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# Electronic Structures and Luminescence Properties of Phenazine Derivatives

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The electronic structures and luminescence properties of phenazine derivatives (1, 5-dichloro-, -dihydroxy-, -dimethoxy-, and -diamino-phenazine) have been studied. The observed absorption spectra and the solvent effects on the spectra have been interpreted satisfactorily on the basis of the quantum mechanical calculation of the pi-electronic states of these molecules. From the results of this calculation, as well as from the fluorescence properties of these molecules, it has been established that the lowest excited singlet state is $^1(\pi—\pi^*)$ (the $^1L_a$ state more or less modified by the substitution) in all of these molecules, in contrast to the case of the phenazine molecule, where $^1(n—\pi^*)$ is the lowest singlet excited state, leading to the non-fluorescent property of this molecule. The effects of hydrogen bonding and acid-base interactions on the fluorescence properties of the phenazine derivatives have been examined. The inter and intra-molecular hydrogen bonding as well as the protonation interactions at the ring nitrogen cause, in general, a large decrease in the fluorescence yields of these molecules, in contrast to the case of acridine and acridine derivatives, where the interactions with aliphatic alcohols and acids affect the fluorescence yield only slightly or even increase it. The mechanism of this fluorescence quenching has been discussed on the basis of a radiationless vibronic coupling between the relevant electronic states.

The luminescence characteristics of nitrogen heterocycles are of considerable interest from various viewpoints. Previously, we have examined the hydrogen bonding and protonation effects on the luminescence properties of several nitrogen heterocycles, including quinoline, acridine, and some acridine derivatives.[1] The existence of the non-bonding electrons in these molecules plays a predominant role in the determination of the intramolecular electronic processes and the luminescence properties of these molecules. Quite similar circumstances seem to prevail in the case of phenazine.

In the present study, we have examined the fluorescence properties and electronic structures of four kinds of 1, 5-disubstituted phenazines and have found out new information concerning the hydrogen-bonding effects on the fluorescence of the pi-electron systems.

## Experimental

**Materials.** Phenazine derivatives 1, 5-dichloro-, -dihydroxy-, -dimethoxy- and -diamino-phenazine, which had been synthesized and purified in the laboratory of Professor E. Imoto of the University of Osaka Prefecture, were kindly supplied to us. They were used without further purification. Ethanol, methanol, benzene, and acetic acid were of an analytical grade and were also used without further purification. Analytical grade phenol was carefully distilled before use. Trichloroacetic acid was recrystallized several times from benzene and stored over concentrated sulfuric acid in a vacuum desiccator.

**Apparatus.** The fluorescence spectra were measured by a spectrometer already described elsewhere,[2] and also by an Aminco-Bauman spectrophotofluorometer. The absorption spectra were measured by a Beckman DU spectrometer and a Hitachi EPU spectrometer.

The deaeration of solutions for the measurement was carried out by an ordinary procedure of repeated freezing, pumping, and thawing.

## Results and Discussion

The energy-level scheme of such nitrogen heterocycles as quinoline, acridine, and phenazine which are non-fluorescent in nonpolar and non-hydrogen bonding solvents may be represented as in Fig. 1. The molecule excited to the $^1(\pi—\pi^*)$ state makes a very efficient internal conversion to the $^1(n—\pi^*)$ state, and then an intersystem crossing to the $^3(\pi—\pi^*)$ state, either directly or *via* the $^3(n—\pi^*)$ state. When they are hydrogen-bonded with a proton donor molecule or, in the case of proton addition, to the lone pair on the ring nitrogen, the excitation energies to the lowest $^1(n—\pi^*)$ and $^3(n—\pi^*)$ states may become larger than the excitation energy to the lowest $^1(\pi—\pi^*)$ state.

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[1] N. Mataga, Y. Kaifu and M. Koizumi, This Bulletin, **29**, 373 (1956); N. Mataga and S. Tsuno, *ibid.*, **30**, 368, 711 (1957).

[2] N. Mataga, Y. Torihashi and Y. Kaifu, *Z. Phys. Chem. N. F.*, **34**, 379 (1962).

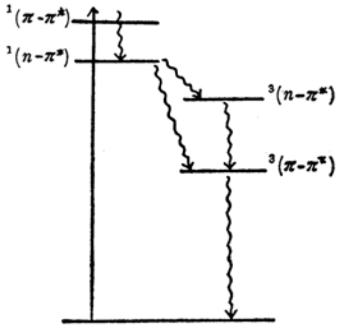

Fig. 1. The energy level scheme for the electronic processes involving the $(n-\pi^*)$ and $(\pi-\pi^*)$ states.

Thus, the fluorescence transition becomes possible in a proton-donating environment.

Quite similar results are obtained when these nitrogen heterocycles are substituted by some appropriate substituents, such as hydroxy-, methoxy-, amino- and dimethylamino-groups. For example, in the case of the 3, 6-diamino- and 3, 6-dimethylamino-acridines, we can observe strong fluorescence even in nonpolar solvents as a result of the red shift of the lowest $^1(\pi-\pi^*)$ ($^1L_a$) state and the blue shift of the $(n-\pi^*)$ states caused by the substitution.

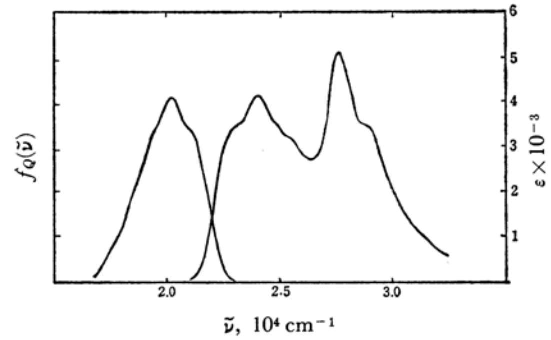

Fig. 2. Absorption and fluorescence spectra of DMP in benzene. $[\mathrm{DMP}]=1.15\times10^{-4}$ mol/$l$

The absorption and fluorescence spectrum of 1, 5-dimethoxy phenazine (DMP) in benzene are shown in Fig. 2. The absorption bands with $\tilde{\nu}_{max}\approx 2.40\times10^4$ cm$^{-1}$ and $\tilde{\nu}_{max}\approx2.76\times10^4$ cm$^{-1}$ may be related to the $^1L_a$ and $^1L_b$ bands, respectively, of the phenazine molecule. This assignment is consistent with the result of quantum mechanical calculations on the pi-electronic states, as well as with the experimental findings on the solvent effects on the spectra to be described below. For the calculation of the pi-electronic states of the 1, 5-disubstituted phenazine, we employ here the method of the composite molecule.(3) We denote the pi-orbitals on the substituents as $s_1$ and $s_2$. Therefore, we have the symmetry orbitals:

$$\left.\begin{aligned}\sigma_b &= (s_1+s_2)/\sqrt{2} \in a_u\\ \sigma_a &= (s_1-s_2)/\sqrt{2} \in b_g\end{aligned}\right\}\qquad(1)$$

According to our previous calculation, the wave functions for the lower-excited pi-electronic states of phenazine are:

$$\left.\begin{aligned}\Psi(^1L_a) &= 0.9870\,{}^1\chi_{78} + 0.1608\,{}^1\chi_{69}\\ \Psi(^1L_b) &= 0.8368\,{}^1\chi_{68} - 0.5748\,{}^1\chi_{79}\\ \Psi(^1B_a) &= 0.1608\,{}^1\chi_{78} - 0.9870\,{}^1\chi_{69}\\ \Psi(^1B_b) &= 0.5748\,{}^1\chi_{68} + 0.8368\,{}^1\chi_{79}\end{aligned}\right\}\qquad(2)$$

where ${}^1\chi_{ik}$ represents the wave function for the electron configuration where one electron is raised from the $i$th MO to the $k$th MO. We take into account the following configurations, in which one electron is transferred from the symmetry orbital, $\sigma$, to the orbitals of phenazine unoccupied in the ground state:

$$\left.\begin{aligned}&{}^1\chi_{\sigma_a8}\in B_u \qquad {}^1\chi_{\sigma_a9}\in B_u\\ &{}^1\chi_{\sigma_b8}\in A_g \qquad {}^1\chi_{\sigma_b9}\in A_g\end{aligned}\right\}\qquad(3)$$

If the MO's of phenazine are written $\phi_1\cdots\phi_n$, then the energy of the electron transfer configuration, ${}^1\chi_{\sigma k}$, is given by:

$$\langle{}^1\chi_{\sigma k}|\mathscr{H}|{}^1\chi_{\sigma k}\rangle = \varepsilon_k - \varepsilon_\sigma - \langle\sigma(1)\psi_k(2)|g_{12}|\sigma(1)\psi_k(2)\rangle \qquad (4)$$

where $\varepsilon_k$ and $\varepsilon_\sigma$ are the energies of $\psi_k$ and $\sigma$ respectively, and where the $\psi_k$'s are linear combinations of $2p\pi$ AO's $\phi_1\cdots\phi_n$:

$$\psi_k = \sum_\mu c_{k\mu}\phi_\mu \qquad (5)$$

$g_{12}$ is the interelectronic repulsion operator, $e^2/r_{12}$. In the present case, it is a good approximation for $\varepsilon_\sigma$ to put:

$$\varepsilon_\sigma \approx \varepsilon_{s_1} = \varepsilon_{s_2} \qquad (6)$$

Accordingly, for DMP, $\varepsilon_\sigma$ will be given by the observed ionization potential of methanol, *i. e.*, $\varepsilon_\sigma=-10.85$ eV. The difference between the observed and calculated values of the electron affinity of benzene has been added to the calculated values of $\varepsilon_k$. Therefore, $\varepsilon_9=0.0774$ eV and $\varepsilon_8=-1.8391$ eV. With zero differential overlap approximation,

$$\begin{aligned}&\langle\sigma(1)\psi_k(2)|g_{12}|\sigma(1)\psi_k(2)\rangle\\ &\quad=(\sum_\mu c^2{}_{k\mu}r_{s_1\mu}+\sum_\mu c^2{}_{k\mu}r_{s_2\mu})/2\\ &\quad=\sum_\mu c^2{}_{k\mu}r_{s_1\mu}=\sum_\mu c^2{}_{k\mu}r_{s_2\mu}\\ &r_{s\mu}=\langle s(1)\phi_\mu(2)|g_{12}|s(1)\phi_\mu(2)\rangle \qquad (7)\end{aligned}$$

For the evaluation of $r_{s\mu}$, the equation(4):

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3) H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc.*, **A68**, 601 (1955).

4) K. Nishimoto and N. Mataga, *Z. Phys. Chem. N. F.*, **12**, 335 (1957); N. Mataga and K. Nishimoto, *ibid.*, **13**, 140 (1957).

$$r_{s\mu} = e^2/(a_{s\mu} + R_{s\mu}) \tag{8}$$

was used, where $R_{s\mu}$ is the distance between the substituent oxygen atom and the $\mu$th atom in the ring. The matrix elements of the interactions between the electron-transfer configurations and the local configurations can be evaluated from the following formulas:

$$\left.\begin{aligned} \langle {}^1\chi_{\sigma k}|\mathscr{H}|{}^1\chi_{jl}\rangle &= -\delta_{kl}\langle\sigma(1)|H(1)|\psi_j(1)\rangle \\ \langle {}^1\chi_{\sigma k}|\mathscr{H}|{}^1\chi_0\rangle &= 2^{1/2}\langle\sigma(1)|H(1)|\psi_k(1)\rangle \end{aligned}\right\} \tag{9}$$

where $\delta_{kl}$ is the Kronecker delta and $\chi_0$ is the ground configuration.

$$\begin{aligned} &\langle {}^1\chi_{\sigma k}|\mathscr{H}|{}^1\chi_{\sigma l}\rangle \\ &\quad = -\langle\sigma(1)\psi_k(2)|g_{12}|\sigma(1)\psi_l(2)\rangle \\ &\quad = -\sum_{\mu} c_{k\mu}c_{l\mu}r_{s\mu} \end{aligned} \tag{10}$$

The $\langle\sigma(1)|H(1)|\psi_j(1)\rangle$ integral can be reduced to: $c_{j\theta}\langle s(1)|H(1)|\phi_\theta(1)\rangle = c_{j\theta}\beta^{\text{core}}$, the substituent being attached to the $\theta$th atom in the ring. For DMP, assuming the proportionality of $\beta^{\text{core}}$ to the overlap integral and taking $R_{\text{CO}}=1.336$ Å, $\beta^{\text{core}}_{\text{CO}}$ was evaluated as $-1.6$ eV. With these approximations for the integrals, and using the observed values for the excitation energies of phenazine ($E({}^1\text{L}_\text{a})=3.09$ eV, $E({}^1\text{L}_\text{b})=3.40$ eV, $E({}^1\text{B}_\text{b})=4.95$ eV, $E({}^1\text{B}_\text{a})=5.88$ eV), the lowest excited states of DMP may be calculated as follows:

$$\left.\begin{aligned} &2.8879\ \text{eV}, \\ &\quad \Psi_1 = 0.9689\,{}^1\text{L}_\text{a} + 0.0065\,{}^1\text{L}_\text{b} \\ &\qquad - 0.0023\,{}^1\text{B}_\text{b} + 0.0106\,{}^1\text{B}_\text{a} \\ &\qquad - 0.2465\,{}^1\chi_{\sigma_\text{a}8} + 0.0072\,{}^1\chi_{\sigma_\text{a}9} \\ &3.3528\ \text{eV}, \\ &\quad \Psi_2 = 0.0083\,{}^1\text{L}_\text{b} - 0.9938\,{}^1\text{L}_\text{b} \\ &\qquad + 0.0427\,{}^1\text{B}_\text{b} - 0.0001\,{}^1\text{B}_\text{a} \\ &\qquad + 0.0027\,{}^1\chi_{\sigma_\text{a}8} - 0.1014\,{}^1\chi_{\sigma_\text{a}9} \end{aligned}\right\} \tag{11}$$

On the other hand, ${}^1\chi_0$ interacts with ${}^1\chi_{\sigma_\text{b}8}$ and is depressed by $-0.1216$ eV. Therefore, the calculated excitation energies to the lowest and the second-lowest excited ($\pi$—$\pi^*$) states are 3.009 eV and 3.474 eV respectively, energies which are in a good agreement with the observed values, 2.98 eV and 3.42 eV respectively. Thus, the substitution causes a small red shift in ${}^1\text{L}_\text{a}$, but it causes very little shift in the ${}^1\text{L}_\text{b}$ band of phenazine. Furthermore, $\Psi_1$ can be regarded as the ${}^1\text{L}_\text{b}$ state of phenazine modified by interaction, mainly with ${}^1\chi_{\sigma_\text{a}8}$, while $\Psi_2$ may approximately be described as the ${}^1\text{L}_\text{b}$ state of phenazine modified a little by interaction with ${}^1\chi_{\sigma_\text{a}9}$ and ${}^1\text{B}_\text{b}$.

Now, the wave numbers of the ${}^1\text{L}_\text{a}$ band of DMP in ethanol and acetic acid are, respectively, $2.35\times10^4$ cm$^{-1}$ and $2.30\times10^4$ cm$^{-1}$, while those of the ${}^1\text{L}_\text{b}$ band are $2.75\times10^4$ cm$^{-1}$ and $2.72\times10^4$ cm$^{-1}$ respectively. The wave numbers of the ${}^1\text{L}_\text{a}$ and ${}^1\text{L}_\text{b}$ bands in benzene are $2.40\times10^4$ cm$^{-1}$ and $2.76\times10^4$ cm$^{-1}$ respectively. Therefore, taking the spectrum in benzene as a reference, the red shift of the ${}^1\text{L}_\text{a}$ band in the polar hydrogen-bonding solvents is larger than that of the ${}^1\text{L}_\text{b}$ band. In these solvents, the hydrogen-bonding interaction between the solute and the solvent molecules may play an important role in the shift of the spectra. In order to make more detailed studies of the hydrogen bonding and/or protonation effect on the spectra, we have examined the DMP-trichloracetic acid system in benzene.

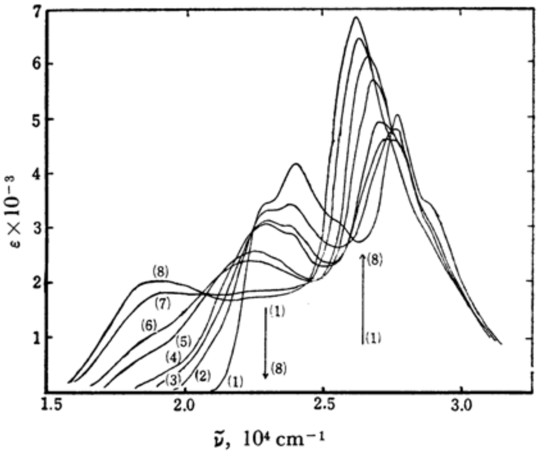

Fig. 3. Change of absorption spectrum of DMP in benzene by added trichloacetic acid.
[DMP]$=1.15\times10^{-4}$ mol/$l$
[D]: (1) 0, (2) $7.0\times10^{-4}$, (3) $9.2\times10^{-4}$, (4) $1.9\times10^{-3}$, (5) $7.6\times10^{-3}$, (6) $1.5\ \times10^{-2}$, (7) $5.0\times10^{-2}$, (8) $1.0\times10^{-1}$ mol/$l$

As Fig. 3 shows the spectral change caused by the added trichloracetic acid is quite remarkable. The change occurs in two stages, which may be ascribed respectively to the following equilibria:

$$\text{DMP} + \text{D} \rightleftarrows \text{DMP}\cdots\text{D}$$
$$\text{DMP}\cdots\text{D} + \text{D} \rightleftarrows \text{D}\cdots\text{DMP}\cdots\text{D}$$

where D represents the proton donor. In the first stage, the ${}^1\text{L}_\text{a}$ and ${}^1\text{L}_\text{b}$ bands shift to $2.27\times10^4$ cm$^{-1}$ and $2.70\times10^4$ cm$^{-1}$ respectively. In the second stage, the ${}^1\text{L}_\text{a}$ band shifts to $1.9\times10^4$ cm$^{-1}$ while the ${}^1\text{L}_\text{b}$ band shifts to $2.64\times10^4$ cm$^{-1}$ and is considerably strengthened. We have evaluated the equilibrium constants for the complex formation as $1.1\times10^3$ $l$/mol and $3.5\times10^2$ $l$/mol at 15°C respectively for the first and the second stages. The spectrum at the end of the second stage is quite similar to that of DMP in a diluted sulfuric acid solution. Therefore, the complexes of DMP with trichloracetic acid in benzene seem to be ion pairs formed by proton transfers from trichloracetic acid to DMP. We have also examined the hydrogen bonding with phenol in benzene. In this case, we can observe only the first stage of the equilibrium: the absorption bands shift to $2.30\times10^4\,\text{cm}^{-1}(^1L_a)$ and $2.73\times10^4\,\text{cm}^{-1}(^1L_b)$ respectively.

The spectral change described above can be well comprehended by means of the wave functions of (11). Among the MO's $\psi_6$, $\psi_7$, $\psi_8$, and $\psi_9$, of phenazine, the coefficients of the AO's on nitrogens are the largest in $\psi_8$, whereas they are zero in $\psi_9$. Accordingly, by the electron promotion $\sigma\rightarrow\psi_8$, the charge density on the nitrogen increases considerably, whereas it does not increase upon $\sigma\rightarrow\psi_9$ promotion. Because the contribution from $\chi_{\sigma a8}$ is much larger in $\Psi_1(^1L_a)$ than in $\Psi_2(^1L_b)$, the red shift caused by the hydrogen bonding or the protonation should be larger in the case of the $^1L_a$ band than in that of the $^1L_b$ band. The intensification of the $^1L_b$ band by the hydrogen bonding and the protonation interaction may be ascribed to the increase in the contribution of the $^1B_b$ of phenazine to $\Psi_2$, resulting from these solvent perturbations. Among the four absorption bands due to the transitions to the lowest excited states of phenazine, the oscillator strength of the $^1B_b$ band is far greater than those of the others, and the contribution of $^1B_b$ in $\Psi_2$ is about twenty times larger than that in $\Psi_1$.

The change in the spectra caused by the substitution is much smaller in 1, 5-dichlorophenazine (DCP) than in DMP, because of the smaller conjugation power of the chlorine atom than that of the methoxy group. The electron-donating power of the hydroxy group is much larger than the chlorine atom, although it may be a little smaller than that of the methoxy group. The absorption spectrum of 1, 5-dihydroxyphenazine (DHP) is very similar to that of DMP, as is indicated in Fig. 4. The $^1L_a$ band lies at $2.25\times10^4\,\text{cm}^{-1}$, and the $^1L_b$ band lies at $2.68\times10^4\,\text{cm}^{-1}$, in a benzene solution. Thus the absorption bands of DHP appear at smaller wave numbers than those of DMP. This fact contradicts the above argument about the conjugation power. However, it seems quite probable that there is a strong hydrogen-bonding interaction between the ring nitrogen and the hydroxy group of DHP. Because of this hydrogen-bonding interaction, the ionization potential of the hydroxy group decreases and the electron affinity of the phenazine ring increases, perhaps leading to the large red shift of the spectrum. Furthermore, the spectra of DHP in ethanol and acetic acid are almost the same as that in benzene, in contrast to the case of DMP. This may be ascribed to the strong intramolecular hydrogen-bonding of DHP, which makes impossible the intermolecular hydrogen-bonding interactions with the solvent molecules.

The spectrum of 1, 5-diaminophenazine (DAP) in benzene as well as that of DHP in an aqueous alkaline solution are shown in Fig. 4. In the latter case, the hydroxy group is completely dissociated. The substitution effect on the absorption spectrum is much larger in these cases than in the case of DMP and DHP in organic solvents. These results may be ascribed to the much larger conjugation power of the amino group and of $-O^-$ compared with those of the methoxy and hydroxy groups.

DCP can fluoresce in benzene as well as in ethanol, in contrast to phenazine, which shows no fluorescence. The wave numbers of the fluorescence band maximum is *ca.* $2.2\times10^4\,\text{cm}^{-1}$ in benzene as well as in ethanol. Accordingly, although the change in the spectrum due to the substitution is rather small, the $^1L_a$ state seems to be lower than the $(n-\pi^*)$ states in DCP.

As we have described already, DMP also can fluoresce rather strongly in a benzene solution. When it is hydrogen-bonded with phenol, however, the fluorescence of DMP is completely quenched. This circumstance is quite similar to the case of acridines hydrogen-bonded with phenol and naphthols.[1] The fluorescence yield of DMP in ethanol and acetic acid is much smaller than in

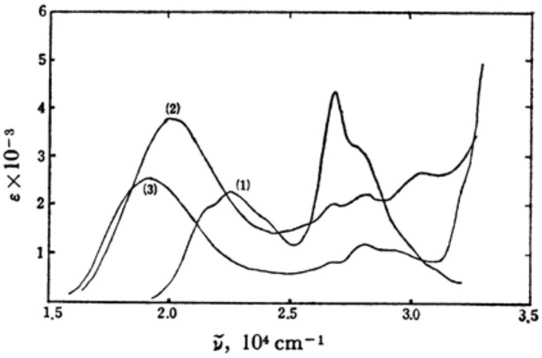

Fig. 4. Absorption spectra of DHP and DAP.
(1) DHP in benzene, [DHP]$=1.15\times10^{-4}$ mol/*l*
(2) DAP in benzene, [DAP]$=1.0\times10^{-4}$ mol/*l*
(3) DHP in aqueous alkaline solution (1 N sodium hydroxide solution), [DHP]$=1.0\times10^{-4}$ mol/*l*

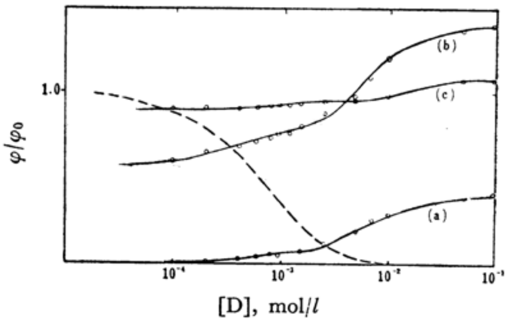

Fig. 5. Change of the relative fluorescence yield $\varphi/\varphi_0$ and the extinction coefficients of DMP caused by added trichloracetic acid.
---- $\varphi/\varphi_0$, —— extinction coefficient, (a) at 500 m$\mu$, (b) at 375 m$\mu$, (c) at 365 m$\mu$

the case of a benzene solution, in contrast to the cases of acridine, 3, 6-diaminoacridine, and 3, 6-dimethylaminoacridine. In the latter molecules, the hydrogen-bonding with aliphatic alcohols and acids enhances, or affects only slightly, the fluorescence yield. Furthermore, the ion-pair complex of DMP with trichloracetic acid in benzene is completely nonfluorescent. As Fig. 5, indicates the change in the relative fluorescence yield of DMP in benzene caused by the complex formation with trichloracetic acid occurs in the same concentration range of added trichloracetic acid as that of the first-stage change in the absorption spectrum. Accordingly, it is evident that the 1 : 2 complex as well as the 1 : 1 complex is nonfluorescent. At any rate, any type of hydrogen-bonding or protonation interactions with ring nitrogens seems to decrease the fluorescence yield of DMP.

DHP is non-fluorescent in all the solvents we have examined. The strong intramolecular hydrogen bonding interaction might play some important role in the fluorescence quenching, which seems to be analogous to the intermolecular hydrogen-bonding interaction of DMP.

The mechanism of the fluorescence quenching caused by the hydrogen bonding and protonation interaction in these molecules cannot be established in the present stage of our investigations. The intermolecular as well as intramolecular hydrogen bonding interactions in these molecules may certainly become much stronger in the excited state than in the ground state. Therefore, the energy difference between the ground state and the first excited singlet state, as well as that between the ground and the lowest-excited triplet state, may become rather small during the lifetime of the excited state. When the energy difference between the excited and the ground state becomes small, the probability of the radiationless transition between these two states may increase in general, because of the increase in the non-radiative vibronic coupling between the two states. Thus, the hydrogen-bonding and the protonation interaction may induce the decrease in the fluorescence yield. If this is the case for the molecules in the present study, the fluorescence yields of DAP in benzene and of DHP di-anion in the aqueous alkaline solution may both be much smaller than the fluorescence yield of DMP in benzene. We have confirmed that this is actually the case, although we have not made any accurate quantitative measurements of the fluorescence quantum yield for the relevant molecules. That is, the DHP di-anion in an aqueous alkaline solution is non-fluorescent, and DAP in benzene fluoresces very weakly.

Finally, we have made a few measurements of the fluorescence spectra of these molecules in the solid state. DMP and DCP can fluoresce rather strongly in the solid state, too, in contrast to DHP, which cannot fluoresce in the solid state as well as in the solution. Figure 6 indicates the fluorescence spectra of DMP film on a quartz plate. The specimen was made by the sublimation of DMP in a vacuum. At 77°K, the spectrum shows a vibrational structure. This result shows quite a different property of DMP as well as of DCP from that of some dyestuffs such as 3, 6-dimethylaminoacridine, which do not fluoresce in the solid state. The molecules of many dyestuffs aggregate very easily in the solid state, as well as in a concentrated solution; these aggregates generally cannot fluoresce.[5] In view of these facts, it may be expected that, in the solid state, DMP and DCP molecules are not in the aggregated state in which the intermolecular interactions are very strong. It has been established by X-ray diffraction that the crystal structure of DMP is not the aggregated form but is quite similar to that of anthracene.[6]

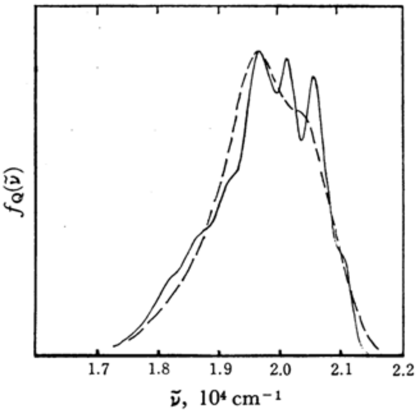

Fig. 6. Fluorescence spectra of DMP solid film. ---- at room temperature, —— at 77°K

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[5] See, for example, Th. Förster, "Fluoreszenz organischer Verbindungen," Vandenhoeck and Ruprecht, Göttingen (1951).

[6] Private communication from Prof. A. Shimada of Osaka City University.