescence band at ~22000 cm^{-1} for **1** and **2**. We therefore attribute this emission band to the keto cation KC* (Scheme 1). The existence of an isoemissive point in the emission spectra indicates that there

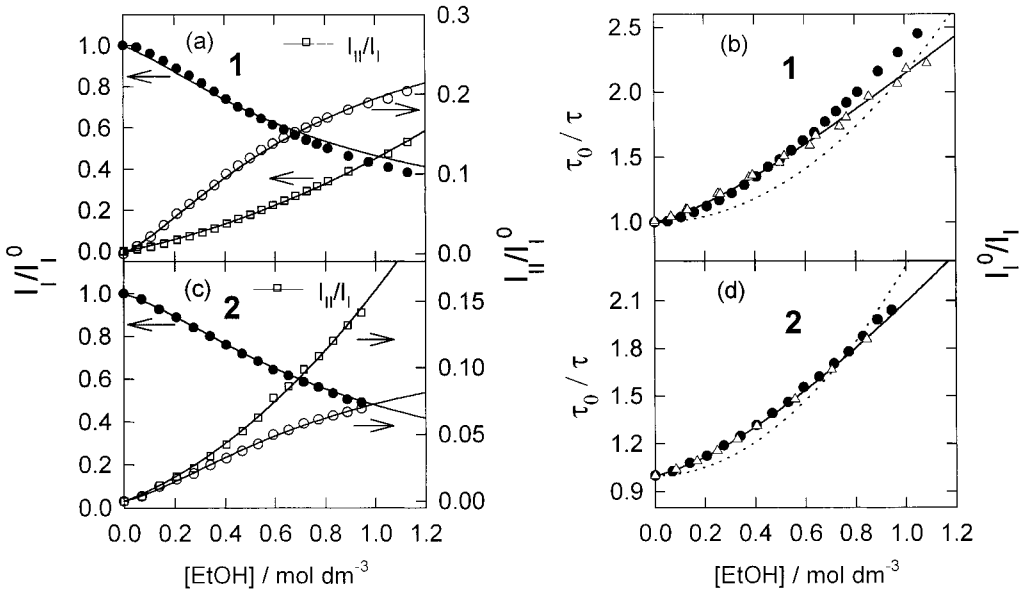
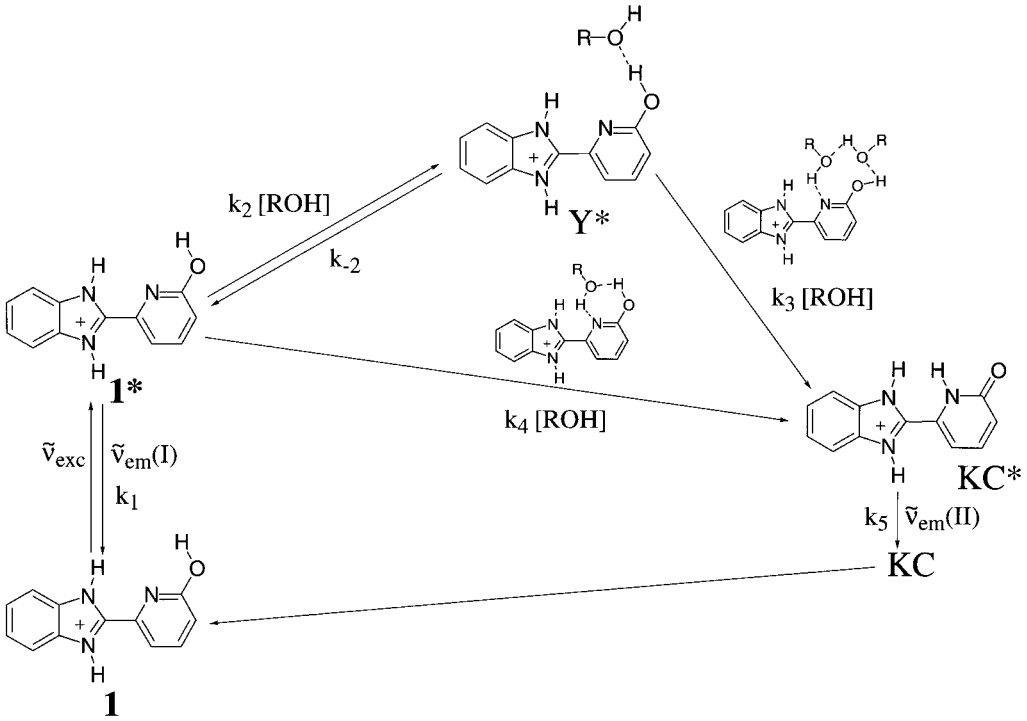


Figure 6. (a) and (c) Dependence of the ratios I_I/I_I^0 (●), I_{II}/I_I^0 (○), and I_{II}/I_I (□) on the concentration of ethanol in an acidified acetonitrile solution of compound **1** (a) and of compound **2** (c). (b) and (d) Dependence of the ratio τ_0/τ (△) and I_I^0/I_I (●) on the concentration of ethanol in an acidified acetonitrile solution of compound **1** (b) and of compound **2** (d). The solid lines in the plots are the result of the global fit of eqs 1 and 2 to the data, according to the proposed mechanism in Scheme 1. The dotted lines (···) in plots (b) and (d) illustrate a quadratic dependence of the ratio τ_0/τ on the concentration of the quencher ethanol.

SCHEME 1: Proposed Mechanism for the Photoinduced Proton Transfer of 1 in Acidified Acetonitrile Solutions in the Presence of an Alcohol; The Same Scheme Is Proposed for 2



are only two emitting species present, the enol cation and the keto cation KC*.

Assuming that the keto form does not emit at 27780 cm^{-1} and subtracting from the intensity at 23530 cm^{-1} the contribution from the emission of the enol form at that wavenumber, the relative contributions of both emitting species to the overall observed fluorescence can be simply expressed by the ratios I_I/I_I^0 and I_{II}/I_I^0 for the excited enol cation and KC*, respectively, where I_I^0 is the intensity at 27780 cm^{-1} in the absence of a quencher, I_I is the intensity in the presence of a quencher at 27780 cm^{-1} and I_{II} is the difference between the intensity at 23530 cm^{-1} in the presence of a quencher and the intensity at the same wavenumber in the absence of quencher corrected for the emission of the enol cation at that wavenumber. In Figures 6a and 6c, the ratios I_I/I_I^0, I_{II}/I_I^0, and I_{II}/I_I obtained for **1** and **2**, respectively, are plotted against the concentration of ethanol. In Figures 6b and 6d, the ratios I_I^0/I_I and τ_0/τ for **1** and **2**, respectively, are plotted against the concentration of ethanol, where τ_0 is the fluorescence lifetime of the **1*** or **2*** species in the absence of ethanol and τ is the lifetime of the same species in the presence of ethanol (both lifetimes measured at 27780 cm^{-1}). Similar plots were obtained for **1** and **2** in the presence

TABLE 1: Kinetic Parameters for the Fluorescence Quenching of Compounds 1 and 2, Obtained by Fitting Eqs 1 and 2, together with the Concentration of the Quencher ($[Q]_{1/2}$/mol dm^{-3}) Needed To Quench 50% the Fluorescence of the 1* and 2* Species[a]

			1				**2**			
quencher	α^b	β^b	$10^{-9}\,k_4$	$10^{-9}\,k_2$	k_3/k_{-2}	$[Q]_{1/2}$	$10^{-9}\,k_4$	$10^{-9}\,k_2$	k_3/k_{-2}	$[Q]_{1/2}$
methanol	0.93	(0.62)	0.09 ± 0.02	0.75 ± 0.09	0.75 ± 0.23	1.15	0.00 ± 0.04	0.73 ± 0.19	0.75 ± 0.44	1.41
ethanol	0.83	(0.77)	0.23 ± 0.06	0.58 ± 0.03	1.6 ± 0.7	0.90	0.18 ± 0.02	0.78 ± 0.08	0.83 ± 0.21	0.94
1-propanol	0.78		0.26 ± 0.11	0.72 ± 0.07	2.7 ± 1.4	0.70	0.00 ± 0.02	0.78 ± 0.05	2.5 ± 1.1	0.90
1-butanol	0.79	(0.88)	0.15 ± 0.03	0.66 ± 0.02	1.8 ± 0.4	0.92	0.19 ± 0.09	0.49 ± 0.07	1.7 ± 1.5	0.98
tert-butyl alcohol	0.68	(1.01)	0.33 ± 0.09	0.3 ± 0.2	0.79 ± 1.9	1.05	0.23 ± 0.02	0.17 ± 0.04	1.1 ± 1.3	1.46
1,2-ethanediol	0.90	(0.52)	0.5 ± 0.2	1.0 ± 0.2	12 ± 5	0.39	0.32 ± 0.05	2 ± 7	0.16 ± 0.79	0.90
2,2,2-trifluoroethanol	1.51	0.00	no quenching observed							
dimethylsulfoxide	0.00	0.76	strong quenching observed							

[a] The rate constants k_2 and k_4 are given in dm^3 mol^{-1} s^{-1} and k_3/k_{-2} in mol^{-1} dm^3. The parameters α and β represent the hydrogen-bond donor ability and the hydrogen-bond acceptor ability of the quencher, respectively. [b] Data are taken from ref 32; values of β in parentheses are relatively less certain.

of the other alcohols. As is illustrated in Figure 6, the observed dependence of the ratio τ_0/τ on the concentration of ethanol cannot be described by a linear or a quadratic function, indicating that the proton transfer in **1** and **2** is not a simple one-step mechanism following first- or second-order kinetics. Furthermore, also the ratio I_{II}/I_I shows a nonlinear dependence on the alcohol concentration (Figures 6a and 6c). This suggests that part of the excited enol cation molecules (**1*** or **2***) give the excited keto cation KC* with the aid of only one alcohol molecule, while another part yield KC* with the assistance of two alcohol molecules. To explain our data, we propose that some excited enol cations are able to yield KC* with the aid of only one alcohol molecule, whereas others form with one alcohol molecule a complex Y* (see Scheme 1) which does not have the suitable geometry to yield KC*. By the involvement of a second alcohol molecule, the proton-transfer process can occur giving KC*. To justify the observed complex dependence of τ_0/τ on the alcohol concentration, we must also assume that part of the Y* complex molecules go back to the excited enol cation. We will now discuss our proposed two-routes mechanism for the photoinduced proton transfer in **1** and **2** in acidified acetonitrile (see Scheme 1).

Upon excitation of the enol cation, it returns to the ground state with rate constant k_1 and emits the blue-shifted fluorescence band. In the presence of an alcohol molecule, however, also a proton-transfer process with rate coefficient k_4[ROH] can occur resulting in the keto species KC*. For this concerted biprotonic transfer to occur, an alcohol molecule must form a cyclical complex with the excited enol cation **1*** or **2*** and that requires that the alcohol approaches the cation with the right orientation. A concerted biprotonic transfer in the cyclical complex yields KC*. If an alcohol molecule reaches the excited cation **1*** or **2*** with an orientation which does not lead to a cyclical complex, an intermediate complex Y* can be formed (rate coefficient k_2 [ROH]). A second alcohol molecule reaching Y* can lead to a cyclical complex involving two alcohol molecules. A concerted triprotonic transfer in that complex yields also KC* (rate coefficient k_3[ROH]). Moreover, Y* can also go back to the initially excited enol cation with rate coefficient k_{-2}. Note that in the latter route two alcohol molecules are involved in the overall proton-transfer process. As an isoemissive point is observed in the emission spectra, it seems reasonable to assume that the intermediate complex does not fluoresce significantly, probably due to its low concentration. The KC* species decays to the ground state with rate constant k_5, emitting the red-shifted fluorescence band.

Equations 1, 2, and 3 show the dependence of the ratios I_I^0/I_I, τ_0/τ, I_{II}/I_I^0, and I_{II}/I_I on the concentration of the quencher [Q] according to the mechanism shown in Scheme 1. Factor γ in eq 2 is a parameter which depends on the fluorescence quantum yields of KC* and the enol cation and on the emission wavenumber.

$$\frac{I_I^0}{I_I} = \frac{\tau_0}{\tau} = 1 + \frac{k_4}{k_1} \times [Q] + \frac{\dfrac{k_2 \times k_3}{k_1 \times k_{-2}} \times [Q]^2}{1 + \left(\dfrac{k_3}{k_{-2}} \times [Q]\right)} \tag{1}$$

$$\frac{I_{II}}{I_I^0} = \gamma \times \frac{\dfrac{k_4}{k_1} \times [Q] \times \left(1 + \dfrac{k_3}{k_{-2}} \times [Q]\right) + \left(\dfrac{k_2 \times k_3}{k_1 \times k_{-2}} \times [Q]^2\right)}{\left(1 + \dfrac{k_4}{k_1} \times [Q]\right) \times \left(1 + \dfrac{k_3}{k_{-2}} \times [Q]\right) + \left(\dfrac{k_2 \times k_3}{k_1 \times k_{-2}} \times [Q]^2\right)} \tag{2}$$

$$\frac{I_{II}}{I_I} = \gamma \times \left(\frac{k_4}{k_1} \times [Q] + \frac{\dfrac{k_2 \times k_3}{k_1 \times k_{-2}} \times [Q]^2}{1 + \dfrac{k_3}{k_{-2}} \times [Q]} \right) \tag{3}$$

The solid lines in Figure 6 represent the global fit of eqs 1 and 2 to the data of both the steady-state and time-resolved fluorescence measurements on **1** and **2** in acidified acetonitrile in the presence of ethanol. As can be seen, the equations can reasonably describe the fluorescence data. In other words, the proton transfer in **1** and **2** might occur as proposed above (Scheme 1). In Table 1 the results of the fits are given, together with the α parameter[32] (a value for the hydrogen-bond donor ability) and the β parameter[32] (a value for the hydrogen-bond acceptor ability) of the quencher and the concentration of the quencher needed to quench 50% the fluorescence of **1*** and **2***.

As can be seen in Table 1, the obtained values of the (ratio of the) rate constants show in some cases large standard deviations. The uncertainty in the values of the (ratio of the) rate constants is mainly due to the existence of correlation between the named parameters. Nevertheless, the following remarks can be made.

Addition of species with both hydrogen-bond donating and accepting capacities quenches the fluorescence of the enol cation species and, concomitant, a new structured red-shifted emission band appears which can be attributed to the KC* species. As can be seen in Table 1, the values of the parameters α and β, as well as the size and geometry of the quencher, play a role in

the quenching process. An increase of the quenching of the fluorescence of **1** and **2** is observed in the series: methanol < ethanol < 1-propanol. In this series, the hydrogen-bond donating capacity of the quencher (the α parameter) decreases, while the hydrogen-bond accepting capacity of the quencher (the β parameter) increases. It seems therefore likely that the quenching of the enol cation fluorescence is related to the formation of a complex between the alcohol and the hydroxyl group of **1** and **2**. The efficiency of this process is affected by the strength of the hydrogen-bond accepting capacity of the quencher and is reflected in an increase of the quenching of the fluorescence of the enol cation. 1-Butanol and *tert*-butyl alcohol are stronger hydrogen-bond accepting molecules than 1-propanol. However, a decrease of the quenching of the fluorescence of **1** and **2** is observed in the series: 1-propanol > 1-butanol > *tert*-butyl alcohol. A reasonable explanation might be that 1-butanol and especially *tert*-butyl alcohol are more bulky quenchers than 1-propanol. As the formation of a cyclical complex between the enol cation and one or two alcohol molecules requires a specific orientation of the alcohol, we would expect an alcohol like *tert*-butyl alcohol, where the hydroxyl group is connected to a bulky group, to have more difficulty approaching the enol cation with the needed orientation to yield a cyclical complex than the isomeric lineal alcohol like 1-butanol, with the same number of C atoms but a smaller unit directly connected to the OH group. Therefore, although *tert*-butyl alcohol is a much stronger hydrogen-bond accepting molecule than methanol, both molecules quench the fluorescence of the enol cation with the same efficiencies. The values of k_2 and k_4 for **1** and **2** are at least 1 order of magnitude lower than the value for the rate constant of diffusion-controlled processes in acetonitrile [k_{diff} (25 °C) = 1.9×10^{10} dm^3 mol^{-1} s^{-1}].[33] This could simply indicate that part of the **1*** and **2*** molecules are solvated by the alcohol in an inefficient way for the occurrence of proton transfer. As the proposed mechanism considers only those excited enol cation molecules forming solvates which yield KC* or go back to the enol cation, the "inactive" solvates will lead to an underestimation of the k_2 and k_4 values.

As can be seen in Table 1, ethanediol is the most effective quencher in the series, despite the fact that the value for the β parameter of this dialcohol is lower than those of the used monoalcohols. An explanation might be that the presence of the extra OH group in the dialcohol compared to the monoalcohols facilitates the formation of a complex in which both OH groups are involved and thereby opens the route for a more efficient proton-transfer process.

Compounds **1** and **2** differ remarkably in the efficiency of the quenching process. This must be due to the presence of the methyl group on the benzimidazole nitrogen N(1) in compound **2**. The most stable structure of **2** in the ground state corresponds to that with the methyl group close to the pyridyl N. It seems therefore likely that in the excited state the proportion of molecules (see Scheme 1) with the right geometry to give KC* is smaller for compound **2** than for **1** because the presence of the methyl group on the benzimidazole hinders the formation of the complex suitable for proton transfer between **2** and one or two alcohol molecules.

Returning to our interpretation of the data, one may think that the complex dependence of the enol cation fluorescence on the alcohol concentration is the result of both an alcohol monomer and an alcohol dimer acting as quenchers. This dimer model, which has been previously proposed for the dissociation of hydroxyaromatic compounds in alcohol−water[34−36] and tetrahydrofuran−water mixtures,[37] would be in agreement with our experimental findings. Both the dimer model and the two-routes model fit the data with the same accuracy because they lead to the same set of equations. This means that in order to decide which mechanism is correct we have to examine the physical meaning of the parameters involved in both models. Taking into account that we observe a second-order contribution to the fluorescence decay of **1*** and **2*** for all the alcohols studied, we would have to conclude that if the dimer model were correct, all these different alcohols dimerize in acetonitrile to a great extent, which is very unlikely for alcohols such as 1-butanol and *tert*-butyl alcohol. We have therefore rejected the dimer model.

Finally, there is no evidence for the occurrence of intramolecular proton transfer in **1** and **2** from the OH group to the pyridyl N in acidified acetonitrile in the absence of a hydroxylic quencher, despite the fact that studies on structurally related compounds 2-(2′-hydroxyphenyl)benzimidazole,[38] 2-(3′-hydroxy-2′-pyridyl)benzimidazole,[26] and 2-(2′-pyridyl)benzimidazole[23] have shown that these compounds experience in the excited state an increase of acidity at the hydroxyl group and an increase of basicity at the pyridyl N. Apparently, the OH group and the pyridyl N in **1** and **2** are not close enough or cannot adopt the suitable geometry to undergo intramolecular proton transfer.

Conclusions

In this article we have demonstrated that in compounds **1** and **2** concerted multiprotonic transfer from the hydroxyl group to the pyridyl nitrogen can occur in acidified acetonitrile in the presence of alcohols. We have discussed a model for the mechanism of this proton-transfer process. Essential for the occurrence of the proton transfer is the presence of a quencher with hydrogen-bond donating and accepting properties. Furthermore, we have shown that the values of these properties, which are represented by the α and the β value, respectively, as well as the size and geometry of the quencher, play a role in the efficiency of the proton-transfer process. Moreover, we have demonstrated that compounds **1** and **2** differ remarkably in the efficiency of this process as a result of the presence of the methyl group on the benzimidazole nitrogen N(1) in compound **2**.

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Supporting Information Available: Tables with the fluorescence lifetimes of **1** and **2** detected at 27780 cm^{-1} in acidified acetonitrile with various concentrations of alcohol (2 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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