BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49 (10), 2706—2712 (1976)

Temperature-independent Delayed Fluorescence of Benzo[*f*]quinoline in Biphenyl Host: A New Interpretation of Delayed Fluorescence Behavior around 77 K

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(Received April 28, 1976)

The delayed fluorescence observed in the mixed crystals of benzo[*f*]quinoline in biphenyl host has been found to be independent of temperature in the low temperature region from 90 K down to liquid helium temperature, and subtraction of this temperature-independent contribution from the observed total delayed fluorescence intensity above 90 K has given straight-line fits of the log I_{DF}/I_P^2 *vs.* $1/T$ plots, that is, a single activation energy has been obtained over the whole temperature range studied, instead of two different ones as usually assumed. Such a correction has also been given to a new attempt of log I_{DF} *vs.* $1/T$ plots successfully. Moreover, the decay behavior of the delayed luminescence has been studied over the wide temperature and concentration range. It has been concluded that the decay behavior of the temperature-independent delayed fluorescence may mainly be responsible for the nonexponential decay of the delayed fluorescence around 77 K.

Since the delayed fluorescence (DF) was first observed in 1958,[1] a number of studies have been made in a variety of liquid solutions,[2] in rigid glassy solutions,[3] in vapor phases[4] and in so-called "pure" crystals[5] as well as mixed crystals.[6–12] Early investigations in the mixed crystal systems were carried out at temperatures higher than 77 K by many investigators, particularly by Hirota *et al.*[8] and McGlynn and his co-workers,[13] and it has been concluded that the guest triplet excitation migration is a thermally activated process and occurs through the host triplet exciton band. In addition, the kinetic model for the delayed luminescence (phosphorescence and delayed fluorescence) has been proposed and substantiated except for the DF behavior in the vicinity of 77 K, that has been a deadlock encountered in the usual kinetic model and some interpretations have been made thereupon.[8b,13] Under such circumstances, we have investigated the temperature and concentration dependence of DF of benzo[*f*]quinoline in biphenyl host crystals, the temperatures and the concentrations extending over a wide range of 4.2—230 K and 10^{-2}—10^{-4} mol/mol, respectively.

We observed the temperature-independent delayed fluorescence (TIDF) in the low temperature region where the nature of DF had never been satisfactorily understood. Similar TIDF had been noticed by several investigators,[8b,14–16] but the significance of TIDF has never been explored. In this paper, we will discuss the significance of this TIDF for the usual temperature-dependent model. Some of these results have been presented previously as brief reports.[17,18]

Experimental

Chemicals and Samples. The chemicals used were obtained from Tokyo Kasei Kogyo Co., Ltd. Biphenyl was recrystallized twice from ethanol, and was further purified by repeated zone refining over 200 passes. Benzo[*f*]quinoline was subjected to the same chemical treatment as described previously,[19] and was finally zone refined with 250 passes. The polycrystalline samples used were prepared from the melts between two fused-silica plates mounted in a brass or a copper block holder, as will be mentioned later on.

Apparatus. The emission spectra were recorded with a photoelectric recording system which was essentially composed of a Bausch & Lomb 500-mm grating monochromator equipped with an RCA 1P28 photomultiplier, a DC preamplifier incorporating a Teledyne Philbrick operational amplifier model 1009, and a Hitachi recorder model QPD-54. The lifetimes of the delayed luminescence were measured with an Iwasaki SS-5004 synchroscope at appropriate wavelengths. A Becquerel-type rotating-disk phosphoroscope was used to exclude normal fluorescence. Excitation radiation was obtained from a 1-kW high-pressure mercury arc lamp, model Orc-CH-612. The excitation light beam was passed through a selective filter combination.

A Dewar cryostat system has been devised to keep the temperature nearly constant during observation. The brass and copper block holders were used for the regions above and below 77 K, respectively. The equipment was constructed according to Nakamura *et al.*[20] The temperature was raised by natural evaporation of the liquid helium or liquid nitrogen, as the case may be. The rate of evaporation was so slow that we were able to monitor constantly the temperatures of the sample crystals and the intensities of luminescence.

The temperatures higher than 77 K were measured by means of a calibrated copper-constantan thermocouple in contact with a fused-silica plate, and by a Yokogawa microammeter type MPs. The temperatures lower than 77 K were measured with a calibrated 1/8-W, 51-Ω Allen-Bradley carbon resistor which was attached to a portion of the copper block holder close enough to the sample to ensure good thermal contact. The resistance was measured with a hand-made DC Wheatstone bridge incorporating a Yokogawa electronic galvanometer type 2707 and a Yokogawa decade resistance box type RV-61.

Results

Observations at 77 K. Figure 1 shows a comparison of the delayed and normal fluorescence of a polycrystalline sample of biphenyl doped with benzo[*f*]quinoline. The normal and the delayed fluorescence spectrum are in good agreement with each other, confirming that the observed DF is genuine. We have already confirmed that the guest-delayed luminescence is genuine in a previous paper.[21]

We examined the temperature and concentration

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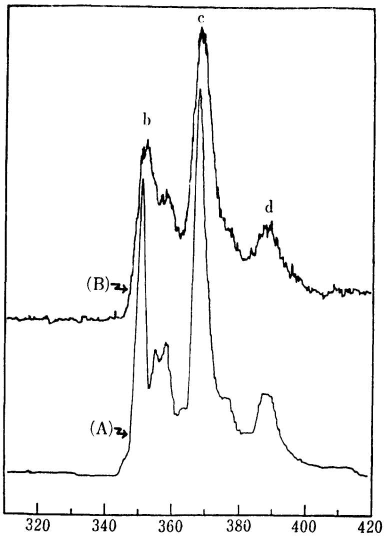

Fig. 1. Comparison of (A) normal and (B) delayed fluorescence of benzo[*f*]quinoline in biphenyl host at 77 K. Concn: 1.0×10^{-3} mol/mol. Slit width: (A) 1.0 mm (corresponding to 1.6 nm), (B) 2.5 mm (4.0 nm).

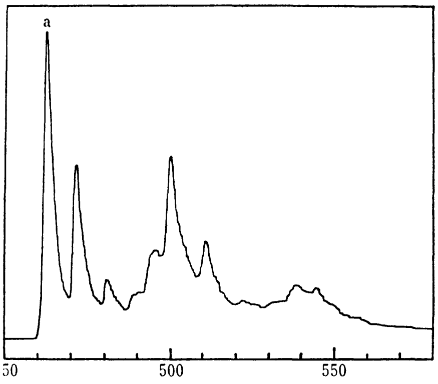

Fig. 2. Phosphorescence spectrum of benzo[*f*]quinoline in biphenyl host at 77 K. Concn: 1.0×10^{-3} mol/mol.

dependence in the delayed luminescence in respect of several bands a, b, c and d shown in Figs. 1 and 2.

Temperature Dependence of Intensity. Results in the Temperature Region above 77 K: General features of the temperature dependence of the delayed luminescence intensity were almost identical with those of Hirota and Hutchison,8a) Hirota,8) and Misra and McGlynn.10) The temperature dependences of the delayed luminescence at a guest concentration of 1.2×10^{-2} mol/mol are shown in Fig. 3 as a typical example; results obtained at more dilute concentrations (10^{-3} and 10^{-4} mol/mol) were essentially the same. It can be inferred from Fig. 3 that the DF intensity seems to become constant in the lower temperature region. This was confirmed experimentally as will be described later.

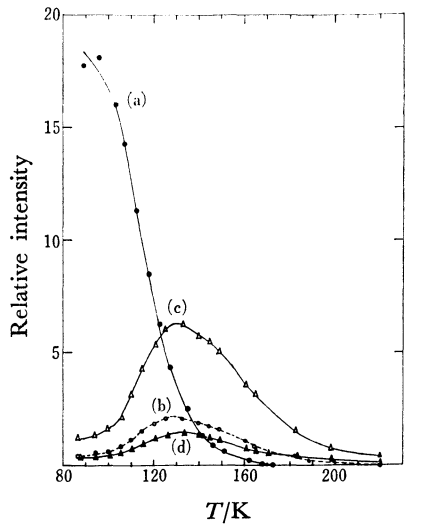

Fig. 3. Temperature dependence of the delayed luminescence of benzo[*f*]quinoline in biphenyl host in the temperature region above 77 K. Concn: 1.2×10^{-2} mol/mol. (a): Phosphorescence intensity observed at 464 nm, *i.e.*, the 0,0-band shown in Fig. 2; (b), (c), and (d): delayed fluorescence intensities observed at the corresponding bands shown in Fig. 1. No correction was made for the spectral response of the apparatus.

Results in the 4.2—77 K Temperature Range: The temperature dependences of the delayed luminescence intensity at various guest concentrations are shown in Figs. 4a, 4b, and 4c. At a concentration of 1.2×10^{-2} mol/mol (Fig. 4a), the DF intensity was essentially independent of temperature in the range of 25—77 K, while at lower temperatures it was dependent on temperature and reached a sharp maximum around 10 K. Similar behavior was also observed at a guest concentration of 1.25×10^{-3} mol/mol (see Fig. 4b). However, the maxima around 13 K were fairly lower than those in Fig. 4a. At a more dilute concentration of 1.0×10^{-4} mol/mol, the DF intensity remained constant over a wider range (4.2—77 K), without any appreciable maximum around 10 K (see Fig. 4c). This is quite different from the behavior of the other two cases as shown in Figs. 4a and 4b. By application of an empirical relation of Misra and McGlynn,10) $T_{\text{max}}=0.06\,\Delta E/k$, to the maximum around 10 K, an activation energy of the order of 100 cm^{-1} was predicted. This shallow depth and the disappearance of the maximum around 10 K in the concentration as low as 10^{-4} mol/mol lead to a conclusion that the pertinent trap is of the so-called X-trap. In this connection, it may be noted that the mixed crystals studied in the temperature range of 4.2—77 K are sufficiently pure in the sense that this shallow depth is smaller by a factor of 10 than the depth involved in the thermal activation process to be discussed later on, and hence the presence of this shallow trap does not give any influence on the later discussion.

The phosphorescence intensity appeared to be independent of temperature at lower temperatures, while at higher temperatures it fell off with an increase in temperature, in every case shown in Figs. 4a, 4b, and 4c.

Decay Behavior. Results in the Temperature Region above 77 K: The decay behavior of the delayed lumines-

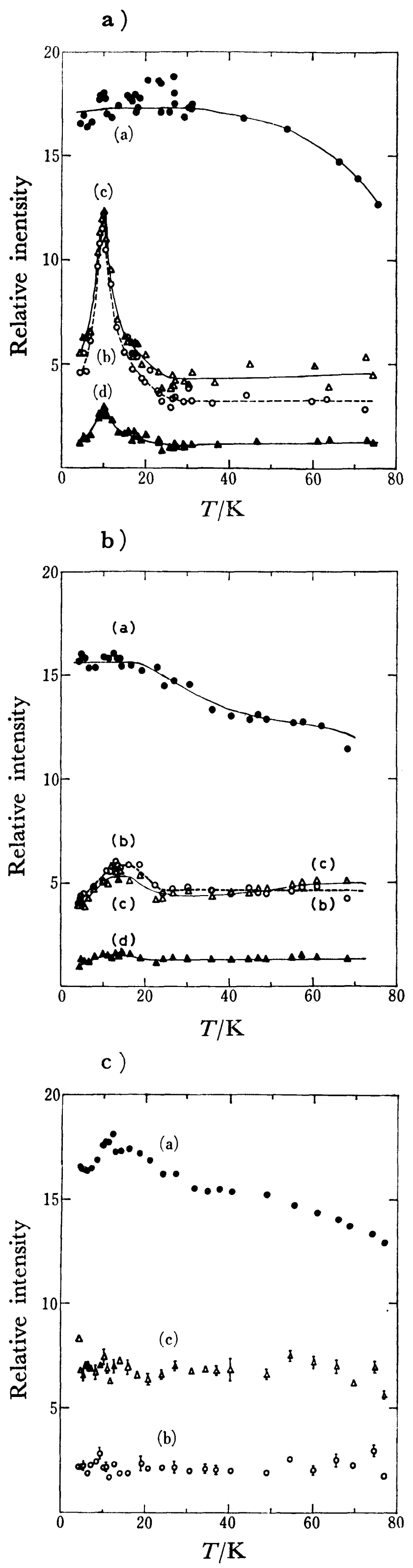

Fig. 4. Temperature dependence of the delayed luminescence of benzo[*f*]quinoline in biphenyl host in the 4.2—77 K temperature range. For the notation (a), (b), (c), and (d), see the figure caption to Fig. 3. Concn: a) 1.2×10^{-2}, b) 1.25×10^{-3}, c) 1.0×10^{-4} mol/mol. Magnification of the delayed fluorescence intensity to the phosphorescence intensity: a) × 10, b) × 20, c) × 25. No correction was made for the spectral response of the apparatus.

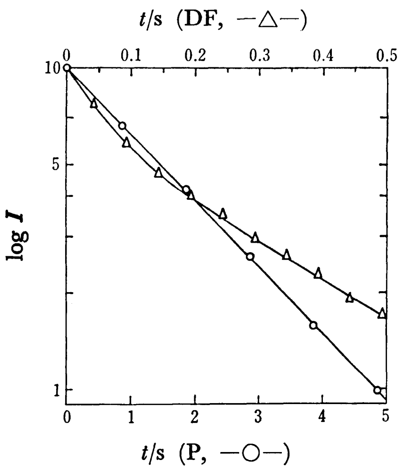

Fig. 5. Phosphorescence (P) and delayed fluorescence (DF) decays of benzo[*f*]quinoline in biphenyl host at 31 K. Concn: 1.2×10^{-2} mol/mol. The upper scale is for the plots of DF decay, and the lower scale for the plots of P decay. The initial intensities are obtained by extrapolation and arbitrarily normalized to 10.

cence at temperatures above 77 K is essentially in agreement with those observed by Hirota and Hutchison[8a] and Hirota.[8] The decay of the phosphorescence was observed to be exponential up to about 100 K and became nonexponential at higher temperatures. The decay of DF was nonexponential in a short time decay region even around 77 K, while it was exponential in a long time decay region. Such an apparently exponential decay behavior only in the long time region was also observed for the overall nonexponential decay of the phosphorescence.

Results in the 4.2—77 K Temperature Range: The decay characteristics of the delayed luminescence observed in the temperature range of 4.2—77 K were investigated for the concentration range of 10^{-2}—10^{-4} mol/mol. The phosphorescence decays were exponential in this temperature range, whereas the DF decays were generally nonexponential in the same temperature range. A typical decay behavior of the delayed luminescence observed for a concentration of 1.2×10^{-2} mol/mol at 31 K is shown in Fig. 5. At long times, however, the DF decay became exponential. As for DF, therefore, we will confine our discussion hereafter to the exponential decay region, that is, the long time decay region. In Fig. 6 is shown the temperature dependence of the delayed luminescence lifetimes measured at the concentration of 1.2×10^{-2} mol/mol. The phosphorescence lifetimes at the temperatures above about 100 K were obtained only in the long time decay region, whereas those below about 100 K were obtained in the whole decay region due to the exponential decay behavior of the phosphorescence. The point observed at the so-called characteristic temperature,[8b,22] where deviation from exponential decay behavior of the phosphorescence begins to appear, is marked with an arrow in Fig. 6. The temperature dependences of the decay behavior observed at the more dilute concentrations of 1.25×10^{-3} and 1.0×10^{-4} mol/mol were similar to that at the higher concentration just mentioned above. As

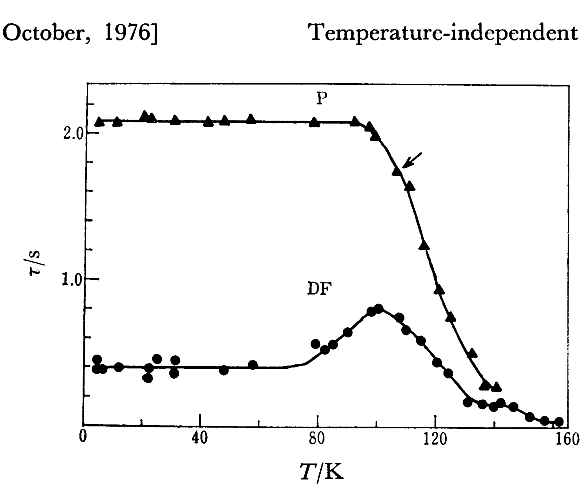

Fig. 6. Temperature dependence of the P and DF lifetimes of benzo[*f*]quinoline in biphenyl host. Concn: 1.2×10^{-2} mol/mol. The arrow refers to the characteristic temperature.

shown in Fig. 6, the decay behavior of the DF and phosphorescence remains constant at least in the temperature range of 4.2—70 K. The mean lifetimes obtained in this temperature range are 2.09 and 0.39 s for the phosphorescence and DF decays, respectively.

Table 1. Definition of the rate processes involved in the triplet-triplet annihilation

	Process[a)]	Rate constant	Remarks[b)]	
(0)	$S_{0H}\rightarrow S_{1G}$	R_0	Over-all rate constant	
(1)	$S_{1G}\rightarrow S_{0G}+h\nu$	k_1^*	Radiative	$K_1\equiv k_1+k_1^*$
(1′)	$S_{1G}\rightarrow S_{0G}$	k_1	Nonradiative	
(2)	$S_{1G}\rightarrow T_{1G}$	k_2	Intersystem crossing	
(3)	$T_{1G}\rightarrow S_{0G}+h\nu$	k_3^*	Radiative	$K_3\equiv k_3+k_3^*$
(3′)	$T_{1G}\rightarrow S_{0G}$	k_3	Nonradiative	
(4)	$T_{1G}+T_{1G}\rightarrow S_{1G}+S_{0G}$	K_4	Triplet-triplet annihilation producing excited singlet state of guest	
(5)	$T_{1G}+T_{1G}\rightarrow T_{1G}+S_{0G}$	K_5	Bimolecular triplet quenching	

a) S_0: Ground singlet state; S_1: lowest excited singlet state; T_1: lowest excited triplet state; G: guest; H: host. b) For detail, see text.

Discussion

Kinetics. Since the kinetic model used here has been discussed in detail by many authors,[3a,6a,8,10–12,22] we will briefly summarize the usual temperature-dependent kinetic model for the convenience of discussion. The rate processes with the relevant rate constants are identified in Table 1.[11b] The rate equations for the singlet and triplet guest populations are given by

$$\frac{\mathrm{d}[S_{1G}]}{\mathrm{d}t}=R_0-(K_1+k_2)[S_{1G}]+K_4[T_{1G}]^2 \tag{1}$$

$$\frac{\mathrm{d}[T_{1G}]}{\mathrm{d}t}=\frac{k_2R_0}{K_1+k_2}-K_3[T_{1G}]-k_6[T_{1G}]^2 \tag{2}$$

where

$$k_6=K_4(2K_1+k_2)/(K_1+k_2)+K_5 \tag{3}$$

From straightforward manipulation of Eqs. 1 and 2, the expressions for the steady-state intensities and the decays of phosphorescence (P) and DF are given by

$$I_P=k_3^*k_3[(4K+1)^{1/2}-1]/2k_6 \tag{4}$$

$$I_{DF}=k_1^*K_4K_3^2[(4K+1)^{1/2}-1]^2/[4k_6^2(K_1+k_2)] \tag{5}$$

$$I/I_P=(1-A)/[\exp(K_3t)-A] \tag{6}$$

$$I/I_{DF}=(1-A)^2/[\exp(K_3t)-A]^2 \tag{7}$$

where

$$K=k_2k_6R_0/(K_1+k_2)K_3^2=A/(1-A)^2 \tag{8}$$

$$A=\frac{k_6[T_{1G}]_0}{K_3+k_6[T_{1G}]_0}=\frac{(1+4K)^{1/2}-1}{(1+4K)^{1/2}+1} \tag{9}$$

From Eqs. 4 and 5, one obtains

$$I_{DF}/I_P^2=k_1^*K_4/[(K_1+k_2)k_3^{*2}] \tag{10}$$

The temperature dependences of the quantities K_4, K_5, k_6, and K are given as

$$K_4,\ K_5,\ k_6,\ K\propto\exp(-\Delta E/kT) \tag{11}$$

where ΔE is the energy separation between the host and guest triplet states, and k Boltzmann's constant. With these expressions for the quantities K_4, K_5, k_6, and K, one may predict the temperature dependences of the delayed luminescence intensities and decays, assuming all the other rate constants to be independent of these quantities.[11] In the temperature-dependent triplet-triplet annihilation kinetics described above, it is assumed that there is no significant temperature-independent long range direct interaction between guest triplet states.[11b] It will be shown, however, that such an assumption does not necessarily hold, at least phenomenologically, in the vicinity of 77 K and below.[17,18] Since the kinetic model used here is the temperature-dependent one, the DF intensity (I_{DF}) in Eqs. 4 and 10 should duly be temperature-dependent. Since our experiment revealed the presence of the temperature-independent portion in I_{DF} (I_{TIDF}), the above-described expressions should be applied only for $[(I_{DF})_{total}-I_{TIDF}]$, where $(I_{DF})_{total}$ is the observed total I_{DF}.

Significance of TIDF in Evaluation of Activation Energy. As shown in Figs. 3 and 4, I_P observed in the lower temperature region was dependent on temperature, contrary to the prediction from the kinetic model. The origin of this temperature dependence of I_P in the lower temperature region is not clear at present, although some explanations have been offered.[14,15] From expressions (4), (5), and (10), and relations (11) on the temperature dependence, one can obtain the following three Arrhenius plots:[11]

(1) In the higher temperature region,
log I_P *vs.* $1/T$ (plot (1))
(2) in the lower temperature region,
log I_{DF} *vs.* $1/T$ (plot (2))
(3) in the whole temperature region,
log I_{DF}/I_P^2 *vs.* $1/T$ (plot (3))

Accordingly, we can obtain the activation energy ΔE from the above three plots. Plot (2) has for the first time been attempted by us. Figure 7 shows that the plot of log $[(I_{DF})_{total}-I_{TIDF}]$ *vs.* $1/T$ instead of log $(I_{DF})_{total}$ *vs.* $1/T$ gives a good straight-line fit for plot (2). The straight-line fit of log I_P *vs.* $1/T$ plot in the higher temperature region as predicted from plot

TABLE 2. ACTIVATION ENERGIES[a] AND RATIOS $(I_{DF})_c/(I_{DF})_m$

Guest concn (mol/mol)	Band[c]	T_{max}/K[d]	ΔE (cm^{-1})[b]					$(I_{DF})_c$[h] / $(I_{DF})_m$
			From T_{max}[e]	log I_{DF}/I_P^2 *vs.* $1/T$		log I_{DF} *vs.* $1/T$	log I_P *vs.* $1/T$	
				Uncorrected[f]	Corrected[f]	Corrected[g]		
1.2×10^{-2}	b	129	1495	1630	1700	1470	1810	0.2
	c	130	1507	1640	1680	—	—	0.2
	d	132	1530	—	—	—	—	0.25
1.25×10^{-3}	b	125	1450	1950	1900	1440	1850	0.07
	c	124	1437	1920	1900	—	—	0.06
	d	124.5	1443	—	—	—	—	0.07
1.0×10^{-4}	b	129	1495	2000	2080	1550	1840	0.07
	c	128	1484	2090	2160	—	—	0.08
	d	128.5	1489	—	—	—	—	0.06

a) See Ref. 23. b) Activation energy calculated from the temperature dependence of the delayed luminescence. See text. c) See Fig. 1. d) T_{max} is the temperature at which maximum intensity of DF occurs. e) Calculated from an empirical relation, $T_{max}=0.06\Delta E/k$. See Ref. 10. f) See text. g) Only the corrected plot gives a good fit to a straight line. See text. h) $(I_{DF})_c$ denotes the DF intensity at 85 K, where I_{DF} approximately equals the temperature-independent contribution, *i.e.*, I_{TIDF}. $(I_{DF})_m$ refers to T_{max}.

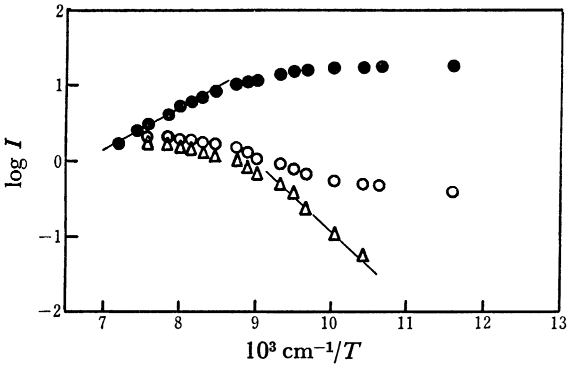

Fig. 7. Plots of log $(I_{DF})_{total}$ (○), log $[(I_{DF})_{total}-I_{TIDF}]$ (△), and log I_P (●) *vs.* $1/T$ with I_{DF} at band b shown in Fig. 1. Concn: 1.2×10^{-2} mol/mol.

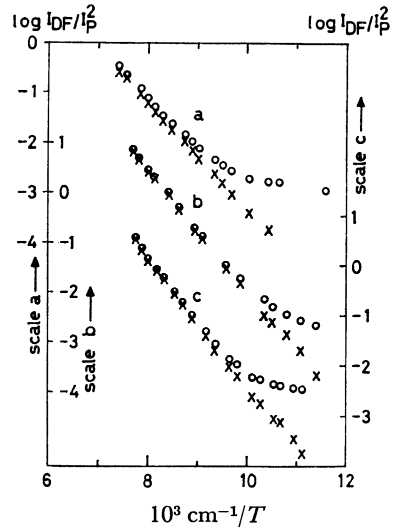

Fig. 8. Plots of log $(I_{DF})_{total}/I_P^2$ (○) and log $[(I_{DF})_{total}-I_{TIDF}]/I_P^2$ (×) *vs.* $1/T$ with I_{DF} at band b. Concn: a) 1.2×10^{-2}, b) 1.25×10^{-3}, c) 1.0×10^{-4} mol/mol.

(1) is also shown in Fig. 7. The thermal activation energies thus obtained are listed in Table 2. According to Misra and McGlynn,[10] plot (3) gave a good fit to a straight line in the high temperature region, whereas the deviation therefrom was observed in the low temperature region, showing a much smaller slope in the latter temperature region. They have suggested on the basis of the smaller activation energy obtained from this smaller slope that DF observed in the vicinity of 77 K may well be due to the annihilation involving thermal depopulation of defect states. However, DF around 77 K was independent of temperature in our cases as shown in Fig. 4. Moreover, as mentioned above, I_{DF} was independent of temperature in a wide range below 90 K. Therefore, such an analysis as given by Misra and McGlynn should be re-examined taking into account of this TIDF.[17] As Fig. 8 shows, subtraction of the temperature-independent contribution gave straight-line fits of the semilog plots over the whole temperature region studied. The thermal activation energies thus obtained are also listed in Table 2 in the column "corrected," while the corresponding "uncorrected" values are listed in the neighboring column. The activation energies obtained from the semilog plots, as seen in Table 2, are comparable with the corresponding spectroscopic value[23] of 1465 cm^{-1}, in particular for those obtained from plot (2). The activation energies obtained from plot (3) seem to be dependent on concentration. This may be due to the presence of the trap giving rise to another very weak delayed fluorescence observed at very low concentrations and high temperatures.[24] In order to check the "concentration effect" of the activation energies obtained from plot (3), an exhaustive purification of biphenyl host crystals has been made by repeated zone refining and taking the non-emissive portions of the specimen. The semilog plots for the trap-free benzo[*f*]quinoline–biphenyl mixed crystals are shown in Figs. 9 and 10, and the activation energies evaluated from the corrected plots are listed in Table 3. The validity of the

TABLE 3. ACTIVATION ENERGIES AND RATIOS $(I_{DF})_c/(I_{DF})_m$ OBTAINED FROM THE TRAP-FREE MIXED CRYSTALS^a)

Guest concn (mol/mol)	Band	ΔE (cm^{-1})				$(I_{DF})_c$^b) / $(I_{DF})_m$
		$\log I_{DF}/I_P^2$ vs. $1/T$		$\log I_{DF}$ vs. $1/T$ Corrected	$\log I_P$ vs. $1/T$	
		Uncorrected	Corrected			
1.0×10^{-2}	c	1580	1530	1540	1550	0.12
1.0×10^{-3}	c	1590	1560	1210	1820	0.04

a) Refer to footnotes to Table 2.

b) The other values of the ratio are 0.06 and 0.05 for bands b and d at the guest concentration of 1.0×10^{-3} mol/mol respectively, and 0.17 for band b at the guest concentration of 1.0×10^{-2} mol/mol.

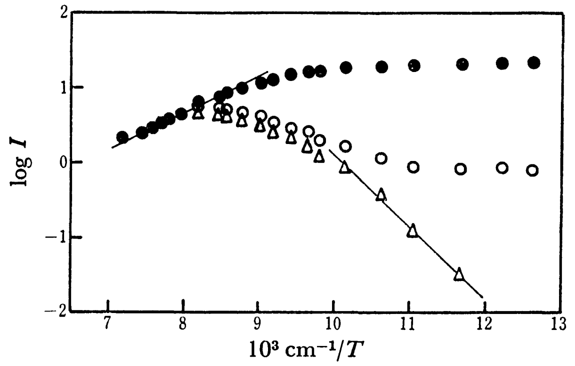

Fig. 9. The same plots as shown in Fig. 7 with I_{DF} at band c, using the trap-free benzo[*f*]quinoline-biphenyl mixed crystals. Concn: 1.0×10^{-2} mol/mol.

correction emphasized above is evident. Moreover, the activation energies obtained from plot (3) at two different concentrations are in accordance with each other within the experimental error. Therefore, it may be concluded that the thermal activation energy is in principle independent of concentration.

For comparison, we have also applied this type of correction to plot (3) of the experimental results on the phenanthrene–biphenyl system published by Misra and McGlynn,10) obtaining a straight line that covers the whole temperature range studied. Accordingly, above-described suggestion made by McGlynn *et al.*10,11b,13) on DF in the low temperature region, in particular in the vicinity of 77 K, is hardly convincible.

In Table 2 are also collected the values of $T_{\max}$, the temperature at which maximum intensity of DF occurs, and the host-guest triplet separations ΔE deduced from $T_{\max}$ through the empirical relation.10) The values of $T_{\max}$ seem to be in agreement with one another within the experimental error, and hence so seem the corresponding values of ΔE.

A New Interpretation of Decay Behavior around 77 K. The experimental results on the decay behavior are in good agreement with the kinetic model except for the unusual decay behavior of DF around 77 K. The decay deviates considerably from the exponential behavior in the lower temperature region, where the exponential decay would be expected from the usual temperature-dependent model. This peculiarity in the DF decay around 77 K has already been pointed out by Hirota8b) and Misra and McGlynn.10) Hirota8b) reported that the DF decays in the vicinity of 77 K were independent of temperature. On the other hand, Misra and McGlynn10) suggested on the nonexponential decays of DF around 77 K that some kinds of traps, probably imperfections in the host-crystal lattice, might be responsible for this decay behavior. Incidentally, Misra15) found the temperature-independent decays in the temperature range 6—77 K for the phenanthrene–biphenyl and naphthalene–biphenyl mixed crystal systems. As can be seen in Figs. 5 and 6, the TIDF decay behavior remains constant at temperatures below about 70 K and is still nonexponential in this temperature range. Here, it should be noted that the existence of this temperature-independent delayed-luminescence decay observed over a wide range of temperature is compatible with Hirota's observation of the temperature-independent decay in a smaller range of temperature. Thus, it may be concluded that the unusual decay behavior of DF around 77 K may be due to the presence of TIDF portion. In other words, if no TIDF existed practically, the decay law of DF in the vicinity of 77 K would be exponential, as have been observed experimentally in some mixed crystals.10,22) The phosphorescence decay that is exponential even in the vicinity of 77 K, is not affected at all by the nonexponential decay behavior of TIDF, as can be understood through the fact that DF around 77 K is much weaker than the phospho-

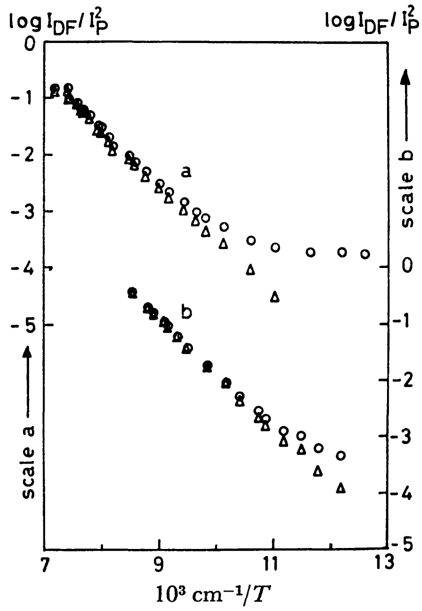

Fig. 10. Plots of $\log(I_{DF})_{\rm total}/I_P^2$ (○) and $\log[(I_{DF})_{\rm total}-I_{\rm TIDF}]/I_P^2$ (△) vs. $1/T$ with I_{DF} at band c, using the trap-free benzo[*f*]quinoline-biphenyl mixed crystals. Concn: a) 1.0×10^{-2}, b) 1.0×10^{-3} mol/mol.

rescence.

Nature of TIDF. We evaluated the intensity ratio of DF at 85 K and at $T_{\max}$, I_{DF} (85 K)/$I_{DF}(T_{\max})$, since I_{DF} at 85 K equals approximately to its temperature-independent contribution. This ratio gives an approximate value for the fraction of all triplets which decay *via* a second-order mechanism, namely triplet-triplet annihilation, in the temperature-independent range.[14,15] The ratios thus obtained with different guest concentrations are also listed in the last columns of Tables 2 and 3. It may be noted that these ratios seem to depend on the guest concentration. Particularly, the ratios at the concentration of the order of 10^{-2} mol/mol are larger than those at the other lower concentrations. This concentration effect is definitely beyond the experimental error. Since average distances between guests in the biphenyl host crystals are 15.3, 32.9, and 71.2 Å in the concentrations of 10^{-2}, 10^{-3}, and 10^{-4} mol/mol respectively according to Chandrasekhar's expression,[25] the direct triplet-triplet annihilation between guests hardly seems to be operative except for the case of the concentration of 10^{-2} mol/mol. At the high concentration of 10^{-2} mol/mol, the triplet-triplet annihilation due to exchange interaction might be responsible for the existence of TIDF in connection with the relatively higher values of the ratios described above. The fact that we observed TIDF at the low guest concentration of 10^{-4} mol/mol seems to suggest that it may be significant to study the problem of the distribution of guest molecules in mixed crystals.[26]

In the hope to decide whether such an opportune overlap of the T-T absorption and T-S emission as occuring in benzo[*f*]quinoline is responsible for the existence of TIDF,[3b] we have undertaken a similar study with naphthalene as guest in place of benzo[*f*]-quinoline, since this kind of overlap does not take place with this guest. We also observed TIDF and obtained a value of 0.012 for the ratio described above at the concentration of 10^{-2} mol/mol.[27] Thus, the above-mentioned overlap of T-T and T-S transitions is not necessarily required for the occurrence of TIDF.

In conclusion, on the sound basis of the observation of TIDF, we show a new way in which we refrain from invoking traps arbitrarily. The experimental results presented above, however, are not enough to elucidate the nature of TIDF. Further detailed experiments are required to clarify this question fully. Detailed results of this study will be given in Ref. 28.

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23) The spectroscopic energy gap of host triplet-guest triplet state is 1465 cm^{-1} for the benzo[*f*]quinoline–biphenyl system, which is obtained by adopting a value of 23010 cm^{-1} for the triplet state of biphenyl.[8] Incidentally, a preliminary study of the X-trap phosphorescence of biphenyl crystal locates the crystal lowest triplet state around 23150 cm^{-1}, a much more favorable value (S. Wada, Y. Gondo, and Y. Kanda, unpublished results).

24) With lower concentrations and higher temperatures, we detected the very weak trap-delayed fluorescence as well as a trap-fluorescence in a shorter wavelength region than that of the guest emission. It should be particularly emphasized that the trap emission became weaker by a more extensive purification of the host biphenyl crystal. For further details, see Ref. 28.

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