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Excited-State Protonation and Photophysical Properties of Azaphenanthrenes

Charles J. Marzzacco,* George Deckey, Rosemary Colarulli, Gary Siuzdak,

Department of Physical Science, Rhode Island College, Providence, Rhode Island 02908

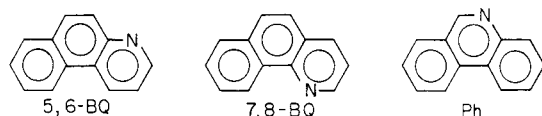
and Arthur M. Halpern

Department of Chemistry, Northeastern University, Boston, Massachusetts 02115 (Received: May 19, 1988;
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The photophysical properties of 5,6-benzoquinoline (5,6-BQ), 7,8-benzoquinoline (7,8-BQ), and phenanthridine (Ph) have been investigated in aqueous solutions at 296 K. Fluorescence lifetimes and quantum yields for both the free base and conjugate acid forms of the molecules have been determined. Rate constants for excited-state protonation by water and by NH_4^+ have also been determined. It is found that the rate constant for protonation by D_2O is one-third as large as that by H_2O . The addition of methanol to the solvent has the effect of decreasing the rate of solvent-assisted protonation while the addition of Mg^{2+} , Li^+ , or Na^+ ions increases the rate. The former result is consistent with excited-state-deprotonation reactions in naphthols while the latter is contrary to what is observed for such reactions.

Introduction

In this study, we examine the photophysical properties and the kinetics of the protonation of the azaphenanthrenes 5,6-benzoquinoline, 7,8-benzoquinoline, and phenanthridine in their lowest excited singlet states in aqueous solutions.



Although these molecules are expected to have low-lying excited states of $n\pi^*$ character, they are all similar to phenanthrene in having lowest energy excited singlet states of $^1L_b \pi\pi^*$ character.¹⁻³ They are all weak bases in their ground states with the pK_a s of their conjugate acids being 5.1, 4.2, and 4.6 for 5,6-BQ, 7,8-BQ, and Ph, respectively.^{1,4,5} They are strong fluorophores in protic solvents and show large red shifts in their spectra upon protonation.^{1-3,5-7} Application of the Forster cycle to these shifts indicates that the molecules are much stronger bases in their lowest excited singlet states. Values on the order of 10–11 have been reported for the pK_a^* of 5,6-BQ and 7,8-BQ,^{1-3,5,7} while a value of 9.6 has been reported for Ph.¹

As a result of the increase in basicity upon going from the ground to the excited singlet state, these molecules are able to undergo excited-state protonation under suitable conditions of pH. Nakamizo determined the rate constant for the protonation of

TABLE I: Lifetimes, Fluorescence Quantum Yields, and Radiative and Nonradiative Rate Constants for Free Base and Conjugate Acid Forms of Ph, 5,6-BQ, and 7,8-BQ

	Ph	5,6-BQ	7,8-BQ
τ , ns	10.2	8.4	9.1
Φ^0	0.19	0.30	0.28
k_f , s^{-1}	1.8×10^7	3.6×10^7	3.1×10^7
k_{nr} , s^{-1}	8.0×10^7	8.3×10^7	7.9×10^7
	PhH^+	5,6-BQH ⁺	7,8-BQH ⁺
τ , ns	10.3	9.4	9.8
Φ^0	0.28	0.53	0.27
k_f , s^{-1}	2.7×10^7	5.6×10^7	2.8×10^7
k_{nr} , s^{-1}	7.0×10^7	5.0×10^7	7.4×10^7

singlet excited 5,6-BQ by water from steady-state measurements of the relative fluorescence intensities of the free base and the conjugate acid as a function of pH.⁵ In this analysis, a value for the fluorescence lifetime of the free base in the absence of protonation was needed. Nakamizo estimated the fluorescence lifetime from the measured quantum yield and the integrated intensity of the lowest energy absorption band. Since such estimates of lifetimes may be in error, the reliability of Nakamizo's value is questionable. In view of the fact that no further attempts have been made to study the excited-state protonation of these molecules, we have undertaken a systematic study of the kinetics of excited-state protonation of these azaphenanthrenes in aqueous solutions.

Results and Discussion

The fluorescence spectra of 5,6-BQ in basic and acidic aqueous solutions are shown in Figure 1 and are attributed to emissions from the free base and the conjugate acid forms of the molecule, respectively. The two other azaphenanthrenes show similar spectral behavior, although the difference in the λ_{max} between the free base and conjugate acid emissions of Ph is somewhat smaller than that in the other two molecules. This fact is reflected in the

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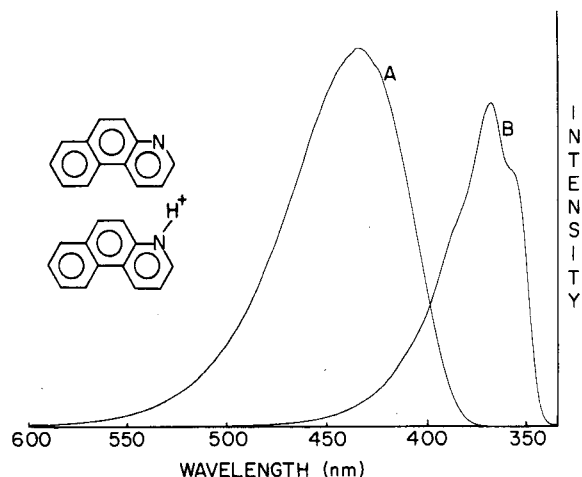


Figure 1. Fluorescence spectra of 5,6-benzoquinoline in 0.10 M HClO_4 (A) and in 0.20 M NaOH (B) excited at 320 nm at 296 K. The latter is the spectrum of the free base and the former is that of the conjugate acid.

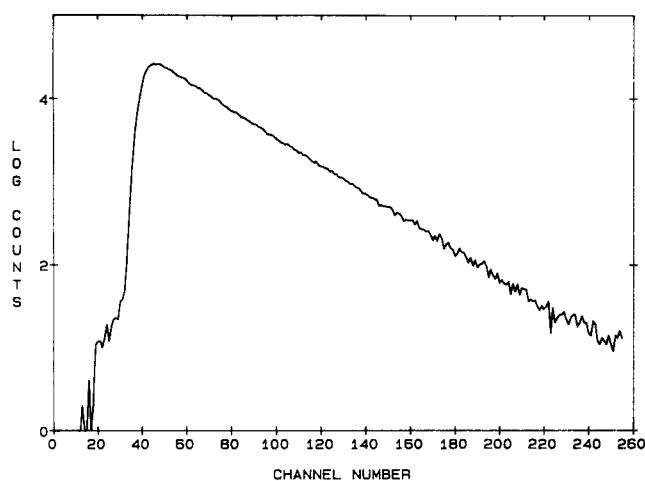


Figure 2. Fluorescence decay curve for 5,6-BQ in 0.20 M NaOH solution. The sample was excited at 320 nm, and the emission was monitored at 360 nm. The time scale is 0.35 ns per channel. The fluorescence lifetime was 8.4 ns and the χ^2 fit was 1.65.

smaller change in $\text{p}K_a$ upon excitation in Ph relative to the other two molecules.¹

The fluorescence decay curve for 5,6-BQ in basic aqueous solution is shown in Figure 2. Decay curves for both the free base and conjugate acid forms of the molecules exhibit single-exponential behavior with χ^2 values typically below 3.0. The lifetimes and fluorescence quantum yields for the free base molecules as well their conjugate acids are listed in Table I along with the fluorescence and nonradiative rate constants. Although the three free base molecules have similar lifetimes, the fluorescence quantum yield of Ph is only about two-thirds as large as those of the other two molecules. This is reflected in a smaller rate constant for fluorescence, a result consistent with the relative strengths of the first absorption band for the three systems. The three molecules have similar nonradiative rate constants.

Although the three protonated molecules have similar lifetimes, the fluorescence quantum yield of 5,6-BQH⁺ is about twice that of the other two ions. This is largely due to a fluorescence rate constant that is twice that in the other two ions, a result also consistent with the relative absorption strengths of the three systems.

The fluorescence spectra of 5,6-benzoquinoline in aqueous sodium hydroxide and in aqueous solutions of varying concentrations of ammonium acetate are shown in Figure 3. The fluorescence spectrum of 5,6-BQ in 0.20 M NaOH (spectrum A) has λ_{max} at 369 nm and is attributed to emission from the free base form of the molecule. The fluorescence spectra of 5,6-BQ

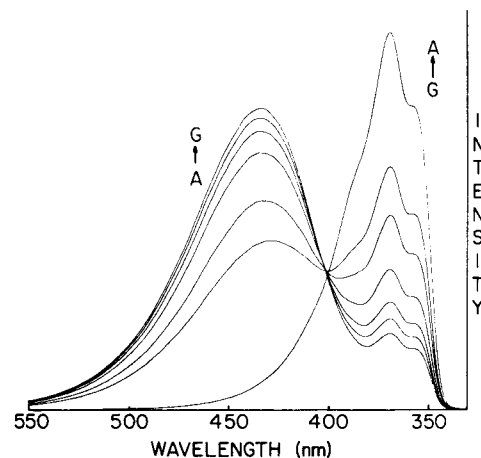


Figure 3. Fluorescence spectra of 5,6-BQ in 0.20 M NaOH (A) and in solutions of increasing concentrations of NH_4OAc at 296 K excited at 320 nm. The concentrations of NH_4OAc are 0.050 (B), 0.10 (C), 0.20 (D), 0.30 (E), 0.40 (F), and 0.50 M (G). The ionic strength of solutions B–G was kept constant at 0.50 M with NaOAc .

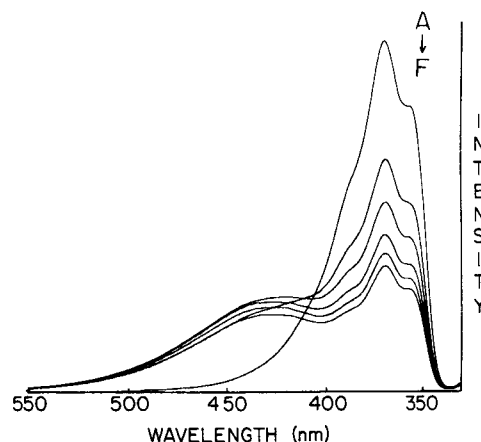


Figure 4. Fluorescence spectra of 7,8-BQ in 0.20 M NaOH (A) and in solutions with the following concentrations of NH_4OAc : 0.10 (B), 0.20 (C), 0.30 (D), 0.40 (E), and 0.50 M (F). The ionic strength of solutions B–F was kept constant at 0.50 M with NaClO_4 .

in solutions of varying concentrations of ammonium acetate (maintained at a constant ionic strength of 0.50 M with sodium acetate) show the 369-nm emission band, as well as another band with λ_{max} at 435 nm, which is characteristic of emission from the conjugate acid form of 5,6-BQ. Since these latter solutions are in the pH range of 7.00–7.35, and all display absorption spectra which are identical with that of 5,6-BQ in basic solution, namely, that of free base 5,6-BQ, it is clear that some of the molecules are undergoing protonation in the excited state. Increasing the concentration of the ammonium acetate has the effect of decreasing the intensity of the free base emission band and increasing the intensity of the conjugate acid band; an isostilbic point is observed at 400 nm. We attribute this observation to the protonation of the excited 5,6-BQ molecule by the ammonium ion. It will be shown that some protonation of the excited 5,6-BQ molecules by water also occurs.

Although increasing concentrations of ammonium acetate produce similar changes in the fluorescence spectra of 7,8-BQ and Ph, the resulting fluorescence intensity of the conjugate acid in these two systems does not reach the high intensity that it does for 5,6-BQ. Although this can be attributed in part to the lower quantum yield of fluorescence of the conjugate acid forms of 7,8-BQ and Ph relative to that of 5,6-BQ, fluorescence quenching of the conjugate acid forms of 7,8-BQ and Ph by acetate ions appears to be the main cause of this observation. This conclusion is based on the observation that when the concentration of the acetate ion is not kept constant, 7,8-BQ and Ph do not exhibit an isostilbic point. This is also true for 5,6-BQ but to a lesser

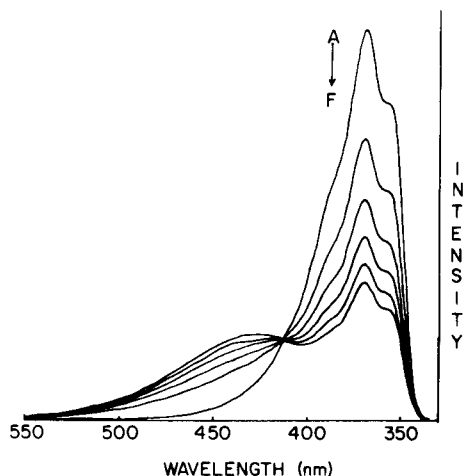
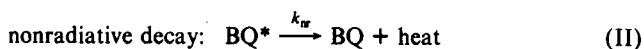
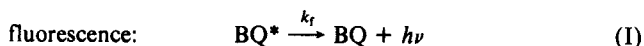
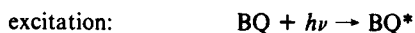


Figure 5. Fluorescence spectra of 7,8-BQ in 0.20 M NaOH (A) and in solutions with the following concentrations of NH_4OAc : 0.10 (B), 0.20 (C), 0.30 (D), 0.40 (E), and 0.50 M (F). The ionic strength of solutions B–F was kept constant at 0.50 M with NaOAc.

extent. This is illustrated in Figure 4, which shows the spectra of 7,8-BQ in solutions with varying concentrations of ammonium acetate, but with sodium perchlorate used instead of sodium acetate to maintain a constant ionic strength. Although the initial additions of ammonium acetate cause an increase in the conjugate acid emission band at 435 nm, further increases in the concentration result in a decrease in the intensity of this band. However, when sodium acetate is used to maintain a constant ionic strength (see Figure 5), an isosbestic point is observed and the conjugate acid emission band shows a steady increase with increasing concentrations of ammonium acetate. We interpret these observations to be the result of quenching of the fluorescence of the conjugate acid forms of 7,8-BQ and Ph (and 5,6-BQ to a lesser extent) by acetate ions. To further substantiate this interpretation, we measured the fluorescence lifetime of the conjugate acid forms of each molecule in 3:1 acetic acid/sodium acetate buffers of various strengths. Each solution was maintained at a constant ionic strength of 0.60 M with appropriate additions of sodium perchlorate. In each case the conjugate acid was directly excited, and a decrease in the fluorescence lifetime with increasing acetate concentration was observed. The application of Stern–Volmer kinetics to the three systems provides acetate fluorescence quenching constants of 6×10^7 , 6×10^7 , and $9 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$ for 7,8-BQ, Ph, and 5,6-BQ, respectively. It should be noted that the Stern–Volmer plots showed some scatter and produced correlation coefficients of 0.973, 0.997, and 0.986, respectively.

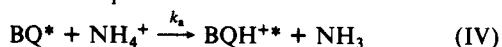
We have determined the rate constants for the excited-state protonation of the three azines by application of a modified Stern–Volmer kinetic scheme. The mechanism shown below illustrates the method that was used to analyze the data:



solvent-assisted protonation:



ammonium ion assisted protonation:



It should be noted that the reverse processes for the third and fourth steps can be neglected when the reaction takes place in ammonium acetate/sodium acetate solutions because the concentrations of OH^- and NH_3 are so low that the probability of them occurring before the BQH^{+*} decays to the ground state would be negligible even if they are diffusion-controlled reactions. The deprotonation of BQH^{+*} by acetate to produce BQ^* can also

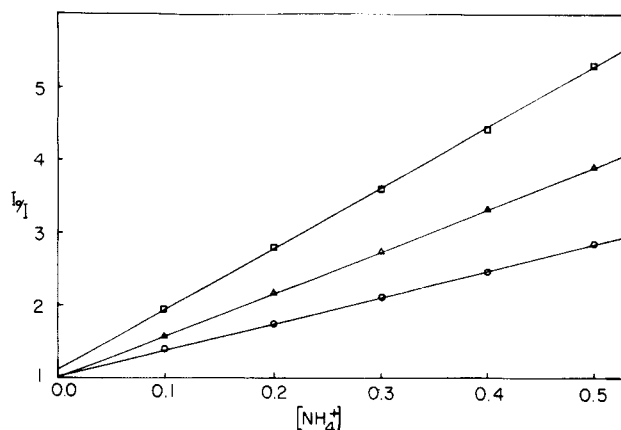
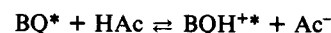


Figure 6. Stern–Volmer plots for the fluorescence quenching of free base 5,6-BQ (\square), 7,8-BQ (\circ), and Ph (Δ) by NH_4^+ at 296 K. I_0 refers to the fluorescence intensity of the free base in a 0.20 M NaOH solution.

be shown to be insignificant. We base this conclusion on the magnitude of the equilibrium constant for the reaction



The equilibrium constant for this reaction is calculated to be on the order of 2×10^7 from the K_a^* of BQH^{+*} and the K_a of acetic acid. Therefore, even if it is assumed that the forward reaction is diffusion controlled, the rate constant for the reverse reaction could only be on the order of 10^2 – $10^3 \text{ L mol}^{-1} \text{ s}^{-1}$. It can therefore be concluded that the reverse reaction is unimportant under the conditions of the experiment.

When 5,6-BQ is photoexcited in solutions containing sodium hydroxide, only steps I and II are important, and steps III and IV can be neglected. The molecule cannot become protonated by NH_4^+ , since none is present, and whatever molecules become protonated by water will be immediately deprotonated by the hydroxide ion. Therefore, the quantum yield of fluorescence of the free base is given by

$$\Phi^0 = k_f / (k_f + k_{nr}) \quad (1)$$

In the presence of ammonium acetate, the third and fourth steps also become important and the quantum yield of fluorescence is given by

$$\Phi = k_f / (k_f + k_{nr} + k_p + k_a[\text{NH}_4^+]) \quad (2)$$

Dividing Φ^0 by Φ , we obtain the result

$$\Phi^0 / \Phi = 1 + k_p / (k_f + k_{nr}) + k_a[\text{NH}_4^+] / (k_f + k_{nr}) \quad (3)$$

Since the ratio of the quantum yields of fluorescence is equal to the ratio of the fluorescence intensities of the free base and since the reciprocal of $(k_f + k_{nr})$ is equal to the fluorescence lifetime in the absence of excited-state protonation, the following relationship results:

$$I_0/I = 1 + k_p\tau_0 + k_a\tau_0[\text{NH}_4^+] \quad (4)$$

Therefore, a plot of I_0/I vs $[\text{NH}_4^+]$ should yield a straight line from which k_a and k_p can be determined from the slope and intercept, respectively. The plots for the three molecules are shown in Figure 6 and are found to show good linearity. The intercept for 5,6-BQ is greater than 1.0 while those of the other two molecules do not differ from 1.0 within the precision of the measurements. Accordingly, only an upper limit can be placed on the k_p values for these molecules. The magnitude of the slopes also show significant differences with 5,6-BQ having the largest and 7,8-BQ having the smallest. These values are reflected in the associated values of the rate constants for protonation by the ammonium ion.

Since the intercepts for the plots are so close to 1.0, it is not possible to get a good estimate for the rate constants for solvent-assisted protonation, especially in the cases of 7,8-BQ and Ph. In order to get a better estimate for such rate constants, a

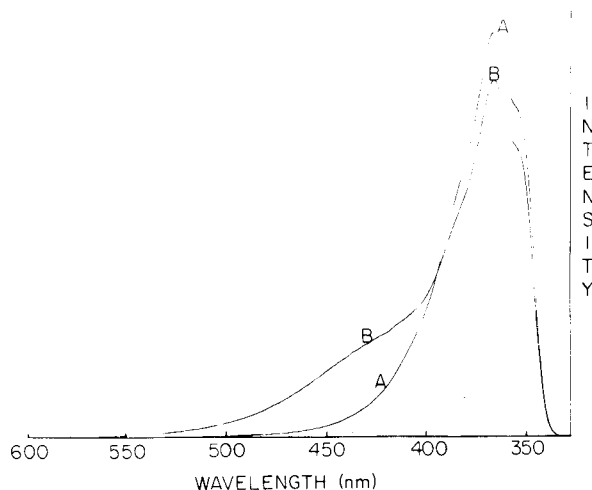


Figure 7. Fluorescence spectrum of 5,6-BQ in 0.20 M NaOH and in 0.020 M NaOAc at 296 K excited at 320 nm.

TABLE II: Rate Constants for Water-Assisted, k_p , and Ammonium Ion Assisted, k_a , Protonation of Excited Ph, 5,6-BQ, and 7,8-BQ at 296 K^a

	Ph	5,6-BQ	7,8-BQ
k_p, s^{-1}	1×10^6 (1×10^6)	1.7×10^7 (1.8×10^7)	3×10^6 (3×10^6)
$k_a, L \cdot mol^{-1} s^{-1}$	5.7×10^8	9.9×10^8	4.0×10^8

^a The values in parentheses were obtained from the lifetime changes through application of eq 6.

more sensitive method has been employed. The spectra in Figure 7 illustrate this method. Spectrum A is that of 5,6-BQ in 0.20 M NaOH and shows the emission of the free base only. Spectrum B is for 5,6-BQ in a 0.020 M NaAc solution. The NaAc is added to make the solution slightly basic in order to ensure that only the free base form of 5,6-BQ is initially present. The absorption spectrum of solution B confirms this. Although no conjugate acid is initially present in either solution, the spectrum of the second solution shows emission from both the free acid and the conjugate base. From the decrease in intensity of the free base peak at 369 nm or from the decrease in the fluorescence lifetime, the rate constant for solvent-assisted protonation can be determined. Since water-assisted protonation should be an irreversible process under such conditions, the following relationships apply:

$$\Phi^0/\Phi - 1 = I_0/I - 1 = k_p/(k_f + k_{nr}) = k_p\tau_0 \quad (5)$$

$$\tau_0/\tau - 1 = k_p/(k_f + k_{nr}) = k_p\tau_0 \quad (6)$$

We have used these relationships to determine k_p for the three azines. The values of k_p obtained this way, along with the values of k_a obtained from the plots of I_0/I vs $[NH_4^+]$, are shown in Table II. As can be seen from the table, the values of k_p obtained from the fluorescence intensity measurements (eq 5) are in good agreement with those obtained from lifetime measurements (eq 6).

The values for the rate constants for water-assisted protonation, k_p , are shown in Table II. The value of $1.7 \times 10^7 s^{-1}$ that we obtain for the protonation of excited 5,6-BQ by water compares with a value of $7.2 \times 10^6 s^{-1}$, which was obtained by Nakamizo.⁵ Nakamizo's value differs from ours because his fluorescence lifetime of 16.6 ns, which was obtained from the measured quantum yield and an estimate of k_f from the integrated absorption spectrum, is roughly twice our measured value. If we apply our fluorescence lifetime to Nakamizo's results, a value of $1.5 \times 10^7 s^{-1}$ is obtained. The k_p values of 1.7×10^7 , 3×10^6 , and $1 \times 10^6 s^{-1}$ that we obtained for 5,6-BQ, 7,8-BQ, and Ph, respectively, can be compared with values of $2.9 \times 10^8 s^{-1}$ and $1.2 \times 10^7 s^{-1}$ recently reported for 6-methoxyquinoline and acridine, respectively.¹³

The variation in the k_p values among the three molecules is consistent with the ordering of their excited-state basicities as determined by the Forster cycle method. Our values of pK_a^*

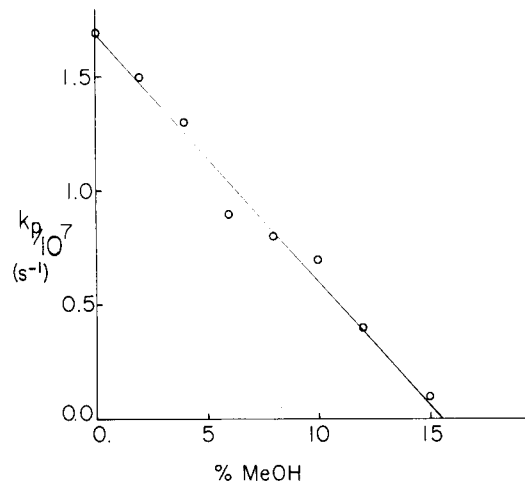


Figure 8. Plot of the rate constant for solvent protonation vs the volume percent of methanol in the solvent.

obtained by this method are 11.4, 10.6, and 10.1 for 5,6-BQ, 7,8-BQ, and Ph, respectively.

The rate constants for ammonium ion assisted protonation, k_a , are also shown in Table II. These second-order rate constants are all well below the diffusion-controlled limit. It is interesting to note that the relative ordering of these rate constants is different than that found for the k_p values. Although the rate constant for protonation by ammonium ion is largest for 5,6-BQ as before, 7,8-BQ replaces Ph in having the smallest value. The reversal in the ordering for 7,8-BQ and Ph may be due to a greater amount of steric hindrance of the ammonium ion by the adjacent hydrogen atom. Such steric hindrance is expected to be greater in 7,8-BQ.

We have also measured the rate constant for the excited-state protonation of 5,6-BQ in D_2O . From the decrease in the fluorescence intensity of free bases 5,6-BQ upon going from 0.20 M NaOH to 0.02 M NaAc, and the measured fluorescence lifetime of the free base (8.7 ns), we obtain a rate constant of $4 \times 10^6 s^{-1}$ for the k_p in D_2O . A value of $5 \times 10^6 s^{-1}$ is obtained from changes in the lifetime upon going from the 0.20 M NaOH solution to 0.02 M NaAc solution. The reduction in k_p upon going from H_2O to D_2O is similar to that found for acridine.¹³ Reductions in the excited-state solvent-assisted deprotonation rate constants of naphthols upon going from H_2O to D_2O are also found to decrease by a similar amount.¹¹

We have also investigated the effect of the presence of small amounts of methanol in the solvent on the rate constants for excited-state solvent-assisted protonation. This was done by comparing the free base fluorescence intensity of 5,6-BQ in 0.20 M NaOH with that in 0.020 M NaAc with each solution having the desired amount of alcohol present. We find that the presence of alcohol results in a substantial decrease in the rate of protonation to the point where it can no longer be measured at 15% methanol. The results are plotted in Figure 8.

The effect of alcohol on the excited-state-deprotonation reactions of naphthols and hydroxypyrenes has been extensively studied.⁸⁻¹¹ It has been shown that alcohols are effective in diminishing the rate constants for such solvent-assisted-deprotonation reactions. This result has been interpreted as being due to a breaking of the water structure by the organic solvent. It would appear that a similar interpretation can be applied to the protonation reactions of the azines.

We have also examined the effect of strong electrolyte on the rate constants for solvent-assisted protonation. Figure 9 illustrates the effect of increasing concentrations of $LiClO_4$ on the fluorescence spectra of 5,6-BQ in aqueous solutions made slightly

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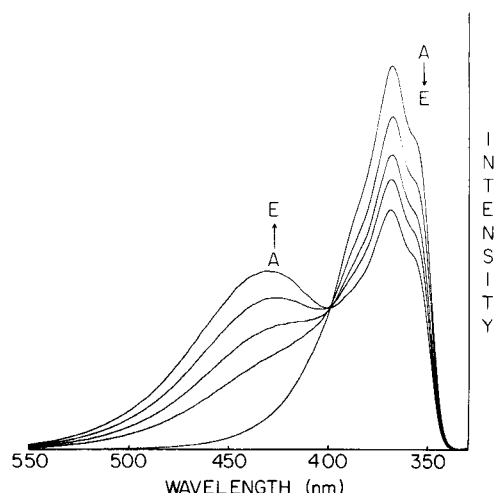


Figure 9. Effect of increasing concentrations of LiClO_4 on the fluorescence spectrum of 5,6-BQ. Spectrum A is that of 5,6-BQ in 0.20 M NaOH. The concentrations of LiClO_4 in solutions B-G were 0.0, 0.50, 1.0, and 1.50 M. Solutions B-G also were 0.020 M in NaOAc in order to maintain the pH slightly above 7.

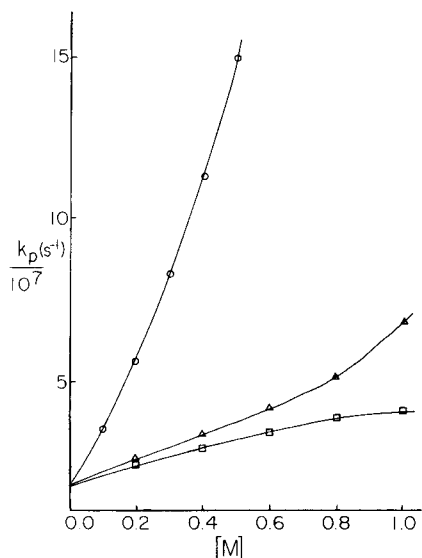


Figure 10. Plots of the rate constant for solvent-assisted excited-state protonation of 5,6-BQ vs the concentration of Mg^{2+} (O), Li^+ (Δ), and Na^+ (\square).

basic with sodium acetate. It can be seen that, as the concentration of the salt increases, the intensity of the free base emission decreases and that of the conjugate acid increases. Clearly, increasing concentrations of the salt result in an increase in the rate of protonation. We have also examined the effect of $\text{Mg}(\text{ClO}_4)_2$ and NaClO_4 on the rate of protonation. In Figure 10, the plots of the k_p vs metal ion concentration are shown. The results indicate that smaller ions are more effective than larger ions in enhancing the rate of solvent protonation, a result that is consistent with recent excited-state-protonation studies on acridine.¹³ It is interesting to note, however, that these results are just the opposite to what is observed for the excited-state-deprotonation reactions of naphthols and hydroxypyrenes.¹² In those systems, the rate

constants decrease with increasing salt concentration. It is also found that the data for these hydroxy systems fit a single straight line when the log of the rate constant is plotted vs the log of the activity of the water. Clearly, the effect of salts on the rates of protonation reactions in azines is different than that on deprotonation reactions in hydroxy systems. Pines et al.¹³ have interpreted the effect of salts on the rates of protonation of excited acridine as being due to metal ions causing water to become a stronger proton donor. We are in agreement with this interpretation.

In summary, the photophysical properties of 5,6-benzoquinoline, 7,8-benzoquinoline, and phenanthridine have been investigated. All three molecules are found to exhibit water-assisted and ammonium ion assisted protonation in their lowest excited singlet state. The rate constant for water-assisted protonation of excited 5,6-benzoquinoline is found to decrease by about one-third as the water is replaced by D_2O . The addition of alcohol to the solvent results in a decrease in the solvent-assisted protonation while the addition of metal ions results in an increase. The former effect is similar to what is observed for excited-state-deprotonation reactions of naphthols and hydroxypyrenes while the latter is opposite to what is observed in these compounds.

Experimental Section

Phenanthridine, 5,6-benzoquinoline, and 7,8-benzoquinoline were obtained from Aldrich Chemical Co. and were recrystallized from 10/90 ethanol/water mixture and vacuum sublimed prior to use. Sulfuric acid, sodium hydroxide, sodium acetate, ammonium acetate, sodium perchlorate, and magnesium perchlorate were all Fisher Scientific reagent grade and were used without further purification. Methanol (certified ACS spectroanalyzed) was also obtained from Fisher Scientific and was used without further purification. Reagent grade lithium perchlorate was obtained from G. Frederick Smith Chemical Co. and was used without further purification. D_2O (99.8%) was obtained from Aldrich Chemical Co. and was used without further purification.

Absorption spectra were obtained with a Perkin-Elmer 330 UV-vis near-IR spectrophotometer, and emission spectra were obtained with a Perkin-Elmer LS-5 fluorescence spectrophotometer. Decay curves were obtained by the time-correlated single-photon method. The technique and the apparatus employed have been discussed elsewhere.^{14,15} Although quenching by oxygen was not significant, all solutions were purged with nitrogen prior to quantitative measurements.

The fluorescence quantum yields for the free base molecules were obtained by using 2-naphthol in cyclohexane as a standard.¹⁶ Those of the conjugate acid were obtained with quinine sulfate used as a standard.

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Registry No. Ph, 229-87-8; 5,6-BQ, 85-02-9; 7,8-BQ, 230-27-3; PhH^+ , 23686-76-2; 5,6-BQH⁺, 22559-74-6; 7,8-BQH⁺, 22559-73-5; Mg^{2+} , 22537-22-0; Li^+ , 17341-24-1; Na^+ , 17341-25-2; H_2O , 7732-18-5; D_2O , 7789-20-0; methanol, 67-56-1.

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