With respect to the detailed mechanism of hydrogenation and these exchange reactions, various kinds of species have been proposed, *e.g.*, formations of π-bonded chemisorbed species,[2] the inclined cyclohexadienyl intermediate,[2] and σ-diadsorbed species.[1,5] From the present experimental data alone, it is difficult to make a final decision on their existence. However, from the present research, it can be suggested that the chemisorbed tolyl species or the intermediate in eq 6 rearranges itself, making its benzene ring vertical or inclined to the surface, because of the reasons already explained.

The above dissociative process ought to be applied also to the exchange reactions, eq 1 and 4, and the hydrogenation, eq 2, but there are two problems which would be worthy of future investigations.

First, are the benzyl and tolyl intermediates the important adsorptive species produced in the hydrogenation of aromatic hydrocarbons besides nondissociative species, especially under higher hydrogen pressure than in the present research? Under sufficiently high pressures, the chemisorbed hydrogen which is produced from gaseous hydrogen would depress the dissociative processes of toluene, eq 6 and 7. At present, it is uncertain, however, above what hydrogen pressure the dissociative process becomes negligibly small. This problem would be interesting in order to clarify the origin of hydrogen in the hydrogenation of alkylbenzenes.

Second, is the present conclusion on the dissociative chemisorbed intermediate applicable to similar exchange reactions[17] of gaseous aromatic hydrocarbons? Since the present research is carried out on liquid aromatic hydrocarbons alone, such an ambiguity may be allowed, in the case of discussion on gaseous reactions.

6. Conclusions

The self-exchange reaction of deuterium in monodeuteriotoluenes catalyzed by platinum or nickel was confirmed on three ring-substituted toluenes, and the dissociative chemisorbed species of the tolyl and benzyl types were suggested as the important intermediates in the reaction, as shown by eq 6 and 7.

This reaction gives us not only useful knowledge on the chemisorbed state of liquid alkylbenzenes but also knowledge on the mechanisms of their exchange reactions and hydrogenation.

A Fluorescence Study of Aminopyridines

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The fluorescence properties of 2-, 3-, and 4-aminopyridines have been studied in a variety of solvents. The 2- and 3- isomers are very efficient fluorescers with quantum yields approaching unity in 0.1 N sulfuric acid. 4-Aminopyridine is characterized by a very weak fluorescence which is attributed to an n,π* lowest excited singlet and a second excited state which has large charge-transfer character. In contrast, the 2- and 3- isomers have more π,π* character in the lowest excited state. Determination of excited pK values for the 2- and 3-aminopyridines indicates that the excited state is a weaker acid than the ground state. Mirror-image plots of the fluorescence and absorption spectra for the 2- and 3- isomers were used to determine the O–O bands for a variety of solvents. Fluorescence quantum yields were measured by comparison to tryptophan.

The structure of the aminopyridines has been the subject of many investigations.[1] Although there was controversy for many years concerning whether these molecules existed in the amino or imino form, it was shown in the early fifties that the amino form is by far the more important structure.[1,2] Murrell[3] showed that the uv absorption spectra of these compounds supported a molecular-orbital model of charge-transfer character better than a valence-bond model. In contrast to this model, Mason[4,5] developed a benzyl anion model to explain the absorption spectra of the aminopyridines using heteroatom perturbation in the Hückel MO framework at the exocyclic and the appropriate nuclear position. His results predict the correct order for the

(1) S. J. Angyal and C. L. Angyal, *J. Chem. Soc.*, 1461 (1952).

(2) C. L. Angyal and R. E. Werner, *ibid.*, 2911 (1952).

(3) J. N. Murrell, *ibid.*, 296 (1959).

(4) S. F. Mason, *ibid.*, 219 (1960).

(5) S. F. Mason, *ibid.*, 493 (1962).

transitions; *i.e.*, the first absorption band lies at wavelengths which depend upon the position of substitution in the order 3- > 2- > 4-. In the two models, however, the importance of n,π* character was not discussed, despite the fact that the allowed n,π* transition of pyridine appears as a shoulder at 2700 Å (ε 450).[5-7]

Recently, Favini, *et al.*,[8] reported theoretical calculations using the localized orbital method with configuration interaction for the electronic transitions of the aminopyridines. The interaction between the amino group and the pyridine ring was accounted for by considering the ground configuration, the locally excited states of pyridine, and the charge-transfer configurations.

In view of the absence of or very weak fluorescence associated with n,π* transitions, which is exemplified by the diazines,[9,10] the fluorescence characteristics of the aminopyridines should provide information regarding the nature of the excited state. With this purpose in mind, we investigated the fluorescence of these molecules in order to elucidate the nature of the lowest excited singlet.

Experimental Section

Materials. The isomeric aminopyridines were obtained from Aldrich Chemical Co. and were purified by recrystallization from *n*-hexane or carbon tetrachloride, followed by drying in a vacuum desiccator. Gas chromatography with a Perkin-Elmer 154 glpc (thermal-conductivity detector) on a 6-ft Apiezon L column at 147° and helium carrier gas resolved the three recrystallized isomers and indicated no impurities. The uv absorption data presented in Table I (*vide infra*) are in good agreement with literature values.[4,8,11] *dl*-Tryptophan was obtained from K & K Laboratories, Plainview, N. Y., and was recrystallized from water with decolorizing carbon and dried in a vacuum desiccator.

Matheson Coleman and Bell Spectrograde solvents were used in absorption and emission work and Harelco Fluorimetric grade HCl and NaOH were used for acid and base solutions. Quartz distilled water was used for preparing aqueous solutions. Reagent grade H_2SO_4, NaCl, NaBr, and NaI were used as received.

Apparatus. Ultraviolet absorption spectra were obtained with a Bausch and Lomb 505 recording spectrophotometer; however, most of the molar extinction coefficients reported were measured with a Beckman Model DU spectrophotometer. Fluorescence spectra were obtained with an Aminco grating monochromator and a 1P21 photomultiplier tube. The output from an Aminco photometer was displayed on a Moseley Model 7030A X-Y recorder.

Excitation was achieved with an Osram HBO 100 W/2 high-pressure mercury lamp which was filtered with a 285-mμ interference filter (band width = 10 mμ) obtained from Thin Films Products, Cambridge, Mass.

Isolation of the 254-mμ line of mercury was achieved with a reflection filter UV-R-250, available from Fish-Schurman Corp., New Rochelle, N. Y. Fluorescence was detected at right angles to excitation and the fluorescence spectra were not corrected for wavelength sensitivity of the photomultiplier tube and the wavelength efficiency of the monochromator. All measurements were made at room temperature in 1-cm quartz cells. Since oxygen quenching was found to be unimportant, no precautions were taken to exclude oxygen. In order to minimize inner filter effects, the optical densities of samples at the exciting wavelengths were kept in the range 0.15–0.165; however, the weak fluorescence of 4-aminopyridine was observed by using samples with optical densities close to unity. The monochromator entrance and exit slits were 0.20–0.25 mm for 2- and 3-aminopyridine; however, with 4-aminopyridine the slits were 0.50 mm.

Relative Fluorescence Yields. The fluorescence quantum yields of the aminopyridines were determined according to the method of Parker and Rees[12] using *dl*-tryptophan, which has emission in the same wavelength region as the aminopyridines and permits the same excitation wavelength (285 mμ) for both molecules. There is disagreement concerning the fluorescence quantum yield of *dl*-tryptophan, since Teale and Weber[13] reported a value of 0.20 in water, while Shore and Pardee[14] reported a value of 0.09 (pH 6.5, 280-mμ excitation). In the present work, we used the smaller value, since the value of 0.20 leads to quantum yields greater than unity (in fact, greater than 2) for 2- and 3-aminopyridines. Our results with aminopyridines suggest that the Teale and Weber value of 0.20 may be incorrect. In view of the larger difference between the values reported in the literature for the fluorescence quantum yield of *dl*-tryptophan, the accuracy of the fluorescence quantum yields is estimated to be ±50%. The relative yields, however, are reliable to ±10%.

Determination of O-O Bands. The position of the O-O band for the lowest singlet was determined by two methods: (a) when plots of relative absorption and emission intensities *vs.* wavelength exhibited good mirror-image symmetry (as with 2- and 3-aminopyridines), the O-O band was taken as the frequency of

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(7) M. Kasha, "A Symposium on Light and Life," W. D. McElroy and B. Glass, Ed., The John Hopkins Press, Baltimore, Md., 1961, p 31.

(8) G. Favini, A. Gamba, and I. R. Bellobono, *Spectrochim. Acta*, **23A**, 89 (1967).

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(12) C. A. Parker and W. T. Rees, *Analyst*, **85**, 587 (1960).

(13) F. W. J. Teale and G. Weber, *Biochem. J.*, **65**, 476 (1957).

(14) V. G. Shore and A. B. Pardee, *Archiv. Biochem. Biophys.*, **60**, 100 (1956).

Table I: Absorption and Fluorescence Characteristics of the Aminopyridines[a]

Solvent	2-Amino (pKa = 6.86)					3-Amino (pKa = 5.98)					4-Amino (pKa = 9.17)				
	λmax(absorp), mμ	εmax	λmax(fl), mμ	φf[b]	O-O[c] band, cm⁻¹	λmax(absorp), mμ	εmax	λmax(fl), mμ	φf	O-O band, cm⁻¹	λmax(absorp), mμ	εmax	λmax(fl), mμ	φf	O-O band, cm⁻¹
Cyclohexane	290	4250	332	0.07	32,200	294	3420	337	0.02	31,900	234 (250 sh)	...	362	...	32,350
Ethyl ether	295	...	345	0.21	31,500	299	...	348	0.06	31,000	241 (262 sh)	...	360	0.0004	32,100
Acetonitrile	293	4800	345	0.19	31,500	298	4000	350	0.10	30,750	241 (260 sh)	11,400	368	0.0006	31,900
Ethanol	296	4400	352	0.37	31,000	302	3250	359	0.23	29,950	247 (270 sh)	16,000	331	0.003	...
Water	292	4100	363	0.71	30,400	290	2800	390	0.32	29,550	262	11,600	335[d]	0.001	...
0.1 N H2SO4	301	...	365	1.20	...	317	...	400	1.07	...	262	...	NF	0.000	...
0.1 N HCl (monocation)	300	6380	367	0.95	30,300	316	3620	400	0.15	27,800	...	17,420	NF	0.000	...
0.1 N NaOH	287	4000	355	0.05	31,300	289	3060	366	0.03	30,300	244	11,900	337	0.001	...
10 N HCl (dication)	...	...	...	...	...	261	...	392	...	...	...	...	...	...	...

[a] Excitation at 285 mμ, except for 4-AMP in 0.1 N NaOH, where 254 mμ was used. [b] Fluorescence yields are normalized to a value of 0.09 for dl-tryptophan at pH 6.5. See ref 14. [c] O-O bands determined from mirror-image plots. [d] The fluorescence of 4-AMP in water solution is predominantly that of the monocation.

intersection of the two curves,[15] and (b) when mirror-image symmetry was not satisfactory (as with 4-aminopyridine), the position of the O-O band was taken to be the mean of the absorption and emission maxima.

Results

The most significant differences in the observed fluorescence characteristics of the aminopyridines (AMP) are that the 2- and 3- isomers fluoresce very efficiently when compared to the 4- isomer and, more importantly, the fluorescence yield increases with polarity of the solvent. The absorption spectra of 2- and 3-AMP are similar, whereas 4-AMP exhibits a shoulder at 250 mμ in cyclohexane, which disappears in polar and hydrogen-bonding solvents. This shoulder is likely to be the n,π* transition observed in pyridine and other azine molecules[5] and would account for the very weak fluorescence. A summary of the absorption and fluorescence characteristics of the three isomers in a variety of solvents is presented in Table I.

The absorption spectra of 2- and 3-AMP show a shift to longer wavelengths with increasing polarity, which is typical of π,π* transitions. This solvent shift is reversed when going from ethanol to water, which arises from two competing effects, i.e., solvent polarity producing a red shift and hydrogen bonding producing a blue shift. In the case of ethanol, the former effect prevails, whereas in water, the latter predominates. The net effect is that the absorption maximum in water solutions is about the same as in cyclohexane (see Table I). A similar result has been reported for aniline.[16,17]

The fluorescence spectra of the 2- and 3-AMP are very similar in their behavior; i.e., the wavelength of maximum fluorescence increases with polarity and hydrogen-bonding ability of the solvent. It appears that the excited state is more polar than the ground state, since the dipolar excited state is more stabilized by an increase in the dielectric constant than the ground state,[18] thereby resulting in a fluorescence shift to longer wavelength with increasing solvent polarity. Reorganization during the excitation process is unimportant, whereas when fluorescence is studied, the molecule lives long enough (ca. 10^{-8} sec) for a reorganization to occur with respect to the solvent cage[15] (see Figure 2 below).

The fluorescence yield of 2-AMP in 0.1 N HCl (monocation) is about 20 times greater than in 0.1 N NaOH (see Table I). Although the fluorescence of the monocation appears to be more efficient than the neutral molecule, the result in 0.1 N NaOH is unusually

(15) E. J. Bowen in "Advances in Photochemistry," Vol. I, W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Jr., Ed., John Wiley and Sons, Inc., New York, N. Y., 1964, pp 27–28.
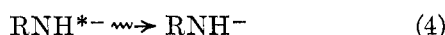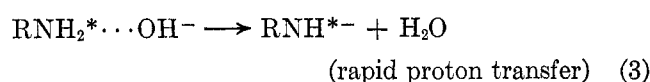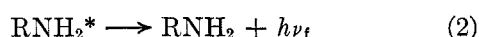
(16) K. B. Wiberg, "Physical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1964, pp 187–190.

(17) W. M. Schubert and J. M. Craven, J. Amer. Chem. Soc., 82, 1357 (1960).

(18) N. S. Bayliss and E. G. McRae, J. Phys. Chem., 58, 1002 (1954).

low. A comparison of the fluorescence data for 2- and 3-AMP in 0.1 N NaOH and ethanol solutions indicates that the emitting states are similar, *i.e.*, $\lambda_{max}(\text{fl}) = 355$ mμ in 0.1 N NaOH and 352 mμ in ethanol; consequently, the hydroxide ion appears to be a quencher of the excited singlet. Hydroxide ion quenching has been reported by Boaz and Rollefson,[19] for the fluorescence of α- and β-naphthylamine.

A possible explanation for the fluorescence quenching of 2- and 3-AMP in the presence of hydroxide ion is that a proton transfer occurs in the hydrogen-bonded species formed between the excited aminopyridine (RNH_2^*) and the hydroxide ion, *i.e.*, $RNH_2^* \cdots OH^-$, followed by radiationless decay of the imine anion. The sequence of reactions may be represented by the scheme

$$RNH_2^* + OH^- \longrightarrow RNH_2^* \cdots OH^- \quad (1)$$

$$RNH_2^* \longrightarrow RNH_2 + h\nu_f \quad (2)$$

$$RNH_2^* \cdots OH^- \longrightarrow RNH^{*-} + H_2O$$
$$\text{(rapid proton transfer)} \quad (3)$$

$$RNH^{*-} \xrightarrow{\sim\sim} RNH^- \quad (4)$$

$$RNH^- + H_2O \longrightarrow RNH_2 + OH^- \quad (5)$$

It is important to note that the formation of the hydrogen-bonded complex can occur either in the excited state (reaction 1) or by excitation of the complex in the ground state, *i.e.*, $RNH_2 + OH^- \rightleftharpoons RNH_2 \cdots OH^-$, which is determined by the equilibrium constant. It is unlikely that the low fluorescence yields for 2-AMP in cyclohexane and 0.1 N NaOH are related, since the wavelength maximum for the two solvents differ by 23 mμ (see Table I). 3-AMP exhibits similar fluorescence behavior in cyclohexane and 0.1 N NaOH. In this case the shift in the fluorescence maximum between the two solvents is 29 mμ. The low fluorescence efficiencies in cyclohexane are probably due to significant n,π^* character in the first excited singlet.

Mirror-image plots were made with all absorption and emission spectra and were found to be satisfactory for the identification of the absorbing and emitting species. 4-AMP is exceptional, in that it exhibits an n,π^* shoulder in nonpolar solvents, which disappears under the higher energy π,π^* transition in polar solvents. Both solvent polarity and hydrogen bonding raise the energy of the low-lying n,π^* state above that of the π,π^* state. The inversion of these energy levels leaves the π,π^* state as the emitting state, resulting in an increased fluorescence when going from cyclohexane to water. The small fluorescence quantum yield for 4-AMP in water is attributed to a significant charge-transfer character in the second excited state.[8]

The mirror-image plot for 3-AMP in 10 N HCl, which is shown in Figure 1, provides an example of excited-state dissociation. The absorption spectrum is
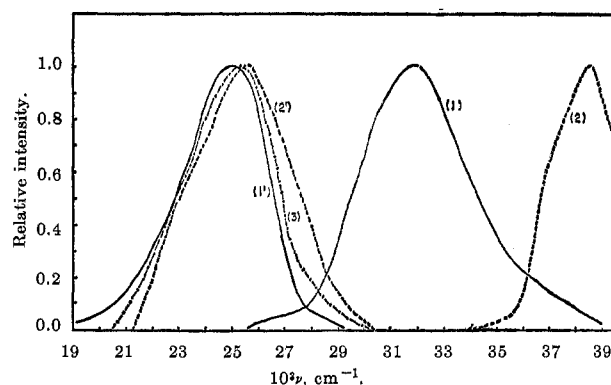

Figure 1. A Fluorescence study of aminopyridines. Mirror-image plots for 3-aminopyridine in HCl solutions:
——— (1 and 1'), absorption and fluorescence of monocation of 3-AMP, respectively, in 0.1 N HCl (285-mμ excitation);
- - - - - (2 and 2'), absorption and fluorescence of dication of 3-AMP, respectively, in 10 N HCl (285-mμ excitation);
—·—·—·—·— (3), fluorescence of 3-AMP in 10 N HCl (254-mμ excitation).

that of the dication; however, the emission spectrum is that of the monocation. It appears that an excited-state dissociation occurs within the lifetime of the excited state to produce fluorescence of the monocation. The process can be represented by
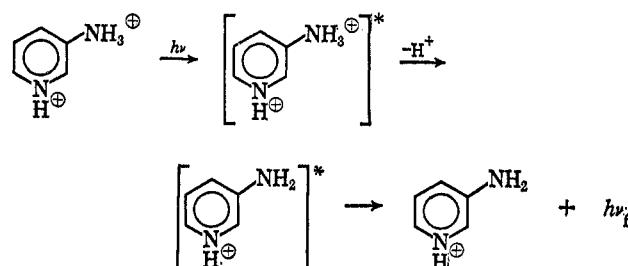
An alternative explanation is that fluorescence arises from a small amount of monocation absorption in 10 N HCl and that the dication does not fluoresce. The dications of 2- and 4-AMP could not be generated because of their large negative pK_a values. The second pK_a values for 2-, 3-, and 4-AMP are -7.6, -1.5, and -6.3, respectively.[20]

An apparent anomaly exists for the fluorescence yields of the monocations of 2- and 3-AMP in 0.1 N HCl, since in the former the fluorescence yield is 0.95; whereas in the latter, the value is 0.15. More importantly, the yield for 3-AMP in water is larger than the value for 0.1 N HCl. Since the first protonation, which occurs at the ring nitrogen, should remove any n,π^* character of the lowest state, an increase in the fluorescence efficiency is expected. When the two isomers are excited in 0.1 N H_2SO_4, however, the fluores-

(19) H. Boaz and G. K. Rollefson, *J. Amer. Chem. Soc.*, **72**, 3435 (1950).

(20) A. Albert in "Physical Methods in Heterocyclic Chemistry," Vol. I, A. R. Katritzky, Ed., Academic Press Inc., New York, N. Y., 1963, p 73.

cence yields for the 2- and 3- isomers approach unity, which suggests that the halogen ion may be responsible for an external heavy-atom effect.[21] In order to test this possibility, the fluorescence of 2- and 3-AMP was studied in 0.1 N NaCl, NaBr, and NaI. As expected, the fluorescence yields of 2- and 3-AMP decrease in the order NaCl > NaBr > NaI. The results are presented in Table II.

Table II: Effect of Halogen Ions on Fluorescence Quantum Yields of 2- and 3-Aminopyridines

	2-Aminopyridine			3-Aminopyridine		
	λ_{max}(ab-sorp), mμ	ϕ_f	λ_{max}(fl), mμ	λ_{max}(ab-sorp), mμ	ϕ_f	λ_{max}(fl), mμ
H$_2$O	292	0.71	363	290	0.32	390
0.1 N NaCl	291	0.79	362	290	0.20	368
0.1 N NaBr	292	0.26	356	290	0.15	365
0.1 N NaI	290	0.07	356	290	0.04	365

A striking result which appears in Table II is the fluorescence shift of 3-AMP from 390 to 365 mμ when going from water to the sodium halide solutions, whereas with 2-AMP, there is no shift. This increased energy from the emitting state of 3-AMP in ionic solutions may arise from a dipole moment reversal in the excited state (*vide infra*).

Discussion

The results in this work demonstrate that 2- and 3-AMP can fluoresce with high quantum efficiencies. By contrast, it is well known that pyridine and pyridinium do not exhibit fluorescence.[22] While aniline fluoresces with a quantum yield of 0.08 in cyclohexane,[23] anilinium does not exhibit any fluorescence.[22,24] These observations are in contrast to the behavior of 2- and 3-AMP, since the monocations fluoresce more efficiently than the neutral molecules.

The absorption and fluorescence spectra of the isomeric pyridines are complicated by the polar effects and the basic character of the heteroatoms. The ground-state dipole moments and the pK_a values (protonation of ring nitrogen) reported in the literature are summarized in Table III.

Table III: Values of pK_a and Dipole Moments for the Isomeric Aminopyridines

	p$K_a{}^a$	μ^{b-d}
2-Aminopyridine	6.86	2.06
3-Aminopyridine	5.98	3.11
4-Aminopyridine	9.17	3.94

[a] A. Albert, R. Goldacre, and J. Phillips, *J. Chem. Soc.*, 2240 (1948). [b] M. T. Rogers, *J. Phys. Chem.*, **60**, 125 (1956). [c] J. Barassin and H. Lumbroso, *Bull. Soc. Chim. Fr.*, 492 (1961). [d] C. W. N. Cumper, R. F. A. Ginman, D. G. Redford, and A. I. Vogel, *J. Chem. Soc.*, 1731 (1963).

In view of the pK_a values of these compounds and the possibility of excited-state dissociation, it follows that the fluorescence spectrum of the monocation is obtained in 0.1 N HCl and the fluorescence of the neutral molecule is obtained in 0.1 N NaOH. In the case of 2-AMP, the cation fluoresces at a higher wavelength than the neutral molecule. The 0-0 band for the cation is 30,300 cm^{-1}, and for the neutral molecule, 31,300 cm^{-1}. When these data are used in the Förster cycle,[25,26] *i.e.*

$$pK - pK^* = hc\Delta\bar{\nu}/2.303kT$$

where pK and pK^* refer to the equilibrium constant in ground and excited state, respectively, and $\Delta\bar{\nu}$ represents the shift in centimeter^{-1} between the fluorescence spectrum of the neutral and protonated forms of the molecule, the excited-state pK value for 2-AMP is determined to be 8.95, compared with 6.86 in the ground state; *i.e.*, the excited state is a weaker acid and should favor protonation. In 3-AMP a similar effect is observed with the 0-0 band at 27,800 cm^{-1} in 0.1 N HCl and at 30,300 cm^{-1} in 0.1 N NaOH. Analogous to the 2- isomer, 3-AMP is a weaker acid in the excited state: pK = 5.98 and pK^* = 11.2. It is known that heterocyclic nitrogens are more basic in the excited state relative to the ground state. For acridine Weller[27] has reported the pK value of 5.45 in the ground state and 10.3 for the excited state. The analysis of pK^* for 4-AMP was not made because of its low fluorescence efficiency; however, it is reasonable to expect a similar trend as was observed with 2- and 3-AMP.

Recently, Goodman, *et al.*,[9] have determined the excited-state dipole moments of diazines using the shifts of absorption and fluorescence spectra together with the ground-state dipole moment and the simple relationship

$$\frac{\mu_e}{\mu_g} = \frac{\Delta\bar{\nu}_f}{\Delta\bar{\nu}_a}$$

where μ_e and μ_g represent excited- and ground-state dipole moments, respectively, and $\Delta\bar{\nu}_f$ and $\Delta\bar{\nu}_a$ represent shifts of fluorescence and absorption peaks in centimeter^{-1} between two polar solvents relative to a nonpolar solvent. Using ether and acetonitrile as the polar solvents and measuring shifts from cyclohexane, it appears, qualitatively, that the excited-state

(21) M. Kasha, *Radiat. Res., Suppl.*, **2**, 243 (1960).

(22) T. Förster, "Fluoreszenz Organischer Verbindungen," Vandenhoeck and Ruprecht, Göttingen, Germany, 1951, p 105.

(23) I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press Inc., New York, N. Y., 1965, p 59.

(24) W. West in "Technique of Organic Chemistry," Vol. IX, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1956, p 707.

(25) T. Förster, *Z. Elektrochem.*, **54**, 42 (1950).

(26) A. Weller, *Progr. Reaction Kinetics*, **1**, 189 (1961).

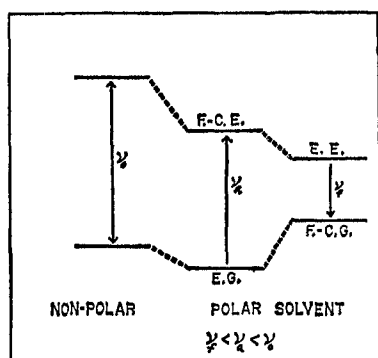(27) A. Weller, *Z. Elektrochem.*, **61**, 956 (1957).

Figure 2. Energy-level diagram illustrating the shift in the observed absorption and fluorescence spectra of aminopyridines with solvent polarity.

dipole moment maintains the same direction for the 2-AMP; however, a reversal occurs with 3-AMP. It would appear that for 3-AMP the excited singlet is in an unfavorable environment relative to the situation which occurs with 2-AMP. An indication of the predicted dipole reversal for 3-AMP in the excited singlet is suggested by the observation that the fluorescence shifts to shorter wavelengths in salt solutions relative to water, while 2-AMP does not exhibit a shift (see Table II). It is expected that the unfavorable solvent cage in the excited state could produce a destabilization in converting to the equilibrium excited state, which would be manifested as a fluorescence shift to shorter wavelengths.

It has been shown that for π,π^* states, the usual condition for dipole moment changes is $\mu_e > \mu_g$.[28,29] This generalization is in agreement with the absorption and fluorescence of the aminopyridines, since greater stabilization of the excited state with increasing solvent polarity causes a shift to higher wavelengths. The energetics of the reorganization in the excited state between the Franck–Condon excited state (FCE) and the equilibrium excited state (EE) and between the Franck–Condon ground state (FCG) and the equilibrium ground state (EG) can be represented by the diagram in Figure 2.

For the aminopyridines the presence of hydrogen-bonding solvents results in a stabilization of the ground state, which is manifested by a shift to shorter wavelengths for the absorption spectrum. In contrast, the fluorescence continues to show a shift to higher wavelengths with increasing polarity and hydrogen-bonding ability of the solvent. This observation suggests that the hydrogen bond is strengthened in the reorganization from the Franck–Condon excited state to the equilibrium excited state, which precedes the fluorescence phenomenon. Goodman, et al.,[9] have found a similar behavior in the fluorescence of diazines.

Since the fluorescence of 4-AMP is very weak com-pared to the 2- and 3-AMP, an explanation should be provided for this behavior. It is reasonable to attribute n,π^* character to the lowest electronic transition, since it disappears in polar solvents. The second transition, however, may be expected to be π,π^* and would normally result in a significant increase of fluorescence efficiency. This is not observed experimentally and, therefore, suggests that charge-transfer character in the second excited state accounts for the very weak fluorescence. Supporting this hypothesis, Favini, et al.,[8] have calculated that the second transition in the aminopyridines has a relatively large charge-transfer character. In addition, the extinction coefficients presented in Table I for 4-AMP are in the range of 11,000–17,000, as compared to 3000–4000 for 2- and 3-AMP. These high extinction coefficients for 4-AMP could be indicative of charge-transfer bands.[30]

Summary

1. The fluorescence efficiency of 2- and 3-AMP approaches unity in 0.1 N H_2SO_4 and is in sharp contrast to the low fluorescence efficiency of 4-AMP.

2. Absorption and fluorescence peaks for 2- and 3-AMP shift to higher wavelengths with increasing solvent polarity, implying greater stabilization of the excited state relative to the ground state.

3. In nonpolar solvents the low fluorescence efficiencies of 2- and 3-AMP are attributed to significant n,π^* character in the first excited singlet. In polar solvents, however, the lowest singlet transition of 2- and 3-AMP appears to be predominantly π,π^*, in view of their high fluorescence efficiencies.

4. The absorption spectrum of 4-AMP exhibits a shoulder in nonpolar solvents which disappears in polar solvents and is, therefore, interpreted as an n,π^* transition. This behavior coupled with significant charge-transfer excitation for the second transition accounts for its low fluorescence efficiency.

5. Determination of the excited-state pK values for 2- and 3-AMP indicate that the excited state is a stronger base relative to the ground state.

6. Excited-state dissociation of the dication in 3-AMP is observed in 10 N HCl.

7. The decrease in the fluorescence efficiencies of 2- and 3-AMP in the presence of halogen ions is the result of spin–orbit coupling.

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