Excitation Wavelength Dependence of Phosphorescence and Hydrogen-Bonding Formation of Thioxanthone and 2,4-Diisopentylthioxanthone

Hiroshi MORITA,* Shigeyasu MORI, and Tsuguo YAMAOKA
Department of Image Science and Technology, Faculty of Engineering, Chiba University, Yayoi-cho, Chiba 260
(Received June 8, 1987)

Phosphorescence spectra of the ethanol solutions of thioxanthone(TX) and 2,4-diisopentylthioxanthone (DITX) exhibited excitation wavelength dependence at 77 K. In addition to the normal phosphorescence observed at 450 nm for TX and at 460 nm for DITX, a new red-shifted phosphorescence was resolved at 470 nm and 485 nm, respectively, when TX and DITX were excited at the absorption tail. The lifetimes and excitation spectra of the red-shifted phosphorescence were found to differ from those of the normal phosphorescence. Based on the study on UV absorption spectra and phosphorescence spectra measured with hydrated species of TX and DITX in ethanol-water solution at 77 K, the red-shifted phosphorescence is ascribed to the hydrogen-bonded species with water. In 2-methyltetrahydrofuran, phosphorescences of TX and DITX shift to the longer wavelengths and the lifetimes become longer when excited at the longer absorption tail, although the phosphorescence excitation spectra do not change appreciably.

In polymer photochemistry, thioxanthone[9*H*-thioxanthen-9-one](TX) and its derivatives are effective sensitizers in radical polymerization of vinyl monomers,[1-3] in photocrosslinking of polyacrylates and polystyrenes,[4,5] and in photocuring of coating systems.[6] In order to understand the sensitization mechanisms, photophysical and photochemical properties of TX and its derivatives have been studied extensively.[1,3,5,7,8] As is widely recognized in aromatic carbonyl compounds,[9-12] TX has close-lying $S_1(\pi-\pi^*)$ and $S_2(n-\pi^*)$, and $T_1(\pi-\pi^*)$ and $T_2(n-\pi^*)$ states.[13-15] Due to the proximity of the S_1 and S_2 states, S_1-S_0 internal conversion rate of TX is influenced significantly by the solvent polarity, and hence fluorescence intensity, peak position, and lifetime largely change depending on solvents.[16]

Nature of the triplet state of TX and its derivatives is of particular interest in relation to the photochemical behavior as a sensitizer. Because the T_1 state of TX is assigned to $\pi-\pi^*$ state even in nonpolar solvents,[13-15] the phosphorescent behavior of TX and its derivatives is not expected to change significantly depending on solvents in contrast to the case of xanthone.[12]

Recently, however, we have observed that the phosphorescence spectra observed with the ethanol and 2-methyltetrahydrofuran (MTHF) solutions of TX and 2,4-diisopentylthioxanthone (DITX) change significantly depending on excitation wavelengths. To investigate this in detail, we have measured in the present paper, the phosphorescence and UV absorption spectra of TX and DITX in ethanol, in ethanol-water, and in MTHF at 77 K, and found that TX and DITX form hydrogen-bonded(H-bonded) species with water even in freshly distilled ethanol solution.

Experimental

TX (Kanto G.R. grade) and DITX (Toshin Kayacure) were purified by repeated recrystallization from benzene three times and finally by vacuum sublimation. Ethanol (Wako G.R. grade) used as a solvent was purified by fractional distillation, and MTHF (Tokyo Kasei G.R. grade), by fractional distillation immediately before use in the dark. Degassed solutions of TX and DITX were prepared by freeze-pump-thaw cycles under a background pressure of 6×10^{-3} Pa.

Phosphorescence spectra and phosphorescence excitation spectra were measured at 77 K with the combination of a phosphoroscope, a monochromator (JASCO CT-50), and a photomultiplier tube (EMI 6256S), exciting light from a 150 W xenon arc lamp (Ushio UXL-150D) being monochromatized with a monochromator (Nikon G250). Phosphorescence decay curves were recorded with the use of a transient memory (Kawasaki Electronica MR100E). UV absorption spectra were measured at 77 K and at room temperature with a Hitachi 200-20 and a Hitachi 330 recording spectrophotometers in cells of 1 and 10 mm light path lengths. The effect of photoproducts[5,7] of the ethanol and MTHF solutions of TX and DITX on phosphorescence lifetimes and spectra, and on UV spectra is negligible under the present experimental conditions.

Results and Discussion

Phosphorescence of TX and DITX in Ethanol. Phosphorescence spectrum observed with the ethanol solution of TX (2.4×10^{-4} M†) excited at 380 nm is shown in Fig. 1A. Observed spectrum is broad and has a peak at 450 nm and a shoulder at ≈480 nm (hereafter this phosphorescence is called the normal phosphorescence). Phosphorescence excitation spectra of TX monitored at 450 and 480 nm are shown in Fig. 1B; the excitation spectrum monitored at 450 nm has peaks at 384, 366, and 299 nm, and coincides well with the UV absorption spectrum of TX measured at 77 K (Fig. 1C). On the other hand, the excitation spectrum monitored at 480 nm shows an additional new band at ≈400 nm. Hence, phosphorescence spectrum was further measured by exciting TX at

† 1 M=1 mol dm^{-3}.

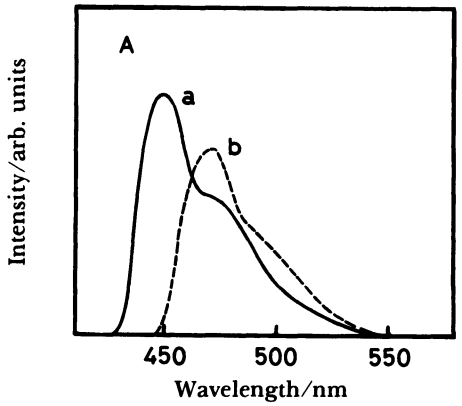

Fig. 1A. Phosphorescence spectra measured with the ethanol solution of TX (2.4×10^{-4} M) excited at (a) 380 nm and (b) 400 nm. The phosphorescence spectra in this and the following other figures are not corrected for the detector responce of a monochromator and photomultiplier tube unless otherwise stated.

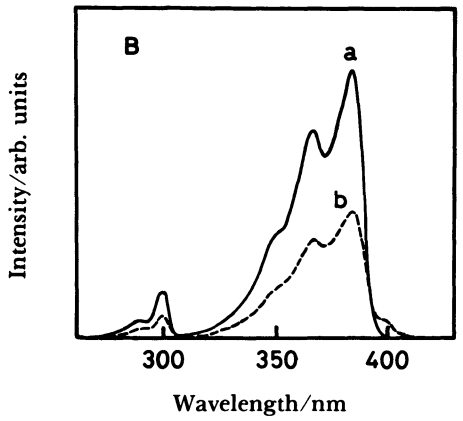

Fig. 1B. Phosphorescence excitation spectra measured with the ethanol solution of TX (2.4×10^{-4} M) monitored at (a) 450 nm and (b) 480 nm. The excitation spectra in this and the following other figures are not corrected for the spectral intensity of an exciting light source unless otherwise stated.

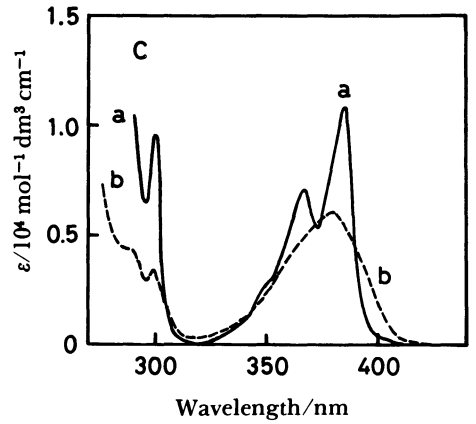

Fig. 1C. UV absorption spectra measured with the ethanol solutions of (a) TX (5.5×10^{-5} M) at 77 K and (b) TX (2.0×10^{-3} M) at room temperature.

400 nm; the result is also shown in Fig. 1A. The weak and broad phosphorescence spectrum with a peak at ≈470 nm and a shoulder at ≈500 nm was observed (referring to the normal phosphorescence, this is called the red-shifted phosphorescence). The red-

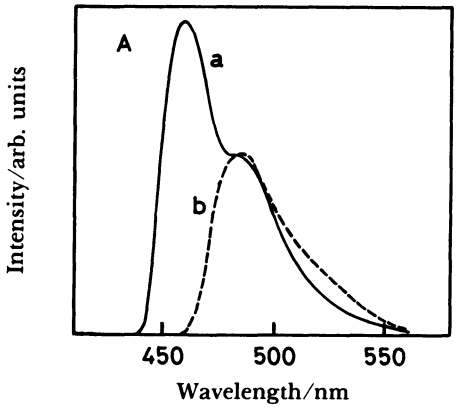

Fig. 2A. Phosphorescence spectra measured with the ethanol solution of DITX (4.4×10^{-4} M) excited at (a) 392 nm and (b) 410 nm.

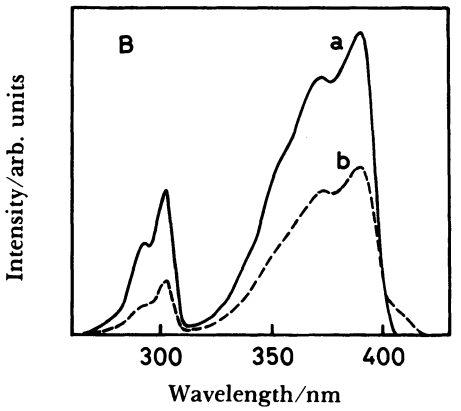

Fig. 2B. Phosphorescence excitation spectra measured with the ethanol solution of DITX (4.4×10^{-4} M) monitored at (a) 460 nm and (b) 490 nm.

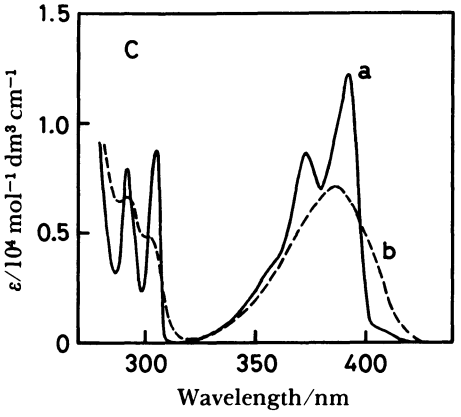

Fig. 2C. UV absorption spectra measured with the ethanol solutions of (a) DITX (7.3×10^{-5} M) at 77 K and (b) DITX (8.3×10^{-5} M) at room temperature.

shifted phosphorescence monitored at 480 nm decays single-exponentially, and the lifetime is 213 ms. This is longer than the one (160 ms) of the normal phosphorescence monitored at 450 nm and also at 475 nm which decays single-exponentially. From the lifetime measurement, the normal and the red-shifted phosphorescences can be assigned to different species of TX.

As in the case of TX, phosphorescence observed with the ethanol solution of DITX exhibits excitation wavelength dependence. Phosphorescence spectrum of DITX excited at 392 nm (near an absorption maximum) has a peak at 460 nm and a shoulder at ≈490 nm, whereas the one excited at 410 nm has a peak at 485 nm and a shoulder at ≈520 nm (Fig. 2A). The lifetime of the latter (i.e., of the red-shifted phosphorescence) is 226 ms and is longer than the one (173 ms) of the former (i.e., of the normal phosphorescence). In phosphorescence excitation spectrum, a new 410 nm band was observed when monitored at ≈490 nm (Fig. 2B). From these results, the normal and the red-shifted phosphorescences can be assigned to different species of DITX.

It is worthwhile to notice that the red-shifted phosphorescence can be observed with the ethanol solution of such a low concentration as 6×10^{-6} M of TX. The extra 400 nm(or 410 nm) band in the excitation spectrum of TX(or DITX) corresponds to the tail of the strong UV absorption measured at 77 K (Figs. 1C and 2C). Intensity of the absorption tail (in terms of apparent extinction coefficient) is rather unaffected by the concentration change of TX from 6×10^{-5} M to 2×10^{-3} M. These results indicate that the new chemical species which gives rise to the red-shifted phosphorescence is neither an associate such as a dimer or an aggregate, nor triplet excimer state which is suggested in naphthoquinones and anthraquinones.[17] Furthermore, the phosphorescence lifetimes were measured with degassed solutions. The lifetimes for the normal and the red-shifted phosphorescences of TX and DITX agree well with the values of the corresponding aerated solutions. The result suggests that a radical species and a light-absorbing transient (LAT) therefrom[7,18,19] are not responsible for the observation of the red-shifted phosphorescence. Judging from the experimental results mentioned above, formation of a hydrated species due to a little dissolved water in ethanol as an impurity is suggested.

Hydrogen-Bonded Species of TX and DITX. To investigate the nature of the hydrated species of TX and DITX in ethanol, UV absorption spectra of TX and DITX were measured at 77 K in ethanol–water mixed solutions; the results are shown in Fig. 3. As the water content is increased, a new band appears at ≈398 nm in the spectrum of TX and at ≈405 nm in the spectrum of DITX with isosbestic points.

The spectral change can be analysed on the basis of

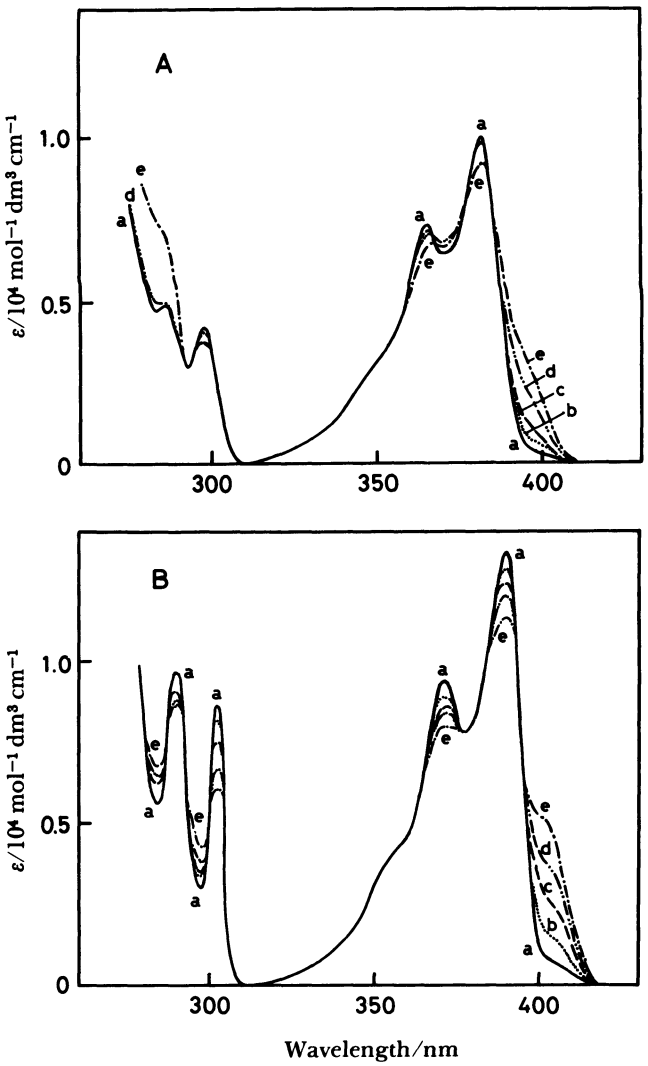

Fig. 3. UV absorption spectra measured with the ethanol–water solutions of (A) TX (9.0×10^{-5} M) and (B) DITX (9.7×10^{-5} M) at 77 K. Water content is (A):(a) 0, (b) 1, (c) 2, (d) 4, and (e) 6 vol%; and (B):(a) 0, (b) 1, (c) 2.5, (d) 4, and (e) 6 vol%.

formation of an associate between TX(or DITX) (A) and water (B):A+B→AB(or C). The association constant, K, was evaluated by the use of the equation;[20,21]

$$(d/[A]_0-\varepsilon_A)^{-1} = ((\varepsilon_C-\varepsilon_A)K[B]_0)^{-1} + (\varepsilon_C-\varepsilon_A)^{-1}, \quad (1)$$

where d is the apparent absorbance (per 1 cm light path length) for the system, ε_A and ε_C, the molar extinction coefficients of TX(or DITX) and the associate, respectively, and $[A]_0$ and $[B]_0$, the initial concentrations of TX(or DITX) and water, respectively. The equation is applicable to the case where $[B]_0 \gg [A]_0$ and $\varepsilon_B \approx 0$ are satisfied. Taking into account of the volume change of ethanol–water mixed solution at 77 K, $(d/[A]_0-\varepsilon_A)^{-1}$ was plotted against $[B]_0^{-1}$ at several wavelengths; the results are shown in Fig. 4. Linear relationship holds for both TX and

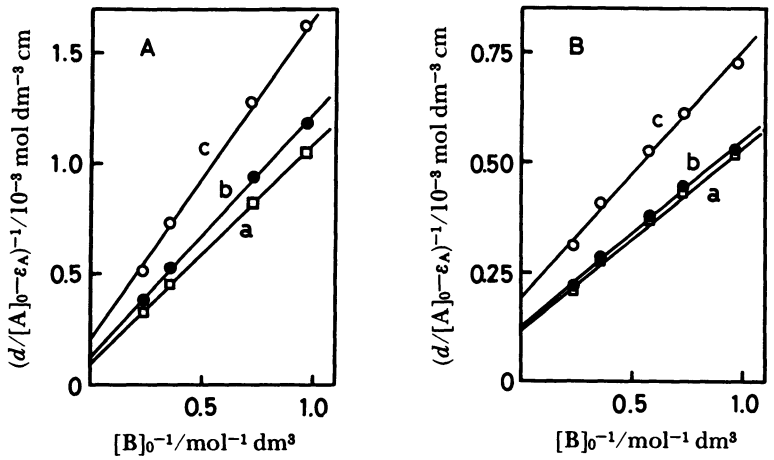

Fig. 4. Plots of $(d/[A]_0-\varepsilon_A)^{-1}$ against $[B]_0^{-1}$ for (A) TX at (a) 392.5 nm, (b) 397.5 nm, and (c) 400 nm; and (B) DITX at (a) 402 nm, (b) 404 nm, and (c) 408 nm in ethanol-water solution at 77 K.

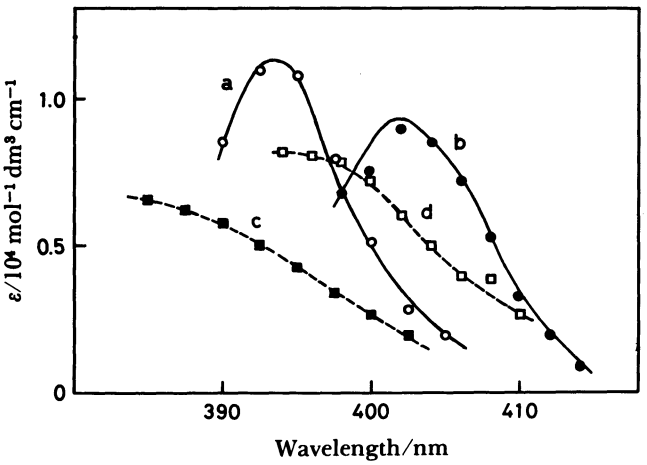

Fig. 5. UV absorption spectra of H-bonded species in ethanol-water solution of (a) TX and (b) DITX at 77 K, and (c) TX and (d) DITX at room temperature. For a detailed procedure, see the text.

DITX, indicating that the 1:1 associated species between TX(or DITX) and water is predominantly formed in ethanol. From the slopes and intercepts of the straight lines in Fig. 4, K and ε_C values were evaluated; the average of K's evaluated for TX-water in 392.5—400 nm region is 0.11±0.03, and the one evaluated for DITX-water in 400—408 nm region is 0.29±0.05. The observed K values are small in ethanol. In the case of xanthone in ethanol-water mixed solvent, a strongly hydrated species in which water molecule is H-bonded to carbonyl group was also reported from the measurement of time-resolved EPR spectrum at 77 K.[22] Considering the similarity between TX(or DITX) and xanthone in H-bond formation, and also considering the small K values in protic solvents being characteristic for H-bond formation,[23,24] the associate between TX(or DITX) and water may be assigned to the H-bonded species. By the use of the ε_C values, absorption spectra of the H-bonded species are shown in Fig. 5. The H-bonded species of TX-water has an absorption maximum at ≈394 nm, and the one of DITX-water, at ≈402 nm. It is noticed that as the water content is decreased, a slight shift to the longer wavelengths was observed with the absorption peak as is easily seen in Fig. 3.

The electronic structure of TX was calculated theoretically by the Pariser-Parr-Pople method in π-electron approximation.[25,26] The first π-π^* state (i.e., 384 nm band in ethanol) of TX is rich in intramolecular charge-transfer character from sulfur atom to carbonyl group as in the case of xanthone.[27] In the calculation procedure of π-electron structure, H-bond formation with water mainly affect the core Coulomb integral, α_P, of the H-bonded atom.[25] In TX, the H-bond, =O···H-O, between the carbonyl oxygen and water is thought to be more stable than the H-bond, S···H-O, between the sulfur atom and water.[23] Actual calculations have been done for the above two cases; theoretical results predict that the first π-π^* band shifts to longer wavelengths for =O···H-O H-bonding formation and to shorter wavelengths for S···H-O H-bonding formation. The observed longer wavelength shift of the first π-π^* band in Fig. 5 qualitatively supports the =O···H-O H-bond formation between TX and water.

The hydrated species between TX(or DITX) and water is also formed at room temperature as is shown in Fig. 6. The UV spectral change can be attributed to the formation of H-bonded species as in the case at 77 K, and K and ε_C values were evaluated from Eq. 1. The average K value is 0.26±0.03 for TX-water and 0.16±0.04 for DITX-water. By the use of the ε_C values, absorption spectra of the H-bonded species are also shown in Fig. 5.

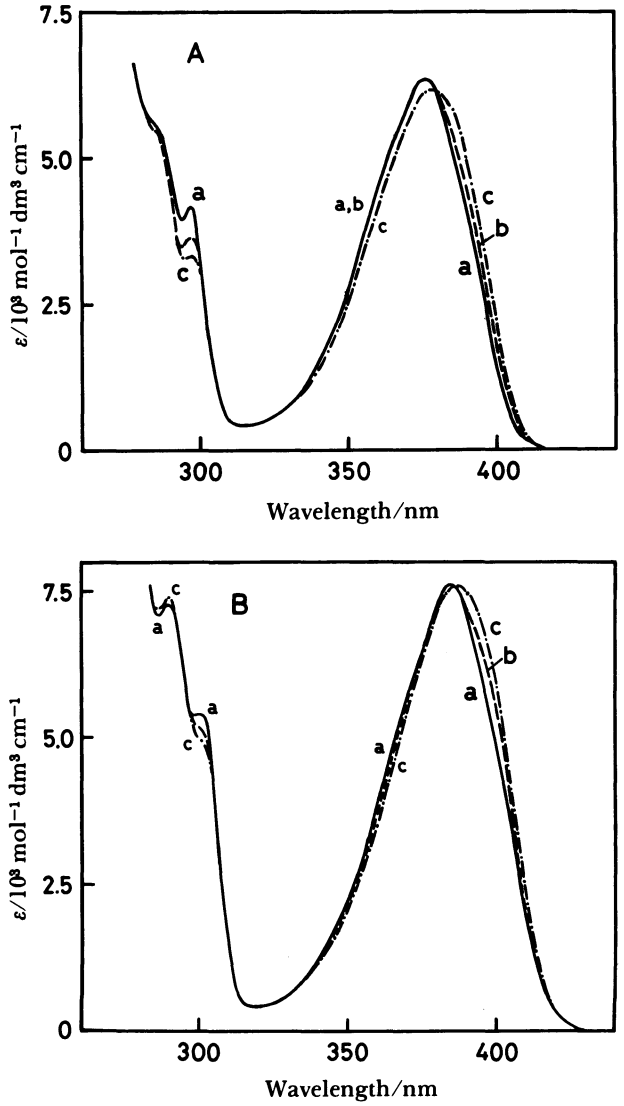

Fig. 6. UV absorption spectra measured with the ethanol-water solutions of (A) TX (7.2×10^{-5} M) and (B) DITX (7.9×10^{-5} M) at room temperature. Water content is (A):(a) 0, (b) 2, and (c) 10 vol%, and (B):(a) 0, (b) 4, and (c) 10 vol%.

Phosphorescence of TX and DITX in Ethanol-Water Solution. Phosphorescence spectra observed with the ethanol-water mixed solution of TX excited at 385 nm are shown in Fig. 7A. As the water content is increased, ≈470 nm and ≈442 nm regions increase their intensities relative to the 452 nm band. This result suggests that at least two phosphorescent species coexist in ethanol-water solution. This is confirmed by measuring the excitation wavelength dependence of phosphorescence spectrum (Fig. 7B) and also by observing excitation spectrum at several monitoring wavelengths (Fig. 7C). In Fig. 7B, besides the normal phosphorescence observed at 452 nm, ≈470 nm phosphorescence was resolved by exciting TX at 400 nm. The ≈470 nm phosphorescence increases its intensity as the water content is increased.

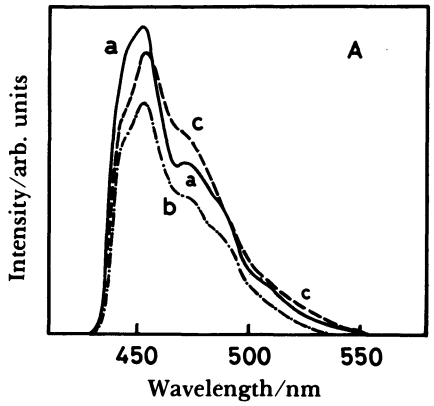

Fig. 7A. Phosphorescence spectra measured with the ethanol-water mixed solutions of TX (2.0×10^{-4} M) excited at 385 nm. Water content is (a) 1.0, (b) 4.8, and (c) 9.1 vol%.

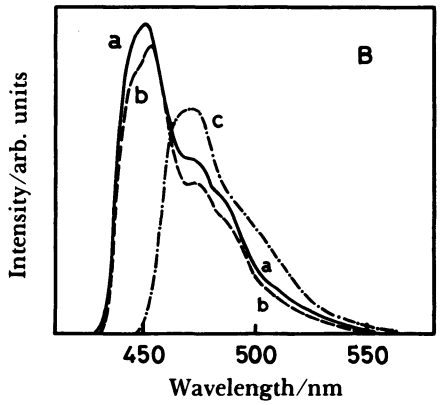

Fig. 7B. Phosphorescence spectra measured with the ethanol-water (100:1 by volume) solution of TX (2.7×10^{-4} M) excited at (a) 350 nm, (b) 385 nm, and (c) 400 nm.

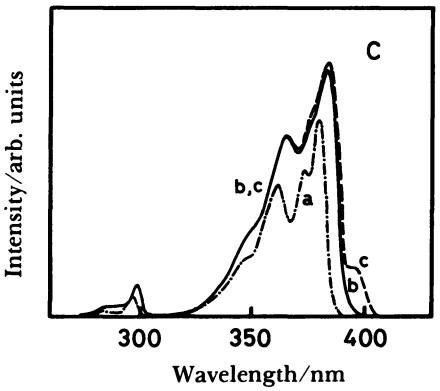

Fig. 7C. Phosphorescence excitation spectra measured with the ethanol-water (100:1 by volume) solution of TX (2.7×10^{-4} M) monitored at (a) 433 nm, (b) 450 nm, and (c) 475 nm.

The same intensity increase was also observed for 397 nm band in the excitation spectrum. Referring to the UV absorption spectrum of TX in ethanol-water at 77 K (Fig. 3), the ≈470 nm phosphorescence is safely

assigned to the hydrated (H-bonded) species. The phosphorescences monitored at 475 nm and at 450 nm decay single-exponentially, and the lifetimes are 212 ms and 160 ms, respectively, in good agreement with the corresponding values of the red-shifted and the normal phosphorescences of TX in pure ethanol. From these results, the red-shifted phosphorescence observed weakly in ethanol can be assigned to the H-bonded species between TX and water.

To understand the phosphorescent behavior in the 442 nm region, the phosphorescence excitation spectra were measured at several monitoring wavelengths; the result monitored at 433—435 nm (Fig. 7C) shows a new distinct band at 374 nm, revealing that the 442 nm phosphorescence can be ascribed to another (i.e., the third) chemical species. Coexistence of three chemical species in ethanol-water solution was also reported in the case of xanthone.[22]

In Fig. 7C, ≈380 nm band in the excitation spectrum shifts to shorter wavelengths (from 384 nm to 380 nm) as the monitoring wavelength becomes shorter (from 475 nm to 433 nm). This may suggest that the normal phosphorescence of TX shows inhomogeneous broadening by solute-solvent interaction.

Phosphorescent behavior of DITX in ethanol-water solution is similar to the one of TX mentioned above. In addition to the normal phosphorescence at 458 nm,

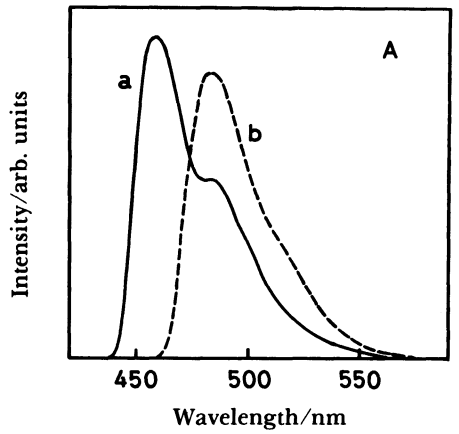

Fig. 8A. Phosphorescence spectra measured with the ethanol-water (100:1 by volume) solution of DITX (3.0×10^{-4} M) excited at (a) 392 nm and (b) 410 nm.

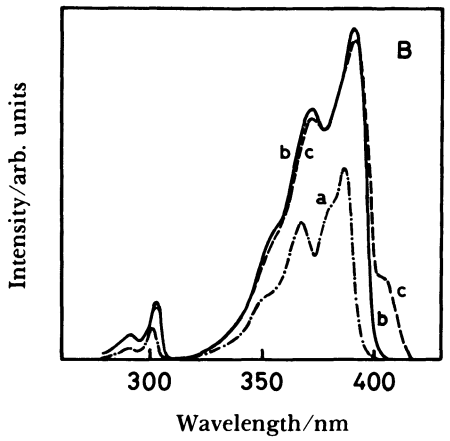

Fig. 8B. Phosphorescence excitation spectra measured with the ethanol-water (100:1 by volume) solution of DITX (3.0×10^{-4} M) monitored at (a) 442 nm, (b) 458 nm, and (c) 490 nm.

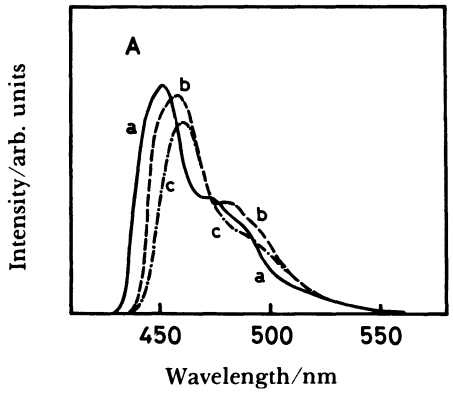

Fig. 9A. Phosphorescence spectra measured with the MTHF solution of TX (3.1×10^{-4} M) excited at (a) 385 nm, (b) 395 nm, and (c) 398 nm.

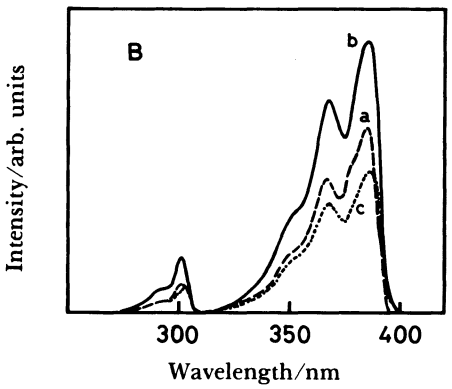

Fig. 9B. Phosphorescence excitation spectra measured with the MTHF solution of TX (3.1×10^{-4} M) monitored at (a) 440 nm, (b) 450 nm, and (c) 475 nm.

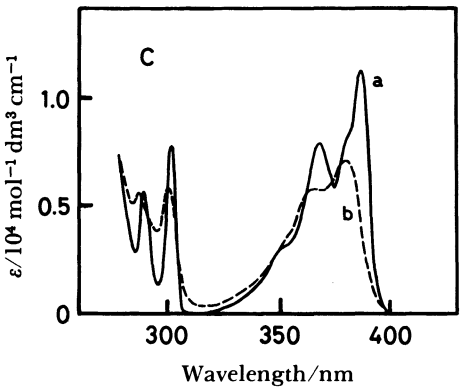

Fig. 9C. UV absorption spectra measured with the MTHF solutions of (a) TX (5.2×10^{-5} M) at 77 K and (b) TX (1.6×10^{-4} M) at room temperature.

phosphorescence due to the H-bonded species is resolved at 485 nm by exciting DITX at 410 nm (Fig. 8A). Furthermore, excitation spectrum monitored at 442 nm shows a new band at ≈380 nm as a shoulder (Fig. 8B), revealing that the third chemical species exists and phosphoresces in shorter wavelength region of the normal phosphorescence.

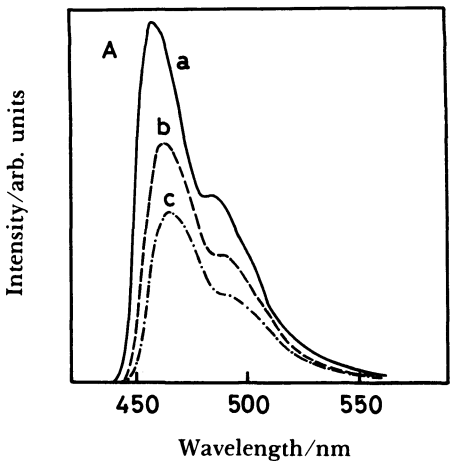

Fig. 10A. Phosphorescence spectra measured with the MTHF solution of DITX (1.7×10^{-4} M) excited at (a) 394 nm, (b) 400 nm, and (c) 403 nm.

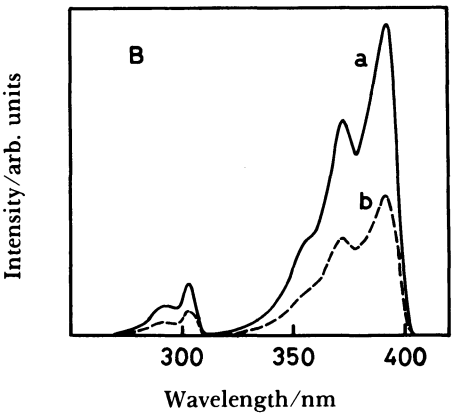

Fig. 10B. Phosphorescence excitation spectra measured with the MTHF solution of DITX (1.7×10^{-4} M) monitored at (a) 458 nm and (b) 490 nm.

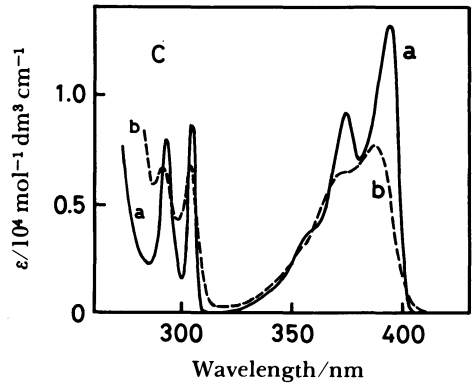

Fig. 10C. UV absorption spectra measured with the MTHF solution of DITX (8.6×10^{-5} M) at (a) 77 K and (b) room temperature.

As in the case of TX, ≈390 nm band in the excitation spectrum shifts to shorter wavelengths (from 391 nm to 386 nm) as the monitoring wavelength becomes shorter (from 490 nm to 442 nm), suggesting that phosphorescence of DITX exhibits inhomogeneous broadening by solute–solvent interaction.

Phosphorescence of TX and DITX in MTHF. Phosphorescence spectra being excited at several wavelengths were measured with the MTHF solutions of TX and DITX. The results are shown in Figs. 9A and 10A. As the longer excitation wavelength is used, the phosphorescence shifts to the longer wavelengths (by ≈10 nm for TX, and by ≈6 nm for DITX), and the longer is the phosphorescence lifetime. The lifetime of TX varies from 150 ms (excited at 385 nm) to 177 ms (excited at 398 nm), and the one of DITX, from 163 ms (excited at 394 nm) to 186 ms (excited at 403 nm). In phosphorescence decay of DITX excited at 403 nm, a slight deviation from a single-exponential decay was observed. Although the phosphorescence excitation spectra and UV absorption spectra in MTHF (Figs. 9B, 9C, 10B, and 10C) did not exhibit any new band in ≈400 nm region in contrast to the cases of TX and DITX in ethanol, these results may suggest that another chemical species, phosphorescence of which can be resolved poorly in the present study, may coexist in MTHF, too.

References

1) G. Amirzadeh and W. Schnabel, *Makromol. Chem.*, **182**, 2821 (1981).
2) A. Hult and B. Ranby, "Primary and Secondary Reactions in Photoinitiated Free-Radical Polymerization of Organic Coatings," in "ACS Symposium Series, No. 266," American Chemical Society, Washington, D. C. (1984), Chap. 23, pp. 457—472.
3) J. P. Fouassier, P. Jacques, D. L. Lougnot, and T. Pilot, *Polym. Photochem.*, **5**, 57 (1984).
4) M. F. Molaire, *J. Polym. Sci.*, **20**, 847 (1982).
5) Y-C. Zhang, H. Morita, and T. Yamaoka, *J. Appl. Polym. Sci.*, **32**, 6005 (1986).
6) V. D. McGinniss, *J. Radiat. Curing*, **5**, 35 (1978); *Photogr. Sci. Eng.*, **23**, 124 (1979).
7) S. F. Yates and G. B. Schuster, *J. Org. Chem.*, **49**, 3349 (1984).
8) R. W. Yip, A. G. Szabo, and P. K. Tolg, *J. Am. Chem. Soc.*, **95**, 4471 (1973).
9) H. Hayashi and S. Nagakura, *Mol. Phys.*, **24**, 801 (1972); **27**, 969 (1974).
10) C. R. Jones, A. H. Pappano, A. H. Maki, and D. R. Kearns, *Chem. Phys. Lett.*, **13**, 521 (1972).
11) M. Batley and R. Bramley, *Chem. Phys. Lett.*, **15**, 337 (1972).
12) J. C. Scaiano, *J. Am. Chem. Soc.*, **102**, 7747 (1980).
13) K. Suga and M. Kinoshita, *Bull. Chem. Soc. Jpn.*, **54**,

1651 (1981).
14) H. J. Griesser and R. Bramley, *Chem. Phys. Lett.*, **86**, 144 (1982).
15) J. C. Dalton and F. C. Montgomery, *J. Am. Chem. Soc.*, **96**, 6230 (1974).
16) T. Lai and E. C. Lim, *Chem. Phys. Lett.*, **73**, 244 (1980); **84**, 303 (1981).
17) A. Kuboyama, Y. Kojima, and S. Y. Matsuzaki, *Bull. Chem. Soc. Jpn.*, **56**, 2572 (1983); A. Kuboyama and S. Y. Matsuzaki, *ibid.*, **58**, 73 (1985).
18) J. Chilton, L. Giering, and C. Steel, *J. Am. Chem. Soc.*, **98**, 1865 (1976).
19) J. C. Scaiano, E. B. Abuin, and L. C. Stewart, *J. Am. Chem. Soc.*, **104**, 5673 (1982).
20) J. A. A. Ketelaar, C. van de Stolpe, A. Goudsmidt, and W. Dzcubas, *Recl. Trav. Chim. Pays-Bas*, **71**, 1104 (1952).
21) H. Nakanishi, H. Morita, and S. Nagakura, *J. Mol. Spectrosc.*, **65**, 295 (1977).
22) M. Minami, H. Murai, Y. I'Haya, T. Imamura, and K. Obi, 49th National Meeting of the Chemical Society of Japan, Tokyo, April 1984, Abstr. No. 1B03; H. Murai, M. Minami, and Y. J. I'Haya, Preprint submitted to J. Phys. Chem.
23) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman & Co., London (1960), pp. 365—386.
24) D. R. Cartwright and C. B. Monk, *J. Chem. Soc.*, **1955**, 2500.
25) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466 (1953); **21**, 767 (1953).
26) J. A. Pople, *Proc. Phys. Soc., London, Sect. A*, **68**, 81 (1955).
27) T. Minegishi, T. Hoshi, H. Hiratsuka, and Y. Tanizaki, *Bull. Chem. Soc. Jpn.*, **50**, 3140 (1977).