Solvent-Controlled Excited State Behavior: 2-(2′-Pyridyl)indoles in Alcohols

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Received August 14, 1995[⊗]

Abstract: Efficient fluorescence quenching caused by rapid internal conversion from the first excited singlet state is observed in alcohol solutions of 2-(2′-pyridyl)indoles, molecules which may simultaneously act as hydrogen bonding donors and acceptors. Electronic and infrared absorption studies show that upon adding alcohols to nonpolar solutions of pyridylindoles, 1:1 complexes are formed in the ground state, with hydrogen bonding occurring to the indole NH group. At higher alcohol concentrations 1:*n* ($n \geq 2$) solvates dominate. Investigations of the fluorescence intensity as a function of temperature and deuterium substitution in the hydroxylic group of the alcohol, and the results obtained for the N-methylated derivatives and 2-phenylindole show that the quenching may be described by a stepwise mechanism. First, a 1:1 cyclic, doubly hydrogen-bonded complex between alcohol and pyridylindole is formed after photoexcitation. This process is controlled by solvent reorientation. Excited state double proton transfer in such a complex opens up a fast internal conversion channel. The driving force for phototautomerization arises as a result of the excited state increase of the basicity of the pyridine nitrogen atom and the enhanced acidity of the indole NH group. This effect was also predicted by calculations of excited state valence electron potentials, parameters that can be used as acido-basic reactivity indices.

Introduction

Formation of intermolecular hydrogen bonding has been shown to influence the photophysical behavior of many heteroaromatic systems.[1−98] For instance, different energy shifts of close-lying nπ^* and $\pi\pi^*$ states upon hydrogen bonding may result in the reversal of state ordering or lead to large changes in the strength of vibronic or spin-orbit coupling ("proximity effects").[4] Another mechanism of altering the photophysical properties operates when the hydrogen bonding strength is not the same in the ground and excited states. This leads to different shapes and positions of the minima in the potential energy hypersurfaces of the two states, which, in turn, may activate rapid internal conversion from S_1.[90−96] In many systems, fluorescence quenching has been explained on the basis of charge transfer interactions between the proton donor and acceptor[5−20] or by a hydrogen transfer[21] mechanism.

A particular case occurs for molecules that can simultaneously act as hydrogen bonding donors and acceptors. In such systems, formation of cyclic complexes, usually with alcohol, may lead to excited state tautomerization involving the cooperative movement of two or even more protons. The most investigated system of this kind are alcohol complexes of 7-azaindole;[22−53] similar behavior has been observed for 1-azacarbazole,[54−58]

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[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1996.

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0002-7863/96/1518-3508$12.00/0

hydroxyquinolines,[59−67] indoloquinoxalines,[68,69] 2-hydroxy-4,5-benzotropone,[70] 2-(2′-pyridyl)benzimidazole,[71−73] 3-hydroxyflavone,[74−82] and lumichromes.[83−86]

Although the phototautomerization of 7-azaindole alcohol and water complexes has been studied for more than two decades, basic controversies still remain. The structure of the ground state species is not definitely solved. The nature of the rate-determining step for phototautomerization is being discussed: it may involve proton movement, solvent reorientation, or a combination of both.

In this work, we address problems of the ground state structure and the excited state deactivation mechanism in order to understand the process of fluorescence quenching by alcohols observed in 2-(2′-pyridyl)indoles.[97,98] We have postulated that this phenomenon must involve a cyclic, doubly hydrogen-bonded complex with alcohol, which strongly suggests that the shift of two protons, occurring in the excited state, is responsible for the process. Still, several problems remained to be solved. It was not clear whether the attainment of a structure predisposed to tautomerization occurs prior to or after excitation. The origin of the rate-determining step for the quenching has not been elucidated.

The results presented in this work are based on a study of the ground state equilibria followed by calculations and the investigation of the quenching efficiency as a function of temperature, solvent properties, and the isotope substitution. We show that the stepwise mechanism of quenching involves: (i) solvent rearrangement leading to the formation of a doubly hydrogen-bonded alcohol complex and (ii) internal conversion induced by the concerted motion of two protons.

Experiment and Calculations

The synthesis of 2-(2′-pyridyl)indole (**Pyln-0**), 3,3′-methylene-2-(2′-pyridyl)indole (**Pyln-1**), 3,3′-dimethylene-2-(2′-pyridyl)indole (**Pyln-2**), 3,3′-trimethylene-2-(2′-pyridyl)indole (**Pyln-3**), and 3,3′-tetramethylene-2-(2′-pyridyl)indole (**Pyln-4**) has been described previously.[99] The N-methylated derivatives were obtained as follows:

1-Methyl-2-(2′-pyridyl)indole (MePyln-0). A mixture of 2-acetylpyridine (0.88 g, 7.27 mmol) and 1-methyl-1-phenylhydrazine (1.10 g, 9.02 mmol) in EtOH (5 mL) with one drop of concentrated H_2SO_4 was refluxed for 2 h. The mixture was cooled, and the crude product was collected and purified by chromatography on SiO_2, eluting with CH_2Cl_2, to obtain 1.22 g (74%) of the corresponding *N*-methylphenylhydrazone. This hydrazone (0.85 g, 3.78 mmol) was heated with polyphosphoric acid (PPA, 1.15 g) at 115 °C for 2 h. The mixture was cooled, made basic with 50% NaOH, and extracted with CH_2Cl_2. Chromatography on SiO_2, eluting with 10:1 CH_2Cl_2/EtOAc provided 0.29 g (37%) of 1-methyl-2-(2′-pyridyl)indole, mp 86−86.5 °C: ^{1}H

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Table 1. The maxima of Room Temperature Fluorescence (in Units of 10^3 cm^{-1})[a]

	n-hexane	benzene	ethyl ether	BuCN	pyridine	DMSO	CH_3CN	BuOH	PrOH	EtOH	MeOH
Pyln-0	27.5	26.6	26.8	26.4	26.0	25.6	26.1	24.6	24.5	24.3	24.4
MePyln-0	26.8	25.9	26.5	25.8	25.5	25.3	25.5	25.3	25.0	24.6	24.7
Pyln-1	27.8	27.0	26.9	26.7	26.2	26.0	26.4	25.9	25.8	25.6	25.4
Pyln-2	26.3	25.5	25.6	25.6	24.9	24.9	25.3	25.1	25.0	25.0	24.8
MePyln-2	25.5	24.9	25.3	25.0	24.6	24.5	24.7	24.5	24.4	24.4	24.2
Pyln-3	26.5	25.7	25.9	25.7	25.3	24.9	25.4	25.3	25.3	25.1	24.9
Pyln-4	26.2	25.7	25.7	25.2	24.9	24.4	24.6	24.5	24.2	23.9	23.6
2-PI	28.5	27.7	27.9	27.7	26.9	27.1	27.6	27.6	27.6	27.6	27.6

[a] The error is estimated to be ±200 cm^{-1}.

NMR (300 MHz, $CDCl_3$) δ 8.70 (d, 1H, J = 4.4 Hz), 7.8−7.7 (overlapping m, 2H), 7.66 (d, 1H, J = 7.8 Hz), 7.41 (d, 1H, J = 8.2 Hz), 7.3−7.2 (overlapping M, 2H), 7.14 (t, 1H, J = 7.7 Hz), 6.87 (s, 1H), 4.07 (s, 3H); IR (KBr) 3010, 2960, 1550, 1525, 1430, 1395, 1295, 1130 cm^{-1}.

1-Methyl-3,3′-dimethylene-2-(2′-pyridyl)indole (MePyln-2). Following the procedure described above, the reaction of 5,6,7,8-tetrahydro-8-quinolone[100] (0.62 g, 4.22 mmol) with 1-methyl-1-phenylhydrazine (0.72 g, 5.9 mmol) afforded a crude hydrazone which was purified by chromatography on Al_2O_3 eluting with CH_2Cl_2. The hydrazone was then treated with PPA (10.5 g) in toluene (4 mL) at 115 °C for 2 h. Workup provided a crude product which was purified by chromatography on SiO_2 eluting with CH_2Cl_2 to afford the pure indole (0.41 g, 41%), mp 99−100 °C: ^{1}H NMR (300 MHz, $CDCl_3$) 8.43 (d, 1H, J = 4.9 Hz), 7.59 (d, 1H, J = 7.7 Hz), 7.51 (d, 1H, J = 7.1 Hz), 7.38 (d, 1H, J = 8.4 Hz), 7.27 (t, 1H, J = 7.2 Hz), 7.13 (t, 1H, J = 7.4 Hz), 7.03 (dd, 1H, J = 4.9, 7.5 Hz), 4.32 (s, 3H), 3.01 (m, 4H); IR (KBr) 2600, 1528, 1426, 1204, 782, 735 cm^{-1}. Anal. Calcd for $C_{16}H_{14}N_2$−$0.2H_2O$: C, 80.80; H, 6.06; N, 11.78. Found: C, 80.85; H, 5.64; N, 11.89.

Commercially available 2-phenylindole (Aldrich, tech.), was purified by thin layer chromatography and recrystallization from *n*-hexane and/or methanol.

Fluorescence quantum yields of pyridylindoles were measured on a Jasny spectrofluorimeter and corrected for the sensitivity of the instrument. Quinine sulfate (ϕ = 0.51) was used as a standard. Special care was taken to ensure that the solvent did not contain impurities that might quench the luminescence. Solvents: *n*-hexane, ethyl ether, acetonitrile, methanol, ethanol, *n*-propanol, butanol, pyridine, benzene, 1,1,1,3,3,3-hexafluoropropanol-2, and dimethylsulfoxide (DMSO) were of fluorescence or spectral grade (Merck). Butyronitrile (Merck, for synthesis) was purified as previously described.[97] The solutions used for isotope substitution studies were prepared in a drybox under a nitrogen atmosphere.

Absorption spectra were run on a Shimadzu UV 3100 spectrophotometer. Transient absorption spectra were recorded on a custom-built nanosecond spectrophotometer with dye laser probing and computer control.[101] Infrared spectra were obtained on a NICOLET SX-170 FTIR spectrometer.

Excited state energies were computed using the INDO/S method, with 200 singly excited configurations taken into account in the CI procedure. Ground state geometry optimizations were performed by molecular mechanics (MMX force field, PCMODEL). In some cases, the AM1 method was also used.

Results

Figure 1 presents room temperature fluorescence spectra of **Pyln-2** and **MePyln-2** in various solvents. Fluorescence maxima of all the compounds studied are given in Table 1. Although not dramatic, solvent dependence of the fluorescence band position clearly indicates specific intermolecular hydrogen-bonding interactions. This is illustrated in Figure 2 for the pair **Pyln-2/MePyln-2.** For the N-methylated derivative, the values of the fluorescence maxima plotted against the values of the

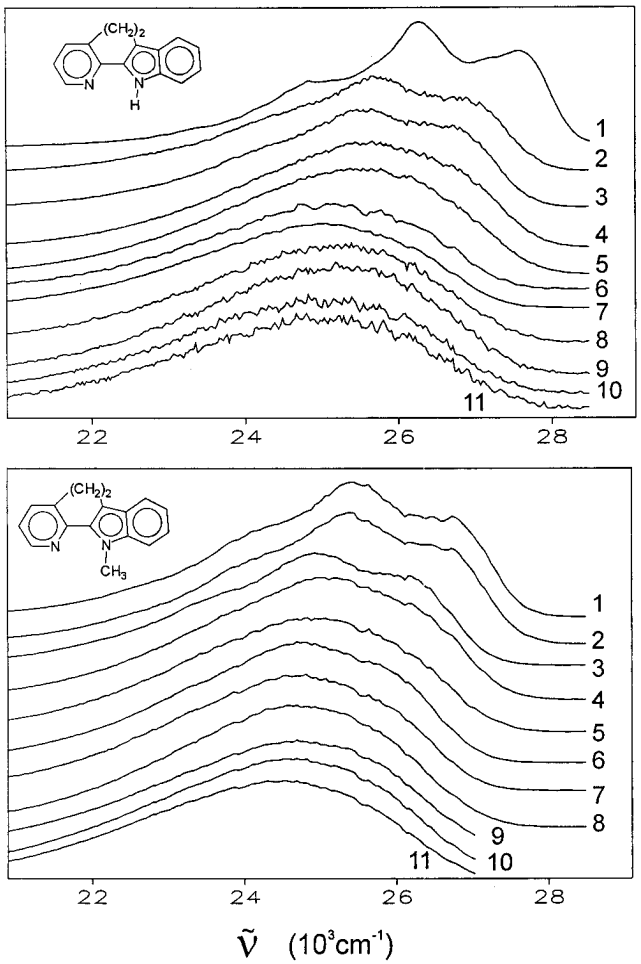

Figure 1. Fluorescence spectra of **Pyln-2** and **MePyln-2** at 293 K in various solvents: *n*-hexane (1), ethyl ether (2), benzene (3), butyronitrile (4), acetonitrile (5), pyridine (6), DMSO (7), butanol (8), *n*-propanol (9), ethanol (10), and methanol (11).

local solvent polarity parameter, π^*,[102,103] fall on a straight line. **Pyln-2** reveals the same behavior only for non-hydrogen bonding solvents, whereas in pyridine, DMSO, and even in ethyl ether the fluorescence is shifted to the red more than could have been expected on the basis of the solvatochromic curve. These results point to an increase in the hydrogen bonding strength between the indole NH group and the proton-accepting solvent upon excitation to S_1. We observe this effect for all the investigated compounds that contain the NH group.

In alcohols, the situation is more complicated. Fluorescence shifts may now reflect excited state changes in two types of hydrogen bonds, occurring between the alcohol and either the indole NH group or the pyridine nitrogen atom. In the former,

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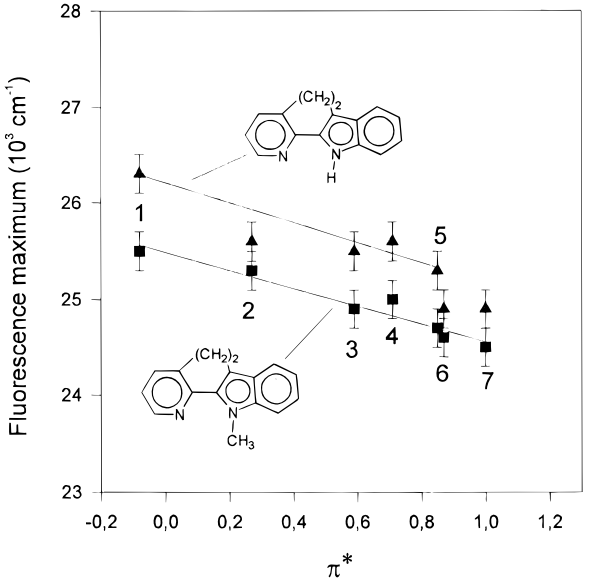

Figure 2. Fluorescence maxima of **Pyln-2** (triangles) and **MePyln-2** (squares) at 293 K plotted against the values of the local polarizability parameter, π^*.[102,103] (1) *n*-hexane, (2) diethyl ether, (3) benzene, (4) butyronitrile, (5) acetonitrile, (6) pyridine, and (7) DMSO.

the alcohol molecule acts as proton acceptor, in the latter, as a donor. The proton donating and accepting abilities of the alcohols vary in opposite directions in the sequence: butanol, *n*-propanol, ethanol, and methanol. Thus, it is not possible to predict *a priori* the spectral shifts along the series of alcohols, since they will depend on which of the two hydrogen bond types is more affected by excitation.

The experimentally observed energies corresponding to fluorescence maxima in alcohols are generally lower than those in pyridine and DMSO. The values of the local polarity parameter, π^*, are smaller for the alcohols (0.87, 1.00, 0.46, 0.51, 0.54, and 0.60 for pyridine, DMSO, butanol, *n*-propanol, ethanol, and methanol, respectively); the values of the solvent basicity parameter, β,[102,103] are similar (0.64, 0.76, 0.88, 0.78, 0.77, and 0.62, in the same order). Therefore, the additional red shift can be explained by the increased hydrogen bonding strength between the pyridine nitrogen atom and the alcohol. This is in agreement with the observation that the emission shift in alcohols can be correlated with the parameter α, which describes the hydrogen bonding acidity of the solvent[103] (0.79, 0.78, 0.83, and 0.93 for butanol, *n*-propanol, ethanol, and methanol).

We thus conclude that upon electronic excitation both the indole NH group and the pyridine nitrogen atom increase their hydrogen bonding ability: the former becomes more acidic, the latter, more basic. A possibility of excited state proton transfer between the two centers can be envisaged, provided that a chemical "link" between the two parts of the chromophore could be established. We have postulated the existence of a cyclic 1:1 complex with alcohol in order to explain the photophysical properties of pyridylindoles.[97,98] In particular, a strong fluorescence quenching in alcohols is observed only for the compounds containing both groups (Table 2). No quenching occurs in the **MePyln-2** as well as in **2-PI**.

Fluorescence quenching was also observed in pyridine. The mechanism of this process will be dealt with separately.[104] Here, we focus on the ground and excited state structure and dynamics of alcohol complexes.

(104) Herbich, J.; Dobkowski, J.; Karpiuk, J.; Thummel, R. P.; Waluk, J. Manuscript in preparation.

Chart 1. Formulae

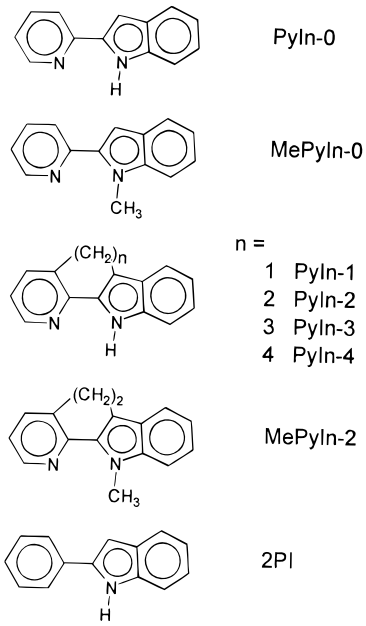

Table 2. Room Temperature Fluorescence Quantum yields[a]

	methanol	ethanol	*n*-propanol	butanol
Pyln-0	0.015	0.08	0.11	0.12
MePyln-0	0.008	0.05	0.09	0.14
Pyln-1	0.004	0.009	0.009	0.012
Pyln-2	0.003	0.005	0.006	0.008
MePyln-2	0.54	0.67	0.69	0.71
Pyln-3	0.004	0.007	0.011	0.017
Pyln-4	0.004	0.007	0.011	0.012
2PI	0.70	0.80	0.75	0.79

[a] Accuracy ±20%.

Ground State Structure of Alcohol Complexes. In order to accurately determine the stoichiometry of alcohol solvates, it is crucial to work in the range where the concentration of alcohol oligomers is negligible. To ensure that, we have measured the IR spectra of methanol and butanol in CCl_4. The formation of oligomeric species is readily detected by the appearance of broad bands around 3300−3500 cm^{-1}. We found that in CCl_4 at 293 K, the concentration range where only monomeric species of the alcohol are observed is below 2×10^{-2} M for butanol and 5×10^{-2} M for methanol.

Adding alcohol to a solution of pyridylindole in a nonpolar solvent results in spectral changes that testify to the formation of ground state complexes. A new absorption band appears on the low energy side of the electronic spectrum, and isosbestic points are observed (Figure 3). This effect is quite strong for **Pyln-0**, **Pyln-1**, and **Pyln-2**, weaker for **Pyln-3** and **Pyln-4** and even weaker for **2-PI**. These variations correlate with the H-bonding ability of the N−H group determined from the NMR chemical shift.[99] If, instead of the alcohol, DMSO (which can only act as a hydrogen bond acceptor) is added to the solution, very similar spectral behavior is observed. No changes are observed upon adding alcohols to solutions of the N-methylated derivatives.

These results strongly suggest that the bonding with alcohol in the ground state occurs preferentially to the NH proton. The direct proof is provided by the IR measurements (Figure 4). In CCl_4, a band at 3473 cm^{-1} for **Pyln-2** may be assigned to the NH stretch of the unbound molecule. Adding alcohol leads to a decrease in the intensity of this peak. Simultaneously, a broad band appears at 3288 ± 5 cm^{-1}.

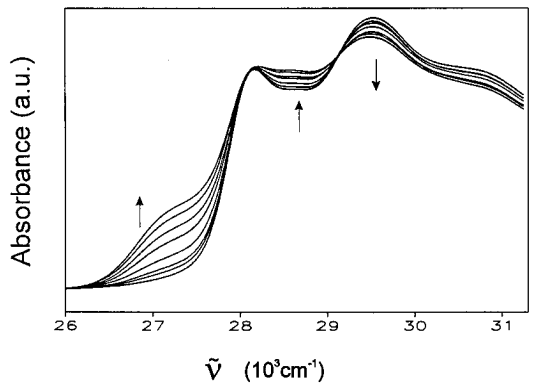

Figure 3. Absorption changes observed upon adding butanol to a 10^{-5} M solution of **Pyln-2** in *n*-hexane at 293 K. The concentrations of butanol were 0, 8.8×10^{-4}, 1.76×10^{-3}, 3.51×10^{-3}, 7.02×10^{-3}, 1.05×10^{-2}, 1.40×10^{-2}, and 1.76×10^{-2} M. The arrow indicates increasing alcohol concentration.

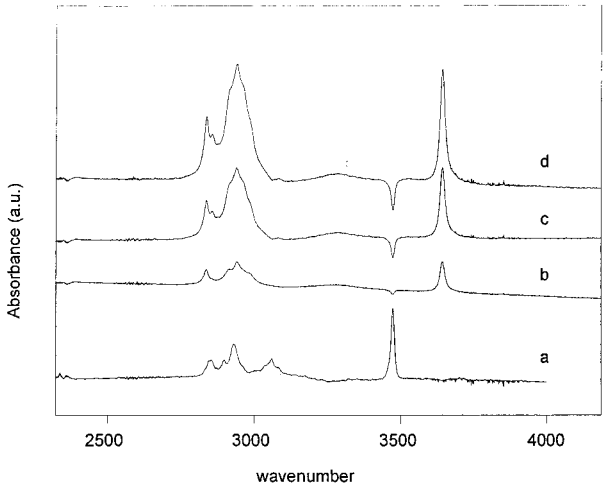

Figure 4. Portion of the IR spectrum of **Pyln-2** ($c = 1.7 \times 10^{-3}$ M) in CCl_4; changes in the spectrum after adding methanol: 1.3×10^{-2} M (b), 3.5×10^{-2} M (c) and 5×10^{-2} M (d).

The ratio of the intensity of the OH stretching band of the alcohol (3644 cm^{-1}) to the intensities of the other bands, not involving the OH vibrations (e.g., 2938 cm^{-1}), does not change in mixed solutions of pyridylindoles and alcohols in CCl_4 and remains the same as observed in the absence of pyridylindoles. This would mean that the hydroxylic proton of the alcohol, and thus the pyridine nitrogen atom of pyridylindole, is not engaged in the ground state hydrogen bonding. However, this result must be treated with caution, since the alcohol concentration was always larger than that of the pyridylindoles, so that the fraction of complexed alcohol molecules did not exceed 10%. Still, this observation agrees well with the finding that adding alcohol did not lead to any spectral changes in the IR spectrum of pyridylindoles in the region 950−1100 cm^{-1}, i.e., the expected location of a band corresponding to a vibration involving the pyridine nitrogen atom (and thus sensitive to hydrogen bonding to the pyridine nitrogen).

There are several ways to determine the stoichiometry of the complex. For a reaction

$$P + nA = PA_n \quad K_{1n} = [PA_n]/([P][A]^n) \tag{1}$$

the equilibrium constant may be expressed as

$$K_{1n} = (OD - OD_0)/\{(OD_\infty - OD_0)\cdot[A]^n\} \tag{2}$$

where OD_0 and OD_∞ denote the optical density measured when only the uncomplexed or complexed forms are present, and OD is the optical density measured at an alcohol concentration [A]. Plotting $\ln[(OD - OD_0)/(OD_\infty - OD_0)]$ vs ln[A] should yield the slope equal to *n*, the number of alcohol molecules in a complex. An example is shown in Figure 5 for **Pyln-2** in butanol. The slope obtained for various wavelengths was in the range 1.04 ± 0.06. Thus, the 1:1 stoichiometry was determined, in accordance with our earlier investigations.[97]

The above result is based on the assumption that the absorption coefficients of both forms are known. While this is true for the uncomplexed species, the value for the complex must be approximated from the measurements performed in large excess of the alcohol. We have therefore checked the validity of the results by using different procedures. The following equations may be written,[105] relating the measured quantities to the equilibrium constants of the complex formation:

$$\frac{([P]_0[A]_0 + [PA]^2)}{\Delta OD} = \frac{[P]_0 + [A]_0}{\Delta\epsilon} + \frac{1}{K_{11}\Delta\epsilon} \tag{3}$$

$$\Delta OD = \frac{[P]_0 K_{11}[A](\Delta\epsilon_1 + \Delta\epsilon_2 K_{12}[A])}{1 + K_{11}[A] + K_{11}K_{12}[A]^2} \tag{4}$$

$$[A]_0 = [A] + \frac{[P]_0 K_{11}[A](1 + 2K_{12}[A])}{1 + K_{11}[A] + K_{11}K_{12}[A]^2} \tag{5}$$

Equation 3 assumes that only a 1:1 complex is formed, while eqs 4 and 5 describe the formation of both 1:1 and 1:2 species, with equilibrium constants K_{11} and K_{12} (note that the units of both K_{11} and K_{12} are the same (M^{-1}), since the latter is now expressed as $[PA_2]/[PA][A]$). $\Delta OD = OD - OD_0$, $[P]_0$ and $[A]_0$ are the initial concentrations of pyridylindole and alcohol, respectively, [PA] is the concentration of a 1:1 complex, $\Delta\epsilon_1 = \epsilon_{11} - \epsilon_P$; $\Delta\epsilon_2 = \epsilon_{12} - \epsilon_P$, where ϵ_P is the extinction coefficient of the uncomplexed molecule.

Using the nonlinear least squares method, we have fitted the experimental data to eq 3 or simultaneously to eqs 4 and 5, optimizing the values of K_{11}, K_{12}, $\Delta\epsilon_{11}$, and $\Delta\epsilon_{12}$.

Yet another approach[14,15] is to assume the formation of a 1:1 complex and to use the relation

$$(1 - OD_0/OD)/[A] = -K_{11} + (\epsilon_{11}/\epsilon_P)K_{11}(OD_0/OD) \tag{6}$$

The intercept of the plot of $(1 - OD_0/OD)/[A]$ vs (OD_0/OD) should yield K_{11}.

The analysis of the experimental data using these three different procedures is shown in Figure 5 for **Pyln-2** in butanol at 293 K. All the methods yield very similar values of the equilibrium constant $K_{11} = 40 \pm 5$ M^{-1}.

Figure 6 shows the temperature dependence of the complexation, measured by the changes in the absorption. For **Pyln-2**, we have determined the values of K_{11} in mixtures of *n*-hexane with methanol and butanol in the temperature range 278−313 K at intervals of 5 K. From the van't Hoff plot (Figure 6) we obtain $\Delta H = -8.6 \pm 0.2$ kcal/mol and -8.7 ± 0.2 kcal/mol, $\Delta S = -22.3 \pm 0.6$ eu and -23.0 ± 0.6 eu for butanol and methanol, respectively. From somewhat less detailed studies of the other pyridylindoles, we estimate that the thermodynamic parameters for **Pyln-0** and **Pyln-1** are similar to those of **Pyln-2**, whereas alcohol complexes of **Pyln-3** and **Pyln-4** have smaller values of the heats of formation ($\Delta H \approx -7$ kcal/mol for the former, −5 kcal/mol for the latter). It is observed that the equilibrium constants are always larger in butanol than in methanol. This confirms that the alcohol binds to the NH group, since butanol is a stronger base but a weaker acid than methanol.

(105) Pipkin, J. D.; Stella, V. J. *J. Am. Chem. Soc.* **1982**, *104*, 6672.

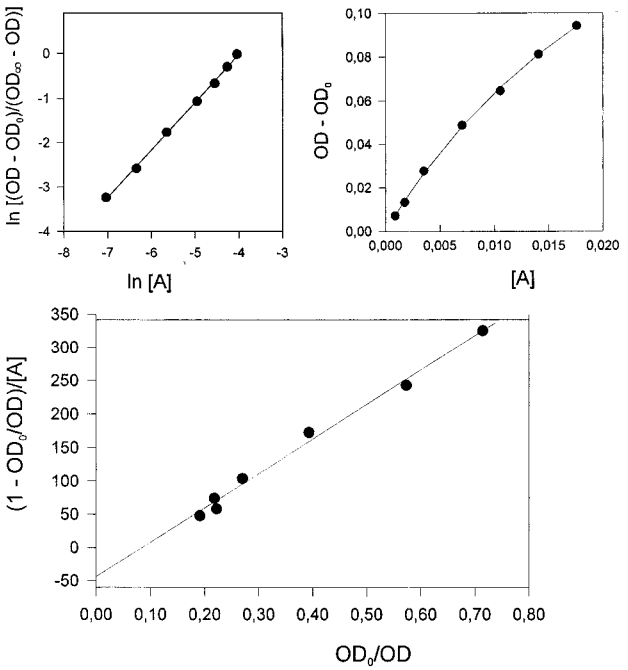

Figure 5. Determination of the stoichiometry of the alcohol solvates of **Pyln-2** using eq 2 (top left), eqs 3−5 (top right) and eq 6 (bottom). The absorbance values at 27 000 cm^{-1} were used for calculations. Similar results were obtained using the values at 26 800 and 27 500 cm^{-1}.

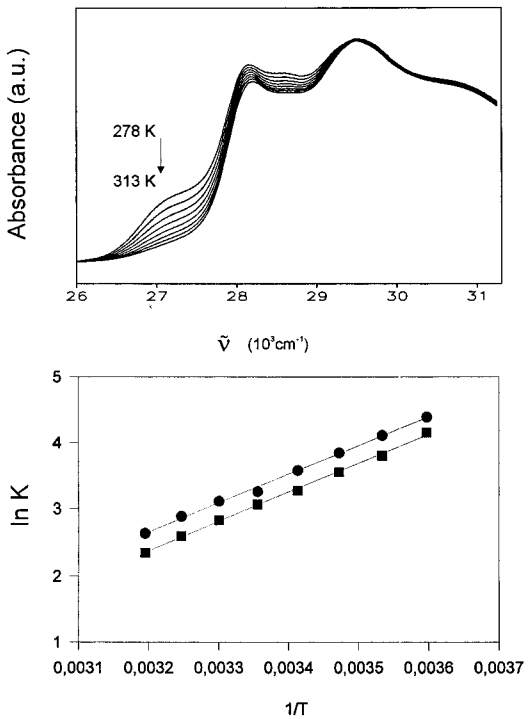

Figure 6. Top, temperature dependence of absorption of **Pyln-2** in *n*-hexane with 10^{-2} M of butanol. The temperature was varied from 278 to 313 K in 5 K steps. Bottom, the van't Hoff plots for methanol (squares) and butanol (circles), obtained from absorption changes at 27 000 cm^{-1}.

Comparison of the results of the fitting procedures that assume only the formation of 1:1 complexes with those based on the method which optimized both K_{11} and K_{12} shows that the spectral behavior in the low alcohol concentration range is satisfactorily explained by the presence of only 1:1 solvates. Such a result does not warrant, however, that the situation is the same at higher alcohol concentrations. Indeed, we have noticed that the slope of $\ln[(OD - OD_0)/(OD_\infty - OD_0)]$ vs $\ln[A]$ systematically deviated from the values close to 1 toward larger values upon discarding the experimental points corresponding to low alcohol concentrations. This can be interpreted as a sign of formation of 1:2 (or even higher order) complexes. Since we could not extend the alcohol concentration range to larger values, due to the aggregation of alcohol molecules, we used the approximate procedure for the evaluation of K_{12}: ϵ_{11} and ϵ_{12} were assumed to be equal; the concentration of the uncomplexed species, [P], was calculated as $[P]_0(OD_\infty - OD)/[(OD_\infty - OD_0)$. Then, $[PA] \approx K_{11}[P][A]$ (true for $[A]_0 \gg [P]_0$: in our case, the latter was always smaller than 2×10^{-5} M). Finally, $[PA_2] = [P_0] - [PA]$, and the value of K_{12} could be estimated. For **Pyln-2** in hexane at 293 ($K_{11} = 40$ M^{-1}) with admixtures of butanol in the range 0.01−0.02 M, the obtained values of K_{12} varied between 10 and 50 M^{-1}. More important than the exact value is the finding that the 1:2 complexes should begin to dominate the 1:1 species already at relatively small alcohol concentrations. Let us denote by α(P), α(PA), and $\alpha(PA_2)$ the molar fractions of the uncomplexed species, 1:1 and 1:2 solvates, respectively. For **Pyln-2** in hexane at 293, even if the smallest value of $K_{12} = 10$ M^{-1} is assumed, the fractions of 1:1 and 1:2 species will be equal at [A] = 0.1 M: α(P) = 0.11, α(PA) = $\alpha(PA_2)$ = 0.44. For $K_{12} = 30$ M^{-1}, we get α(P) ≈ 0.22, α(PA) ≈ 0.35, and $\alpha(PA_2) \approx 0.42$ when [A] = 0.03 M. In the bulk alcohol, more than 99% of the complexes should not be present as a 1:1 form. Naturally, with increasing alcohol concentration the formation of higher order (1:*n*, $n \geq 2$) solvates with alcohol oligomers is also possible.

The results we obtain from the ground state studies may be summarized as follows: upon adding alcohols to nonpolar solutions of pyridylindoles, 1:1 complexes are formed, with the bonding occurring to the NH group. No spectral evidence for the participation of the pyridine nitrogen atom in the hydrogen bonding was found. Thus, cyclic ground state 1:1 complexes seem highly improbable. As the alcohol concentration increases, 1:*n* species ($n \geq 2$) begin to dominate. The second alcohol molecule may become attached either to the pyridine nitrogen atom or to the alcohol molecule that is already involved in the complex. Several observations support the latter possibility: (i) the electronic spectra in alcohols and DMSO (which can only act as a hydrogen bond acceptor) are very similar; (ii) no significant spectral shifts are detected upon passing from mixed solutions of nonpolar solvents with alcohols (where mostly 1:1 species are present) to bulk alkohols; (iii) the absorption spectra of the N-methylated derivatives in aprotic solvents are completely insensitive to the addition of alcohols; (iv) the IR spectra clearly indicate formation of hydrogen bonding between alcohol and the NH group but not between the alcohol and the pyridine nitrogen. The somewhat surprising absence of the ground state hydrogen bonding to the pyridine nitrogen atom may be related to the pK_a values (Table 5), which are significantly lower than 5.2, the pK_a value of pyridine.[106]

The most important implication of the ground state studies is that the cyclic, doubly hydrogen-bonded 1:1 complex, crucial for the understanding of the fluorescence quenching process, must be formed after photoexcitation.

Temperature Dependence of Fluorescence Intensity. In all pyridylindoles that reveal quenching by alcohols, temperature decrease leads to the recovery of the emissive properties. At low temperatures, both quantum yields (higher than 60%) and lifetimes (2.3−2.8 ns) are very similar for all the compounds, including the methylated derivatives, and practically solvent-

(106) Kasende, O.; Zeegers-Huyskens, Th. *J. Phys. Chem.* **1984**, *88*, 2132.

Table 3. Arrhenius Parameters for Pyridylindoles in Alcohols

		ΔE (kcal/mol)	k' (s^{-1})[a]
Pyln-2	Methanol	3.5 ± 0.5	$(2.6 \pm 1.3) \times 10^{13}$
	ethanol	3.9 ± 0.5	$(3.0 \pm 1.5) \times 10^{13}$
	ethanol-*O*-*d*	3.7 ± 0.5	$(1.0 \pm 0.5) \times 10^{13}$
	propanol	4.6 ± 0.5	$(8.6 \pm 4.3) \times 10^{13}$
	butanol[b]	5.0 ± 0.5	$(3.6 \pm 1.8) \times 10^{13}$
Pyln-3	ethanol	4.3 ± 0.2	$(4.4 \pm 1.0) \times 10^{13}$
	ethanol-*O*-*d*	4.4 ± 0.2	$(3.0 \pm 0.9) \times 10^{13}$
	propanol	5.0 ± 0.3	$(9.3 \pm 4.0) \times 10^{13}$
Pyln-0	methanol	1.8 ± 0.4	$(3.0 \pm 0.7) \times 10^{11}$
	ethanol	1.7 ± 0.4	$(3.4 \pm 1.7) \times 10^{10}$
	ethanol-*O*-*d*	2.1 ± 0.5	$(3.0 \pm 1.5) \times 10^{10}$
	propanol	1.7 ± 0.4	$(3.0 \pm 1.5) \times 10^{10}$
Me-Pyln-0	methanol	2.0 ± 0.5	$(7.4 \pm 3.7) \times 10^{11}$
	ethanol	2.2 ± 0.4	$(1.4 \pm 0.7) \times 10^{11}$
	propanol	3.2 ± 0.4	$(4.4 \pm 2.2) \times 10^{11}$
	butanol[b]	3.5 ± 0.5	$(3.8 \pm 1.9) \times 10^{11}$

[a] Obtained assuming the radiative rate of S_1 depopulation, $k_r = 2 \times 10^8$ s^{-1}. [b] From fluorescence lifetime measurements.

independent. The values of the radiative rate constant, k_r, calculated from quantum yields and lifetimes, are also similar (all lie in the range $2-3 \times 10^8$ s^{-1}) and only weakly dependent on the solvent. For instance, the k_r values calculated for **Pyln-2** are $(2.9 \pm 0.8) \times 10^8$ s^{-1} (*n*-hexane, 293 K), $(2.2 \pm 0.7) \times 10^8$ s^{-1} (butyronitrile, 293 K), and $(2.2 \pm 0.7) \times 10^8$ s^{-1} (butanol, 77 K).

Thus, the quenching process in alcohols is strongly temperature-dependent. If one assumes that the nonradiative rate of excited singlet state deactivation may be expressed as $k^0_{nr} + k'\exp(-\Delta E/RT)$, a sum of a temperature independent and a temperature dependent process, the Arrhenius-type expression results

$$1/\phi(T) = 1 + (k^0_{nr}/k_r) + (k'/k_r)\exp(-\Delta E/RT) = a + b\exp(-\Delta E/RT) \quad (7)$$

Fitting the experimental data to this equation enabled the determination of the Arrhenius parameters, k' and ΔE. The results are presented in Table 3. An example of the fit is shown in Figure 7.

The activation energy of the temperature-dependent quenching process in **Pyln-2** is correlated with the activation energy of viscous flow of the solvent (2.5, 3.5, 4.4, and 4.6 kcal/mol for methanol, ethanol, *n*-propanol, and butanol, respectively).[107] A very significant result is that the activation energy in **Pyln-2** and **Pyln-3** does not change upon replacing the hydroxylic proton of the alcohol by deuterium. The isotope effect is observed, however, in the decreased value of the preexponential factor in deuterated ethanol. This finding will be the basis of the model we use for the explanation of the quenching mechanism.

The values of k^0_{nr}/k_r obtained from the fit are of the order of one. This is in agreement with the fact that the fluorescence quantum yields observed when no quenching occurs are of the order of 50%. Thus, the radiative and radiationless deactivation processes occur with similar rates. We attribute the nonradiative, temperature-insensitive channel to intersystem crossing, based on the results of transient absorption measurements which will be discussed below.

Both the unbridged and methylated derivatives reveal completely different temperature dependence. In **2PI** and **MePyln-2**, fluorescence yields are very high already at room temperature. In **Pyln-0** and **MePyln-0**, emission intensity changes with temperature obey a completely different pattern than that observed in the bridged, nonmethylated derivatives. Lower activation energies and preexponential factors are obtained. This and other observations discussed below provide arguments that the Arrhenius parameters extracted from the temperature dependence of fluorescence of **Pyln-0** do not describe the species that undergoes efficient quenching, but another conformer.

Photophysics of Pyln-0 and MePyln-0. **Pyln-0** and its methylated derivative may exist as *syn* and *anti* conformers, whereas the *syn* conformation of all the other pyridylindoles is imposed by bridging. Spectral evidence points to the existence of two conformations of **Pyln-0**. The fluorescence decay is biexponential in alcohols and in mixtures of alcohol with either a nonpolar or a polar, aprotic solvent.[97] The value of the shorter component is practically the same as the decay time observed for the bridged pyridylindoles. Therefore, it is assigned to the *syn* conformation. The other component would thus correspond to the *anti* conformation. Characteristically enough, its fluorescence lifetime, 3.3 ns in both *n*-propanol and butanol, is longer than that observed for **Pyln-0** in aprotic solvents (1.3 ns in *n*-hexane, 1.8 ns in butyronitrile[97]).

The quantum yields measured for **Pyln-0** at 293 K in alcohols are much larger than those of the bridged compounds (cf. Table 2). On the other hand, these yields are smaller than the yield measured for **Pyln-0** in aprotic solvents (0.48 in *n*-hexane, 0.47 in ethyl ether, 0.53 in butyronitrile, and 0.55 in benzene[98]). It should also be noted that the emission maxima of **Pyln-0** in alcohols are shifted considerably to the red from those measured in hydrogen-bonding solvents that can only act as proton acceptors (e.g., pyridine and DMSO). This solvent dependence is not observed for the other derivatives. These findings indicate that the emission of **Pyln-0** observed at room temperature in alcohols is mostly due to the *anti*-conformer. Indeed, fluorescence decay studies performed in mixtures of *n*-hexane with *n*-propanol or butanol show that the fraction of the *anti*-conformer increases upon adding the alcohol. In pure alcohols, more than 90% of the population may be assigned to the *anti* form. It is noteworthy that the radiative constant of the fluorescence of the *anti*-conformer is about one order of magnitude smaller than that of the *syn*-conformer of all pyridylindoles (4×10^7 s^{-1} as compared to $2-3 \times 10^8$ s^{-1}). This difference suggests a conformational change, such as twisting. Transient singlet−singlet absorption spectra for **Pyln-0**, with nanosecond resolution, reveal a band at around 580 nm, which decays with the same rate (about 3.5 ns) as the longer-lived fluorescence component. Such a band is not observed in other pyridylindoles (cf. Figure 8). A more detailed analysis of the photophysics of the *anti* conformation of **Pyln-0** is being carried out and will be presented elsewhere.[104]

Table 2 shows that the quantum yields of **Pyln-0** and **MePyln-0** in alcohols are quite similar. However, this similarity is fortuitous. In contrast to the emission of **Pyln-0**, the fluorescence decay of **MePyln-0** measured in *n*-propanol and butanol is purely monoexponential. The radiative rate constant, determined from the values of fluorescence quantum yields and lifetimes, is the same as that obtained for aprotic solvents and similar to the values for other pyridylindoles (2×10^8 s^{-1}). Thus, there is no evidence for the existence of two conformations of **MePyln-0** that would decay according to different mechanisms.

The quenching of **MePyln-0** fluorescence in alcohols is much smaller than that of the *syn* form of **Pyln-0**, the species capable of forming a double cyclic hydrogen bond. The fluorescence

(107) Calculated from the data given in Viswanath, D. S.; Natarajan, G. *Data Book on the Viscosity of Liquids*; Hemisphere Publishing: New York, 1989; Landolt-Börnstein, Bd. II, 5 Teil, Springer Verlag: 1969; pp 209−214.

Table 4. Experimental and Computed Ground and Excited States Parameters

	Θ^a (deg)	$E(S_1)_{exp}$ (10^3 cm^{-1}) np[h]	$E(S_1)_{exp}$ (10^3 cm^{-1}) p[i]	$E(S_1)_{cal.}$ (10^3 cm^{-1})	$\mu(S_0)^b$ (D)	$\mu(S_1)^c$ (D)	$W^N(S_0)^d$ (eV)	$\Delta W^N(S_1)^e$ (eV)	$W^{NH}(S_0)^f$ (eV)	$\Delta W^{NH}(S_1)^e$ (eV)
Pyln-0 (*syn*)	0	30.7	30.9	31.0	2.29(2.59)	1.23	−11.86	1.05	−5.57	−0.33
Pyln-0 (*anti*)	0			31.0	3.10(4.07)	4.57	−11.81	1.15	−5.90	−0.53
MePyln-0 (*syn*)	4	31.3	31.5	31.0	2.13(2.37)	0.50[g]	−11.83[g]	−0.17[g]		
MePyln-0 (*anti*)	40			32.1	2.90(4.16)	3.63[g]	−11.83[g]	0.18[g]		
Pyln-1	0	30.4	30.6	31.4	2.09(1.88)	2.47	−11.71	1.00	−5.68	−0.32
Pyln-2	12	29.5	29.6	29.9	2.46(2.27)	2.55	−11.74	1.14	−5.57	−0.26
MePyln-2	14	29.7	30.0	30.0	2.48(2.21)	2.51	−11.72	1.13		
Pyln-3	14	29.9	30.3	30.5	2.71(2.71)	2.07	−11.77	1.13	−5.42	−0.25
Pyln-4	36	31.0	31.5	31.5	2.90(2.97)	1.59	−11.81	0.41	−5.52	−0.35
Pyln-4[j]	17			29.4	(3.35)	2.69	−11.69	1.38	−5.26	−0.23
2-PI	5	32.7	32.2	31.5	1.19(1.85)	2.04			−5.77	−0.59

[a] The dihedral angle between pyridine and indole rings. [b] Ground state dipole moment; first value obtained by MMX, second, by INDO/S. [c] Calculated by INDO/S. [d] Effective valence electron potential of the pyridine type nitrogen atom obtained by INDO/S. [e] $\Delta W(S_1) = W(S_1) - W(S_0)$. [f] $W^{NH} = (1/2)(W^N + W^H)$ for the NH bond of the indole group. [g] Results for the second calculated excited state, see text. [h] Absorption maximum in a nonpolar solvent (*n*-pentane). [i] Polar solvent (acetonitrile). [j] AM1 optimized ground state geometry.

Table 5. Ground State pK_a Values

	pK_a
Pyln-0	3.8 ± 0.1
Pyln-1	4.4 ± 0.1
Pyln-2	4.4 ± 0.2
Pyln-3	4.4 ± 0.2
Pyln-4	4.3 ± 0.2

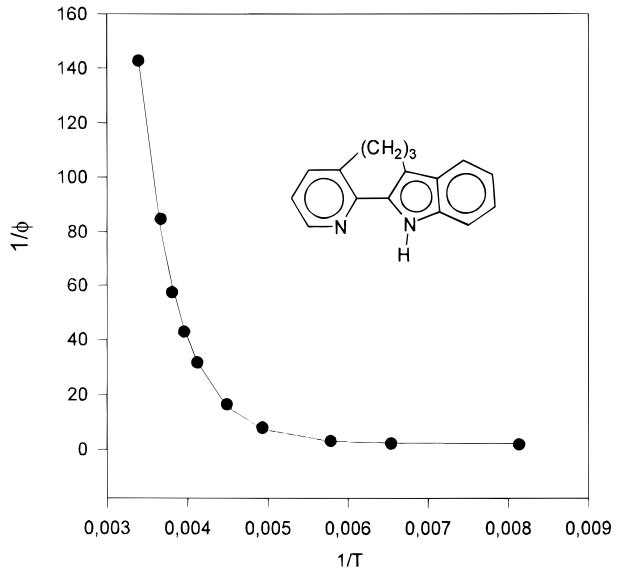

Figure 7. Plot of $1/\phi$ vs $1/T$ for **Pyln-3** in ethanol. Circles show the experimental values, solid line, result of the fit to eq 7.

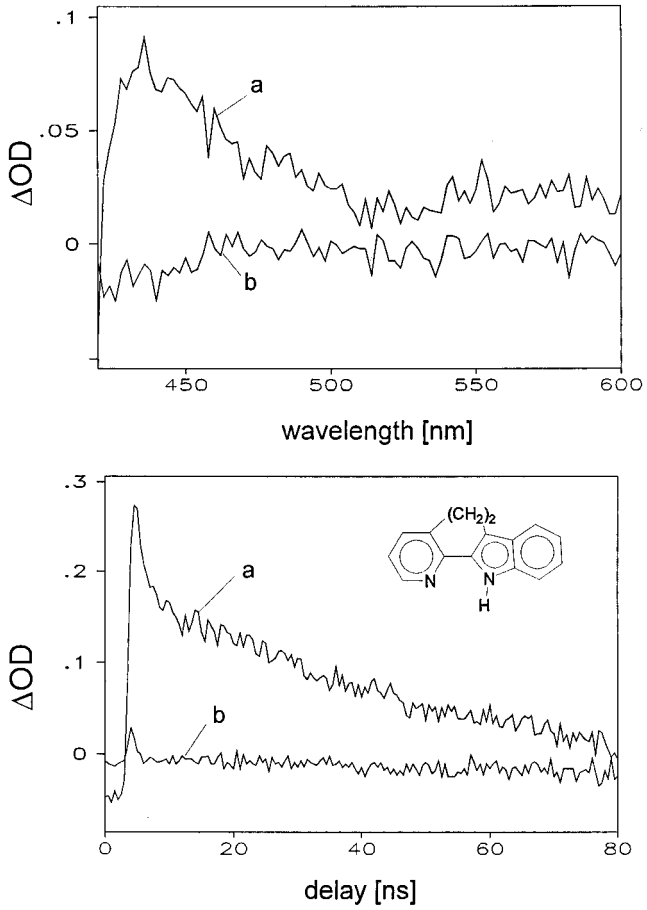

Figure 8. Transient absorption of **Pyln-2** in *n*-hexane (a) and butanol (b). Top, absorption spectrum recorded 40 ns after excitation; bottom, time profile of the absorption monitored at 435 nm.

lifetime of **MePyln-0** in *n*-propanol and butanol (about 0.6 and 0.7 ns at 293 K, respectively) is about 3−4 times lower than that observed in aprotic solvents (2.5 ns in butyronitrile), whereas for the *syn* form of **Pyln-0** about 20-fold decrease is observed (the lifetime is shorter than 100 ps, too short to be accurately measured with the time resolution of our apparatus). The extent of emission quenching of the methylated derivatives is related to two factors. The first factor is the alcohol acidity: methanol shows a much stronger effect than ethanol, *n*-propanol, and butanol. In even more acidic alcohol, 1,1,1,3,3,3-hexafluoropropanol-2, the fluorescence quantum yield drops below 0.001. The second factor is the rigidity of the molecule: fluorescence of the bridged, methylated derivative, **MePyln-2** is not quenched by alcohols.

Quenching of **MePyln-0** fluorescence in alcohols may be explained by the increased basicity of the pyridyl nitrogen in the excited state, followed by the formation of the hydrogen bond and increased internal conversion. As shown below, a large basicity increase upon excitation is determined experimentally and predicted by calculations. Such a mechanism previously has been observed for various azaaromatic compounds.[90] In the present case, comparison of the behavior of **MePyln-0** with the *syn* conformer of **Pyln-0** shows the effect of cooperativity, resulting in a much higher rate of quenching in a molecule capable of forming two hydrogen bonds, both as a donor and an acceptor.

Calculations of Ground and Excited State Acido-Basic Properties. For a quantitative description of excitation-induced changes of the hydrogen bonding abilities on both nitrogen atoms, we have used the concept of effective valence electronic

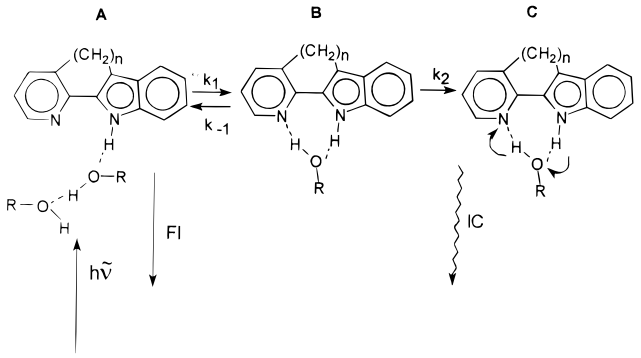

Figure 9. The proposed mechanism of fluorescence quenching: Fl, fluorescence; IC, internal conversion.

potentials.[108−110] These parameters are defined as simple functions of atomic charges and intermolecular distances. For an atomic orbital μ on atom A

$$W_\mu^A = W_\mu^A(q_A) + \sum_{B\neq A} W_\mu^A(q_B) \tag{8}$$

$$W_\mu^A(q_A) = -(a + bq_A)^{3/2} \tag{9}$$

$$W_\mu^A(q_B) = \gamma_{AB}(q_B - Z^c) \tag{10}$$

q_A and q_B are the gross populations; the summation in (8) occurs over all centers in the molecule except A; γ_{AB} is the repulsion integral, Z^c is the number of valence electrons in the neutral atom B. The constants a and b are derived from the valence state ionization potentials for the positive and negative ions.

It has been shown that the effective potentials W_{2p}^A are very reliable in the prediction of ground[108−110] and excited states[109] acidities. The less negative values indicate higher basicity. Relative pK_a values of azaarenes are reproduced also in cases where an approach based only on consideration of charge densities on nitrogen atoms fails.

One can also formally define a bond potential,[110] e.g., for the NH group

$$W^{NH} = (1/2)(W^N + W^H) \tag{11}$$

In this case, the increased acidity is accompanied by W^{NH} becoming more negative.

Using the INDO/S method, we have calculated the values of the effective valence electron potentials for the pyridine nitrogen and for the NH bond in the ground and the first excited singlet state. The results are shown in Table 4. Ground state basicities of the pyridine nitrogen and the acidities of the NH group are predicted to be similar throughout the series. The difference of 0.1 eV in $W^N(S_0)$ corresponds to about 1 pK_a unit. Thus, for instance, pK_a values for **Pyln-1** and **Pyln-0** should differ by that amount, the former being more basic. We have experimentally determined the pK_a values for pyridylindoles using spectrophotometric titration. The results are shown in Table 5. We obtain p$K_a = 3.8 \pm 0.1$ for **Pyln-0** and p$K_a = 4.4 \pm 0.1$ for **Pyln-1**, in nice agreement with the computational results. The pK_a values of all bridged derivatives are practically the same, while the calculations predict somewhat smaller values for **Pyln-3** and, in particular, for **Pyln-4**. However, the latter two molecules may exist in several conformeric forms, with different values of Θ, the dihedral angle between the pyridine and indole rings. Indeed, in **Pyln-4** varying Θ from 36° (the value obtained by MMX) to 17° (the result of AM1 opotimization) results in a calculated pK_a change of about one unit.

The calculations predict that the molecules with longer bridges (**Pyln-3** and **Pyln-4**) should have weaker acidities. Assuming that acidities and hydrogen bonding donor properties are related, this prediction is confirmed by our measurements of the alcohol complex formation.

For pyridine, we obtain $W^N(S_0) = -11.66$ eV. The calculations thus predict that pyridylindoles should be less basic than pyridine and that the pK_a difference should be about 1 unit. This agrees nicely with experiment and may help explain the lack of the ground state hydrogen bonding to the pyridine nitrogen atom in pyridylindoles.

A huge increase in basicity upon excitation—about 10 pK_a units—is calculated for nearly all the compounds. Experimental evaluation, based on the Förster cycle[111] yields $\Delta pK_a \approx 7$ for **Pyln-0** and **Pyln-2**.

The results obtained for the $W^N(S_1)$ in **MePyln-0** are much different from those computed for the other species. However, this may be due to a computational artefact: In all compounds except **MePyln-0**, the first excited singlet state is very well represented by a single configuration corresponding to HOMO−LUMO electron jump. The second and third calculated singlet transitions have small oscillator strengths and different orbital parentage. In **MePyln-0**, however, strong configurational mixing occurs. The three lowest singlet states are computed with similar, fairly large oscillator strengths, and with comparable contributions of three different configurations. Thus, there is no straightforward correlation between the S_1 state of **MePyln-0** and the lowest excited state of other molecules. The excited state parameters given in Table 4 for **MePyln-0** actually refer to the second calculated transition, because it resembles, albeit very weakly, the S_1 state in other pyridylindoles. Since the absorption spectra of **Pyln-0** and **MePyln-0** are very similar, we do not think that the puzzling results for the latter have real physical meaning.

The calculations reproduce well the position of the first absorption maximum and the relative shifts caused by bridging. A small blue shift, observed upon passing from a nonpolar to polar protic solvent indicates a decrease of the dipole moment in the first excited state. This is also in agreement with calculations. For **2PI**, an increase of dipole moment upon excitation, and thus a red shift in absorption in polar solvents is predicted by calculations and experimentally confirmed (Table 4). Actually, for the *anti* isomer of **Pyln-0** a red shift in polar solvents should be expected, as the calculated dipole moment in S_1 is larger than in S_0. Since the opposite is observed, it seems that the *syn* conformer is the dominant form. MMX calculations predict it to be more stable than the *anti* species form by 7.1 kcal/mol; the AM1 method gives 3.1 kcal/mol.

For our present purpose, the most relevant result of the calculations is the prediction of a large increase of basicity of the pyridine nitrogen and of acidity of the indole proton upon electronic excitation. Thus, a driving force for the excited state proton transfer is provided.

Nature of the Quenching Process. Figure 8 presents the transient absorption spectra of **Pyln-2** taken in a nonpolar and a protic solvent. A band centered around 430 nm is observed in *n*-hexane, while there is practically no signal in butanol. The decay of the transient absorption in *n*-hexane occurs in several tens of nanoseconds, suggesting the assignment to a triplet−

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triplet transition (fluorescence lifetime is 1.7 ns[97]). Lack of a signal in alcohol indicates that the triplet population efficiency was greatly reduced and that the quenching process does not involve enhancement of the intersystem crossing to the triplet state. Thus, one can exclude the fluorescence quenching due to solvent-induced shifts of the singlet and triplet levels with respect to each other (in particular, the nπ^* states with respect to those of $\pi\pi^*$ character).

Two other processes may be responsible for the decrease of fluorescence upon hydrogen bonding. One is the excited state double proton transfer. Such a process, leading to the formation of a nonfluorescent tautomeric species, has been proposed to explain the photophysical behavior of 2-(2′-pyridyl)benzimidazole, a molecule structurally similar to pyridylindoles.[71,72] However, in our case the calculations performed for the tautomer predict that the energy of the transition to the first excited singlet state is about 8500 cm^{-1} lower than that of the normal form, and the oscillator strength is about six times weaker. We should thus be able to observe the tautomeric fluorescence in alcohols in the region of 16 000−17 000 cm^{-1}, unless it is very efficiently quenched. Only an extremely weak emission, too weak to measure its excitation spectrum is detected in this region. Also, the absence of transient absorption in alcohol indicates that no significant population of tautomeric species is formed.

There is no doubt that the quenching involves the double hydrogen bond and some form of proton motion. We therefore propose that the mechanism of radiationless depopulation involves an efficient internal conversion process that is activated by the movement of hydrogen-bonded protons. There are two possible sequences for such an event: (i) efficient internal conversion occurring during proton translocation, before reaching the tautomeric conformation, and (ii) rapid deactivation of the phototautomer, faster than the rate of its creation. While both would lead to the same final result—efficient primary fluorescence quenching and lack of the tautomeric emission—they are, in principle, distinguishable kinetically. In the former case, the rate of the process would correspond to internal conversion itself, while for the latter it is the slower step, the proton transfer, which is rate-limiting. The values of the preexponential factor obtained from the temperature dependence of fluorescence are of the order of 10^{13} s^{-1} (Table 3), typical of internal conversion. The analogous factors obtained for azaindole, where the decay of the initially excited state is due to double proton transfer, are 1−2 orders of magnitude smaller.[42] Therefore, it seems that the mechanism (i) is dominant, and the excited molecule becomes deactivated sometimes "on the way" between the initial structure and the phototautomer.

Discussion

The results of ground and excited state studies allow us to propose the cycle of events occurring after excitation of pyridylindoles in alcohols. In the bulk alcoholic solvent, 1:*n* complexes are predominant, where *n*, the number of alcohol molecules is greater than one. After excitation, the complexes may rearrange to form a 1:1 cyclic structure, which undergoes a double proton transfer reaction. During this process, a rapid internal conversion channel brings the complex to the ground state.

Crucial for the understanding of the excited state phenomena was the observation that deuterium substitution in the hydroxylic group of the alcohol does not lead to a change of activation energy. The isotope effect is expressed only through a difference in the preexponential factor. The same behavior has been recently observed in alcohol solutions of 7-azaindole[42] and 7-hydroxyquinoline,[63,67] where a double phototautomerization also occurs with alcohol molecules serving as bridges between proton donor and acceptor centers. The interpretation of the unusual isotope effect is based on a two-step model. According to this scheme, the excited state proton transfer must be preceded by the attainment of a favorable structure of the alcohol complex, which is equivalent to a solvent reorientation process. The reaction may be depicted as

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \xrightarrow{k_2} C$$

where A, B, and C correspond to the primarily excited complex, the structure obtained after solvent reorientation, and the phototautomer, respectively. The rate constants k_1 and k_{-1} refer to solvent rearrangement, and k_2 describes the deactivation of the "prepared" structure involving proton transfer. Thus, k_2 should depend on deuterium substitution, whereas k_1 and k_{-1} should not.

For $k_1 \ll k_{-1}$, i.e., for the case where A is the dominant species, the decay rate of A may be written as

$$k_{obs} = k_1 k_2/(k_{-1} + k_2) \qquad (12)$$

In the high temperature region, where the solvent reorientation is fast, the rate limiting step would correspond to proton transfer, while in the other extreme the reaction is controlled by the solvent rearrangement. The activation energy of the latter should be correlated with the activation energy of viscous flow and not dependent on the isotope substitution.

Fitting of the experimentally observed decay rate of A to eq 12 requires, in general, the determination of six parameters (three preexponential factors and three activation energies) and may only be attempted after making several assumptions, not necessarily well-justified. Instead of trying this procedure, we note that the present results are similar to the ones obtained for 7-azaindole and 7-hydroxyquinoline. In excited pyridylindoles the first step, solvent reorientation, should involve expulsion of one or more alcohol molecules from the complex before a 1:1 structure can be achieved. A driving force for such a process is provided by the excited state increase of basicity on the pyridine nitrogen atom which, as our results suggest, is not hydrogen bonded in the ground state. If both hydrogen bonding centers of pyridylindoles were engaged in the hydrogen bonds already in the ground state, each with a different alcohol molecule, one would predict the increase in the strength of both bonds upon excitation rather than breaking one of them.

The second step in our case actually involves two processes, proton transfer and internal conversion, of which the first provides the driving force for the other. While the rate of both should not be strongly temperature-dependent, the population of molecules able to undergo this process is solvent-controlled and rapidly decreases upon increasing the viscosity or lowering of temperature. Thus, the radiative properties of pyridylindoles are fully recovered in alcohol glasses, which shows that the ground state structure of the complexes is not prone to tautomerization.

It thus seems that the mechanism of excited state proton transfer in hydrogen-bonded solvates can now be generalized to encompass various species. Attainment of a suitable conformation is the prerequisite for a rapid phototautomerization. This process is often associated with the alcohol rearrangement and thus provides an example of a solvent-controlled reaction. There are cases, however, when an appropriate structure of the complex already exists in the ground state. In such a situation, the intermolecular excited state proton transfer can be extremely rapid, even faster than the intramolecular process. Excited state proton transfer in methanol solution of 3-hydroxyflavone is

faster than 125 fs, whereas the rate of the intramolecular reaction occurring in a nonpolar solvent was determined to be 240 ± 50 fs.[82] In 1:1 cyclic hydrogen bonded complexes of 7-azaindole with carboxylic acid, the rate of photoinduced double proton transfer is so fast that only the tautomer emission is observed.[52] This observation is in contrast to the same reaction occurring in alcohols, where the much slower dynamics involves solvent reorganization.[35,42]

We are currently investigating systems related to pyridylindoles with more than two hydrogen bonding centers. Preliminary results for dipyridocarbazole indicate that the quenching of fluorescence by alcohols is even more efficient than in pyridylindoles. A related line of research involves quenching of emission based on coupled photoinduced proton and electron transfer reactions. The results, to be published shortly, depict the quenching properties of azaaromatic hydrogen bond and electron acceptors.[104]

Acknowledgment. Technical assistance from Mrs. A. Zielinska, Mrs. G. Orzanowska, Mr. R. Rodowski, and Mr. J. Karpiuk is deeply appreciated. R.P.T. thanks the Robert A. Welch Foundation and the National Science Foundation (CHE-9224686) for financial support.

JA952797D