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Journal of Photochemistry and Photobiology A: Chemistry 118 (1998) 1–6

Journal of Photochemistry and Photobiology A:Chemistry

Induced fluorescence of phenylpyridines by hydrogen bonding complexation

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Received 1 April 1998; received in revised form 3 June 1998; accepted 6 July 1998

Abstract

Fluorescence of the isomeric 2-, 3-, and 4-phenylpyridines was induced by forming hydrogen-bonded complexes with trifluoroacetic acid (TFA) in a hydrocarbon solvent. The results indicate a high sensitivity of these molecules for TFA with 1:1 H-bonded formation constants of 0.85×10^3, 1.59×10^3, and 1.85×10^3 M^{-1}, respectively, which increase with the basicity of the azine. In each case induced fluorescence occurs as the result of an excited state H-bond transfer. With 2-phenylpyridine in cyclohexane, complexation converts a nonfluorescent molecule to an H-bonded species with a fluorescence quantum yield of 0.24. The application of these molecules as fluorescence probes for acid molecules in a non-polar solvent is suggested.

Keywords: Excited state H-bond transfer; pH dependent fluorescence; Phenylpyridines

1. Introduction

Excited state proton transfer processes have been the focus of interest to many research groups. A review of proton transfer spectroscopy has been presented by Kasha [1]. Arnaut and Formosinho have discussed inter- and intramolecular proton transfer reactions [2,3], and Kuzmin et al. [4] have discussed proton transfer reactions in the excited electronic states of aromatic molecules. A fluorescence study of the excited state proton transfer of 2-heterooxazoles with acetic acid in ethyl alcohol has been reported by Uzhinov et al. [5]. McMorrow and Kasha [6] have demonstrated the application of an excited state intramolecular proton transfer to the detection of trace hydrogen-bonding impurities in hydrocarbons using 3-hydroxyflavone as a fluorescence probe. Studies including molecules such as 3-hydroxybiphenyl [7], 2,2′-dihydroxybiphenyl [8], 2,5-di(biphenyl)oxazole [9], 3,5,6-trimethyl-2(N,N′-diethyl-amino-methyl)phenol [10], and 2,(2′-pyridyl)indoles [11] have also been reported.

In a recent study we demonstrated that the fluorescence yield of 2,6-diphenylpyridine increases significantly by formation of a 1:1 complex with trifluoroacetic acid (TFA), resulting from an excited state H-bond transfer [12]. It has been shown [13] that by choosing substituents which drastically alter the basicity of the pyridine nitrogen, it is possible in a series of complexes between HCl and 4-substituted pyridines to span the range of hydrogen-bond possibilities: (i) hydrogen-bonds between neutral molecules, N···H–A, (ii) hydrogen-bonds between ion-pairs, N–$H^+\cdots A^-$, and (iii) hydrogen-bonds in proton shared complexes, N···H···A. With the phenylpyridines we can vary the nitrogen basicity over the pKa range 3.7 (2,6-diphenylpyridine) to 5.3 (4-phenylpyridine), which when coupled with their increased basicity upon excitation allows us to probe the extent of hydrogen-bonding in a hydrogen solvent.

In contrast to the excited state proton transfer required for the isomeric phenylpyridines to fluoresce in water, the 2,6-derivative has an unexpectedly low pK_a=3.7 that prevents this process from occurring. As an extension of our interest in hydrogen-bonding induced fluorescence we have initiated a study of the isomeric 2-, 3- and 4-phenylpyridines in a low dielectric constant, hydrocarbon solvent, where proton transfer is unfavorable. The major difference between a protonated and an H-bonded species in these systems is that the N–H distance is predicted to be 1.0 Å in the former and 2.5 Å in the latter. Since these molecules in aqueous solutions are effective proton scavengers in the excited state we have been interested in perturbing their fluorescence with hydrogen-bond/proton donors. Of the donors with which we were able to observe interesting complexations effects, trifluoroacetic acid, was chosen to investigate the influence of H-bond complexation on the fluorescence of these molecules. In particular we wanted to address the issue of an

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PII: S1010-6030(98)00345-1

excited state proton transfer vs. an excited state H-bond transfer, i.e., the formation of 1:1 complexes with TFA could be used to perturb their excited state behavior. Mataga et al. [14,15] reported the fluorescence of hydrogen-bonded complexes of 2-naphthol with some alklychloroacetates and amines. By conducting experiments in a solvent of low dielectric constant we hoped to minimize the importance of the excited state proton transfer and focus on the H-bond transfer.

2. Experimental

2.1. Materials

The isomeric phenylpyridines were obtained from Aldrich Chemical Co. and were purified as follows: 2-, and 3-phenylpyridine were vacuum sublimed, and 4-phenylpyridine was recrystallized from hexane. Sealed 1 ml ampules of trifluoroacetic acid were used as received from Aldrich. Spectrograde cyclohexane and hexafluoro-2-propanol were used after verifying that they did not contribute any impurity emissions.

2.2. Apparatus and procedures

Absorption spectra were recorded with an HP8452 diode array spectrophotometer, and fluorescence spectra were recorded with a Perkin–Elmer LS-50 spectrophotofluorometer. Excitations were done with 300 nm., and the fluorescence yields were determined relative to the value (Φ_F=0.20 for 4-phenylpyridine in water [16]. The formation constants of the 1:1 complexes, $K_{H\text{-}bond}$, were determined by measuring the 50% complexation point. At this condition, the reciprocal concentration of free TFA is equal to $K_{H\text{-}bond}$.

3. Results

Although the isomeric phenylpyridines are non-fluorescent in hydrocarbon and polar organic solvents, in the presence of a strong acid such as trifluoroacetic acid, these molecules undergo molecular complexation, induce fluorescence, and lead to a significantly different excited state behavior, attributed to the increased basicity of the azine. The interaction between the two can be followed in the absorption spectrum by adding TFA to a cyclohexane solution of 1.0×10^{-5} M 2-phenylpyridine, which gives rise to a new peak appearing at 301 nm, as is shown in Fig. 1. The absorption peak of the 2-phenylpyridinium ion appears at 294 nm. Photoexcitation at 300 nm induces fluorescence as the H-bonded complex builds in, and the non-fluorescent free azine now exhibits fluorescence with a quantum yield of 0.24 when completely complexed, as can be seen in Fig. 2. A fluorescence wavelength maximum is evident at 359 nm, which provides confirmation for the 1:1 hydrogen-bonded

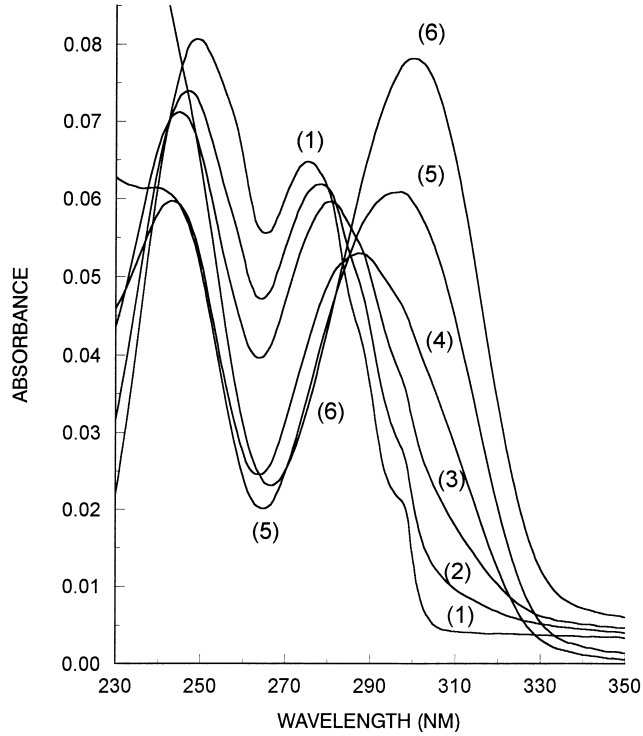

Fig. 1. Effect of trifluoroacetic acid addition on the absorption spectrum of 5.0×10^{-6} M 2-phenylpyridine in cyclohexane: (1) 0 M, (2) 6.0×10^{-4} M, (3) 1.2×10^{-3} M, (4) 2.1×10^{-3} M, (5) 3.0×10^{-3} M, and (6) 7.5×10^{-3}M.

complex formation upon addition of TFA to a 5.0×10^{-6} M solution of 2-phenylpyridine in cyclohexane. With the 2-phenylpyridinium ion in aqueous H_2SO_4 the absorption and fluorescence maxima appear at 294 and 364 nm, respectively. The formation constant of the ground state complex estimated from the 50% complexation point in the absorption and fluorescence spectra was determined to be 0.85×10^3 M^{-1}. The induced fluorescence of 3- and 4-phenylpyridine by complexation with TFA follows a similar pattern upon addition of TFA to a cyclohexane solution of these molecules, where the uncomplexed azine does not show any fluorescence. The fluorescence wavelength maximum for the H-bonded complex of 3- and 4-phenyl derivative with TFA appear at 360 and 340 nm, respectively, while the corresponding pyridinium ion fluorescence wavelength maximum appears at 390 and 380 nm, respectively. With these two molecules a significant increase in fluorescence is observed upon complexation, and the formation constants for the 1:1 hydrogen-bonded complexes were determined to be 1.59×10^3 M^{-1} and 1.85×10^3 M^{-1}, respectively. The rapid growth in the absorbance at 300 nm for the three isomeric phenylpyridines, resulting from addition of TFA is shown in Fig. 3. The steepest growth in the case of 4-phenylpyridine is consistent with it being the most basic of the three derivatives studied. With 2-phenylpyridine, which is the weakest base of the three, it is seen that the 50% complexation point occurs at a higher TFA concentration. In

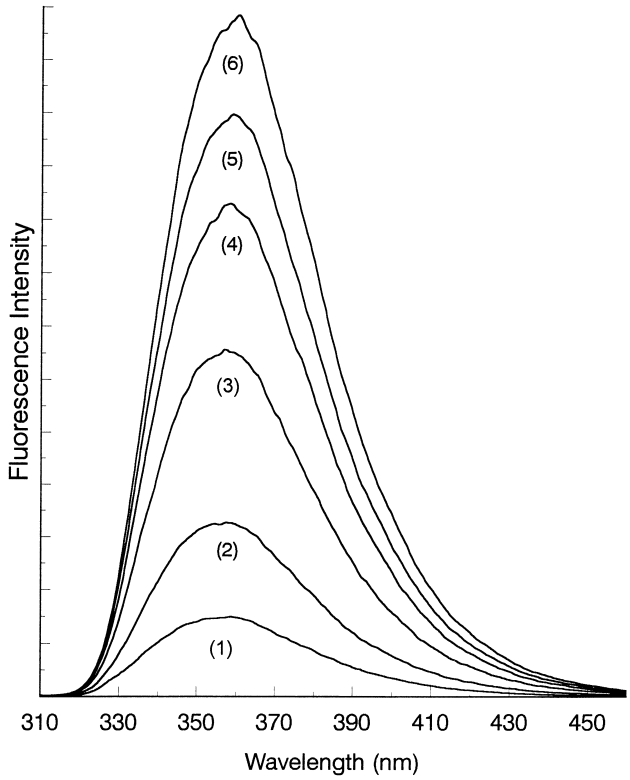

Fig. 2. Induced fluorescence of 1.0×10^{-5} M 2-phenylpyridine in cyclohexane by formation of a 1:1 H-bond complex with increasing trifluoroacetic acid concentration: (1) 3.0×10^{-4} M, (2) 8.0×10^{-4}M, (3) 1.6×10^{-3} M, (4) 3.2×10^{-3} M, (5) 6.4×10^{-3} M and (6) 1.0×10^{-2} M. (300 nm exc.).

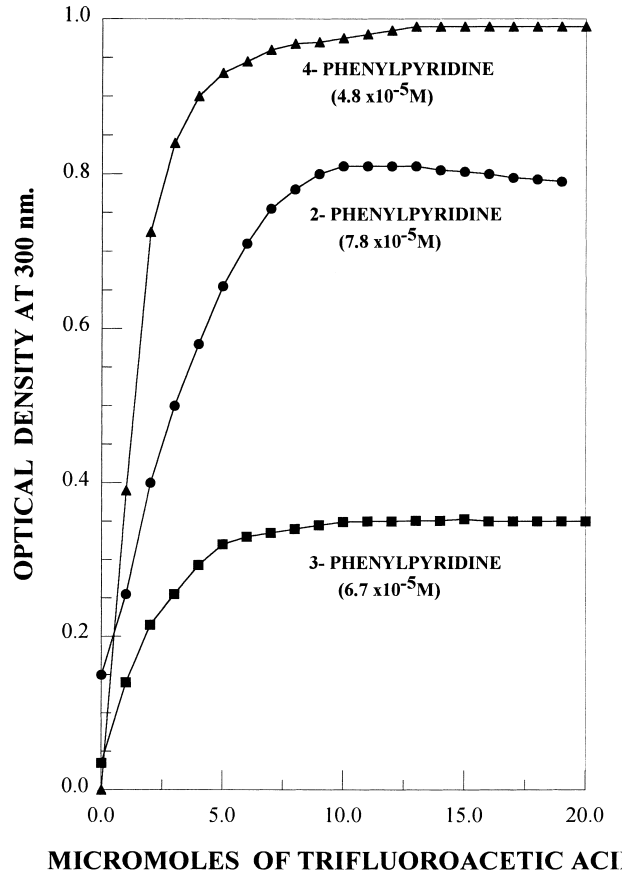

Fig. 3. Optical density increase at 300 nm in the absorption spectrum due to the formation of the 1:1 H-bond complex between TFA and: (1) 2-phenyl- (2) 3-phenyl-, and (3) 4-phenylpyridine.

trying to distinguish a proton transfer from a hydrogen-bond transfer, we noted that the fluorescence peak of the hydrogen-bonded complex for 3-phenylpyridine appeared at 360 nm, while that of the 3-phenylpyridinium ion appeared at 390 nm, indicating two distinguishable species. In contrast with 2,6-diphenylpyridine, which does not undergo an excited state proton transfer the two species appear at 396 nm. A difference in the fluorescence wavelength maximum between the H-bonded complex and the protonated species is also evident with 4-phenylpyridine, where the former exhibits a peak at 340 and 380 nm in the latter. A summary of the data for the induced fluorescence of phenylpyridines, resulting from the hydrogen-bonded complex with TFA is presented in Table 1, where it is seen that the pK_a of the azine correlates well with the formation constant of the 1:1 H-bonded complex.

Experiments to induce the fluorescence of 3-phenylpyridine in a hydrocarbon solvent were also carried out by adding 10 μl increments of hexafluoro-2-propanol to a 1 cm cell containing a solution of 3.0×10^{-4} M 3-phenylpyridine in cyclohexane. An increasing fluorescence signal induced by this hydrogen-bonded complex is shown in Fig. 4. The fluorescence peak appears at ~320 nm suggesting that the levels of hydrogen-bonding in TFA and HFIP are distinguishable, being stronger in the former.

Table 1
Summary of the fluorescence behavior for 1:1 H-bonded complexes between phenylpyridines and trifluoroacetic acid

		Solvent: cylcohexane				
		Free azine			1:1 H-Bonded complex	
	pK_a	Φ_F	λ_{max} (nm)	Φ_F	λ_{max} (nm)	$K_{H\text{-bond}}\times10^{-3}$ (M^{-1})
2-phenylpyridine	4.2	NF[a]	–	0.24	359	0.85
3-phenylpyridine	4.8	NF	–		360	1.59
4-phenylpyridine	5.3	NF	–		340	1.85
2,6-diphenylpyridine	3.7	0.014	342	0.61	396	1.23

[a]NF – non-fluorescent

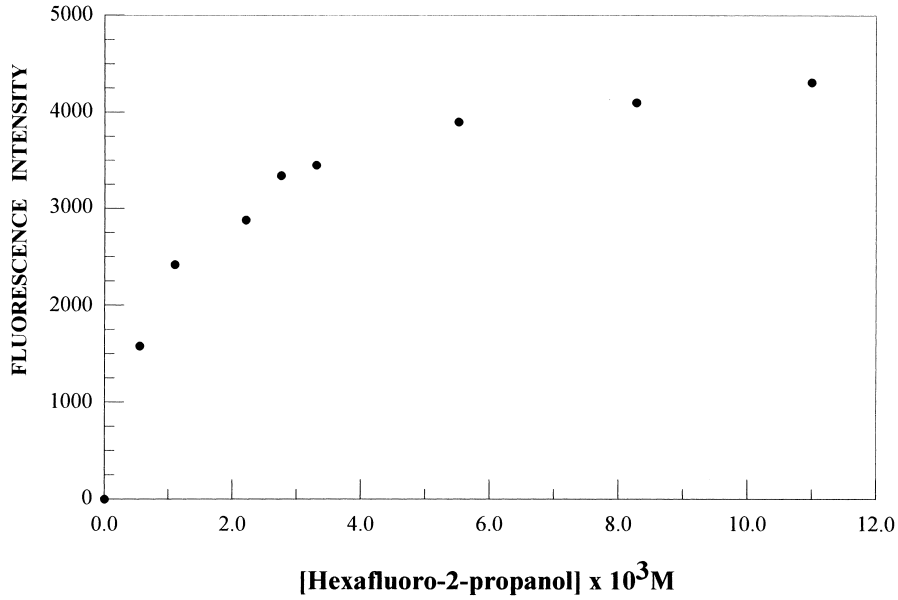

Fig. 4. Induced fluorescence of 3-phenylpyridine in cylcohexane from addition of hexafluoro-2-propanol (300 nm exc.).

The fluorescence of 2-phenylpyridine from ethyl alcohol solutions can be induced by adding water and it is seen that the signal intensity is weak until the water level exceeds 70% – see Fig. 5. In this case the solution changes from non-fluorescent to a fluorescent solution with a quantum yield of 0.12 in 100% water. We have previously reported that the excited state protonation of this molecule in water is required for the fluorescence [17].

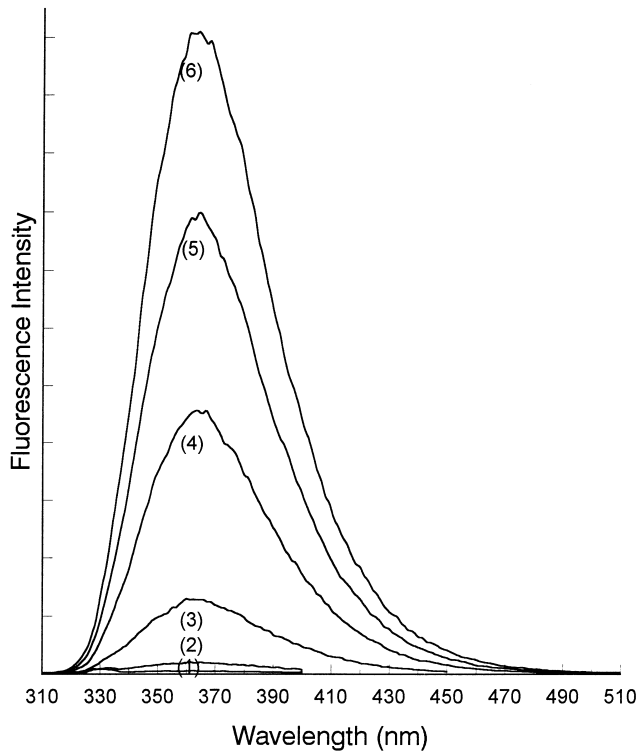

Fig. 5. Effect of water addition on the fluorescence of 3.0×10^{-6} M 2-phenylpyridine in ethyl alcohol. (300 nm exc.). Percent water: (1) 40, (2) 55, (3) 70, (4) 85, (5) 94, (6) 100.

4. Discussion

The data presented above indicate that the formation of 1:1 H-bonded complexes between the phenylpyridines and TFA in a hydrocarbon solvent lead to dramatic changes in the excited state behavior of the free azine, resulting in an induced fluorescence with a significant quantum yield. In all the three cases complexation of the azine raises the n, π transition, increases the oscillator strength of the transition to the lowest excited Frank–Condon state, thereby increasing the probability of fluorescence. In an earlier study with 2,6-diphenylpyridine, we demonstrated that in a non-polar solvent a proton transfer is unlikely, but rather that an excited state H-bond transfer occurs [12]. The data for the 2-,3- and 4-phenylpyridines presented in this study are also consistent with an induced fluorescence resulting from an excited state H-bond transfer. The fact that the H-bonded complex and the corresponding pyridinium ions show different peaks support the view that the absorption and fluorescence spectra are not due to the pyridinium cations. We do not consider the shifts to result from a solvent effect because of their correlation with the basicity of the azines. Furthermore, the fact that 2,6-diphenylpyridine, which is a weaker base than the molecules investigated here, shows the same fluorescence peak for the H-bonded complex and the corresponding pyridinium cation, underscores the importance of the increased basicity in the excited state. The magnitude of the formation constants indicate a strong interaction between the azine and

acid. It is noted that the induced fluorescence resulting from an excited state H-bond transfer has the potential application of sensing trace amounts of generated acid molecules in non-polar solvents with a low dielectric constant that inhibit proton transfer. The 1:1 complexation of the azine with an acid produces a strongly fluorescent species, and the large formation constants shown in Table 1 correlate well with the basicities of the three phenylpyridines. Although, all the three molecules exhibit induced fluorescence as a result of the formation of the ground state 1:1 H-bonded complex, the higher quantum yield in 2,6-diphenylpyridine suggests that it is the best sensor of the molecules investigated.

Since the N–H distance in hydrogen-bonded complexes are generally $\geq$2.5 Å, and much larger than the 1.0 Å distance seen in the protonated species, there should be varying degrees of H-bonding occurring between these two distances which should relate to the observed fluorescence yields, i.e., within these two limits of N-H separation how do we describe the events at distances between 1.0 Å and 2.5 Å? In addressing this issue we carried out an AM1 calculation of the dependence of the heat of formation for 2-, 3-, and 4-phenylpyridine, summarized in Fig. 6, which indicates that they all form the pyridinium ions at 1.0 Å, which is much shorter than the value in a hydrogen-bonded system. If we assume that a proton transfer should provide the largest fluorescence yield, then there is the possibility that the level of hydrogen-bonding should influence the fluorescence yield and wavelength maximum. The fact that

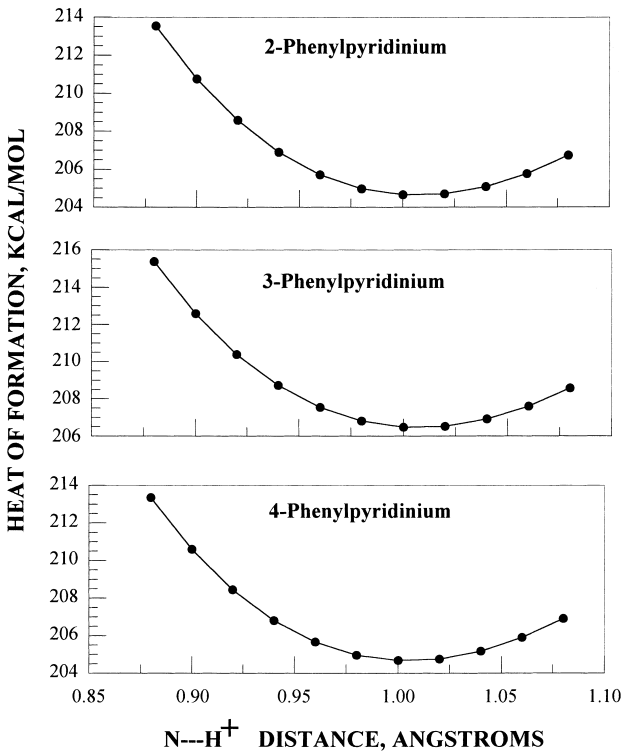

Fig. 6. AM1 calculation for the dependence of the heat of formation on the N–H^+ distance in 2-, 3- and 4-phenylpyridinium ions.

the 2- and 3- and 4-isomer show fluorescence peak wavelength differences for the H-bonded complexes with TFA in cyclohexane and in HFIP, relative to their respective pyridinium ions in water, seems to support this view. In a recent study Linschitz et al. [18] have shown that different levels of hydrogen-bonding could be distinguished in electrochemical studies. In the case of the phenylpyridines the fluorescence wavelength peak separation between the pyridinium ion and the H-bonded complex in cyclohexane increases with the basicity of the azine in the order 2,6- (pK_a=3.7) <2- (pK_a=4.2) <3- (pK_a=4.8) <4- (pK_a=5.3), with values of 0, 5, 30 and 40 nm, respectively. From the present study it appears that intermolecular H-bonding effects can lead to interesting luminescence effects in solution photophysics.

The concept of differing degrees of hydrogen-bonding has been discussed by Scheiner [19]. The increased basicity of the azine in the excited state has the effect of moving the proton of the TFA closer to the pyridine nitrogen, but at N–H distances that are larger than the 1.0 Å found in the pyridinium ion. As the hydrogen atom of the acid moves closer to the azine, the increased basicity induced by electronic excitation would gradually convert over from a neutral complex to the ion pair, i.e., B···H-A $\rightarrow$ B···H···$\rightarrow$ B-H^+···A^-, if the base becomes a strong acceptor. In principle if the proton affinity of B and A^- are the same, the hydrogen would be equidistant between the acid and base, a separation distance which would be larger than the protonation distance. It is in the presence of a polarizable solvent that the complete proton transfer would be facilitated. It has been shown that when various 4-substituted pyridines are complexed with an acid such as HCl, the distance $R_{H–Cl}$ increases as the substituted pyridine is made more basic [13]. Concomitantly, the distance $R_{N–H}$ gets shorter. These effects are manifested in a decreasing stretching frequency, $\nu_{H–Cl}$, and an increasing ν_{NH} as the proton moves toward the pyridine. The different fluorescence wavelength maxima for the H-bonded complex and the pyridinium ion for the phenylpyridines are consistent with the excited state H-bond transfer rather than a proton transfer.

In summary, we have shown that the fluorescence of phenylpyridines can be induced in a non-polar solvent by formation of 1:1 hydrogen-bonded complexes with an acid, which undergoes an excited state H-bond transfer. The sensitivity of this fluorescence method suggests that it can be used to detect trace amounts of acid in a non-polar solvent.

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