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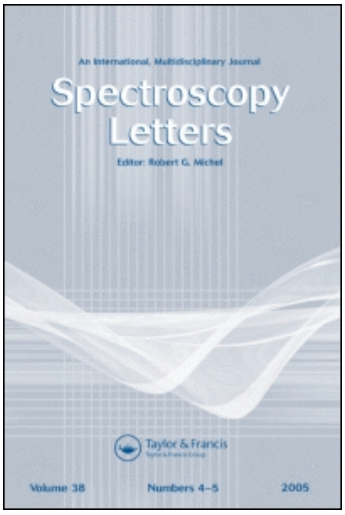

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Steady-State and Time-Resolved Emission Studies of 6-Methoxy Quinoline

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Steady-State and Time-Resolved Emission Studies of 6-Methoxy Quinoline

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Abstract: Steady-state absorption, fluorescence excitation, and emission spectra of 6-methoxy quinoline (6-MQ) were measured at room temperature in cyclohexane, dioxane, ethanol, acetonitrile, water, and water–dioxane solvents. Absorption spectra of cyclohexane, *n*-hexane, and isopentane solutions show resolved vibronic structure at room temperature. However, the excitation spectrum of cyclohexane solution is structureless and is found to be emission wavelength dependent, indicating the formation of at least two distinct species in the ground state. Similar behavior was observed in dioxane and water–dioxane solutions. For all other solutions, the fluorescence excitation spectrum of 6-MQ was found to be the same for different emissions. Emission of 6-MQ in all solvents consisted of two bands with their maxima around 355 nm (I) and 430 nm (II), the actual positions and the relative intensities being dependent on the solvent used. The bands I and II were respectively attributed to normal and protonated/H-bonded species of either ^1L_a or ^1L_b states or mixed ($^1L_a/^1L_b$) state of $\pi\pi^*$ character. Fluorescence decay of this dye in all solvents monitored over each emission maximum showed biexponential behavior, and the analysis yielded two different lifetime components for each emission band. The short and long fluorescence decay components were respectively in the range of 0.30–3.00 ns and 18–20 ns. The observed emission characteristics coupled with the nature of the fluorescence polarization spectra and two different decay components for each emission suggest the existence of two different conformers having two different excited electronic states.

Keywords: Conformers, emission, fluorescence decay, polarization

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INTRODUCTION

6-Methoxy quinoline (6-MQ) is a simple aromatic compound containing a methoxy group at the sixth position and a nitrogen atom in the aromatic ring, both being electron donating groups and, as such, the molecule in its ground state seems to be more basic. When such a molecule is excited, the electron transfer from the methoxy group to the aromatic ring may lead to various possible resonance structures. The interaction of polar solvents with lone pair electrons in the nitrogen atom and the π-electron cloud of the quinoline ring might result in the modification of the photophysical behavior of the molecule. There have been a few reports on the luminescence spectra of 6-MQ at low temperature dealing mainly with the relative quantum yield of fluorescence and phosphorescence and also on the shift of the emission spectra upon varying excitation energy at room temperature.[1–3] According to these reports, 6-MQ is known to show a single emission band around 350–360 nm, the peak position being solvent dependent, and the spectra are red-shifted upon excitation at the long wavelength absorption (edge excitation red shift, EERS). As shown in Ref.[2] at excitation wavelengths longer than the absorption maximum, the emission from 6-MQ in glycerol-water (4:1) mixed solvents containing 0.02 N NaOH at 293 K shows a main band at 348 nm, the weak band at 440 nm appearing as shoulder. The longer wavelength band was attributed to the protonated species. Upon acidification, the longer wavelength band characteristic of protonated species alone appears. EERS effect observed both in acidic and basic media was attributed to the slow solvent reorientation rate ($\tau_r = 10$ ns) relative to emission rate ($\tau_f = 2.8$ ns).

During the course of our studies on fluorescence excitation and emission and decay of emission in various solvents, some new observations, as far as previous studies are concerned, emerged under experimental conditions somewhat different from those used earlier. The noteworthy features of the current study are as follows:

1. The absorption spectra of 6-MQ only, in hydrocarbon solvents such as cyclohexane, *n*-hexane, and isopentane, show well-resolved vibronic structure resembling very closely the excitation spectrum found by Itoh and Azumi[3] for this compound in EPA at 77 K. At room temperature, and for all solvents studied here, the corresponding excitation spectra are structureless, suggesting a large chromophoric geometry difference between the ground and fluorescent states.
2. The dual fluorescence is observed in all solvents under study but it is distinctly seen in water and binary solvents containing water. Cyclohexane and dioxane solutions show dual emissions at 350 nm and 440 nm, and a clear isoemissive point is detected in a series of emission spectra taken as a function of excitation wavelength λ_{ex}. As the λ_{ex} is raised just beyond 375 nm, only the longer wavelength band with the

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resolved vibronic structure is observed. Similar spectral features are found in dioxane–water solutions with a systematic variation of composition of solvents and also as a function of excitation wavelength. However, in the latter case, the long wavelength band at 440 nm does not show any vibronic structure. Thus the formation of long wavelength bands in these solutions may stem from the product of an adiabatic process in the excited state.

3. Fluorescence excitation spectra of 6-methoxy quinoline in cyclohexane and also in binary solvents show emission wavelength dependence, while in the case of water, the excitation spectra are the same for both the emissions.
4. Fluorescence decay, monitored over each emission maximum for most of the solutions, is characterized by a single component τ, while for a few others two components are obtained.
5. The fluorescence polarization factor as a function of λ_{ex} varies continuously over the entire range of emission, indicating the existence of more than one emitting species.

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EXPERIMENTAL

6-MQ was obtained from Merck (Germany) and used without further purification. All solvents were of spectroscopic grade (Fluka, USA) and were used as received. Doubly distilled water was used for the preparation of aqueous solutions. The purity of the solvents was checked before use by HPLC-MS. The fluorescence excitation and emission spectra were recorded using a Hitachi model F-2000 fluorescence spectrophotometer (Japan) setting an effective band pass at about 5 nm. A Hitachi model 3200 UV-Vis spectrophotometer (Japan) was employed for obtaining the absorption spectra. The fluorescence lifetimes were determined by a picosecond operated time-correlated single photon counting unit, which is described elsewhere.[4] The frequency doubled radiation at $\lambda_{ex} = 300$ nm derived from a cavity dumped rhodamine 6G dye laser synchronously pumped by a mode locked cw Nd-YAG laser (FWHM, 6–10 ps; repetition rate, 800 kHz) was used as a source of excitation. The fluorescence decays were analyzed using the maximum entropy method (MEM).[5] This method gives a distribution of lifetimes and the peak of the distributions is generally consistent with discrete lifetimes. The error in the lifetime measurements was around 3–5%.

RESULTS AND DISCUSSION

Absorption and Fluorescence Excitation Studies

Figure 1 shows the absorption spectra of 6-MQ (1×10^{-5} mol dm^{-3}) in typical solvents at room temperature along with the corrected excitation

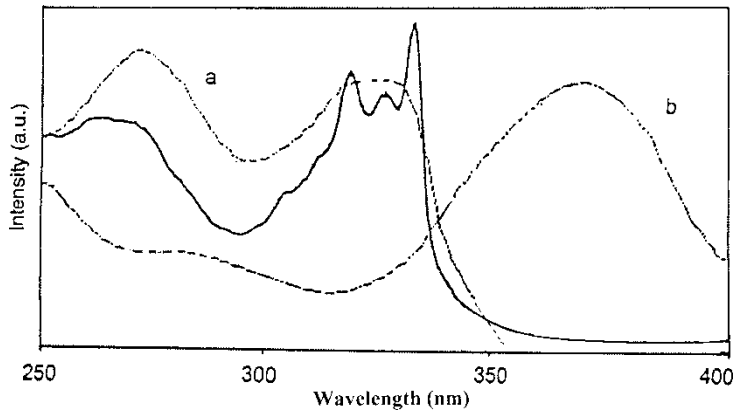

Figure 1. Comparison of absorption and excitation spectra of 6-MQ in cyclohexane at 1×10^{-5} mol dm^{-3}; absorption (thick line), excitation spectra detected at (a) 355 nm and (b) 440 nm.

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spectra of two fluorescence components in dioxane solution detected at 440 nm and 355 nm. The main absorption bands are located in the region 250–290 nm and 300–350 nm with peaks at about 271 and 320 nm, respectively. These bands as described in Ref.[6] belong to $^1L_a \leftarrow {}^1A$ and $^1L_b \leftarrow {}^1A$ transitions, where ^1L_a and ^1L_b are the two low-lying excited states in the singlet manifold of 6-MQ. The ^1L_a and ^1L_b states are, in fact, impure due to perturbation of the symmetry of the molecule caused by the methoxy substituent in position 6. The relative positions of the state depend very much on the polarity of the solvent. The mixing up of the vibration levels of the states under certain conditions might alter the fluorescence lifetime of 6-MQ. Transition to ^1L_b shows little or no vibronic structure in all solutions except cyclohexane, *n*-hexane, and isopentane, and the absorption spectra closely resemble the excitation spectra reported by Itoh and Azumi[3] for the same compound in EPA at 77 K, and such a structure probably arises due to weak solute–solvent interactions of general type such as polarization and dispersive force. The ^1L_a band, on the other hand, is broad and sensitive to solvent polarity. As the solvent polarity increases, the ^1L_a band is red-shifted with respect to that of cyclohexane, whereas ^1L_b band is slightly blue shifted. This shows that the energy gap between ^1L_a and ^1L_b will increase with increasing solvent polarity. The net result for 6-MQ in nonpolar solvents would be to reduce the level separation, leading to increase in the vibronic coupling in acidic solutions: the resultant spectrum is broad and more significantly extended toward longer wavelength compared to that of nonacidic solutions. The ^1L_a state undergoes larger shift in proportion to dielectric constant and is nearly degenerate with the ^1L_a state.

In polar solvents such as alcohols, acetonitrile, and water relative to nonpolar solvents such as cyclohexane, the absorption band is slightly

blue-shifted, reflecting the increased dipole moment in S_o-S_1 excitation. To understand the origin of emitting species, the excitation spectra were measured at different emission peaks for all solutions, and the results show that in case of cyclohexane, dioxane, and mixture of water–dioxane solutions, excitation spectra show emission wavelength dependence. Two distinct excitation spectra were obtained corresponding to emissions at 360 and 430 nm. The excitation spectrum of the emission at 350 nm resembles the absorption, whereas that at longer wavelength is structureless and considerably red-shifted relative to the first absorption band. Two distinct excitation spectra observed corresponding to two emission bands clearly indicate the formation of at least two distinct species in the ground state. In alcohol and aqueous solutions, the excitation spectra at $\lambda_{em} = 340$ and 440 nm are found to be the same for two emissions, indicating that both the distinct peaks have a common origin in the same compound. In all acidic solutions, both the absorption and the excitation spectra are the characteristic of protonated species. The spectra are broadened and red-shifted relative to that of neutral species. All the excitation spectra were measured at sufficiently low concentrations ($\sim 10^{-5}$ mol dm^{-3}) in order to avoid the possibility of spectral distortion at high concentrations. We believe that the broad and red-shifted nature of the excitation spectra relative to their corresponding absorption spectra may be associated with the geometrical changes in the compound after photoexcitation.

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Fluorescence Emission Studies

Fluorescence emission of 6-MQ in alcohols (ethanol, methanol, propanol, butanol), cyclohexane, dioxane, acetonitrile, dimethylformamide, water, and binary solvents of dioxane and water consists of two bands with their peak positions ranging from 350 to 375 nm (band I) and 431 to 440 nm (band II). The emissions corresponding to these bands arise from either ^1L_a or ^1L_b states or mixed ($^1L_a/^1L_b$) state depending on the solvent and the experimental conditions. In 6-MQ, although the energy of the ^1L_a is higher than the ^1L_b state, the locations and conformational changes occur mostly in cases where π-bonding interaction is possible. The detailed solvent-dependent behavior of these two states has been discussed in Refs.[7,8] in case of indoles. The spectral data corresponding to these two bands are collected in Table 1. We find that the peak positions of emission bands are solvent dependent and are red-shifted with increasing polarity of the solvent, indicating the increased basicity of the compound. In all the solvents studied here, except water, band I is relatively stronger than the band II. Concentration studies show that with increasing concentration in the range of 10^{-5}–10^{-3} mol dm^{-3}, the relative intensities of two bands do not change greatly, revealing that the long wavelength band is not associated with excimers. Dioxane solution shows the main band at

Table 1. Fluorescence emission characteristics of 6-methoxy quinoline in various solvents at 1×10^{-5} mol dm^{-3}

Solvents	λ_{ex} (nm)	λ_{em} (nm)	
Cyclohexane	300	351 (3003)	—
	345	355 (2021)	415 (177)
Dioxane	300	355 (7038)	—
	345	366 (6226)	431(4495)
Dioxane + 0.1 N H_2SO_4	300	—	442 (692)
	345	—	440 (796)
Dioxane + 0.1 N NaOH	300	360 (270)	—
	345	369 (208)	435 (16)
Ethanol	300	358 (548)	416 (16)
	345	363 (378)	430 (111)
Ethanol + 0.1 N H_2SO_4	300	—	436 (1115)
Ethanol + 0.1 N NaOH	300	359 (272)	—
Acetonitrile	300	358 (402)	—
Water	300	369 (376)	438 (649)
	345	377 (270)	442 (680)
Water + 0.1 N H_2SO_4	300	—	438 (842)
Water + 0.1 N NaOH	300	366 (138)	—

Quantities in parentheses are the relative intensities.

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350 nm and a weak structureless band at about 430 nm even at very low concentration (10^{-5} mol dm^{-3}). A series of emission spectra recorded as a function of excitation wavelength (λ_{ex}) ranging from 330 to 350 nm display a clear isoemissive point at 420 nm, reflecting the equilibrium between two distinct emitting species (Fig. 2). The peak position of the band is considerably red-shifted, whereas that of band II is slightly red-shifted upon the change of excitation wavelength from 300 to 350 nm. However, with $\lambda_{ex} = 375$ nm, which lies beyond the emission region of band I, the long wavelength band alone is observed. This finding clearly indicates that two emissions originate from different species originally formed in the ground state. Apart from this, the emission spectra of dioxane–water solutions display the quasi-isoemissive points with the variation of compositions of solvents, reflecting the quasi-equilibrium between two distinct emitting species. We observe that as the concentration of water increases in the mixture, the intensity of the longer wavelength band increases gradually and becomes relatively stronger compared to the low wavelength band. In all the solutions with acid content, band II alone was detected, and its spectrum resembles closely the spectrum as observed by the authors of Ref.[9] This band is obviously ascribed to the protonated species originally formed in the ground state. The protonation of 6-MQ by acid produces major changes in absorption and emission spectra. However,

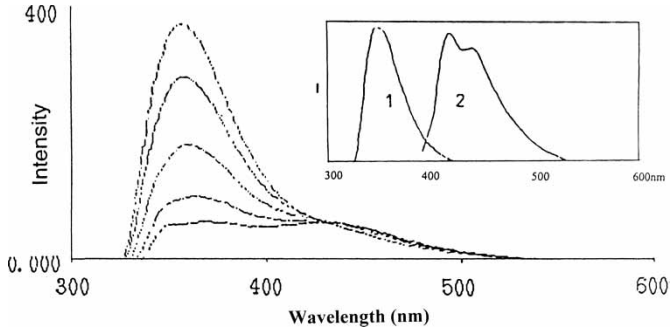

Figure 2. Fluorescence emission spectra of 6-MQ in dioxane at 1×10^{-4} mol dm^{-3} as a function of λ_{ex}, from top to bottom: 340, 342, 345, and 348 nm. Insert: Emission spectra of 6-MQ in cyclohaxane at 1×10^{-4} mol dm^{-3} with λ_{ex} (1) 320 nm and (2) 350 nm.

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the addition of NaOH to the solution does not affect the absorption and emission characteristics, and the spectral features are in favor of the formation of only the neutral species.

In case of cyclohexane solution, the curious observation is that with $\lambda_{ex} = 350$ nm, the long wavelength band II exhibits splitting, which may be ascribed to either the vibronic structure (spectra inserted in Fig. 2) or π-type interactions in 6-MQ or the charge distribution in the S_1 state due to the strength of solvation. Similar observation has been reported for coumarin 153 in cyclohaxane.[10] This band is attributed to the hydrogen-bonded species as it closely resembles the spectra of the protonated form, and the source of H-donor may be a small trace of proton present in the solution as an impurity.

Interestingly, in the case of ethanol, a typical polar protic solvent, band II is not enhanced either with the variation of concentration or the excitation wavelength. At room temperature, it seems that apart from dipole–dipole interactions, possibly specific H-bonding between the active sites and OH group of alcohol also takes place. Hydrogen-bonded molecules may undergo a partial proton transfer in the excited state, as H-bonding is likely to hinder the degree of protonation. If band II is assumed to be associated with protonation process, then its low intensity may be due to inefficiency of the photochemical transfer of proton from alcohol to 6-MQ. It is therefore concluded that with the exception of water, in all other polar solvents, the weak emission at 430 nm may be due to lesser degree of protonation. All this could lead to the formation of complexes between 6-MQ and ethanol. This is further confirmed by the superposition of the excitation spectra taken at various emission wavelengths with the corresponding absorption spectra of 6-MQ. The existence of the ground state of H-bonded species is not evident in absorption, perhaps owing to very low extinction coefficient.

It is interesting to note that only in the case of aqueous solutions, as can be seen from Fig. 3, two emission bands centered around 367 and 438 nm are observed upon short wavelength excitation ($\lambda_{ex} \sim 300$ nm). The peak positions of bands I and II are respectively red-shifted by 6 and 3 nm with the change of λ_{ex} from 300 to 340 nm. The ratio of emission intensities of the band II to the band I is found to increase linearly, and at $\lambda_{ex} \sim 340$ nm, only the long wavelength emission with enhanced intensity was detected and no isoemissive point was observed.

In order to check the effect of polarity on the emission behavior, dioxane–water mixture was chosen because of its high dielectric constant and hydrogen bonding ability. Such a system allows the possibility of varying the polarity continuously between two extremes and/or even beyond extremes corresponding to that of pure dioxane and water. In this system, as illustrated in Figs. 3 and 4, the relative intensity of two bands depends on both excitation wavelength as well as on the composition of component solvents in the mixture corresponding to that of pure dioxane and water. Figure 4 shows fluorescence spectra of 6 -MQ in dioxane with various amounts of added water. At the lowest concentration of water, as can be seen from figure, the fluorescence spectra show two bands. As the concentration is further increased, band I corresponding to normal species almost disappears while band II corresponding to species/exciplex dominates.

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Fluorescence Polarization Studies

It is well-known that the polarization measurements with linearly polarized light yield information on the orientation of molecules or transition dipole moments of molecules. The quantity most commonly measured in

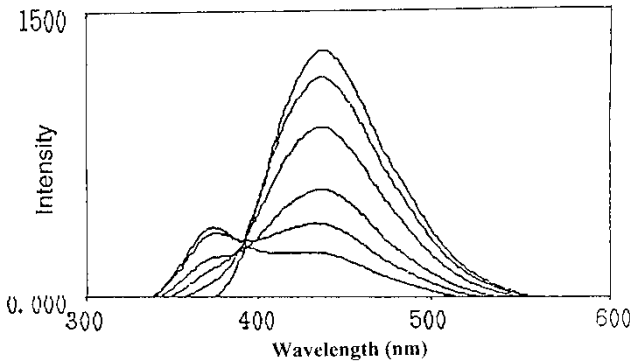

Figure 3. Excitation wavelength dependence of emission of 6-MQ in dioxane:water (4:6) at 1×10^{-4} mol dm^{-3} with λ_{ex}, (bottom to top on the long wavelength band): 275, 285, 300, 340, 345, and 355 nm.

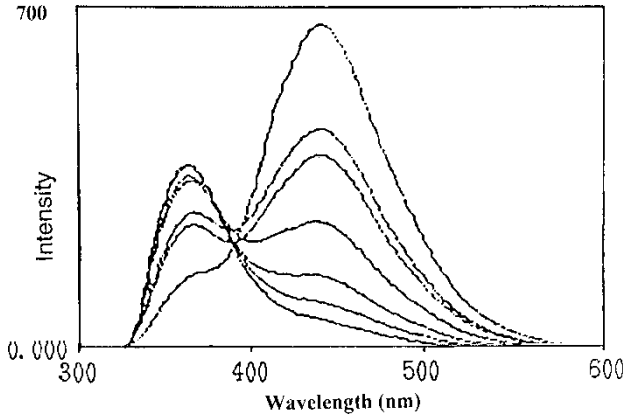

Figure 4. Fluorescence emission spectra of 6-MQ in dioxane + water as a function of water concentration. Concentration (top to bottom on the long wavelength band): 1.00, 0.83, 0.69, 0.56, 0.45, 0.40, and 0.35 M with $\lambda_{ex} = 300$ nm.

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fluorescence polarization studies is the fluorescence polarization degree P, which is expressed as

$$P = (I_{\parallel} - I_{\perp})/(I_{\parallel} + I_{\perp}) \tag{1}$$

where $I_{\parallel}$ and $I_{\perp}$ are respectively the fluorescence intensity for parallel and perpendicular polarization with respect to that of excitation. Cross or parallel polarization components were achieved by inserting a polarizer followed by half wave plate before the detection. The apparatus was calibrated with respect to its sensitivity for parallel and perpendicular components. The components $I_{\parallel}$ and $I_{\perp}$ were recorded separately and normalized during the processing of the data. A typical polarization spectrum along with the corresponding fluorescence emission spectra is shown in Fig. 5. We find that the polarization factor, P, varies continuously over the entire region of emission displaying four distinct regions. When the detector analyzer is polarized perpendicular to the excitation beam polarization, the intensity of the band I (340 nm) is enhanced while that of band II (440 nm) is reduced. This indicates that the emission of 6-MQ contains at least two differently polarized transitions. Polarization dependence of emission wavelength can be explained in terms of the shift of the energy levels during motion from perpendicular to the coplanar configuration. This result clearly indicates the overlapping transitions of different moment directions. In the spectral region of band I, the value of P increases toward zero value as wavelength increases. This finding reveals that the excitation and fluorescence transition dipole moments are not aligned and the emitting state is an overlapping state corresponding to those of two conformers. In the spectral region of band II (500–580 nm), the value of P changes from 0.00 to 0.12 toward

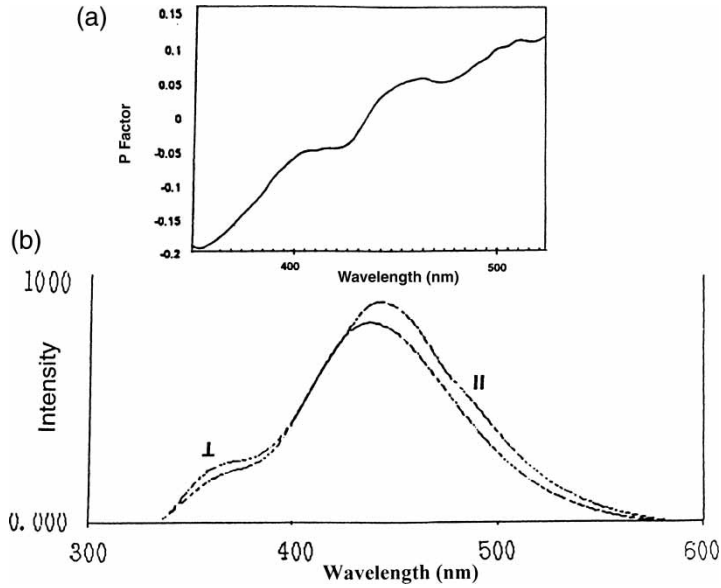

Figure 5. (a) Polarization spectra of 6-MQ in water at 1×10^{-4} mol dm^{-3} with $\lambda_{ex} = 340$ nm. (b) Emission spectra of 6-MQ at 1×10^{-4} mol dm^{-3} in parallel and perpendicular geometry with respect to excitation beam polarization.

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higher wavelength. The high degree of polarization indicates that the transition dipole moments are basically in the same direction, the emitting state is very probably of $\pi\pi^*$ character of the ($^1L_a/^1L_b$) state. When excitation and emission dipoles are parallel, according to the theory, $P = 0.4$[11]; in practice, this value is rarely observed. The polarization spectrum shows four distinct regions, which can be identified with four distinct excited species.

Fluorescence Lifetime Studies

The fluorescence decays were measured at two emission wavelengths, 360 nm and 430 nm, corresponding to the peak positions of band I and band II, respectively, keeping the excitation wavelength at 300 nm. Fluorescence decay for each emission was fitted to a biexponential function.

$$I(t) = a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2) \tag{2}$$

where τ_1 and τ_2 are the lifetimes of the two decay components and a_1 and a_2 are their respective amplitudes such that $a_1 + a_2 = 1$. The parameters of the biexponential fit are listed in Table 2. As can be seen from Table 2, the decay parameters depend on the emission wavelength and the nature of the solvent. For each emission in the current solutions, there is a large difference between the two lifetimes τ_1 and τ_2 and their relative amplitudes

Table 2. Fluorescence lifetimes of 6-methoxy quinoline in different solvents at 1×10^{-4} mol dm^{-3} ($\lambda_{ex} = 300$ nm)

Solvents	λ_{em} (nm)	τ_1 (ns)	τ_2 (ns)	τ_{av} (ns)	χ^2
Cyclohexane	360	1.01 [0.08]	0.29 [0.92]	0.36	1.73
Dioxane	355	1.93 [0.05]	0.48 [0.95]	0.56	1.55
Ethanol	360	3.38 [0.11]	2.00 [0.89]	2.16	1.19
	430	4.27 [0.15]	2.39 [0.85]	2.67	1.06
Acetonitrile	360	2.55 [0.30]	1.48 [0.70]	1.80	1.33
Water	369	3.41 [0.06]	1.65 [0.94]	1.75	1.12
	430	21.62 [0.90]	17.75 [0.10]	21.23	1.36
Water + 0.1 N H_2SO_4	430	21.81 [0.95]	14.10 [0.05]	21.40	1.31
Water + 0.1 N NaOH	369	4.10 [0.26]	1.45 [0.74]	2.14	0.92
Dioxane:H_2O					
1:9	360	4.37 [0.06]	2.46 [0.94]	2.60	1.11
	430	21.24 [0.84]	4.40 [0.16]	18.60	1.06
2:8	360	4.30 [0.23]	2.72 [0.77]	3.08	1.01
	430	20.94 [0.98]	5.02 [0.20]	17.73	1.29
3:7	360	5.20 [0.18]	2.89 [0.82]	3.30	1.07
	430	20.36 [0.72]	4.20 [0.28]	15.80	1.32
4:6	360	6.06 [0.12]	2.96 [0.88]	3.34	0.99
	430	19.90 [0.70]	4.10 [0.30]	15.10	1.41
5:5	360	5.34 [0.18]	2.70 [0.82]	3.17	1.06
	430	19.50 [0.47]	4.20 [0.53]	11.40	1.27

Quantities in brackets are relative amplitudes.

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a_1 and a_2. It is also seen that with the change of solvent from nonpolar cyclohexane to highly polar acetonitrile or water, both τ_1 and τ_2 and fluorescence quantum yield increase, indicating that the decays are controlled by solvent polarity/viscosity. Note that the relative intensities of bands I and II are almost consistent with the amplitudes. In all solvents except water, for emission at 360 nm, $\tau_1 \gg \tau_2$ and $a_2 \ll a_1$. In case of ethanol, for both emissions, the fast decay component is the dominant one with $a_2/a_1 = 5$ to 8. The average lifetime, $\langle \tau_f \rangle = \tau_1 a_1 + a_2 \tau_2$ obtained in the current work agrees closely with the previously reported value of $\tau_f = 2.8$ ns.[9] In case of cyclohexane and dioxane, we measured the decay of 360-nm emissions only as the 430-nm emission was too weak to be detected.

In case of water, acidic water, and dioxane–water solutions, the emission decay (τ_1, τ_2) and the amplitudes (a_1, a_2) at two wavelengths differ dramatically. For example, at 360-nm emission, 5–20% of the intensity decays with a time constant of 2–7 ns (τ_1), and 70–90% of the fluorescent intensity decays with a time constant of ~1–3 ns (τ_2). However, for emission at 430 nm, both the decay times increase considerably while the relative contributions get reversed [$\tau_1 \sim 20$ ns (50–90%); $\tau_2 \sim 4$ ns (10–50%)].

In contrast to the decay behavior found in ethanol and other solutions, for 430-nm emissions from water and water–dioxane solutions, τ_1 becomes dominant, and low intensity component τ_2 increases greatly ($\tau_1 = 21$ ns, $\tau_2 = 14$ to 17 ns). τ_1 values of the current work agree closely with earlier reported value of 22.8 ns.[6] These long-lived components are attributed to protonated complexes/H-bonding complexes. The positive amplitudes obtained within the spectral region investigated indicate that both the emissions corresponding to these species decay independently.

CONCLUSIONS

The fluorescence emission bands I and II are respectively attributed to the coexistence of normal and protonated/H-bonded species. Associated with each emission, two different decay components with different positive amplitudes were obtained, and the fluorescence polarization varies drastically over the region of two emissions. For example, in the steady-state fluorescence polarization studies, the value of polarization factor P is low and varies from 0.15 to -0.20. These findings reflect electronic depolarization by partial conversion of locally excited ^1L_a state to the ^1L_b via a large number of intermediate configurations. The excitation wavelength dependence of emission and also different excitation spectra monitored over different emissions in some solutions suggest the existence of at least two distinct species in the ground and the excited states. In case of water solution, however, the same excitation spectrum was obtained for both emissions, indicating that the absorption takes place by the same species, but the fluorescing states/species being different. In some solutions, particularly for 430 nm emissions, the excitation spectra are considerably red-shifted relative to the absorption spectra. This fact implies that the interconversion between two species is appreciable in the excited states. These experimentally observed trends could be understood as follows:

(i) Because the dominant decay component (τ_1) of 430-nm emission is considerably longer than that of 360 nm emission, these emissions are assigned to ^1L_b and ^1L_a states, respectively. This assignment is based on the fact that ^1L_b is forbidden while ^1L_a is allowed in nature. The observed dual decay components can be explained by assuming the interference from overlapping of ^1L_b and ^1L_a emissions coming from the neighboring species. Consequently, at the detection wavelength, each emission may contain a small fraction of the other emission. However, this is not in accordance with the variation of decay amplitudes as evidenced from Table 2. For example, in dioxane–water solution, a_1 and a_2 values are nearly equal in contrast to the behavior of relative intensities of ^1L_b and ^1L_a emissions. We therefore conclude that our assumption that the

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dual decay components result from the mixing up of emissions from two states of the two different species is not correct.

(ii) In absorption spectra of neutral or cationic species, ^1L_a band is well separated from ^1L_b band, whereas in emission these bands exhibit composite nature. Geometrical change and solvent relaxation upon photoexcitation play a major role in the modification of emission characteristics. If these states become very nearly degenerate, it would be possible to excite both simultaneously. If the solvent and experimental conditions are such that thermal equilibrium is established between them, then the emission from both states are expected at the same wavelength. In this case, when the detection wavelength

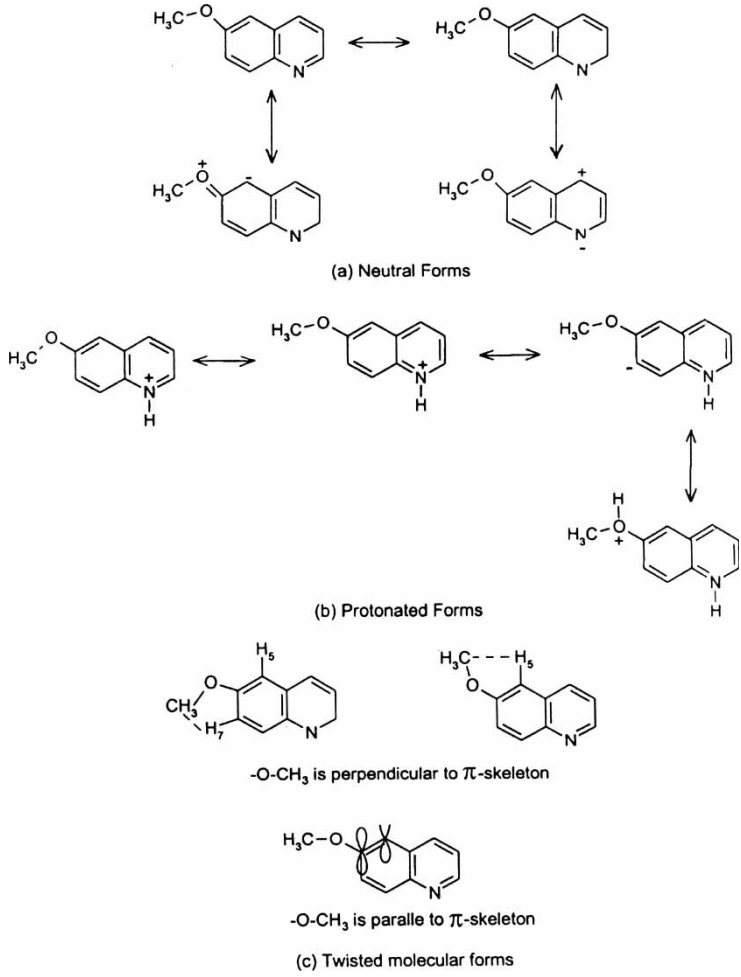

Figure 6. Possible resonance structures of 6-methoxy quinoline.

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corresponds to the maxima of the composite band, dual decay components may be obtained corresponding to these two states. There is a possibility of interconversion of ^1L_a state into ^1L_b via solvent relaxation and/or geometrical relaxation. Therefore, the ^1L_b is populated by both direct excitations as well as by interconversion. When the two emitting states are almost degenerate, each emission is an admixture of ^1L_a and ^1L_b states of isolated molecules resulting in different decay components. The dependence of emission on the excitation energy may be related to the geometrical relaxation process.

(iii) The data clearly indicate the composite nature of each emission band, which presumably results from the overlap of two different electronic transitions corresponding to two different conformers in each species. In this molecule, the conformational change is assumed to arise from the twisting of methoxy group with respect to the chromophore. Upon excitation, electron transfer can take place from methoxy group to the aromatic ring, and the corresponding state gets a charge transfer character. It is quite possible that the molecule adapts a suitable geometry or conformation, which is favorable to the charge transfer process. In the absence of theoretical studies, we predict that the methoxy group may exhibit a hypothetical twist about the molecular plane; this motion producing nonplanarity with the change in the transition moment direction. The proposed structures for the molecule are shown in Fig. 6.

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In conclusion, two decay components for each emission are due to two different conformations of the corresponding species, which are distinguishable from lifetimes and polarization measurements. However, to identify the fluorescing states, further studies on the time-resolved fluorescence anisotropy measurements and on the characterization conformers are underway.

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REFERENCES

1. Itoh, K.; Azumi, T. Shift of emission band upon excitation at the long-wavelength absorption edge. I. A preliminary survey for quinoline and related compounds. *Chem. Phys. Lett.* **1973**, *22* (2), 395–399.

2. Itoh, K.; Azumi, T. Shift of the emission band upon excitation at the long-wavelength absorption edge. II. Importance of the solute-solvent interaction and solvent reorientation relaxation process. *J. Chem. Phys.* **1975**, *62* (9), 3431–3438.
3. Azumi, T.; Itoh, K.; Shiraishi, H. Shift of emission band upon the excitation at the long-wavelength absorption edge. III. Temperature dependence of the shift and correlation with the time dependent spectral shift. *J. Chem. Phys.* **1976**, *65* (7), 2550–2555.
4. Dutt, G. B.; Doraiswamy, S.; Periyasamy, N. Molecular reorientation dynamics of polar dye probes in tertiary-butyl alcohol-water mixtures. *J. Chem. Phys.* **1991**, *94* (8), 5360–5368.
5. Brochon, J. *Methods in Enzymology*; Academic Press: London, 1994; Vol. 240.
6. Schulman, S. G.; Capomacchia, A. C. Dual fluorescence of quinolinium cation. *J. Chem. Soc.* **1973**, *95* (9), 2763–2766.
7. Arnold, S.; Sulkes, M. Spectroscopy of solvent complexes with indoles: Induction of $^1L_a - {}^1L_b$ state coupling. *J. Phys. Chem.* **1992**, *96* (12), 4768–4778.
8. Tubergen, M. J.; Levy, D. H. Spectroscopy of indol van der waals complexes. Evidence for a conformation-dependent excited state. *J. Phys. Chem.* **1991**, *95* (6), 2175–2181.
9. Ikeyama, J.; Azumi, T. Shift of emission band upon excitation at long-wavelength absorption edge, time-dependent fluorescence shift of a fluid ethanol solution of 6-methoxy quinoline. *Chem. Phys. Letts.* **1983**, *96* (4), 419–421.
10. Maroncelli, M.; Fleming, G. R. Picosecond solvation dynamics of coumarin 153: The importance of molecular aspects of solvation. *J. Chem. Phys.* **1987**, *86* (11), 6221–6239.
11. Kliger, D. S.; Lewis, J. W.; Randall, C. E. *Polarized Light in Optics and Spectroscopy*; Academic Press: NY, 1990, Chap. 6, 185–190.

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