Hydrogen Bonding Effect on the Fluorescence of Some Nitrogen Heterocycles. I

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1. Introduction

It is well known that whereas the aromatic hydrocarbons such as benzene, naphthalene and anthracene fluoresce fairy well or strongly in the near ultraviolet or visible spectral region, the corresponding aza-derivatives such as pyridine, quinoline and acridine are completely non-fluorescent or emit very weakly in spite of their comparable or stronger absorption intensity compared with aromatic hydrocarbons. Some interpretations have been made for these behaviors of nitrogen heterocycles; for example according to Bowen[1], this effect has been ascribed to the increase in spin-orbital interaction by a nitrogen atom, while Förster[2], has interpreted this phenomenon in the case of pyridine as due to the predissociation of CN bond, though he has made no interpretation on the very weak fluorescence of acridine or quinoline. We will propose another interpretation, perhaps more plausible, for the phenomenon in question, on the basis of the solvent effects upon the absorption spectra and fluorescence yields of these nitrogen heterocycles. One of the present authors has previously reported[3] that, although quinoline and acridine are almost non-fluorescent in non-polar solvent such as hexane and benzene, they fluoresce fairy well in alcohols which are capable of making hydrogen bond with nitrogen atoms of these heterocycles. Moreover, the fluorescence yield has been found greatly enhanced in quinolinium and acridinium ion in the aqueous solution. He has suggested, from these facts, that the non-bonding electron pair on a nitrogen atom may play an important role in the inner quenching of fluorescence in these molecules. To elucidate the problem further, we have measured the absorption spectra and relative fluorescence yields of these molecules hydrogen bonded with various proton donors in non-polar solvent. The results obtained clearly show the parallel relation between relative fluorescence yield and proton donating power, i. e., the greater the proton donating power, the larger the increase in relative fluorescence yield. Moreover, we have found an interesting fact that the difference in the emitting π-electronic state leads to the different behavior of these nitrogen heterocycles in fluorescence quenching by a halogen atom.

The object of the present paper is to report these facts with some discussions on the role of the interaction between n- and π-electrons, and also the character of emitting π-electronic state in the fluorescence of these molecules.

2. Experimental

Apparatus: Absorption spectra were measured with a Beckman spectrophotometer model DU. The fluorometer was the same as described previously[4]. The fluorescence spectra were photographed with a Hilger E_2 type quartz spectrograph or a small type glass prism spectrograph, using a high-pressure mercury lamp with appropriate filters[3] as an exciting light source.

Reagents: Quinoline and acridine were the same samples as reported previously[3]. Chemical pure grade *n*-hexane was shaken with fuming sulfuric acid diluted with conc. sulfuric acid and distilled carefully. Extra pure grade benzene was dried over metallic sodium and distilled before use. Carbon tetrachloride and chloroform were shaken with conc. solfuric acid, washed with water, and after being dried over phosphorus pentoxide, distilled carefully. Ethanol was refluxed with silver nitrate to remove aldehyde, and after refluxing with calcium oxide, distilled carefully. Commercial β-phenylethylalcohol was fractionally distilled. Benzylalcohol was dried over potassium carbonate, and distilled under an atmosphere of dry nitrogen. Chemical pure grade mono- and trichloracetic acid were recrystallized several times from benzene, then stored over concentrated sulfuric acid in a vacuum

1) E. J. Bowen and F. Wokes, "Fluorescence of Solutions", Longmans (1953), p. 26.
2) Th. Förster, "Fluoreszenz Organischer Verbindungen", Vandenhoech and Ruprecht (1951), p. 118.
3) N. Mataga, Y. Kaifu and M. Koizumi, This Bulletin, **29**, 373 (1956).
4) N. Mataga, Y. Kaifu and M. Koizumi, ibid., **29**, 115 (1956).

desiccator. Dichloracetic acid was fractionally distilled under a pressure of 17 mm.

3. Experimental Results

A. Remarks on the Electronic Spectra of Nitrogen Heterocycles. — The π-electronic spectra of nitrogen heterocycles such as pyridine, quinoline and acridine are very similar to those of isoelectronic aromatic hydrocarbons such as benzene, naphthalene and anthracene, and their excitation energies are almost the same. A systematization of this correspondence between nitrogen heterocycles and aromatic hydrocarbons was made by Zanker[5] using Platt's perimeter model[6]. According to Platt's notation, the lowest excited singlet state ($\pi \rightarrow \pi^*$) is ^1L_b in pyridine and quinoline, and ^1L_a in acridine, and these are regarded as the emitting state of fluorescence, respectively. The second excited singlet state is ^1L_a in pyridine and quinoline, and ^1L_b in acridine.

B. Change in Absorption Spectrum by Hydrogen Bonding. — When various proton donors are added to the solutions of quinoline and acridine in non-polar solvent, the absorption spectra show characteristic changes due to the hydrogen bonding equilibrium. In both quinoline and acridine, hydrogen bonding strengthens the ^1L_b band somewhat, its wave length being not altered, but induces the red shift of ^1L_a band. The stronger the donating power, the larger the degree of the increase of absorption intensity of ^1L_b band and the red shift of ^1L_a band. In the case of the acid-base interaction in which trichloracetic acid was used as proton donor, the degree of the change of absorption spectrum is very close to the case of quinolinium or acridinium ion in the aqueous solution, but slightly less prominent.

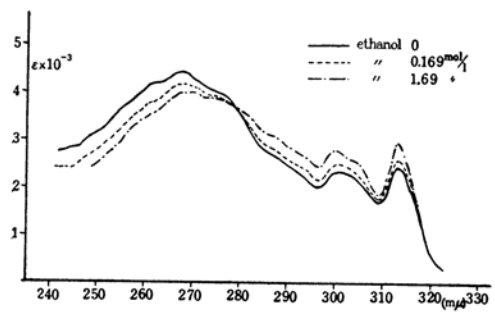

Fig. 1. Change in absorption spectrum of quinoline in *n*-hexane with addition of ethanol.
Concentration of quinoline $\sim 10^{-4}$ mol./l.

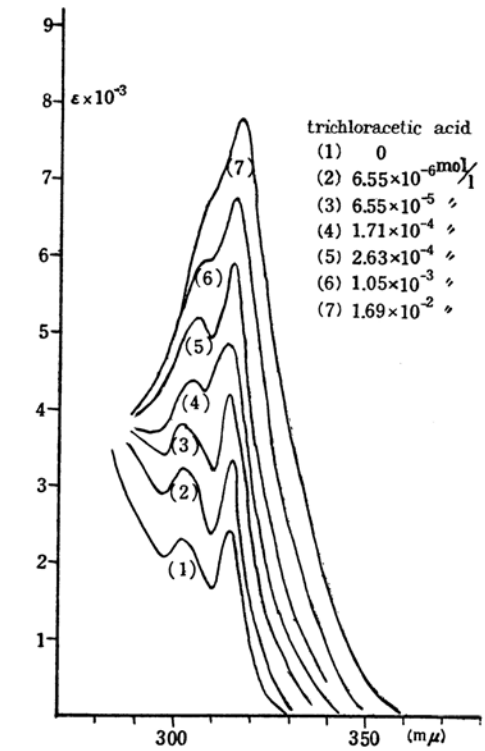

Fig. 2. Change in absorption spectrum of quinoline in benzene with addition of trichloracetic acid.
Concentration of quinoline $\sim 10^{-4}$ mol./l.

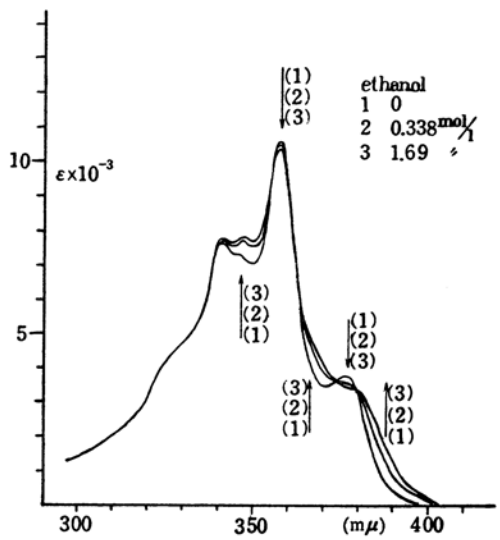

Fig. 3. Change in absorption spectrum of acridine in benzene with addition of ethanol.
Concentration of acridine: 5×10^{-5} mol./l.

5) V. Zanker, *Z. Physikal. Chem.*, N. F., **2**, 52 (1954). see also Ref. 3).
6) J. R. Platt, *J. Chem. Phys.*, **17**, 484 (1949). H. B. Klevens and J. R. Platt, ibid., **17**, 470 (1949).

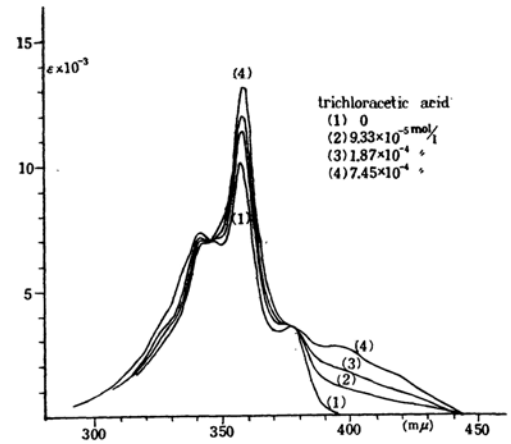

Fig. 4. Change in absorption spectrum of acridine in benzene with addition of trichloracetic acid.
Concentration of acridine: 5×10^{-5} mol./l.

Some examples of these spectral changes caused by hydrogen bonding are shown in Figs. 1—4.

These spectral changes caused by the perturbation of π-electronic states by hydrogen bonding, seem to correspond definitely to the above-mentioned Zanker's assignment. The same correspondence seems to hold also in pyridine[5,7]. From these spectral changes we can obtain the equilibrium constant of hydrogen bond formation in the ground state.

C. Method of Evaluation of Equilibrium Constant from Absorption Spectra. —The optical density at a definite wave length, d, is expressed as follows, using molar extinction coefficients of a free molecule A and a hydrogen bonded one AD, ε_a and ε_c:

$$d=\varepsilon_a[A]+\varepsilon_c[AD]=\varepsilon_a[A]+\varepsilon K[A][D]$$

The optical density of the solution without donor is:

$$d_0=\varepsilon_a[A]_0=\varepsilon_a[A](1+K[D]),$$

where $[A]_0$ is the analytical concentration of A.

From these equations we obtain:

$$\frac{1-(d_0/d)}{[D]}=-K+\left(\frac{\varepsilon_c}{\varepsilon_a}\right)K\left(\frac{d_0}{d}\right) \qquad (1)$$

For moderately weak donors, we can approximately replace [D] by $[D]_0$, the analytical concentration of D.

For a strong donor such as trichloracetic acid, however, we cannot use such an approximate method.

Instead, we put as follows:

$$K=\frac{[AD]}{([D]_0-[AD])([A]_0-[AD])},$$

$$[A]_0(\varepsilon-\varepsilon_a)=[AD](\varepsilon_c-\varepsilon_a),$$

$$[AD]=\frac{[A]_0(\varepsilon-\varepsilon_a)}{(\varepsilon_c-\varepsilon_a)}$$

where ε is the apparent molar extinction coefficient. Hence,

$$K=\frac{(\varepsilon-\varepsilon_a)(\varepsilon_c-\varepsilon_a)}{[D]_0(\varepsilon_c-\varepsilon_a)(\varepsilon_c-\varepsilon)-[A]_0(\varepsilon-\varepsilon_a)(\varepsilon_c-\varepsilon)}.$$

When $\varepsilon_a=0$ at the wave length used for the calculation,

$$[D]_0\left(\frac{\varepsilon_c}{\varepsilon}-1\right)=\frac{1}{K}+[A]_0\left(1-\frac{\varepsilon}{\varepsilon_c}\right) \qquad (2)$$

By means of Tsubomura's method[8], we can obtain [AD], and from $[A]_0\varepsilon=[AD]\varepsilon_c$,

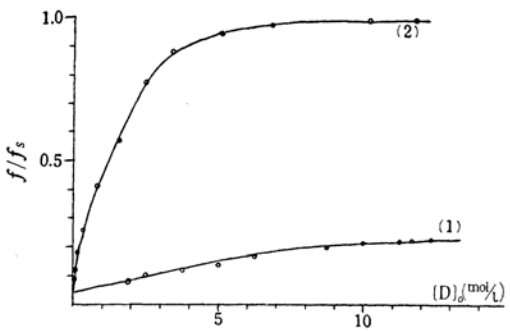

Fig. 5. Change in fluorescence intensity of acridine in benzene with addition of chloroform and ethanol.
Concentration of acridine: 5×10^{-5} mol./l.
(1) chloroform, (2) ethanol.
f_s: fluorescence intensity of ethanol solution used as standard.

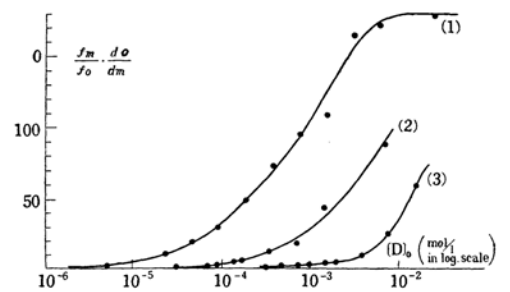

Fig. 6. Change in fluorescence intensity of acridine in benzene with addition of chloracetic acids.
Concentration of acridine: 5×10^{-5} mol./l.
(1) trichloracetic acid
(2) dichloracetic acid
(3) monochloracetic acid

7) L. W. Pickett, et al., *J. Am. Chem. Soc.*, **75**, 1618 (1953).

8) H. Tsubomura, *J. Chem. Phys.*, **23**, 2130 (1955).

ε_c is evaluated. Then, K can be evaluated from (2).

D. Change in Fluorescence Intensity and Its Interpretation on the Basis of Hydrogen Bonding Equilibrium. — In all the cases of hydrogen bonding, the fluorescence intensity is increased. Moreover, the stronger the donating power, the greater the increase in fluorescence intensity. Some examples of those changes in fluorescence intensities are shown in Figs. 5 and 6.

Now it is almost certain that the observed changes in fluorescence intensity may be attributed to the fact that the free and hydrogen bonded heterocycles have different efficiency of fluorescence and that the concentration of these molecular species are determined by the association equilibrium. Hence the experimental results will be analyzed as follows.

(i) When the equilibrium of the ground state is maintained during the course of fluorescence, the fluorescence intensity f_m with addition of D is:

$$f_m = \frac{(\varepsilon_a \Phi_a + \varepsilon_c \Phi_c K[\mathrm{D}])}{1+K[\mathrm{D}]} [\mathrm{A}]_0 I_0 \qquad (3)$$

where ε_a and ε_c are the molar extinction coefficient of A and AD at the wave length of the exciting light, respectively. I_0 is the intensity of the exciting light, and, Φ_a and Φ_c are the quantum yields of fluorescence of A and AD, respectively. It is to be noted that (3) is derived on the condition that the absorption of each molecular species is proportional to its concentration, which approximately holds in the present experiment.

From (3) we derive,

$$\frac{1-(f_0/f_m)}{[D]} = -K + \alpha\left(\frac{\varepsilon_c}{\varepsilon_a}\right)K\left(\frac{f_0}{f_m}\right) \qquad (4)$$

where f_0 is the fluorescence intensity of the solution without D, and $\alpha = \Phi_c/\Phi_a$.

When $\Phi_a \simeq 0$,

$$\frac{1}{f_m} = \mathrm{Const.}\left(1+\frac{1}{K}\frac{1}{[\mathrm{D}]}\right) \qquad (5)$$

(ii) In contradistinction to (i), when an equilibrium in the excited state is different from that of the ground state and the state of association approaches a new equilibrium state during the lifetime of the excited molecule, until a new equilibrium state is almost completely reached prior to the emission, we should use euqation (6) instead of (3):

$$f_m = \frac{(\Phi_a + K'\Phi_c[\mathrm{D}])}{1+K'[\mathrm{D}]} d_m I_0 \qquad (6)$$

$$d_m = \frac{(\varepsilon_a + \varepsilon_c K[\mathrm{D}])[\mathrm{A}]_0}{1+K[\mathrm{D}]}$$

where K' is the equilibrium constant in the excited state. From equation (6) we can easily derive (7) and (8), which correspond to (4) and (5), respectively.

$$\frac{1-(f_0/f_m)(d_m/d_0)}{[\mathrm{D}]} = -K' + \alpha(d_m/d_0)K'(f_0/f_m) \qquad (7)$$

$$d_0 = \varepsilon_a[\mathrm{A}]_0, \quad d_m/f_m = \mathrm{Const.}\left(1+\frac{1}{K'}\frac{1}{[\mathrm{D}]}\right) \qquad (8)$$

For moderately weak donors such as chloroform and ethanol, we can approximate [D] with $[\mathrm{D}]_0$. Since the increase in fluorescence intensity by hydrogen bonding with those donors is not so much remarkable, we cannot neglect the fluorescence of A compared with that of AD, and we should use for these cases equations (4) or (7).

The ranges of fluorescence spectra of A and AD for these cases are practically the same.

Owing to a very small difference in extinction coefficients of A and AD at the wave length of the exciting light, (4) and (7) practically coincide in their forms and it has been established that the experimental results can be reproduced by either equations (4) or (7) satisfactorily, the equilibrium constants evaluated by (4) and (7) being practically the same.

Further, the equilibrium constant obtained in this way from fluorescence intensity measurement agrees with that evaluated from the change in the absorption spectrum.

Therefore, we can conclude that, in these cases, the association equilibrium in the excited state is practically the same as that in the ground state, in contrast to the case of naphthols[4,9].

For strong donors such as trichloracetic acid, we cannot approximate [D] with $[\mathrm{D}]_0$ and [D] should be evaluated using an equilibrium constant obtained from an absorption spectrum.

For acridine-trichloracetic acid system, the spectral range of fluorescence of AD is considerably different from that of A, but the increase of fluorescence intensity by hydrogen bonding is so remarkable, that we can neglect Φ_a compared with Φ_c.

9) N. Mataga, Y. Kaifu and M. Koizumi, *Nature*, **175**, 731 (1955).

TABLE I

Acceptor	Donor	Solvent	T°a)	K_T	$\delta\tilde{\nu}$b)(cm^{-1})	Φ_r
Acridine	Chloroform	Benzene	286	0.1	*	0.6
	Ethanol	Benzene	290	1.0	*	1.0
		Hexane	290	1.6	*	1.0
		CCl_4	291	1.8	*	1.0
	Benzylalcohol	Benzene	287	2.0	*	1.0
	β-phenylethylalcohol	Benzene	287	1.0	*	1.6
	$CH_2ClCOOH$	Benzene	293	1.4×10^2	~600	
	$CHCl_2COOH$	Benzene	293	8×10^2	~800	9.5
	CCl_3COOH	Benzene	293	1.3×10^4	~900	11
Quinoline	$CH_2ClCOOH$	Benzene	295	~10^2	*	
	CCl_3COOH	Benzene	297	5×10^3	*	

a) Temperature at which measurement was made.
b) Wave number shift of ^1L_a band due to hydrogen bonding.
* Uncertain.

Hence it is suitable to employ equation (5) or (8) and the experimental results are really well reproduced by these equations.

In contradistinction to acridine-trichloracetic acid system, the increase in fluorescence intensity is very slight in the quinoline-trichloracetic acid system. In quinolinium ion in aqueous solution, the emitting state is ^1L_a in contrast to ^1L_b of quinoline base, and the range of fluorescence spectrum is considerably different from each other. In the quinoline-trichloracetic acid system, however, it was confirmed that the emitting state is ^1L_b, the spectral range of fluorescence being the same as in non-polar solvent (310–360 mμ).

Some examples of the analysis of fluorescence intensities are shown in Figs. 7, 8.

The concentration ranges of ethanol, benzylalcohol and β-phenylethylalcohol used for the evaluation of equilibrium constants from the results of absorption and fluorescence measurements were approximately 0.03–0.5 mol./l.

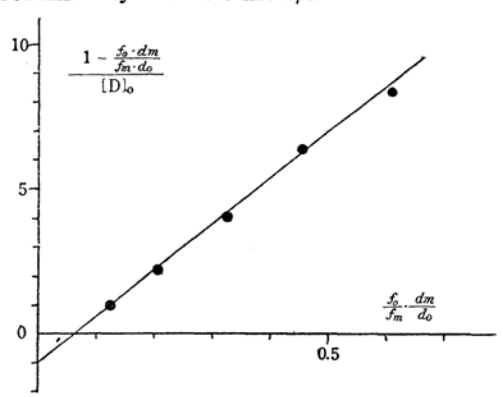

Fig. 7. $\dfrac{1-\dfrac{f_0\cdot d_m}{f_m\cdot d_0}}{[D]_0}\sim\dfrac{f_0\cdot d_m}{f_m\cdot d_0}$ relation for acridine-benzene-ethanol system.
Concentration of acridine: 5×10^{-5} mol./l.

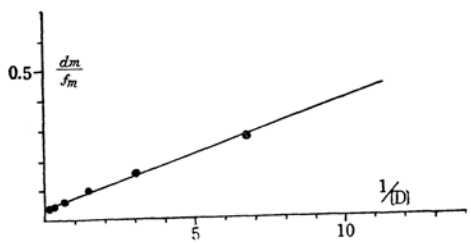

Fig. 8. $\dfrac{d_m}{f_m}\sim\dfrac{1}{[D]}$ relation for acridine-benzene-trichloracetic acid system.
Concentration of acridine: 5×10^{-5} mol./l.

The results of infrared measurements[10] on the dimerization of chloracetic acids were used for the estimation of concentration ranges where the fraction of monomer is at least 80%, and the calculation of equilibrium constants was made in this concentration range.

E. The Relative Fluorescence Yields of Hydrogen Bonded Nitrogen Heterocycles.—It is clear from the above mentioned results, that the change in fluorescence intensity is well interpreted on the basis of hydrogen bonding equilibrium. Further, it is possible to deduce some information on the interelation between the fluorescence yields of hydrogen bonded nitrogen heterocycles and the donating powers of various proton donors.

Ethanol solution was used as a standard. The fluorescence intensity of this standard solution is expressed as follows:

$$f_s=\Phi_s\cdot d_s\cdot I_0 \qquad (10)$$

where d_s is the optical density at the wave length of exciting light and Φ_s is the quantum yields of fluorescence. Then,

10) J. T. Harris, Jr. and M. E. Hobbs, *J. Am. Chem. Soc.*, **76**, 1419 (1954). H. A. Pohl. M. E. Hobbs and P. M. Gross, *J. Chem. Phys.*, **9**, 408 (1941).

from equations (10), (3) and (6), the following equations are derived.

$$f_m/f_s=\frac{\varepsilon_a(\Phi_a/\Phi_s)+\varepsilon_c(\Phi_c/\Phi_s)K[\mathrm{D}]}{1+K[\mathrm{D}]}\frac{[\mathrm{A}]_0}{d_s} \quad (11)$$

$$f_m/f_s=\frac{(\Phi_a/\Phi_s)+(\Phi_c/\Phi_s)K'[\mathrm{D}]}{1+K'[\mathrm{D}]}\frac{d_m}{d_s} \quad (12)$$

From these equations, (Φ_c/Φ_s) can be evaluated, and the ratios of (Φ_c/Φ_s) for various proton donors give the ratio of Φ_c. The results obtained for acridine by (11) and (12) are practically the same. As shown in Table I, Φ_c's of acridine hydrogen bonded with ethanol, benzylalcohol and β-phenylethylalcohol are almost the same, and it is somewhat smaller when acridine is hydrogen bonded with chloroform.

Moreover, Φ_c for ethanol does not change irrespective of whether benzene, hexane, or carbon tetrachloride, is used as solvent. For chloracetic acids, the value of Φ_c is far greater than that for ethanol, and owing to the red shift of fluorescence spectrum, the "true value" of Φ_c may be larger than the value given in the table*.

For quinoline, since the weakness of its fluorescence intensity did not allow precise measurement, we did not attempt extensive study, and measurements were made only for monochlor- and trichloracetic acid. From the increases in fluorescence intensity, we can see, for these cases that Φ_c may be only several times of Φ_B in its order of magnitude, whereas $\Phi_s/\Phi_B\sim 30$[3], therefore, Φ_c may be probably much smaller than Φ_s, for these cases.

Now, $\Phi=\dfrac{k_f}{k_f+k_i}$, where k_f and k_i are the rate constant of fluorescent transition and that of the radiationless process. k_f can be estimated using Ladenburg's formula[11],

$$k_f\simeq 2.88\times 10^{-9}\, n^2\tilde{\nu}^2_{\max}\int_0^\infty \varepsilon(\tilde{\nu})d\tilde{\nu}\ \mathrm{sec}^{-1}$$

Both in acridine and quinoline, the overlapping of ^1L_b and ^1L_a bands is fairy large; nevertheless, in the case of acridine, we can estimate $\int_0^\infty \varepsilon(\tilde{\nu})d\tilde{\nu}$ in its order of magnitude.

For acridine-trichloracetic acid-benzene system,

$$k_f'\sim 5.5\times 10^7\ \mathrm{sec}^{-1},$$

and for acridine-ethanol-benzene system,

$$k_f\sim 2.5\times 10^7\ \mathrm{sec}^{-1}.$$

Putting these k_f' and k_f value into the equation,

$$\Phi'/\Phi=\frac{k_f'}{k_f}\frac{(k_f+k_i)}{(k_f'+k_i')}\sim 11,$$

the following relations are derived.

$$k_i'<\frac{1}{5}k_i,\quad \tau'\simeq 5\tau$$

For quinoline, the estimation of $\int_0^\infty \varepsilon(\tilde{\nu})d\tilde{\nu}$ is more difficult. It is certain, however, that the integrated absorption is far larger in quinoline-trichloracetic acid-benzene system compared with those in benzene or ethanol solution. Therefore, it is clear that k_i of quinoline hydrogen bonded with trichloracetic acid is far greater than k_i in ethanol solution.

4. Discussion

(a) Role of n-Electron in the Inner Quenching of Fluorescence. — From all the facts described above, it is clear that the hydrogen bonding or proton addition plays an important role in the fluorescence of these nitrogen heterocycles. This circumstance is well comprehended by assuming that the n-electrons (non-bonding electrons) on a nitrogen atom is intimately related with the mechanism of fluorescence; the interaction between n- and π-electrons in the excited state may perhaps induce the radiationless transition to the ground state**, directly or indirectly. Such n–π interaction may be weakened more or less owing to the acquisition of bonding character by the n-electron due to hydrogen bonding or proton addition, making the fluorescence transition possible.

In contradistinction to the case of naphthols, the equilibrium constant obtained from the fluorescence intensity is almost the same as that calculated from absorption spectrum, for these nitrogen heterocycles. This fact may be correlated with the proposed mechanism of the inner quenching by n-electron.

The possible interpretations may be as follows.

(i) Although the equilibrium in the excited state is shifted toward hydrogen bonding, the excited free molecule has such a short lifetime, due to high probability of inner quenching, that it has no time to be bonded with neighboring OH

* The phototube used is an ultraviolet sensitive one.

11) See for example, Th. Förster, loc. cit., p. 158.

** An analogous discussion was made recently by Sangster and Irvine in relation to their study of the efficiencies of organic scintillators. R. C. Sangster and J. W. Irvine, Jr., *J. Chem. Phys.*, **24**, 670 (1956).

groups during its life. Thus only the molecules which are hydrogen bonded in the ground state may be able to fluoresce.

(ii) Owing to the n–π interaction the non-bonding character of n-electron may be lost more or less in the excited state, decreasing the proton accepting power, but the π-electron density on the nitrogen atom plausibly be increased in the excited state[3***], thus compensating the decrease in proton accepting power by n-electron, and the accepting power may be the same in the ground and in the excited state. In this case, even when the equilibrium state is reached during the lifetime of an excited free molecule, the equilibrium constant obtained from fluorescence intensity ought to be equal to that evaluated from absorption spectrum. In the present stage it cannot be decided definitely which of (i) and (ii) is the dominant mechanism for the phenomenon question.

(b) Effect of π-Electronic State on the Fluorescence Quenching. — Although the increase in fluorescence yields of quinoline and acridine by hydrogen bonding with ethanol or by proton addition in aqueous solution is almost the same, we see a distinct difference between these molecules in the effect of halogen atom on the fluorescence yields. The fluorescence yield of acridine is greatly enhanced by hydrogen bonding with trichloracetic acid, but the fluorescence yield of quinoline hydrogen bonded with trichloracetic acid is rather small compared with the fluorescence yield in ethanol solution. This distinction in these two molecules may be ascribed to the difference of emitting π-electronic state. In aromatic hydrocarbons, such as benzene, naphthalene and anthracene, there exists an ^3L_b state which has the same energy as ^1L_b[12,13].

If the lowest singlet excited state is ^1L_b, the phosphorescence transition occurs with relative ease probably by the processes, $^1L_b \rightarrow {}^3L_b \rightarrow {}^3L_a \rightarrow$ ground state. However, when the lowest singlet excited state is ^1L_a, phosphorescence transition may be very difficult. The difference between naphthalene and anthracene in the experimental results of T→T absorption[14] may be interpreted by these mechanisms. Now, as the electronic spectra of nitrogen heterocycles are very similar to those of isoelectronic aromatic hydrocarbons, we may be allowed to assume that the analogous situation probably prevails also in these heterocyclic molecules. Thus, in the case of quinoline, the near-by existence of a halogen atom may easily accelerate $^1L_b \rightarrow {}^3L_b$ process owing to the spin-orbital perturbation, but it may be difficult to realize such a situation in acridine.

After all, the results reported in this paper, are well comprehended by assuming that the n–π interaction is a chief cause of inner quenching and also by considering the effect of emitting π-electronic state on the quenching phenomenon. From the present results, the interpretations of the inner quenching in these molecules as due to the spin-orbital perturbation by the existence of nitrogen atom or predissociation of CN bond may not be appropriate.

*** A theoretical study using the molecular orbital method is now in progress.

12) R. Pariser, *J. Chem. Phys.*, **24**, 250 (1956).
13) J. A. Pople, *Proc. Phys. Soc.*, **68A**, 81 (1955).
14) D. P. Craig and I. G. Ross, *J. Chem. Soc.*, **1954**, 1589.

Summary

1. The hydrogen bonding effect on the fluorescence of quinoline and acridine was studied in non-polar solvent mixed with various proton donors.

2. The equilibrium constants of hydrogen bonding calculated from the absorption and fluorescence data were the same for these molecules, in contradistinction to the case of naphthols. Possible mechanisms for this experimental fact were proposed.

3. The larger the relative fluorescence yields of hydrogen bonded nitrogen heterocycles become, the stronger the donating powers of proton donors are, and from this fact, discussions were given on the role of non-bonding electrons in the inner-quenching of these molecules.

4. The difference between quinoline and acridine in their fluorescence quenching caused by the existence of a halogen atom was ascribed to the different emitting π-electronic states in these molecules (^1L_b in quinoline, ^1L_a in acridine), and some considerations by means of analogy to the π-electronic structures of aromatic hydrocarbons were given.

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