simple electrostatic arguments may not totally explain the observed phenomena.

One might consider antibinding to simply be an excluded volume effect based on the repulsion of a charged solute from a similarly charged micelle. As a result of this repulsion, a solute would not only be excluded from the volume of the micelle but also from much of the volume of the double layer surrounding the micelle (which can be appreciable). Theories have been derived for charge–charge interactions in aqueous solution as well as for the effect of added salt on these interactions. For example, both the Debye length for simple ions (i.e., the distance over which the electrostatic field extends) and the thickness of the electric double layer of charged lyophobic colloids are proportional to the inverse of the square root of ionic strength.[22,23] In this work the interaction of organic anions with negatively charged association colloids is analogous to the previous examples, yet there are fundamental differences. From strictly electrostatic arguments (vide supra) one would expect solutes to show decreased micellar antibinding with increasing ionic strength. In fact, this occurs for the majority of solutes studied. Sodium 2-naphthalenesulfonate, alizarin red S, and 2-naphthol-6-sulfonic acid show a linear increase in the value of their measured "coefficients" with increasing salt concentration (Table II). This behavior is typical of many organic anions with SDS micelles. Bromophenol blue (Figure 4) is the only compound found, thus far, in which the relationship is not linear.

In lyophobic colloidal systems, the addition of sufficient salt generally brings about flocculation. In the present system, the addition of sufficient salt can cause organic ions to go from antibinding to binding. It is tempting to draw an analogy between colloidal flocculation values and the nonbinding values observed in this study. In order for the transition from antibinding to nonbinding to binding to occur, the solute ion of interest must have sufficient hydrophobic character to associate with the nonpolar portion of the micelle once electrostatic repulsions have been minimized.

The behavior of ammonium thiocyanate (Table II and Figure 4) is difficult to explain in terms of the aforementioned electrostatic criteria. However, it may be possible to rationalize the increased antibinding of thiocyanate ion with added salt by considering the equilibrium constant of thiocyanate between the bulk aqueous solution and the micellar phase as well as the constant between the micellar and stationary phase. Thiocyanate ion has little hydrophobic character compared to the other solutes in this study. Consequently, when salt is added, the predominate factor may be the ions increased affinity for the bulk solution or for the stationary phase. In contrast, many organic ions tend to be salted into the micelle.

The apparent lack of variation in antibinding of naphthol green B with added salt is a bit of an enigma (Table II and Figure 4). This compound seems to be oblivious to changes in the micelle and in the bulk aqueous solution. It is possible that changes too small to detect by chromatographic techniques are occurring. It may also be possible (although not probable) that the change in the excluded volume effect of the micelle is exactly counterbalanced by an increase in the solution or stationary phase affinity of naphthol green B.

The antibinding phenomena is useful in liquid chromatography because it produces unusual selectivities (Figure 1). It may also be useful in studies involving micelles, liposomes, vesicles, and even membranes. Indeed, unusual salt effects have been noted in kinetic studies in micellar media.[24]

Antibinding and nonbinding phenomena are by no means restricted to negatively charged micelles and solutes. They are easily observed with cationic micelles and positively charged solutes. Indeed, some uncharged solutes behave in an analogous manner with charged micelles. Antibinding behavior has also been observed between micelles composed of amphoteric surfactants and some solutes. These and other studies on this phenomenon, its control, and use are in progress and will be reported subsequently.

Registry No. SDS, 151-21-3; naphthol green B, 19381-50-1; bromophenol blue, 115-39-9; alizarin red S, 130-22-3; 2-naphthol-6-sulfonic acid, 93-01-6; ammonium thiocyanate, 1762-95-4; sodium 2-naphthalenesulfonate, 532-02-5; sodium nitroferricyanide, 14402-89-2.

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Solvent and pH Dependence of Absorption and Fluorescence Spectra of 5-Aminoindazole: Biprotonic Phototautomerism of Singly Protonated Species

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Abstract: Absorption and fluorescence spectra of 5-aminoindazole have shown that the amino group acts as a hydrogen-bond acceptor in S_0 and hydrogen-bond donor in S_1. pH studies have indicated that the monocation and the monoanion of 5-aminoindazole are different in S_0 and S_1 states, respectively, i.e., species II and IV in the ground state and species V and VI in the excited singlet state. Solvent studies have also shown that there exists a biprotonic phototautomerism in the singly protonated species.

Introduction

Excited singlet-state proton-transfer reactions of several bifunctional molecules such as quinoline carboxylic acids[1] and hydroxy aromatic acids[2,3] have been studied. In the ground state of these molecules the electron-donating (OH, NH_2) and electron-withdrawing groups (COOH, pyridinic nitrogen atom) behave in a similar manner to that in monofunctional molecules. But it has been observed that the gain in acidity of an electron-donating

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group and the gain in basicity of the electron-withdrawing group in the same electronically excited molecule are so large that the order of ionization of the two groups is reversed with respect to the normal order observed in the ground state. This could be due to the change in the charge densities at these functional groups in the excited singlet state. The effect of this could be the formation of a species in the excited state which may be an isomer (tautomer) of the species present in the ground state; i.e., the molecule has not gained or lost any proton but the migration of proton has taken place from one functional group to another. This process is termed phototautomerism. When the two functional groups are widely separated as in β-methylumbelliferrone,[4] then this phototautomerism is biprotonic (intermolecular phototautomerism) since it must entail a deprotonation of one functional group and protonation to another. This phototautomerism shows a strong dependence on solvent. If both the groups are ortho or peri (e.g., salicylic acid, hydroxynaphthoic acids) to one another, then this process is called intramolecular phototautomerism since proton exchange occurs through intramolecular hydrogen bonding between the two groups.

Even though many bifunctional molecules have been studied, not much work has been carried out in molecules having more than two functional groups. It would be interesting to study 5-aminoindazole (AI) which has three functional groups. Furthermore, the amino group can behave as a proton donor as well as a proton acceptor. Hence this compound has two sites of protonation and two sites of deprotonation. The different species which might be possible from AI, during protonation or deprotonation, when the pH is varied are shown in Figure 4.

The present study was carried out to identify the species involved in various ground and excited singlet-state equilibria and to calculate the equilibrium constants with the help of the effect of solvents and pH on the absorption and fluorescence spectra. It has been found that the successive deprotonation, from dication to neutral form in the excited singlet state, takes place in a path which is quite different from that observed in the ground state. The monoanion formed in S_1 is also different from that in S_0. Absorption and fluorescence spectral analysis of the singly protonated species indicates the existence of a biprotonic phototautomerism.

Experimental Section

5-Aminoindazole was obtained from Aldrich Chemical Co. and purified by recrystallization from ethanol. Indazoleammonium chloride (chloride of III) was prepared by passing HCl(g) into a pure dry ethereal solution of AI. The purity of this salt was checked by its absorption spectra in different solvents. B.D.H. spectroquality methanol was used as such. AnalaR grade acetonitrile (E. Merck) and hexane (BDH) were further purified by the methods described elseshere.[5] Triply distilled water was used for the preparation of aqueous solutions. AnalaR grade H_2SO_4 and NaOH were used to prepare acidic and basic solutions. A modified Hammett's scale[6] for the H_2SO_4–H_2O mixture and Yagil's basicity scale[7] for the NaOH–H_2O mixture were used for the solutions below pH 1 and above pH 13, respectively.

Absorption spectra were recorded on a Cary 17D spectrophotometer. Fluorescence measurements were made on a scanning spectrofluorimeter fabricated in our laboratory.[8] Excitation and emission monochromators were calibrated using a calibration Hg lamp. Low-temperature fluorescence spectra were recorded using a Aminco-Bowman low-temperature accessory in our instrument. pH measurements were made on a Toshniwal pH meter, Model CL-44A.

The frequency shifts (blue or red) in the study of solvent effects are discussed relative to the maxima in hexane. The solution for absorptiometric and fluorimetric titrations were prepared just before taking the measurements. The concentrations of the solutions were of the order 10^{-4}–10^{-5} M. In fluorimetric titrations, while measuring the relative fluorescence intensities at the analytical wavelength as a function of pH/H_0/H_-, isosbestic wavelength is used for the excitation. These

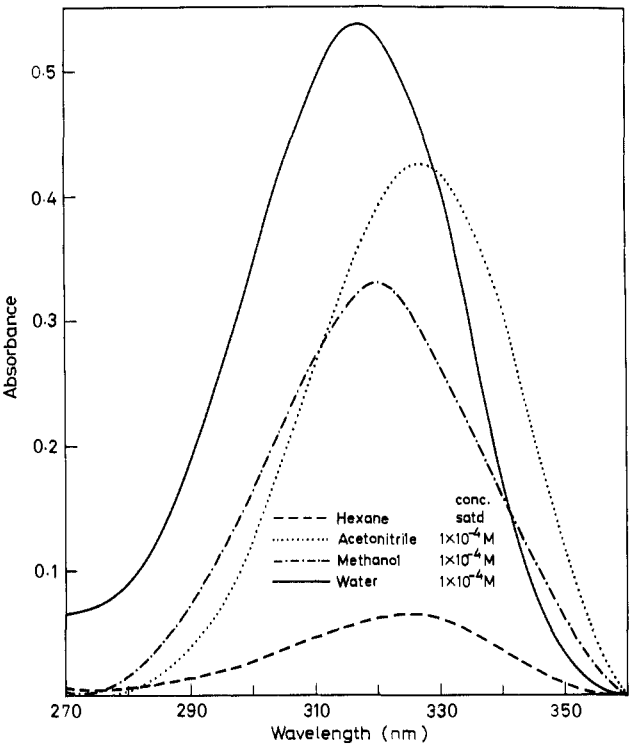

Figure 1. Absorption spectra of 5-aminoindazole in different solvents at 298 K.

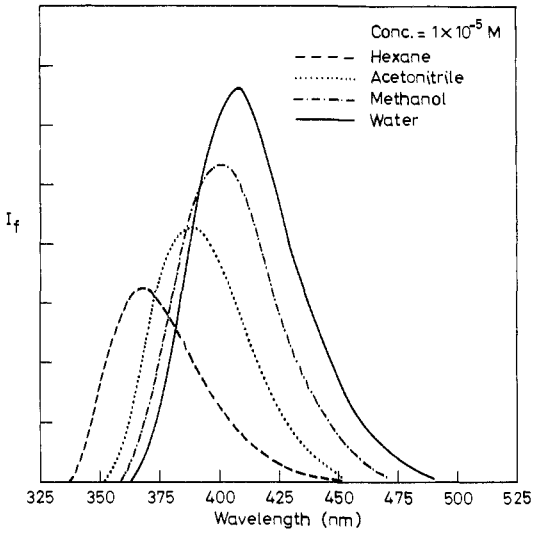

Figure 2. Fluorescence spectra of 5-aminoindazole in different solvents at 298 K.

Table I. Long-Wavelength Absorption Maxima ($\bar{\nu}_{abs}$), log ε, and Fluorescence Maxima ($\bar{\nu}_{flu}$) at 298 K and in Different Solvents

solvent	$\bar{\nu}_{abs}$ (cm^{-1})	log ε	$\bar{\nu}_{flu}$ (cm^{-1})
H_0 −9.0 (H_2SO_4)	34 722		27 548
H_0 −1 (H_2SO_4)	35 211		19 801
water	31 575	3.73	24 449
methanol	31 250	3.52	24 397
acetonitrile	30 627	3.62	25 806
hexane (satd)	30 769		27 210
H_- 16 (NaOH)	30 864		

Hammett's functions[6] represents the actual (or free) amount of proton or hydroxyl ions available in the desired solution to react with a weak base or acid, respectively.

Results and Discussion

Effect of Solvents on Absorption and Fluorescence Spectra. The absorption and fluorescence spectra of AI were observed in dif-

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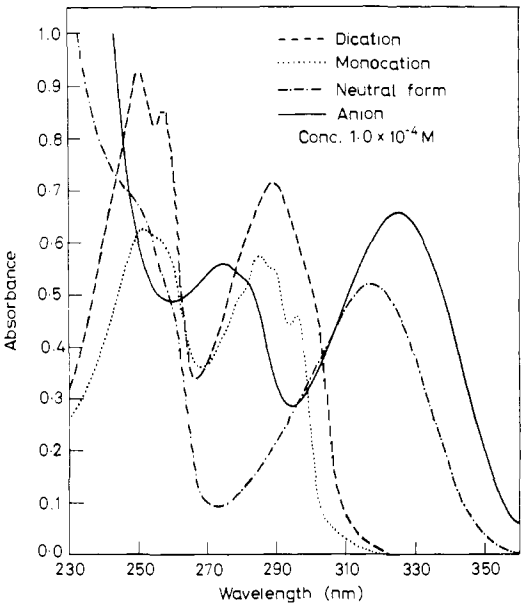

Figure 3. Absorption spectra of dication, monocation, monoanion, and neutral 5-aminoindazole at 298 K.

ferent solvents and are shown in Figures 1 and 2. The $\bar{\nu}_{max}$(abs), log ϵ, and $\bar{\nu}_{max}$(flu) are listed in Table I. As compared with the structured absorption spectrum of indazole,[27] the absorption spectra of AI in all the solvents are broad and structureless. Further, contrary to the red shift in the $\bar{\nu}_{max}$(abs) of indazole with the increase in polarity of solvents, the $\bar{\nu}_{max}$(abs) of AI is red shifted in acetonitrile whereas it is blue shifted in methanol and water. Similar to indazole,[27] the fluorescence spectra of AI is red shifted with the increase in the polarity and hydrogen-bonding capacity of solvents as compared with those in hexane. The red shift is more in the latter than in the former.

The absorption spectrum of AI should have the characteristics similar to that of parent indazole molecule, perturbed by the substituent (amino group); i.e., the lowest energy transition is of $\pi^* \leftarrow \pi$ character. The vibrational structure of the absorption spectrum is lost because of the charge-transfer interaction of the lone pair of amino group with the π cloud of the indazole ring. Further, the amino group can behave in two ways. It can interact with hydrogen-donating solvents through the lone pair on the nitrogen atom of amino group or it can donate a hydrogen atom of the amino group to the hydrogen-accepting solvents. In the former, a blue shift and, in the latter, a red shift in the absorption spectrum should be observed. Thus a blue shift in $\bar{\nu}_{max}$(abs) in methanol and water suggests the formation of a hydrogen bond with the lone pair, thus inhibiting its interaction with the π cloud. The red shift in acetonitrile (which is a poor hydrogen-acceptor solvent) is due to the usual dipole–dipole effect on the $\pi^* \leftarrow \pi$ transition or to the hydrogen-donating character of the amino group. In the extreme case of hydrogen-bond formation, i.e., protonation of amino group, the absorption spectrum is blue shifted relative to AI and resembles the spectrum of indazole[27] (Figure 3).

As stated in the above paragraph, the fluorescence spectrum of aromatic amines resembles that of absorption spectrum in hydrogen-donating or hydrogen-accepting solvents, i.e., blue shift in the former and the red shift in the latter solvents compared with those in hexane.

The regular red shift in the fluorescence spectra of AI with the increase in the polarity of hydrogen-bond formation tendency of solvents clearly indicates the hydrogen-donating capacity of amino group. Further, the red shift of the fluorescence maxima in methanol relative to hexane is quite large, suggesting that the hydrogen bond between the solute and solvent is very strong and may actually result in a stoichiometric complex (exciplex) between the excited solute and solvent molecule. To confirm this, fluorescence spectra of heptane solutions with different amounts

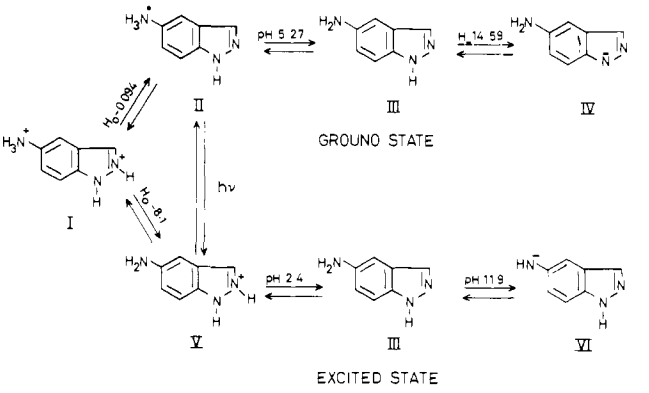

Figure 4. Scheme of ground- and excited-state equilibria of 5-aminoindazole at different H_0/pH/H_-: I, dication; II, indazoleammonium ion; III, neutral form; IV, 5-aminoindazole anion; V, 5-aminoindazole cation; VI, imino anion.

of ethanol were recorded. It was found that addition of ethanol up to 3% (v/v) resulted in a red shift of 1550 cm^{-1}, whereas further addition up to 100% resulted in a gradual red shift of only another 730 cm^{-1}.

Although AI is similar to phenanthroimidazole and isomeric aminoquinolines in having more than one site of hydrogen bonding, the spectral behavior of AI is different from others. Irregular shifts have been observed in PI[9] and aminoquinolines[10] due to change in the site of hydrogen bonding in methanol and water, whereas a regular blue shift in absorption and regular red shift in fluorescence with increasing hydrogen bond formation are observed in AI. This clearly indicates that in both states solvent interacts only with the amino group of the solute.

Effect of pH on the Absorption and Fluorescence Spectra. Absorption spectra of AI have been studied in the basicity/acidity range from H_- 16 to H_0 −4. Four ground-state prototropic species (Figure 4), the neutral molecule (III), a monocation (II), a dication (I), and an anion (IV), have been observed. The absorption spectra of these four compounds are shown in Figure 3 and $\bar{\nu}_{max}$(abs) in Table I. The blue shift observed in the absorption spectrum of monocation and its resemblence to absorption spectrum of indazole[27] shows that the first protonation in the ground state, as stated earlier, occurs at the amino group. The $\bar{\nu}_{max}$(abs) of the dication is red shifted to the monocation and it is due to the protonation at the ring nitrogen atom, as observed in case of pyrazoles[11,12] and aminoquinolines.[10] The absorption spectrum of the anion is red shifted as compared with the neutral form, and the pK_a for the equilibrium between the neutral molecule and anion, determined spectrophotometrically, is found to be 14.59, which is slightly greater than the pK_a of indazole. This is in line with the theory that electron-donating groups, such as amino and methyl, increase the basicity of the molecule.[13] These results indicate that the anion involved in the equilibrium is the one deprotonated at the ring nitrogen atom because the deprotonation equilibrium constant of the amino group in other compounds is much larger than this value. From the absorption spectra of these species the ground-state, equilibrium reactions can be written as shown in Figure 4; pK_a's for the respective equilibria, determined spectrophotometrically, are noted on the arrows.

The fluorescence spectra of AI have been studied in the range H_- 16 to H_0 −10. The neutral species shows a fluorescence maxima at 408 nm. When the pH is lowered below 4.5, the fluorescence intensity at 408 nm starts decreasing and a new band with very low intensity (even at H_0 −1.12 its intensity is less by a factor of

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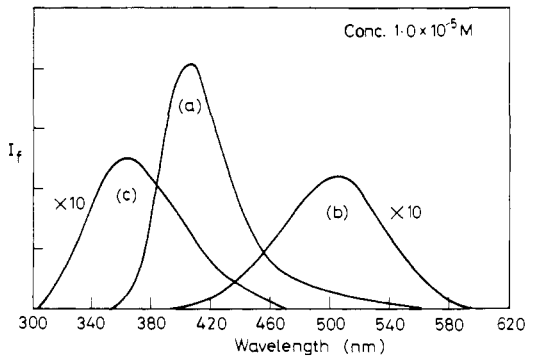

Figure 5. Fluorescence spectra of 5-aminoindazole at different pH's: (a) neutral form (pH 7), (b) monocation (H_0 −0.5), (c) dication (H_0 −9) at 298 K.

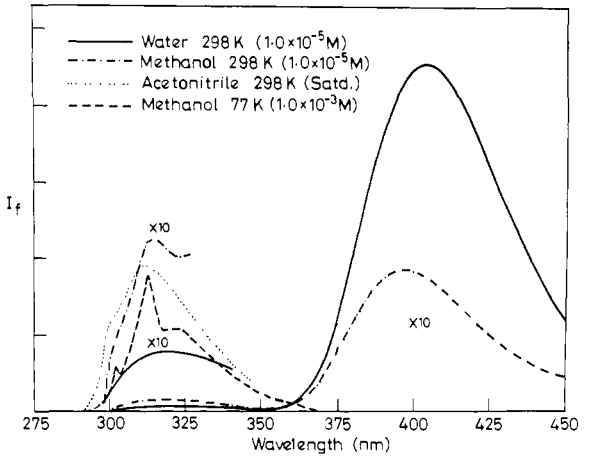

Figure 6. Fluorescence spectra of indazoleammonium chloride in different solvents at 298 K.

30 than that of the neutral form at 408 nm) starts appearing at 505 nm and could be detected only below pH 1.2. This band is due to the formation of the monocation and its formation is complete at pH 0.2. A further decrease of H_0 results in the quenching of the fluorescence at 505 nm and it is nearly complete at H_0 −5. At this stage a new band with λ_{max} at 363 nm starts appearing; this band is found to be due to the formation of the dication. On the other hand, when the pH is increased from 7 to 10, the fluorescence of the neutral form at 408 nm gets quenched and the quenching is complete at pH 14 without the appearance of any other fluorescence band. Above pH 14, no fluorescence is observed at room temperature even up to H_- 16. Fluorescence spectra of the different excited-state species are shown in Figure 5.

(a) Excited-State Equilibrium between the Monocation and Neutral Form. As stated earlier, the monocation fluorescence is strongly red shifted in comparison with the neutral form, and the monocation formed may be due to the protonation either at the ring nitrogen atom or at the amino group. If the protonation had occurred at the latter position, the fluorescence spectrum should have been blue shifted and resembled the indazole fluorescence spectrum,[8] as did the absorption spectrum and also as noticed in other aromatic amines[15,16] where the fluorescence and absorption spectra of the protonated forms resemble those of the parent molecules. To prove the above point, the indazoleammonium chloride salt was prepared; its absorption spectrum taken in acetonitrile, methanol, and water resembles the absorption of the species II. Fluorescence spectra of the salt recorded in different solvents at 298 K and methanol at 77 K are shown in Figure 6.

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Table II. Absorption and Fluorescence Maxima (cm^{-1}) of Indazoleammonium Chloride in Different Solvents at 298 K

solvent	$\bar{\nu}_{abs}$	$\bar{\nu}_{flu}$
acetonitrile	39 682	33 333
	34 843	32 514, 25 940
methanol	39 525	31 796, 25 094
	38 910	
	34 843	
	24 482	
	33 613	
water	39 682	31 250, 24 539
	39 062	
	35 087	
	34 602	
	33 783	

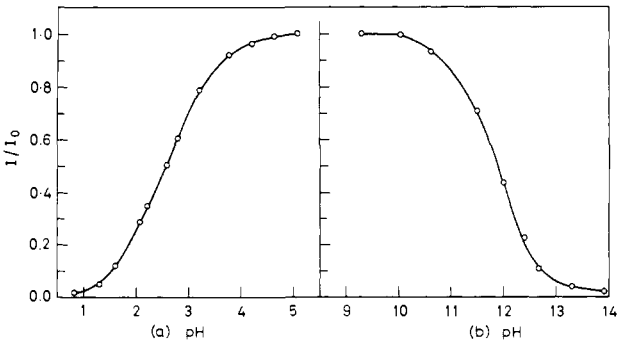

Figure 7. Plot of relative fluorescence intensities of 5-aminoindazole vs. pH at 298 K.

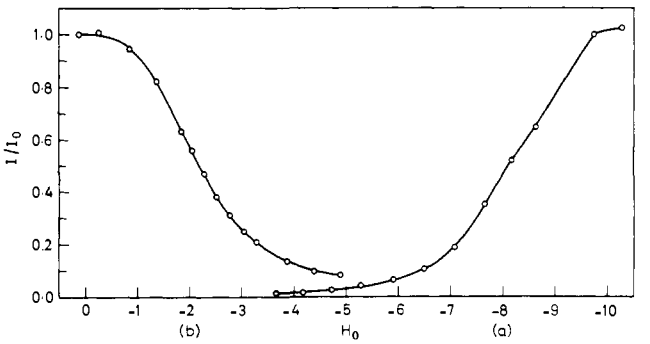

Figure 8. Plot of relative intensities of 5-aminoindazole vs. H_0: (a) dication, (b) monocation at 298 K.

The absorption and fluorescence maxima are reported in Table II. In all the solvents at room temperature two fluorescence bands appear, one near 310 nm, corresponding to indazoleammonium ion (close to the indazole fluorescence), and another at a longer wavelength, corresponding to the neutral form. This shows that indazoleammonium ion, being unstable in the excited state dissociates to the neutral form, and dissociation, as expected, increases with the increase in the hydrogen-bond-accepting tendency of the solvent, i.e., from acetonitrile to water. But at 77 K, the fluorescence spectrum in methanol has no band corresponding to the neutral AI, and the shape of the spectrum matches that of indazole.[27] Because of rigidity of the medium, the dissociation cannot occur. This confirms that the first protonation takes place at the ring nitrogen atom and not at the nitrogen atom of the amino group. The variation of the fluorescence intensity of neutral form vs. pH is plotted in Figure 7, and the middle point of this titration curve gives the pK_a^* (2.58) between the neutral form and the ring nitrogen protonated monocation (V, 5-aminoindazole cation).

(b) Equilibrium between the Mono- and Dication. The 5-aminoindazole cation fluorescence has a maximum at 505 nm whereas the dication has a maximum at 363 nm. The blue shift shows that the protonation has occurred at the amino group and thus reiterates our earlier conclusion that the first protonation

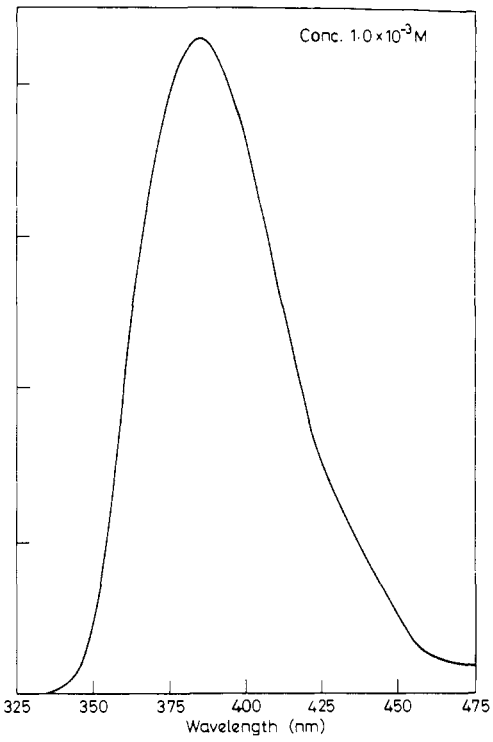

Figure 9. Fluorescence spectrum of 5-aminoindazole anion at 77 K (H_- 16) and 9 M NaOH solution in H_2O (homogeneous rigid glass solution).

occurs at the ring nitrogen atom. Fluorimetric titration was carried out for both species and the titration curves are shown in Figure 8. It is clear from Figure 8 that the fluorescence intensity of species V is quenched with a decrease in pH/H_0. The middle of this quenching occurs at H_0 −2.1 which could not be the pK_a* value for the equilibrium between monocation and dication, as the dication (I) starts fluorescing only from H_0 −4, and its intensity increases with the increase in acidity. The midpoint of this rise occurs at H_0 −8.1, which could be the pK_a* value, as no fluorescence quenching of this species is observed with the further increase in hydrogen ion concentration. The sharp fluorimetric titration curve shows that the formation of species I is complete within the lifetime of species V. The lack of correspondence between quenching of species V and appearance of fluorescence of species I clearly indicates that the fluorimetric titration curves do not correspond to the simple two-component (i.e., conjugate acid–base pair) equilibrium in the lowest excited singlet state, but that it is due to the proton-induced quenching of fluorescence of species V at moderate H^+ concentration as it has been shown that this process competes with the proton-transfer reaction.[17] Similar behavior has also been observed in many aromatic amines[18-20] and naphthols,[21] though under such circumstances accurate values of pK_a*'s can be calculated only with the help of time-dependence fluorimetry, but the midpoint of the rise of species I fluorescence curve will not be far from the true value.

(c) Equilibrium between the Neutral and the Anion. Fluorescence quenching of the neutral form without the appearance of a new band above pH 10 is due to the formation of the imino anion (VI) and not the 5-aminoindazole anion (IV). Similar behavior has been observed in case of aromatic amines such as aminoquinolines[22-24] and 9-phenanthrylamine,[15] where there can be only

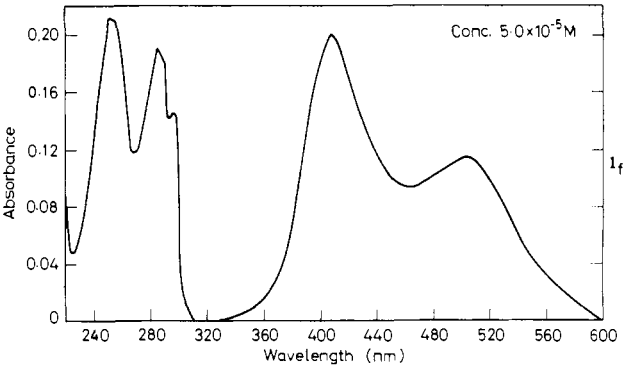

Figure 10. Absorption and fluorescence spectra of 5-aminoindazole at pH 1.4 at 298 K.

the formation of an imino anion. Moreover, if species IV is formed, the fluorescence of the ion might have been observed as noticed in the case of indazole,[27] pyrazoles,[11,12] benzimidazole,[25] and 2-phenylbenzimidazole.[26] To substantiate this further, the fluorescence spectrum of 5-aminoindazole anion at H_- 16 and at 77 K was recorded as shown in Figure 9. At such a low temperature and in the frozen state, only the ground-state species (IV) will be present because of the hindrance of the rearrangement of the atoms; this is confirmed by its fluorescence. These results demonstrate that the quenching behavior is due to the formation of the imino anion in the excited state. The midpoint of the fluorimetric titration curve (Figure 7) occurs at 11.9 which is the pK_a* for the equilibrium between neutral and the imino anion, indicating that aromatic amines are stronger acids in the S_1 state. Further increase in pH does not give rise to any fluorescence as observed in α- and β-naphthylamines[27] and 9-phenanthrylamine,[15] indicating that there is no formation of a dianion in this case nor any fluorescence.

In all the three equilibria discussed so far, it has been found that any of the species involved in the ground-state equilibria are different from those involved in the excited-state equilibria. Since the Förster cycle[28] is applicable only when pK_a and pK_a* correspond to the same equilibrium in the ground and excited states, calculation of pK_a* values by using Förster cycle methods has no meaning in these cases.

Bioprotonic Phototautomerism. The monocation (II) present in the slightly acidic solution (pH ~4) dissociates to neutral form (III) on excitation and gets protonated at the pyridinic nitrogen atom with further increase in the acidity in forming the monocation V. This suggests the existence of phototautomerism. The absorption and fluorescence spectra recorded at pH 1.4 are shown in Figure 10. At this pH in S_0 only monocation II exists (Figure 3), but the fluorescence spectrum has two maxima, one corresponding to III and the other to V, indicating that these two species are in equilibrium in the excited state. The formation of monocation V is not complete and it might be due to the shorter lifetime of the excited species. It is observed that the gain in acidity of amino group and the gain in basicity of the pyridinic nitrogen atom is so great in S_1 that the order of protonation of these two groups is reversed with respect to the normal order in the ground state. Since both groups, protonated amino group and pyridinic nitrogen atom, are widely separated, the phototautomerism should be biprotonic. The solvent-dependent nature of this biprotonic phototautomerism is also revealed in the fluorescence spectra of indazole ammonium ion (II) in different solvents; as seen in Figure 6, the dissociation (deprotonation) increases with increase in hydrogen-bonding capacity of solvents.

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From the above results, the phototautomerism along with ground- and excited-state equilibria is shown in the scheme in Figure 4.

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Registry No. I, 86695-80-9; II, 86695-81-0; III, 19335-11-6; IV, 86695-82-1; VI, 86695-83-2; indazoleammonium chloride, 63725-55-3.

Photoinduced Hydrogen Evolution by a Zwitterionic Diquat Electron Acceptor. The Functions of SiO_2 Colloid in Controlling the Electron-Transfer Process

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Abstract: Photosensitized hydrogen evolution from a basic aqueous SiO_2 colloid (pH 9-10) is accomplished with *N,N'*-bis-(3-sulfonatopropyl)-2,2'-bipyridinium (DQS^0, **1**) and colloidal platinum as mediating catalysts. In this system $Ru(bpy)_3^{2+}$ acts as a photosensitizer and triethanolamine (TEOA) as ultimate electron donor. No hydrogen formation is observed in a homogeneous aqueous solution under similar conditions. The SiO_2 colloid affects the formation and stabilization of the intermediate photoproducts, $Ru(bpy)_3^{3+}$ and $DQS^{-}\cdot$, by means of electrostatic interactions. The electric potential of the particles assists the separation of the products from the initial "encounter cage complex" and results in the repulsion of the reduced product, $DQS^{-}\cdot$, from the colloidal interface. Consequently, the recombination rate of $DQS^{-}\cdot$ with the oxidized product $Ru(bpy)_3^{3+}$ is retarded. The electrostatic functions of the colloid are confirmed by alteration of the ionic strength and pH of the colloid solution. The structure of DQS^0 was determined by X-ray crystallography. The compound crystallizes in space group $P2_1/n$ with unit cell dimensions of a = 10.392 (1) Å, b = 22.390 (3) Å, c = 8.235 (1) Å, β = 95.07 (2)°, V = 1909 (1) Å^3, and Z = 4.

Photosensitized electron-transfer reactions are currently examined as potential processes for solar energy conversion and storage.[1-3] In these reactions, a photoinduced electron transfer from a donor, D, to an acceptor, A, results in the reduced and oxidized products (eq 1). These photoproducts are initially in an "encounter cage complex" and might recombine in this cage structure or dissociate into separated ions. The separated ions A^- and D^+ can then recombine in a diffusion recombination process or be utilized in subsequent oxidation and reduction reactions. Thus, the degradative recombination of the photoproducts by the two pathways results in limitations in utilizing the species in chemical routes.

$$D + A \xrightarrow{h\nu} (D^+ \cdots A^-) \rightarrow D^+ + A^- \qquad (1)$$

The further utilization of the photoproducts in chemical routes has been mainly concentrated in the photolysis of water.[4,5] Reduction of water has been accomplished by using 4,4'-bipyridinium salts (viologens) as mediating electron acceptors, followed by hydrogen evolution by the reduced radical in the presence of colloidal platinum as catalyst.[6,7] In most of the reported systems the oxidized donor is a sacrificial component, i.e., cysteine, EDTA, or triethanolamine. Certainly, the exclusion of such sacrificial components and the direct oxidation of water are desired. Several studies have examined the oxidation of water in the presence of a variety of catalysts,[8,9] though oxygen evolution seems still to be the major difficulty. The oxidation and reduction potentials of water depend strongly on the pH of the aqueous media. While the oxidation of water is favored at basic pH values, hydrogen evolution is facilitated in acidic environments. Indeed, most of the previously described hydrogen-evolving reactions were performed in acidic aqueous solutions. Thus, hydrogen evolution from basic solutions might facilitate the complementary process of water oxidation.

The stabilization of the photoproducts against their degradative recombination reactions has been accomplished with a variety of interfacial organizates such as micelles,[10-12] microemulsions,[13] vesicles,[14,15] and colloids.[15] In these systems electrostatic and/or

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