Fluorescence and Dual Phosphorescence Spectra of Quinoxaline in Fluid Solution

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Fluorescence and phosphorescence spectra of quinoxaline in isooctane (2,2,4-trimethylpentane) have been measured under fluid conditions. The fluorescent emission with a spectral maximum at 410 nm is assigned to the $^1(n,\pi^*)\rightarrow S_0$ fluorescence of quinoxaline. A new phosphorescence spectrum appears in a wavelength region longer than 520 nm as the concentration of quinoxaline increases, in addition to the phosphorescence spectrum of the monomer. From the results of photostationary and transient experiments on the concentration and/or temperature dependence of phosphorescence, it has been confirmed that the phosphorescence consists of two components attributable to the monomer and the excimer.

Triplet excimers have been a subject of considerable interest.[1-8] Recently, we have confirmed the existence of the triplet excimer for naphthalene and its derivatives and phenanthrene in fluid solution by means of photostationary and transient phosphorescence measurements.[1-4] On the other hand, Chandross and Dempster showed that practically no triplet excimer is formed even with a sandwich-pair conformation of the two naphthalene rings in 1,3-di(1-naphthyl)propane in a rigid glass. Such a sandwich-pair is favorable for the formation of singlet excimer.[5]

More recently, Subudhi and Lim observed intramolecular excimer phosphorescence spectra of 1,3-di(1-naphthyl)propane[6] and 1,2-di(1-naphthyl)ethane[7] in a fluid solution. The spectra of these compounds are very similar to those of naphthalene and its derivatives reported by us.[1,2]

The experimental results described above seem to be reasonably explained in terms of the idea that there is a conformational difference between singlet and triplet excimers.[2,7] However, there still remain unsolved problems concerning the stability and geometrical structure of triplet excimers. In order to settle the problems, it is desirable to examine whether or not the triplet excimer is formed in fluid solution in compounds other than aromatic hydrocarbons.

Quinoxaline is similar to naphthalene in electronic structure except that the former has lower-lying (n,π^*) states. The presence of the (n,π^*) states will make it relatively easy to detect the phosphorescence of quinoxaline in fluid solution.

This paper reports the phosphorescence spectrum of quinoxaline in fluid solution, together with its fluorescence spectrum which has not been observed so far. The phosphorescence of quinoxaline is shown to be due to both the monomer and the excimer as in the case of aromatic hydrocarbons.

Experimental

Quinoxaline (Nakarai Chemical Co.) was purified by vacuum sublimation. Isooctane (2,2,4-trimethylpentane, Wako Pure Chemical Co.) was passed through a silica-gel column. The solution of quinoxaline in isooctane was fully degassed by repeated freeze-thaw cycles (7 or 8 times). Emission spectra were measured with a high-resolution, high-sensitivity emission spectrophotometer[1,2] equipped with a photon-counting detector. A specially designed spectrophosphorimeter was used for measuring the phosphorescence or delayed emission spectra as well as the time-resolved emission spectra with the lifetimes ranging from 10^2 to 10^{-5} s by means of the photon-counting method combined with a multichannel digital boxcar technique.[1,2] Representative emission and excitation spectra were corrected for the spectral sensitivity of the monochromator-photomultiplier system and for the spectral intensity of exciting light, respectively. The fluorescence quantum yield of quinoxaline was determined by comparing the corrected fluorescence spectrum with that of quinine sulfate in 1/2 M sulfuric acid used as a reference.

Results and Discussion

Uncorrected emission spectra are shown in Fig. 1, which were measured for both the aerated and the degassed isooctane solutions of 1.1×10^{-4} M quinoxaline at 25 °C. The emission spectrum of the aerated sample (A in Fig. 1) may be assigned to $^1(n,\pi^*)\rightarrow S_0$ fluorescence of quinoxaline on the basis of the following facts: (1) There is a mirror image relation between the emission spectrum and the lowest $^1(n,\pi^*)\leftarrow S_0$ absorption spectrum of quinoxaline; (2) the emission spectrum is very similar to the fluorescence spectrum of gaseous quinoxaline reported by McDonald and Brus,[9,10] and Soep and Tramer,[11] although it differs from the spectrum obtained by Dewey and Hadley;[12] (3) the exci-

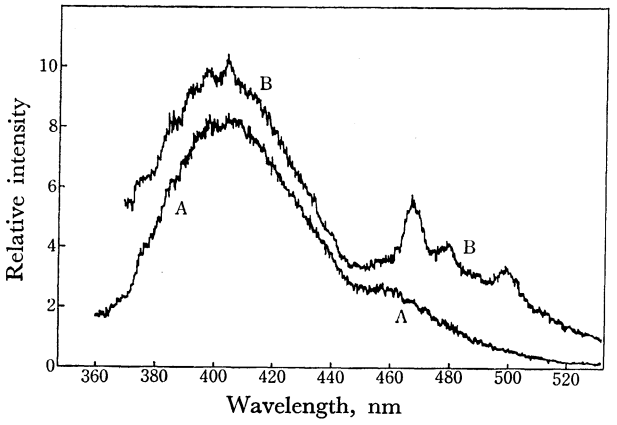


Fig. 1. Emission spectra (uncorrected) of quinoxaline in isooctane at 25 °C: A, aerated sample; B, degassed sample. The exciting wavelength is 315 nm with a band width of 10 nm; the band width for the emission is 3 nm. The concentration of quinoxaline is 1.1×10^{-4} M.

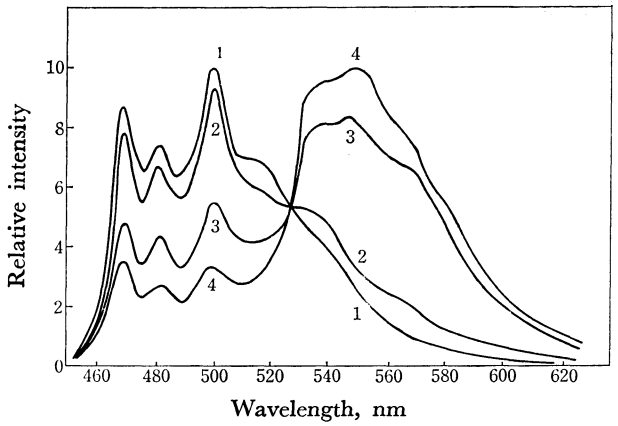


Fig. 2. Changes in the delayed emission spectrum (uncorrected) of quinoxaline in isooctane at 25 °C caused by the increase of the concentration. The concentrations of quinoxaline: (1) 1.1×10^{-4}; (2) 1.1×10^{-3}; (3) 1.1×10^{-2}; (4) 1.1×10^{-1} M. The spectral intensities are normalized at 528 nm.

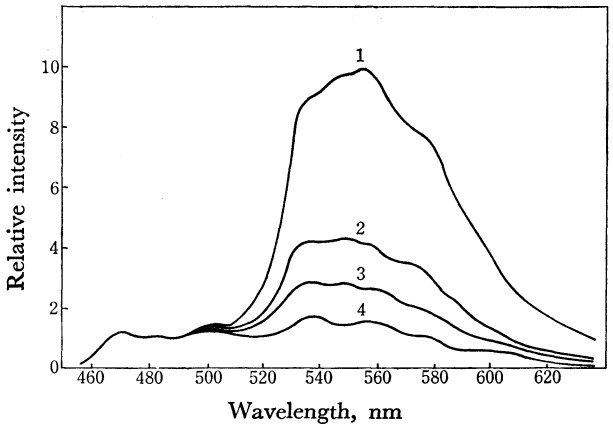


Fig. 3. Changes in the delayed emission spectrum (uncorrected) of quinoxaline in isooctane with temperature. The temperatures of the solution: (1) 0; (2) 25; (3) 43; (4) 60 °C. The concentration of quinoxaline is 6.0×10^{-2} M. The spectral intensities are normalized at 470 nm.

tation spectrum monitored at any emission wavelength between 370 and 520 nm is in fair agreement with the absorption spectrum in the range of the $^1(n,\pi^*)\leftarrow S_0$ transition of quinoxaline; (4) the emission concerned has a quantum yield of 7.5×10^{-5} and a lifetime shorter than 2 ns in isooctane at 25 °C; and (5) the quantum yield is independent of concentration and is not changed by degassing the sample solution. It should be noted here that the appearance of a shoulder at about 460 nm is due to the fact that the spectrum is not corrected for the sensitivity of the spectrophotometer used.

On the other hand, the degassed sample (B in Fig. 1) exhibits, in addition to the fluorescence spectrum described above, a structured emission spectrum in a wavelength region longer than 465 nm. This emission has an apparent lifetime of the order of 10^{-3} s. The excitation spectrum with respect to the structured emission spectrum agrees with the absorption spectrum of quinoxaline.

Figure 2 shows the delayed emission spectra (uncorrected) of quinoxaline in isooctane at 25 °C, which were measured with the spectrophosphorimeter. The emission spectrum of quinoxaline for a relatively low concentration (1.1×10^{-4} M) is in good agreement with the phosphorescence spectrum in EPA at 77 K, but the former spectrum is red-shifted by about 300 cm^{-1} compared with the latter.

The experimental results described above indicate that the structured spectrum extending from 465 nm towards longer wavelengths at a relatively low concentration is attributable to the phosphorescence from the monomer of quinoxaline.

The delayed emission spectrum, however, exhibits strong concentration dependence as shown in Fig. 2, where the spectral intensities are normalized at 528 nm. A new emission spectrum grows in a wavelength region from 520 to 620 nm with the increase of concentration; hereafter, it will be called emission spectrum E. Although the excitation spectrum cannot be obtained accurately by monitoring the emission spectrum E because of the high solute concentration, the onset at the longest wavelength of the excitation spectrum coincides with that of the absorption spectrum of quinoxaline. It is seen in Fig. 2 that the intensity ratio of the emission E to the monomer phosphorescence increases as the concentration increases. It should be noted that the emission E is not due to a photochemical product, because practically no change was produced in the intensity of the emission E by exposing the sample solution to UV light. It is also noted that the solvent used showed no delayed emission under the present experimental conditions.

By reference to the excimer phosphorescence of naphthalene and phenanthrene,[1-4] the experimental results regarding the concentration dependence of the delayed emission are found to suggest that the emission E is due to the excimer phosphorescence of quinoxaline. However, there still remains the possibility that the emission E is an impurity phosphorescence resulting from T-T energy transfer from quinoxaline to an impurity involved originally in the solute.

In order to decide whether the emission E is due to the triplet excimer of quinoxaline or not, temperature dependence of the phosphorescence spectrum must be examined. The temperature dependence of the delayed emission spectrum for 6.0×10^{-2} M quinoxaline in isooctane is shown in Fig. 3, where the intensities of emission spectra are normalized at 470 nm. It is clearly seen in Fig. 3 that the intensity ratio of the emission E to the monomer phosphorescence markedly decreases as the temperature rises. This means that the emission E is not due to an impurity triplet resulting from the T-T energy transfer, since in the case of T-T energy transfer in fluid solution the intensity ratio of phosphorescence of the energy donor to that of the acceptor must be independent of temperature.[13] When the sample solution is frozen, the emission E vanishes, while the monomer phosphorescence intensifies remarkably. Thus, all the experimental results obtained indicate that the emission E is the excimer phosphorescence of quinoxaline itself.

Figure 4 shows collectively the absorption spectrum

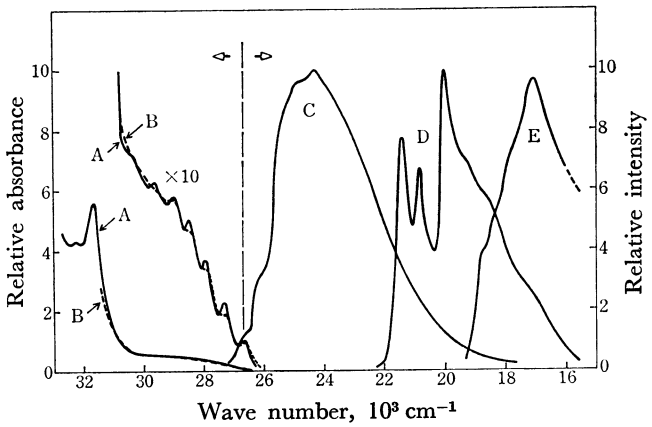
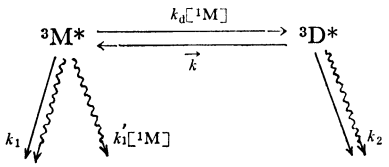


Fig. 4. Absorption, excitation (corrected), and emission (corrected) spectra of quinoxaline in isooctane at 20 °C: A, absorption; B, excitation spectra of the fluorescence and the monomer phosphorescence; C, fluorescence; D, monomer phosphorescence; and E, excimer phosphorescence.

and corrected emission and excitation spectra of quinoxaline in isooctane at 20 °C.

By solving the rate equations with regard to the kinetic scheme 1 appropriate for the deactivation of the triplet state involving excimer formation,[2] one can easily obtain Eqs. 2 and 3 for the time dependence of the intensities, I, of the monomer (m) and excimer (d) phosphorescence:



(1)

$$I_m(t) = \frac{C_1(\theta_2 - X)}{\theta_2 - \theta_1}\{e^{-\theta_1 t} + Ae^{-\theta_2 t}\}, \quad (2)$$

$$I_d(t) = \frac{C_2[^1M]}{\theta_2 - \theta_1}\{e^{-\theta_1 t} - e^{-\theta_2 t}\}, \quad (3)$$

with

$$\left.\begin{matrix}\theta_1 \\ \theta_2\end{matrix}\right\} = \frac{1}{2}[X + Y \mp \{(Y-X)^2 + 4k_d\overleftarrow{k}[^1M]\}^{1/2}], \quad (4)$$

$$X = k_1 + (k_1' + k_d)[^1M], \qquad Y = k_2 + \overleftarrow{k}, \quad (5)$$

$$A = (X - \theta_1)/(\theta_2 - X), \quad (6)$$

and C_1 and C_2 are constants with positive values. Here, ^{1}M, ^{3}M*, and ^{3}D* stand for the ground singlet monomer, excited triplet monomer, and excited triplet dimer (triplet excimer), respectively; k_1 and k_2 are the sums of the radiative and nonradiative decay constants for the triplet monomer and excimer, respectively; k_d and $\overleftarrow{k}$ are the rate constants for the formation and dissociation of the triplet excimer, respectively; and k_1' is the rate constant for quenching by the ground state molecule.

Figure 5 shows representative decay curves of the phosphorescence monitored at 480 nm (M) and at 540 nm (D) for 1.1×10^{-2} M and 1.1×10^{-1} M quinoxaline in isooctane at 20 °C. According to Eqs. 2 and 3, it is expected that $I_m(t)$ should yield a curve consisting of two exponential decays, while $I_d(t)$ a rise-and-

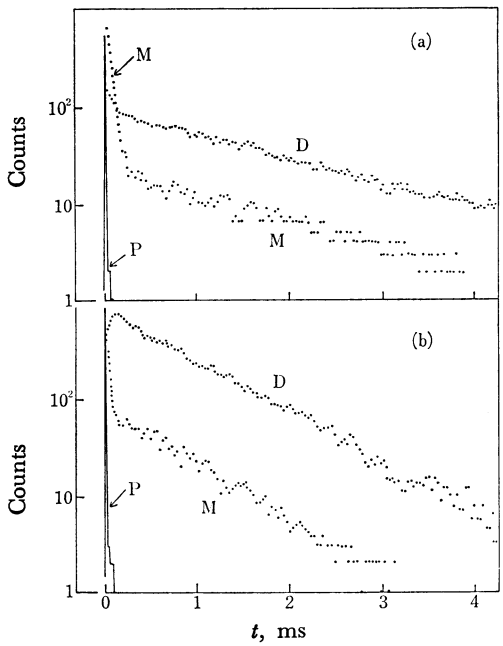


Fig. 5. Representative $I(t)$ curves for the phosphorescence of quinoxaline in isooctane at 20 °C. The concentrations of quinoxaline: (a) 1.1×10^{-2} M; and (b) 1.1×10^{-1} M. Monitoring wavelengths: M, 480 nm (monomer region); D, 540 nm (monomer+excimer region). P represents the exciting light pulse.

decay curve. It is clearly seen in Fig. 5 that the decay curves for the monomer phosphorescence at 480 nm correspond well to $I_m(t)$ predicted by Eq. 2 with $\theta_1 = 5.4\times10^2$ s^{-1} and $\theta_2 = 1.9\times10^4$ s^{-1} for a solute concentration of 1.1×10^{-2} M and with $\theta_1 = 1.2\times10^3$ s^{-1} and $\theta_2 = 2.7\times10^4$ s^{-1} for 1.1×10^{-1} M. The $I(t)$ curve monitored at 540 nm for 1.1×10^{-1} M shows clearly a rise-and-decay curve corresponding to $I_d(t)$ in Eq. 2, with a decaying rate constant very close to the value of θ_1 in $I_m(t)$. On the other hand, the $I(t)$ curve at 540 nm for 1.1×10^{-2} M shows almost a single exponential decay. This fact may be attributed to the coexistence of the monomer and the excimer phosphorescence emissions at 540 nm.

Here again, we shall examine the possibility that the emission E is due to an impurity. In this case, ^{1}M and ^{3}D* in the kinetic scheme (1) must be replaced by ^{1}A and ^{3}A*, respectively, where ^{1}A and ^{3}A* are the ground state and the excited triplet state of the impurity molecule. Since the energy separation between the structured phosphorescence spectrum of the quinoxaline monomer and the broad emission spectrum E is about 3000 cm^{-1}, the reverse T-T energy transfer from the triplet state of the impurity to that of quinoxaline can be completely neglected; that is, $\overleftarrow{k}=0$.

In such a case, the $I(t)$ curve of the phosphorescence observed at 480 nm should give a single exponential decay, since the phosphorescence emission at 480 nm is due to the quinoxaline monomer which is regarded as the energy donor. This contradicts the observation that the $I(t)$ curves M in Fig. 5 consist of two exponential decays. In other words, the results of dynamic measurement of the phosphorescence also indicate that the

broad emission cannot be due to an impurity.

It is thus concluded that the broad emission spectrum, which appears in the range of 520—620 nm upon increasing the concentration of quinoxaline, is ascribable to the triplet excimer of quinoxaline.

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