Experimental and Theoretical Studies of the Proton-Hopping Reaction of 7-Hydroxyquinoline in Viscous Hydroxylic Media

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Experimental and theoretical (PM3) studies of 7-hydroxyquinoline in glycerol and in ethylene glycol show the occurrence of a proton-transfer reaction in the ground as well as in the first singlet electronically excited states. Both studies indicate that the H-bond bridge formed in the 1:1 complex provides a stabilization of the keto form in the S_0 state (λ_{abs}= 420 nm). In S_1, a photoinduced proton-transfer reaction solely occurs in the bridged or well-prepared H-bonded enol form, producing a fraction of the keto tautomer that emits a largely Stokes shifted band (λ_{emis} = 530 nm). The time-resolved fluorescence measurements show that the dynamics of this proton-hopping reaction is viscosity-dependent (0.5 ns in ethylene glycol and 0.8 ns in glycerol). Theoretical calculations indicate the coexistence of cis and trans rotamers of the dye in the gas phase, in agreement with the observation in a jet-cooled molecular beam. The optimized geometries of the 1:1 complexes of both cis-enol and keto tautomers with both solvents indicate that proton-transfer dynamics involves a global nuclear motion of the H-bond bridge. In both associated tautomers, the 2-OH group of the glycerol molecule does not participate in the H-bond bridge involved in the tautomerization. Analysis of the HOMO and LUMO shows that the driving force of the proton-hopping reaction originates in a partial intramolecular charge transfer from the proton-donating site to the accepting group within the dye molecule.

1. Introduction

Processes involving proton translocation over long distances are fundamental for the establishment of proton electrochemical potential gradients across biological membranes and are crucial for the proper function of the energy-transducing membranes.[1] Very recently, Hynes and co-workers suggested the involvement of several proton-transfer elementary steps in the mechanisms of hydrochloric ionization at the surface of stratospheric ice and hydrolysis of chlorine nitrate in the ice lattice.[2] The fast motion of the hydrogen ion is thought to arise from successive protonation−dissociation reactions mediated by hydrogen-bonded water chains, "proton wires".[2−4] As a result of the importance of proton hopping in chemistry and biology, much work has been devoted to elucidating this phenomenon in DNA base pairs, water clusters, and in several H-bonded species.[2−7] From the point of view of experiment, proton-transfer reactions of 7-azaindole (7AI)[5−7] and hydroxyquinoline[8−15] are of particular interest and constitute the most studied chemical systems in this field.

We have recently reported the absorption and fluorescence spectra of 7-hydroxyquinoline (7HQ) and the van der Waals complexes with water and methanol in jet-cooled free conditions[12] and in hydroxylic and carboxylic polymeric matrixes at room temperature.[13,14] The jet-cooled experiment shows the existence of cis and trans rotamers in a way similar to that of 2-naphthol.[16] Microscopic solvation of 7HQ with one or two molecules of water or methanol in the gas phase does not yield the keto phototautomer,[12] which is photoproduced in the condensed phase. In polymeric matrixes, several species have been proposed to explain the excitation-wavelength-dependent fluorescence spectrum.[13,14] Proton switching and stabilization of the keto tautomer in these media at room temperature have been demonstrated, opening a way for storing information at a molecular level.[14] Earlier, Itoh and co-workers[9a−c] reported on the steady-state and time-resolved spectroscopy of 7HQ in methanol solution, showing the occurrence of proton-transfer reactions in 1:2 complexes (7HQ/MeOH). Recently, Tokomura et al.[9e] have measured a lifetime in the microsecond range, which they ascribed to the ground-state keto form generated through an excited-state proton-transfer reaction in the H(D)-bonded 7HQ/methanol. The idea that we introduce in this work is to replace the "floppy" H-bond bridge formed by the two well-arranged alcohol molecules by only one molecule of the solvent (Scheme 1). Thus, a relatively rigid complex might be formed, opening a way to the stabilization of the keto form in the ground state. In this kind of cyclic structure with a H-bond bridge, the proton hopping might be described as a triple proton-transfer reaction. Contrary to the situation in a polymeric medium, in viscous solvents one might easily change the experimental

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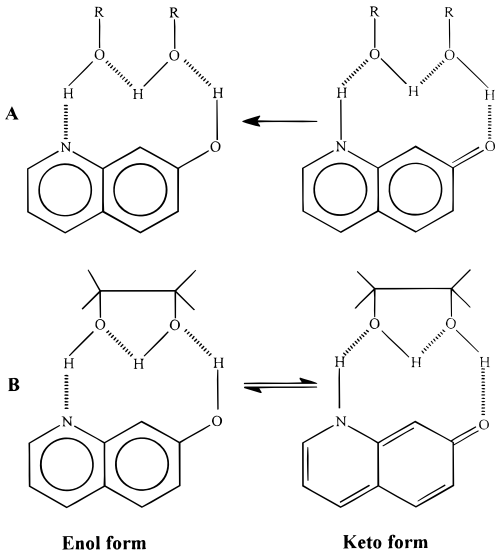
SCHEME 1[a]



[a] (A) Hydrogen-bond bridge formed by two molecules of alcohol (ROH) when complexing the enol form of 7-hydroxyquinoline (7HQ). (B) A similar bridge involving only one molecule of a polyalcohol like ethylene glycol (EG) or glycerol (GL) might stabilize the keto (K) tautomer of 7HQ (see text).

conditions to control the molecular dynamics and spectroscopy of the H-bond species.

The present paper deals with the absorption and fluorescence (steady-state and time-resolved fluorescence) spectra of 7HQ in glycerol (GL) and in ethylene glycol (EG) at room temperature, aiming to reach a better understanding of the energetics and dynamics of the processes, which involve the intermolecular H-bond interactions and the proton hopping in hydroxylic and viscous media in both ground and first excited electronic states. Measurements using mixtures of ethylene glycol with acetonitrile (AC), dioxane, and tetrahydrofuran are also reported. To get more insight into the nature (and length) of the H-bond bridge, which allows the proton-hopping reaction in 7HQ in these media, we also studied 6-hydroxyquinoline (6HQ), a molecule which shows intermolecular proton transfer in aqueous solutions. Results of a theoretical treatment (PM3) of the energetics, electronic density, geometry, and solvation of the implicated species in these solvents are also presented and compared with the experimental observation.

2. Materials and Methods

The compounds 6- and 7-hydroxyquinoline (6HQ and 7HQ, from Across Organics) were dried under vacuum, and the purity was checked and confirmed by fluorescence spectroscopy before use. All the solvents (spectrograde quality of >99%, Aldrich) were used as received. The sample concentrations were approximately $10^{-4}-10^{-5}$ M. The steady-state absorption and fluorescence spectra were measured using Cary (E1) and Perkin-Elmer (LS-50B) spectrophotometers, respectively. The excitation and emission spectra are corrected for spectral responsivity of the instrument. The time-resolved emission measurements were carried out by using the time-correlated single-photon-counting technique with a nanosecond fluorimeter (Edinburgh Instruments, model 199F). An instrument response function having fwhm of ~800 ps and a repetition rate of 20 kHz were used with a thyratron-gated, coaxial, hydrogen-filled flash lamp. A monochromator and an XP2020Q fast photomultiplier were used in the detection electronics. The time resolution of the apparatus after deconvolution of the signal is about 200 ps. The fluorescence decays were deconvoluted by an iterative nonlinear least-squares fitting method with the help of the FLA900 analysis software package (Edinburgh Instruments). The quality of the fits was checked with the χ^2 value and distribution of residuals. All the measurements were done at 293 K.

PM3 semiempirical molecular orbital calculations[17] were performed for the electronic ground state using original parameters of Hyperchem software v4.5, based on the restricted Hartree−Fock (RHF) method and in native MOPAC93 included in Chem3D Pro-MOPAC.PRO.[18,19] For our calculations, the initial geometry of a given molecule or associated molecule was first optimized for minimum energy by molecular mechanics using the MM2 force field. The result of this optimization was employed as input data for PM3 semiempirical calculations. According to this methodology, the optimization were ended in internal coordinates and were stopped when Peter tests were satisfied in BFGS or an enhanced EF method,[20] for a gradient below 0.001 kcal/mol per Å.

Electronic energy calculations on the geometrically SCF-optimized molecule for HOMO and LUMO orbitals were performed with singly excited (5 occupied + 5 unoccupied orbitals) or microstates (3 occupied + 3 unoccupied orbitals, 83 orbitals, 400 configurations) configuration interaction (CI) including electronic correlation, and the calculations were also done without considering CI. The relative energies for the studied tautomers are similar to those for the simple and two-CI method, indicating that at this level CI does not introduce significant structural and energetic changes.

3. Results and Discussion

3.1. Experimental Section. *3.1.1. Steady-State Absorption and Fluorescence Spectra.* The main absorption band (maximum at ~330 nm) of 7HQ in GL and in EG is similar to that found in monoalcohols, losing the vibrational structure observed in the spectrum of AC (Figures 1 and 2). The disappearance of the structure is due to the establishment of H-bonds of 7HQ to these solvents. Taking into account the H-bonding ability of 7HQ and those of GL and EG, the free enol population of the dye in the ground state might be very low or nonexistent in these media. Besides the main band, a relatively weak absorption band at 420 nm appears in these viscous solvents (Figures 1A and 2A). This tail does not appear in monoalcohol solutions, however.[9] The spectrum in GL compared to that in EG shows a relative increase in intensity of the 420 nm band in comparison to that of the one at 330 nm. To further investigate the nature of the band at 420 nm, we recorded the absorption spectra of 7HQ in AC, EG, and their mixtures (Figure 2A). Addition of EG solution to the AC solution results in the appearance of the 420 nm absorption band, which increases in intensity with the concentration of EG. This band is due to the absorption of the keto (K) structure of 7HQ formed through proton transfer with EG (and GL), as proposed in Scheme 1. A similar but transient absorption band of 7HQ in methanol has been observed by Itoh and co-workers.[9d] The maximum of this band does not shift when the concentration of EG is increased. Similar observations can be reached from the fluorescence spectra when exciting at 410 nm (Figure 2C).

The process giving rise to the species absorbing at 420 nm, assuming a 1:1 stoichiometry of the complex between 7HQ and EG, can be formulated as

$$\mathrm{E} + \mathrm{EG} \rightleftharpoons \mathrm{E.EG} \rightleftharpoons \mathrm{K.EG} \qquad (1)$$

where E, E.EG, and K.EG stand for the free enol, H-bond

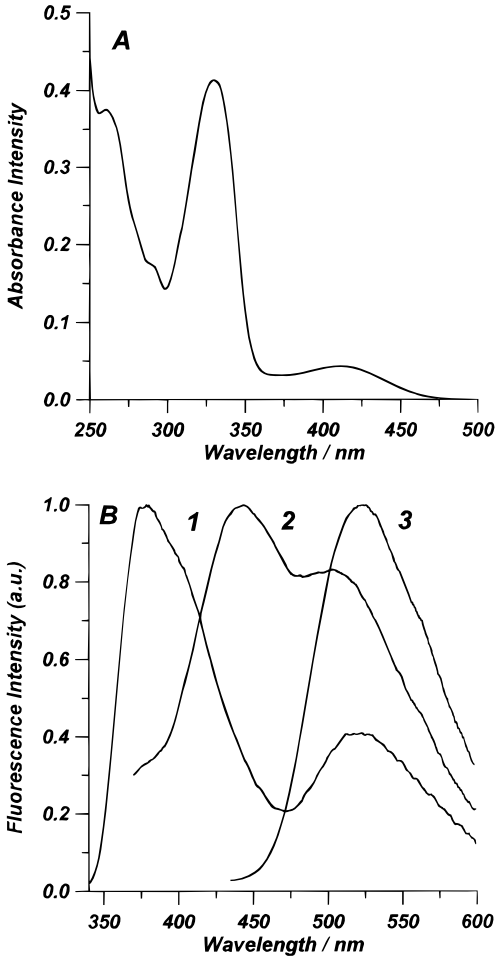


Figure 1. (A) Absorption and (B) normalized fluorescence spectra of 7HQ in GL. Spectra 1, 2, and 3 correspond to $\lambda_{exc} = 320$, 360, and 410 nm, respectively.

complexed enol, and *keto* tautomers of 7HQ, respectively. Thus, the apparent equilibrium constant of (1) is given by

$$K_{app} = [\text{K.EG}]/([\text{E}][\text{EG}]) \qquad (2)$$

With the experimental condition that [EG] ≫ [K.EG], one can derive eq 3, where A and ϵ and $[\text{E}]_0$ and $[\text{EG}]_0$ stand for the absorption and molar absorption coefficient of the complex and the initial concentrations of 7HQ and EG, respectively.

$$1/A = 1/(\epsilon[\text{E}]_0 K_{app}[\text{EG}]_0) + 1/(\epsilon[\text{E}]_0) \qquad (3)$$

A Benesi−Hildebrand (BH) plot[21] (eq 3, which assumes a 1:1 stoichiometry of the H-bonded complex) of the data at 420 nm, where solely the K tautomer absorbs, shown as an inset of Figure 2A, gives an apparent equilibrium constant for reaction 1, $K_{app} = 0.02$ L mol^{-1} at 293 K. This apparent constant reflects those of the equilibria between E, K, and EG as proposed in reaction 1. A model assuming 1:2 (7HQ/EG) stoichiometry of the complex does not fit the experimental data (not shown). The complexes, K/EG (or K/GL), which absorb at 420 nm, are produced and stabilized in the ground state. This is an experimental verification of Scheme 1. The low value of K_{app} indicates that the enol form is the most stabilized one with $\Delta G^\circ = -2.3$ kcal mol^{-1} at 293 K.

The emission spectra in GL and in EG have been recorded as a function of the excitation energy (Figures 1 and 2). Upon excitation in the UV region (i.e., 330 nm), two prominent emission bands are observed with maxima at ∼380 and ∼530

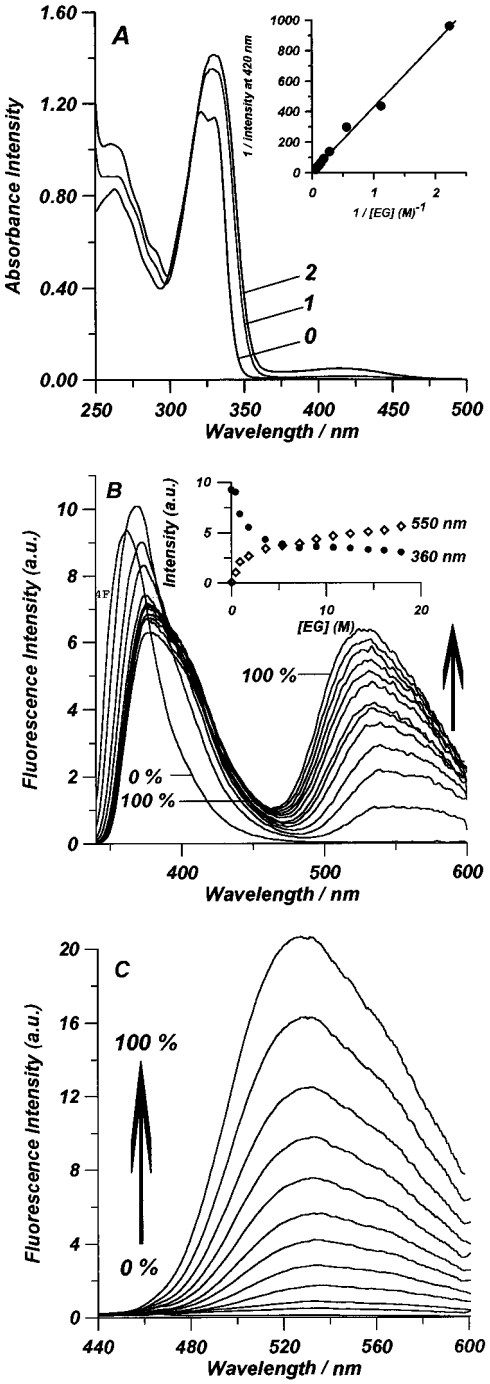


Figure 2. (A) Absorption and (B and C) fluorescence spectra of 3×10^{-4} M 7HQ in mixtures of acetonitrile (AC) and ethylene glycol (EG) solutions. In (A), for clarity, we only show the spectra done in pure AC (0), a binary mixture of AC/EG ([EG] = 5.38 M) (2), and pure EG (3). In (B), spectra from the bottom to the top at 520 nm correspond to $[\text{EG}]_0 = 0$ (pure AC), 0.45, 0.90, 1.79, 3.59, 5.38, 7.17, 8.97, 10.76, 12.55, 14.45, 16.14, and 17.93 (pure EG) M, respectively. The inset in (A) is a Benesi−Hildebrand plot (eq 3) assuming a 1:1 complex (K/EG) for the absorption at 420 nm. $\lambda_{exc} = 330$ nm (B) and 410 nm (C), respectively.

nm. When excitation occurs at 360 nm (Figure 1B), a band in the region of 420−450 nm predominates, however. A further increase in the excitation wavelength (i.e., 420 nm) results in an enhancement of the fluorescence intensity of the only band observed at 530 nm. Figure 2B shows the emission spectra of 7HQ in a binary of mixture of EG and AC when exciting at 330 nm. The inset shows the change of the fluorescence intensity at 360 and 550 nm upon addition of EG solution. In

contrast to the emission band at 380 nm, the emission band at 530 nm shifts toward the blue and increases in intensity upon increasing the concentration of EG. Figure 2C exhibits the fluorescence spectra of 7HQ in the same mixtures but now excitation of at 410 nm.

The observation of a dual emission when exciting around 330 nm suggests that a fraction of the species absorbing in this region undergoes a photoreaction. It is well-known that the green fluorescence band at 530 nm of 7HQ complexed by hydroxylic solvents (liquid or matrixes media) originates from the keto phototautomer, formed by an intermolecular proton-transfer reaction in the electronically first excited state of H-bond-bridged enol species.[8−14] Observation of a similar fluorescence when exciting the keto tautomer (Figures 1 and 2) supports this assignment and is in agreement with the results reported by Itoh and co-workers[9] and those measured in polymeric matrixes.[13,14] The emission spectra suggest that not all of the species absorbing at 330 nm undergo the proton photoreaction. These complexes must have a geometry that does not allow the establishment of the H-bond bridge (HBB) required for the proton dislocation and hence the formation of the K species.[9,14] On the basis of the structure of the HBB suggested to be formed in alcohol solutions[9] and polymeric matrixes,[13,14] we suggest that the photoreaction occurs through a triple proton-transfer process in the bridged complexes, as noted in the Introduction.

As said above, in addition to the enol and keto fluorescence bands, the emission spectra in GL (Figure 1B) and in EG (not shown) exhibit an emission band at 430−440 nm when excited at ∼360 nm. The maximum of the excitation spectra of this band is at 360 nm. Comparison with the absorption and fluorescence spectra of 7HQ in water at different pHs[8] and in acidic polymeric matrixes[14] and use of the proposed mechanism of formation of 1:2 complex of 7HQ/methanol,[9] these species are ascribed to cationic structures. Given the shape of the absorption spectra, the population of these cationic (C) species must be very low compared to those of the E and K tautomers.

The spectral shift in the steady-state proton-transfer fluorescence band in the binary mixtures of EG with AC (Figure 2) is used to get information on the solvation shell around the keto form of 7HQ, when directly excited and when formed through a triple proton-transfer reaction in the H-bond structure. The variation of the dipole moment of E upon electronic excitation can be related to the spectral shifts and K of absorption and emission bands. Therefore, we have plotted in parts A and B of Figure 3 the change of the Stokes shift of the proton-transfer band when exciting (i) the enol form and (ii) only the keto form, with variation of the molar fraction of EG (X_{EG}) in AC. Both solvents have similar reaction field factors,

$$f(\epsilon,n) = [(\epsilon_o - 1)/(\epsilon_o + 2)] - [(n^2 - 1)/(n^2 + 2)] \quad (4)$$

where ϵ_o and n are the static dielectric constant and refractive index of the solvent, respectively (values of $f(\epsilon,n)$ are 0.67 and 0.71 for EG and AC, respectively).[22] However, the H-bond abilities of EG are stronger than those of AC. A direct relationship between $\Delta\nu$ and X_{EG} is observed (parts A and B of Figure 3). The linear dependence is more important when exciting the enol form (slope ≈ 500 cm^{-1}), which suffers a proton-transfer reaction, than when directly exciting the keto species (slope ≈ 200 cm^{-1}). Because the 530 nm emission band originates from the same fluorophore (K), one may consider that the observed difference reflects the difference of the ground-state dipole moments of the enol and K species. However, the absorption spectra of these species do not show a significant

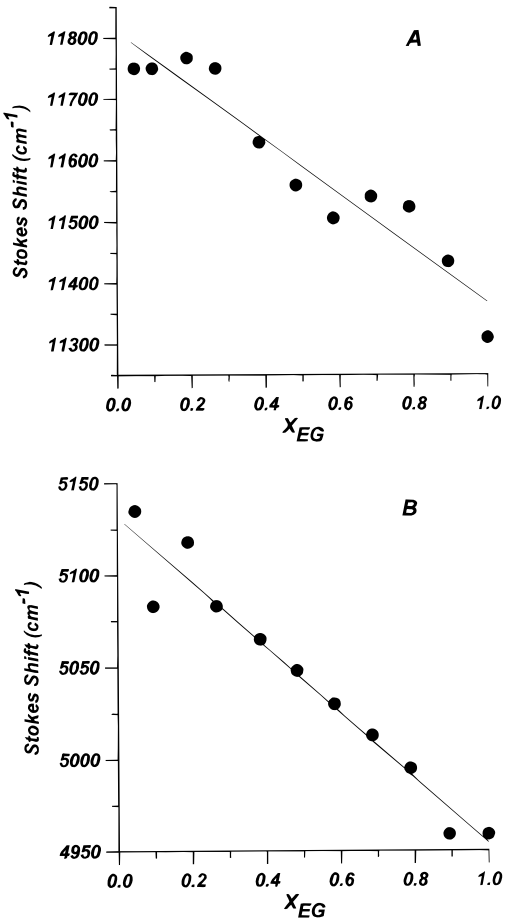


Figure 3. Variation of the Stokes shift of the proton-transferred emission band with the molar fraction of EG (X_{EG}) in the mixtures EG/AC. (A) and (B) correspond to the excitation of the H-bonded enol species and keto tautomer, respectively.

shift upon changing X_{EG} (Figure 2A) or the nature of the noninteracting solvent. In fact, Figure 4 shows that the position of the band of E (not shown) and that of K are not affected upon changing the cosolvent: mixtures of EG with AC, dioxane, and tetrahydrfuran with 50/50 (v/v) parts of EG/cosolvent. A similar feature is observed in the emission spectra. Thus, changing the polarity of the cosolvent does not affect the spectral position of both species, suggesting that the dipole moments of E and K do not experience a significant change upon electronic excitation. On the contrary, the emission bands of E and photoproduced K (Figure 2B) show shifts to opposite sides of the spectrum upon changing solvent composition in the binary mixtures of EG/AC. Thus, we can relate the difference in the relationship between $\Delta\nu$ and X_{EG} (parts A and B of Figure 3) to the difference of the solvation shells of excited K reached by direct excitation (410 nm) and those reached through a proton-hopping reaction in excited E (330 nm). This difference reflects the reorganization energy of the solvation shell (about 300 cm^{-1}) caused by the excited-state proton-hopping reaction in the H-bonded enol form, giving rise to the phototautomer K. A comparable situation has been found to occur in the photophysics of nile blue A in proton-accepting and electron-donating solvents, where the solvation shell and lifetime of the same fluorophore depend on the precursor.[23]

To investigate the nature of the relation between the HBB and the occurrence of proton-transfer reaction, we compared the absorption and emission spectra of 6HQ under similar conditions (Figure 5A). Beside the main absorption band, the absorption spectrum shows a very weak and long tail extending

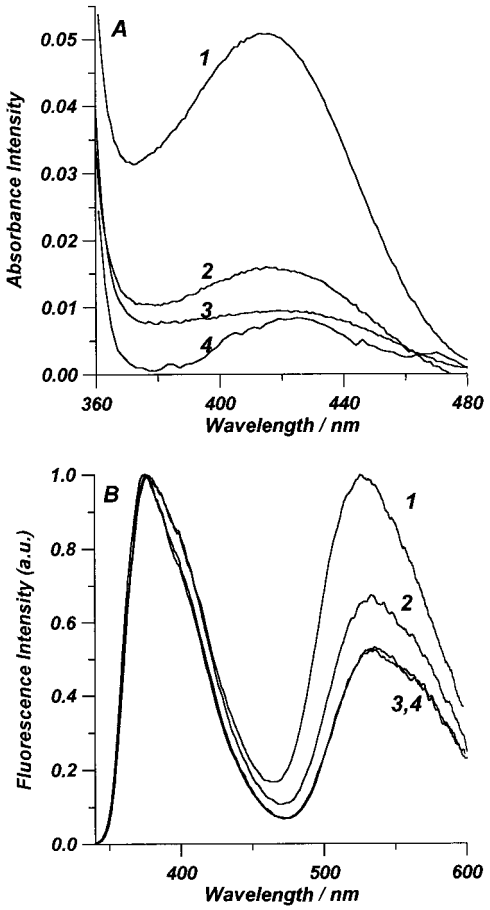


Figure 4. (A) Visible absorption and (B) normalized emission spectra ($\lambda_{exc} = 330$ nm) of 7HQ in EG (1) and in mixtures of 50/50 (v/v) EG and AC (2), dioxane (3), and tetrahydrofuran (4).

up to 600 nm, which could be ascribed to K or other H-bonded species of 6HQ to EG. We observed no new emission band that might be assigned to the proton-transferred structure of 6HQ, like those found in water solution.[8,15] The length of one molecule of EG might not be enough to establish a H-bond bridge between the heterogroups of 6HQ. Therefore, the formation of a proton-transferred species of 6HQ involving one molecule of EG is not expected. Complexation of 6HQ with two molecules of solvent may occur, and the tail in the absorption spectra in EG might be ascribed to the absorption of these structures. However, even in this situation, we observed no proton-transferred species in EG. Of course, this reaction might occur in the excited state, and presumably, the highly efficient nonradiative processes of the tautomer could preclude observation of an emission from the keto species, which should appear at ~580 nm.[8,15] However, in GL (a molecule that is longer than EG) the fluorescence spectrum exhibits two bands due to the enol (380 nm) and keto (575 nm) species (Figure 5B). The observation of a band at 360 nm in the excitation spectrum (Figure 5C), similar to that of the anionic 6HQ in alkaline water,[8,15b] leads us to ascribe this absorption to the keto species stabilized in the ground state through a H-bond bridge with GL. The observed absorption and fluorescence features of 6HQ and those of 7HQ in EG and GL suggest that the formation of tautomeric species mostly involves one solvent molecule. This agrees with a BH analysis of this band in 7HQ/EG (Figure 2A). However, in monoalcohols, two molecules of solvent are needed for the bridge.[9,10]

3.1.2. Time-Resolved Fluorescence. To get information on the proton-transfer dynamics in the excited state, we have

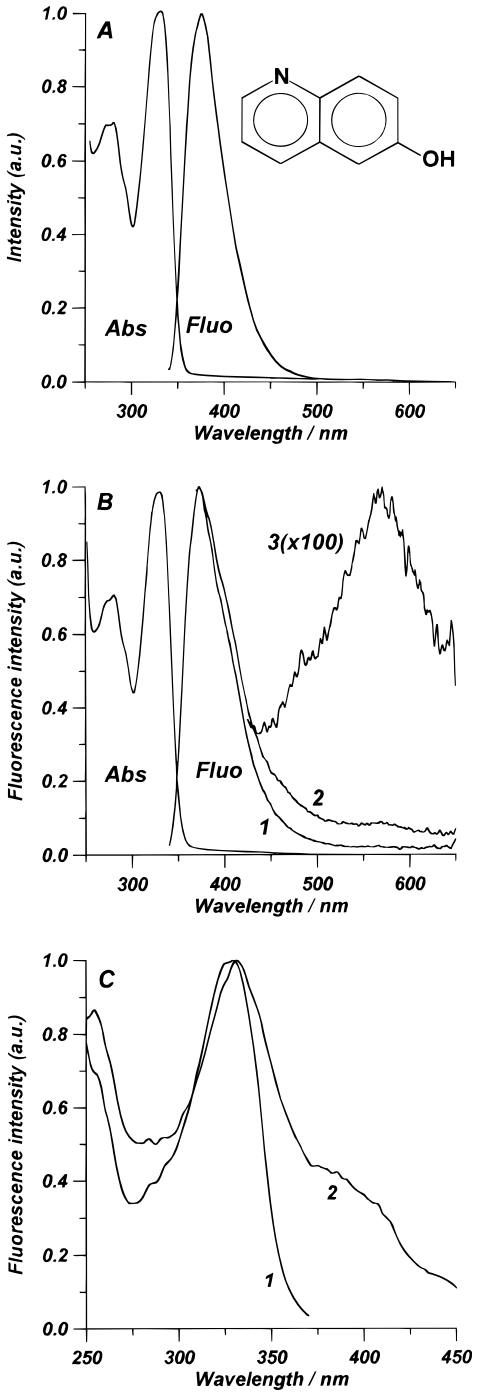


Figure 5. Absorption (Abs) and fluorescence (Fluo) spectra of 6-hydroxyquinoline (6HQ) in EG (A) and in GL (B). $\lambda_{exc} = 330$, 350, and 400 nm for (1), (2), and (3), respectively. (C) Excitation spectra of 6HQ in GL observed at 380 nm (1) and at 570 nm (2).

measured the fluorescence decays of 7HQ in EG, GL, and AC at several wavelengths of excitation and emission. For instance, in GL (Table 1), when excitation occurs at 320 nm and the emission of E at 360 nm is recorded, the decay shows a double-exponential behavior ($\tau_1 = 0.68$ ns, and $\tau_2 = 2.24$ ns). Gating the emission at longer wavelengths up to 400 nm, both lifetimes become longer ($\tau_1 = 1.0$ ns and $\tau_2 = 2.56$ ns). The decay curve observed at 450 nm, however, fails to fit to a double-exponential function. The χ^2 value is larger and involves a considerable error in the value of the lifetimes due to overlap of several species (E, C, and K).[21] At 500 nm, where K emits, the transient signal fits with a 3.99 ns decay and a rise-time component of about 0.77 ns. When the cation is excited at 360 nm and gated

TABLE 1: Data of the Fitted Fluorescence Signal of 7HQ in GL at Different Observation Wavelengths When Pumping with 320 nm[a]

λ_{obs}/nm	τ/ns	χ^2	τ_1/ns	τ_2/ns	a^*_1	a^*_2	χ^2
360	1.80	1.30	0.68	2.24	0.56	0.44	1.11
370			0.89	2.35	0.56	0.44	1.08
400	2.28	1.88	1.00	2.56	0.36	0.64	1.20
450	3.30	2.85	6.01	2.79	0.09	0.91	1.26
500			0.77	3.99	−0.39	1.39	1.09
520	5.01	5.10	0.80	4.17	−0.35	1.35	1.23
400[b]	2.46	3.18	1.66	3.78	0.77	0.23	1.08
500[c]	3.62	1.02					

[a] a_1 and a_2 are the normalized pre-exponential factors of the fitted functions of τ_1 and τ_2, respectively. [b] Corresponds to excitation at 360 nm. [c] Corresponds to excitation at 408 nm.

at 400 nm, a two-exponential function with time constants of 1.66 and 3.78 ns fits the emission decay. However, upon excitation of K at the red edge of the absorption spectrum (408 nm), the decay kinetics of excited K simply fits to a single-exponential function with a time constant of 3.62 ns. Similar studies in EG show that upon pumping with 320 nm and measuring at 360−390 nm range, the decay fits with lifetime values of 0.46 and 2.20 ns. At 520 nm, a rise time of 0.45 ns is recovered with a fluorescence decay of 3.50 ns.

The subnanosecond (sub-ns) component of the double-exponential fluorescence decays in EG and in GL (decay at 380 nm and rise time at 520 nm) indicates that some H-bond-bridged E and K phototautomers are "photophysically" connected with a common channel. In AC, where proton transfer cannot take place, this component is not observed and the fluorescence decay fits to a single-exponential function with a time constant of 0.98 ns. Thus, the sub-ns component in EG and GL can be ascribed to the dynamics involving both solvent motion and proton-switching events in bridged E to yield K. This later relaxes to the ground state within a few nanoseconds (3.5 ns in EG and 4 ns in GL, comparable to 3.5 ns in methanol). The time constant of the sub-ns component agrees with those measured in a series of monoalcohols by a picosecond (ps) apparatus.[9,10] The dynamics of the proton-transfer event in a well-prepared geometry might be on the sub-ps time scale, as it has been observed in the case of clusters of 1-naphthol in H-bonding solvents.[6,25] The present data for EG ($\eta = 26.1$ cP, $\tau = 0.5$ ns) and in GL ($\eta = 1412$ cP, $\tau = 0.8$ ns) are viscosity-dependent. The high viscosity of the medium does not allow a fast rearrangement of the solvent molecules to form the H-bond bridge necessary for the photoreaction. The barrier to solvent reorientation limits the proton-switching photoreaction to occur from only suitable or quite arranged geometries. Part of the sub-ns component in the decay of the normal emission in EG and in GL might be due to the dynamics, which yields OH's and nitrogen atom's solvated species as a final photoproduct in the first singlet electronically excited state of the enol forms. These species might be considered as intermediates in the proton-transfer process of 7HQ in these media as in hydroxylic solvents.[11] This implicates a stepwise mechanism of the triple proton-hopping reaction of 7HQ (vide infra).

We consider now the potential-energy surfaces (PES) in the S_0 and S_1 states. The stabilization of K in S_0 and its photoformation in S_1 allow comparison of the excited-state behavior due to the proton-hopping reaction in the H-bond-bridged enol form ($\lambda_{abs} = 330$ nm) with that directly reached by a vertical excitation of K ($\lambda_{abs} = 420$ nm). In fact, the observation of a single-exponential fluorescence decay of K (3.6 ns in GL and EG) upon vertical excitation (408 nm) reveals interesting points relevant to the PES. First, the absence of the sub-ns rise time corroborates the assignment of this component to the proton-transfer reaction in H-bonded enol species. Second, the lack of a reverse proton-transfer reaction of K in S_1 indicates that this reaction is endothermic and that both excited species (E and K) are not in equilibrium, contrary to the situation in the ground state, where both forms coexist. Third, most of the population of K absorbing at 420 nm is formed by very similarly solvated K, involving one molecule of the solvent, in agreement with the BH analysis (Figure 2A), the single fluorescence lifetime, and the spectral features.

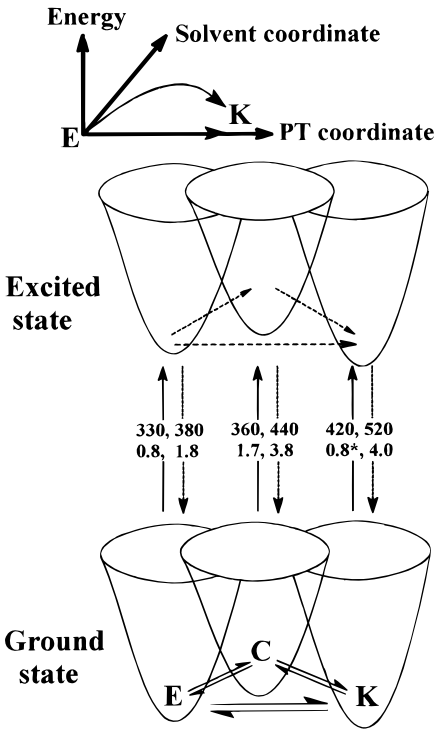


Figure 6. Schematic illustration of the PES of proton-transfer reactions of 7HQ in GL in S_0 and S_1 states. E, C, and K are the solvated enol, cation, and keto species of 7HQ, respectively. The upper numbers between the S_0 and S_1 state transitions correspond to the wavelengths (nm) of the maximum of absorption (left) and emission (right) spectra and the lifetime values of these structures. The star indicates a rise time of the K fluorescence signal when photoproduced from E. Note that, when K is directly excited, no rise time of the fluorescence of K was observed. In S_1, the arrows connecting the wells illustrate a proposed direct and nondirect (solvent rearrangement) proton-hopping reaction of complexed E to yield K. In the upper part of the figure, the direct and indirect arrows from E to K represent proton-transfer reactions in prepared and quite prepared (involving solvent motion) complexes, along proton-transfer and solvent coordinates, respectively. The looping arrow to K is in the plane defined by these coordinates.

Figure 6 is a proposed schematic diagram of the PES of 7HQ in Gl (and EG) in S_0 and S_1 states with direct and two-step (solvent rearrangement) mechanisms of the PT reaction from E to K along proton-transfer and solvent coordinates and where C is the cationic structure.

3.2. Theoretical Section. The main goal of the present calculations is to examine the solvation effects of GL and EG on the stability of the cis-enol (cis-E) and keto (K) species. The formation of a HBB in 1:1 complexes of the types discussed above and the ones to be shown here is the main step responsible for the proton transfer of 7HQ in these solvents. In addition, detailed information on the geometries of these structures is fundamental to understanding the proton-translocation process.

Figure 7 depicts the optimized geometries with the intermolecular H-bond distances of the solvent-bridged cis-E and K

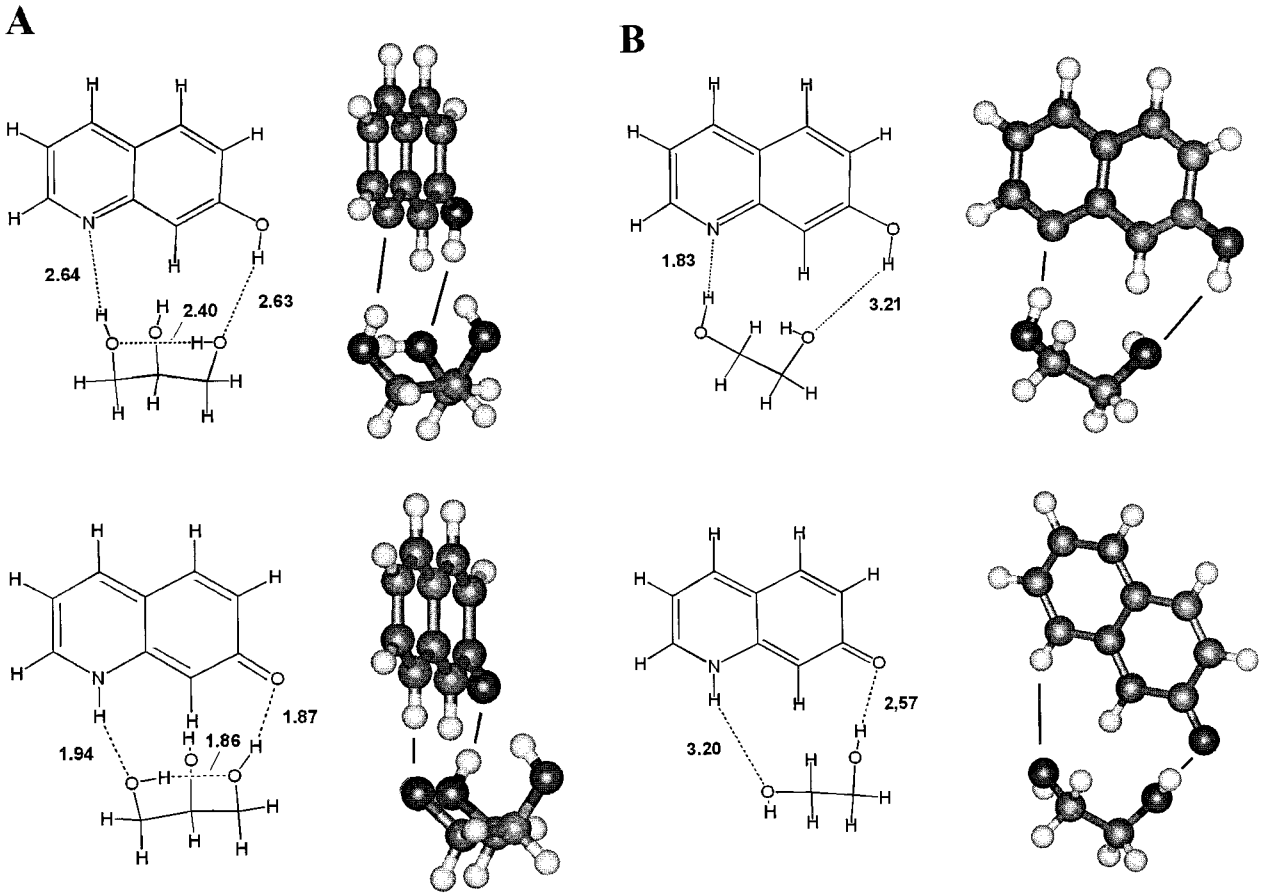


Figure 7. Ground-state geometries of bridged cis-enol (cis-E) and K tautomers with (A) glycerol and (B) ethylene glycol. The right part shows a stereoview with the endo position of the 2-OH group of GL in both complexed tautomers. Distances are given in angstroms.

species in GL and EG. All the calculated structures result in planar geometries except that for the enol rotamer at the top of the barrier corresponding to the cis−trans isomerization. In addition to this, in the glycerol-bridged species, the 2-OH group of the GL molecule is out of the plane of the H-bonded species, pointing to the direction of the aromatic ring (endo position).

Calculations suggest the coexistence of cis and trans rotamers of 7HQ in the gas phase, in accordance with the jet-cooled molecular beam results.[12] The energy of free cis-E is slightly lower (0.71 kcal/mol) than that of trans-E. The energy barrier to the internal rotation of the C−OH bond, from cis-E to trans-E, is 2.89 kcal/mol. The geometry of the rotamer at the top of the barrier has the C−O−H plane perpendicular to that defined by the quinoline ring. Both cis-E and trans-E are more stable than K. For instance, the energy gap between cis-E and K is 16.57 kcal/mol. From the point of view of electronic charge distribution (Figure 8), the striking features are the high total electronic charge density on the oxygen and nitrogen atoms in all the calculated species. K, which is the most polar form (μ = 6.36, 3.20, and 1.16 D for K, trans-E, and cis-E, respectively), is the less stable one. Because of the relatively long distance between the nitrogen and oxygen atoms, both the ground and the first singlet excited electronic states of K are not populated in free conditions.[12]

The geometries of the 1:1 complexes (Figure 7) indicate that the OH groups in positions 1 and 3 of the GL molecule are the ones involved in the chelate ring formed by HBB in both species. The 2-OH group of the GL molecule does not directly participate in the bridge, and the influence of its stereochemistry (exo/endo) on the distance of the HBB is not significant. However, the endo position stabilizes the complex through interaction with the aromatic ring. Here, the theoretical result will only consider the species with the 2-OH group in the endo position in bridged 1:1 complexes. The H-bond distances in enol species are longer than those in the keto ones (Figure 7). In associated K structure, these distances are similar to those found in strongly hydrogen-bonded systems.[6,26−33] In addition, the OH···O intramolecular bond in the glycerol molecule complexed to K is shorter (1.86 Å) than that in the one complexed by cis-E (2.40 Å). This difference suggests a nuclear rearrangement along the HBB, when producing K from the complexed E. The shortening (or compression) of the H-bond distance reduces the energy barrier to the transfer and is fundamental for the occurrence of the reaction as found in numerous systems.[6,30−34]

Figure 8 shows that the HBB induces a stabilization of cis-E and K by 4.89 and 10.27 kcal/mol, respectively.[29] The dipole moments in these species are 1.44 and 4.90 D, respectively. The energy gap between cis-E and K is reduced to 11.20 kcal mol^{-1}. In both structures, the HBB induces an increase of the electronic charge density on the nitrogen and oxygen atoms of 7HQ (Figure 8). Contrary to the situation in free structures, the most polar complex (K) results in the most stabilized one due to the formation of HBB. This is due to the shortening of the H-bonds in associated K, compared to those in associated E. Similar findings have been reported for 2-hydroxypyridine and its tautomer, 2-hydroxypyridone, complexed to H-bonding species.[26−28] The tautomer cis-E is still the most abundant species, in agreement with the experimental result.

In a way similar to that of GL, the HBB through one molecule of EG stabilizes K by 9.58 kcal/mol, while that acting in cis-E brings only a stabilization of 3.67 kcal/mol. The energy gap

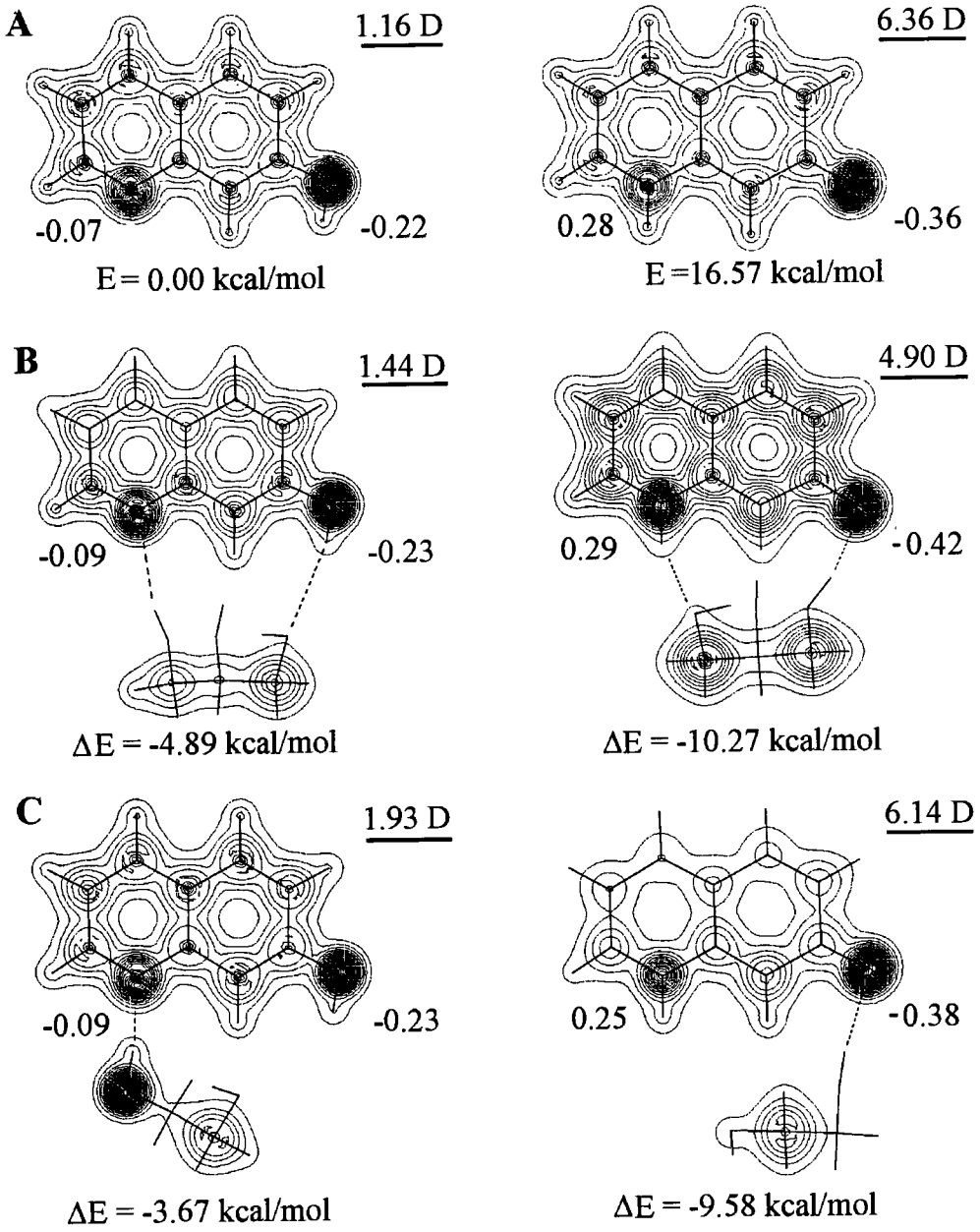


Figure 8. Contour plots of the total electronic charge densities at the (horizontal) molecular plane of (A) free cis-E (left) and K (right) tautomers of 7HQ and their respective complexes with GL (B) and EG (C). The figure also shows the dipole moment values (underlined), the total charge on the heteroatoms of 7HQ, and the relative energy (E) and the stabilization energy (ΔE) due to interactions, mainly for H-bond formation in these structures.[29]

between E and K is now reduced to 10.66 kcal/mol. However, given that the present theoretical calculations only include one molecule of solvent complexed to 7HQ, we cannot make a direct comparison of the energy gaps (between solvated E and K) obtained from theory (10.66 kcal/mol) and experiment (2.4 kcal.mol^{-1}). However, the observed trends are due to formation of HBB confirmed by theory.

The HBB formed by EG induces the largest charge separation between the dye and the solvent molecule, when compared with that of GL. The distance of the N−H···OH bond in K (3.20 Å) is longer than that of the N···H−O bond in cis-E (1.83 Å), contrary to the situation in GL (Figure 7). However, this trend is reversed when examining the distances of C═O···HO (dye···solvent) of K (2.57 Å) and OH···O (dye···solvent) of cis-E (3.21 Å). Assuming that the shortest H-bond distance is the result for the most part of energy of stabilization, we deduce that both N···HO and C═O···HO bonds in H-bridged cis-E and K, respectively, involve the stabilizing interactions. Initially, both structures would first act as H-bond accepting species, and upon the triple proton-switching reaction, the solvent molecule would move to the side of the proton-accepting group of the dye, making the related H-bond stronger (Figure 8). These processes dictate the mechanism by which the proton-hopping reaction occurs in this system (vide infra). While the GL molecule acts in a "symmetrical" fashion to form the HBB, the EG molecule fits in a different way, depending on the nature of the tautomer, and leads to bridged cis-E and K tautomers with some cationic character (Figure 8).

3.3. Mechanism of the Triple Proton Hopping of 7HQ in EG and GL. In accordance with the above results, we only consider the proton hopping involving one molecule of EG or GL. The geometry of the 1:1 complex of cis-E is suitable for the switching of protons in S_1. The motion of the system from the enol well to that of the keto one in the S_1 state is expected to be very fast with dynamics mostly dependent on (i) the electronic redistribution, (ii) the solvent polarization, and (iii)

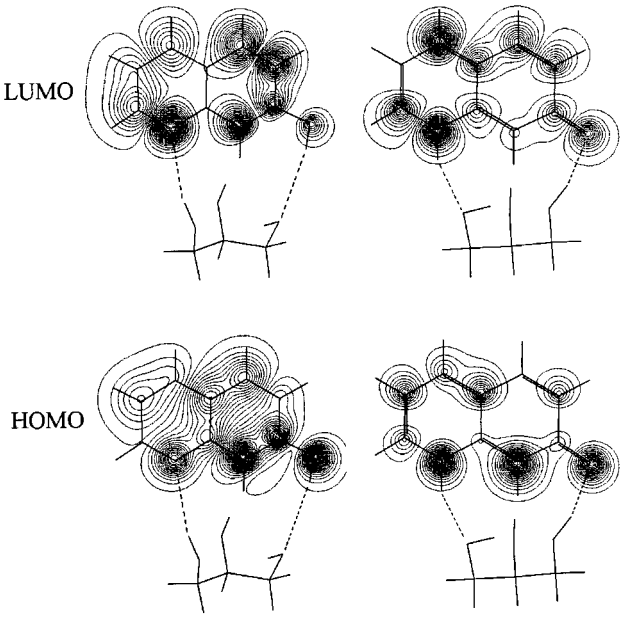


Figure 9. Calculated HOMO and LUMO in the minimum energy of the 1:1 complexed cis-E (left) and K (right) tautomers of 7HQ with GL.

the proton hopping within the bridge. Examination of the HOMO and LUMO explains the fundamental trends of the proton-transfer reactions (Figure 9). For instance, with one molecule of GL, the HOMO of cis-E shows a high electronic density on the oxygen and on the C_7 and C_8 atoms. In the LUMO, the electronic redistribution makes the nitrogen atom the richer electronic site, while the oxygen atom now has a "normal" charge. Then, the HOMO−LUMO π,π^* transition involves a charge transfer from the region of the C═O to that of C═N. This provides a new electronic distribution and thus the driving force to the migration of protons along the HBB of the complexed cis-E. In K, the HOMO shows accumulation of electronic charge densities on the heteroatoms, while in the LUMO, the oxygen atom becomes electronically poor, not able to recuperate the proton lost in S_0 to yield the enol form.

We now consider the solvent polarization/rearrangement and proton event. Two different kinds of mechanisms of the proton motion might act in the bridged species. First, a concerted reaction where all the involved (three) protons move at the same time. Second, a stepwise mechanism involving the formation of intermediates (cation or anion), where only one or two protons have moved in each step of the overall reaction (Figure 9). Further, these intermediates might further produce the final product or relax to the ground state. In all these steps, vibrational motion along the HBB reaction coordinates can be accompanied by a relative compression of the heteroatom distances in the bridge, as found in other systems showing intermolecular or intramolecular proton-transfer reactions.[6,30−34] The former mechanism (concerted reaction) implicates proton motion with synchronous or diffuse (not synchronous, but in one step) dynamics.[7] However, the observation of an emission band in the range of 420−450 nm, similar to those of strongly solvated enol forms at the nitrogen atom or at the OH group, might be an indication of the second mechanism, at least in the excited state of complexed cis-E. In fact, 7HQ in neutral water undergoes protonation of the nitrogen atom to form an excited cation or deportation of the OH group to form the anion intermediate within 10 ps.[11] The OH group in the cation deprotonates in 30 ps, while the nitrogen atom of the anion is protonated in 200 ps.[11] Both intermediates lead to the keto form in the excited state. The lack of symmetry in the 1:1 complex of the present system and the difference in the proton affinities of the involved groups (aliphatic OH and aromatic −N═ groups) lead the reactions in both states to occur in a stepwise fashion. Geometries (H-bond distances) of bridged cis-E and K suggest that these would act first as H-bond-accepting species favoring the formation of a cation as the intermediate of the reaction. It is worth noting that, due to the electronic excitation, the mechanism of the ground state might be different from that of the excited states.[7b] Real-time proton-transfer dynamics,[6,7a,c,35] and ab initio calculations at a high level are needed to elucidate the mechanism of the proton-hopping process in this system. Studies in this direction are currently in progress.

4. Conclusion

Room-temperature absorption and steady-state and time-resolved fluorescence spectra of 7HQ in glycerol and ethylene glycol show that the proton-hopping process takes place in both ground and excited states. The H-bond bridge formed in 1:1 complexes (dye/solvent) stabilizes the keto tautomer in the ground state. A fraction of the electronically excited, solvated enol species produces keto phototautomers on the subnanosecond time scale, with a largely Stokes shifted fluorescence band. In agreement with the experiment, the calculations predict the formation of a 1:1 complex of cis-E and keto structures with glycerol and ethylene glycol. The associated cis-E is the most stable structure. Theoretical results also suggest that charge migration from the OH to the nitrogen parts of complexed enol provides the driving force of the proton-hopping process.

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