Studies on Triplet Energy Transfer by Means of an Emission-Absorption Flash Technique. II. Mixed Triplet-Triplet Annihilation in Ethanol

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The mixed delayed fluorescence due to the processes,

$$A^T + B^T \begin{array}{l} \xrightarrow{p_M{}^A k_{MTT}} A^* + B \\ \searrow\xrightarrow{p_M{}^B k_{MTT}} B^* + A \end{array}$$

in the following systems in ethanol solutions have been quantitatively investigated. a) 1) 9-methylanthracene-anthracene, 2) 9-phenylanthracene-anthracene, 3) 9-methylanthracene-9-phenylanthracene, 4) anthracene-acridine, 5) 9-methylanthracene-acridine, 6) 9-phenylanthracene-acridine. b) 7) eosin-anthracene, 8) proflavine-anthracene, 9) eosin-acridine. It has been found that for class a) in which the separations of singlet excited levels of A and B are less than a few times of kT, the delayed fluorescence of both components occur and the value of $(p_M{}^A+p_M{}^B)$ is close to that of the efficiency of a simple p-type delayed fluorescence, p^A or p^B. The delayed mixed excimer fluorescence also occurs in most cases. For class b) in which the level differences largely exceed kT, only the delayed fluorescence of the lower level component occurs. It has also been established that the delayed excimer fluorescence in a single component system increases in intensity from anthracene through 9-methyl- to 9-phenylanthracene. The $p_M{}^A/p_M{}^B$ values are discussed for systems (1), (2), and (3).

Delayed fluorescence due to T–T annihilation has been studied extensively by Parker[1] and Birks[2] since its discovery by Parker and Hatchard.[3] It seems that the recent work of Birks *et al.*[4] has terminated the debates upon its mechanism. Their conclusion is that T–T annihilation occurs according to the dual paths

$$\text{(I)}\quad A^T+A^T \rightarrow A_2^{**} \begin{array}{l} \rightarrow A_2^* \rightarrow 2A + h\nu \quad \text{(excimer fluorescence)} \\ \rightarrow A^* + A \rightarrow 2A + h\nu' \quad \text{(monomer fluorescence)} \end{array}$$

$$\text{(II)}\quad A^T + A^T \rightarrow A^* + A$$

in which process (I) goes through encounter whereas (II) proceeds by a long range interaction. This scheme is essentially the same as the one proposed earlier by Parker.[5] Birks *et al.* and Parker also agree on the point that process (I) is temperature dependent while (II) is not, the former predominating at room temperature.

One purpose of the present work is to compare the efficiency of *mixed T–T annihilation* with that of simple type T–T annihilation at room temperature assuming that process (I) is predominant. Since the discovery of mixed T–T annihilation by Parker,[6] no quantitative investigation seems to have been made. Although there is no doubt that in the anthracene (donor)-naphthacene (acceptor) system,[7] the delayed fluorescence of the latter is brought about by $D^T+A^T \rightarrow D+A^*$, there is some ambiguity as to the mechanism of the enhanced delayed fluorescence in the eosin-anthracene system.[8] Parker's observation gave no quantitative information as to what extent the enhanced delayed fluorescence of both eosin (D) and anthracene (A) occurs *via*

$$\text{(III)}\quad D^T + A^T \begin{array}{l} \nearrow D^* + A \quad \text{(M-type 1)} \\ \searrow D + A^* \quad \text{(M-type 2)} \end{array}$$

or

$$\left.\begin{array}{l} D^T + D^T \rightarrow D^* + D \\ A^T + A^T \rightarrow A^* + A \end{array}\right\} \text{(P-type)}$$

We developed a method of separating M-type from P-type using the flash technique involving absorption and emission measurements.[9] By means of this method, we established that (M-1) occurs very efficiently and that (M-2) does not occur at all in the alcoholic solution of eosin and anthracene. In the present work, the proflavine-anthracene and eosin-acridine systems have been studied. They are similar with respect to the singlet energy separation between donor and acceptor. Further, systems consisting of donor and acceptor with almost the same singlet excited levels have been studied. As such compounds, we have chosen anthracene and its substituted compounds which are well known to give only very weak excimer fluorescence. It is expected that the dependence of the relative fluorescence yield of donor and acceptor (processes (M-1) and (M-2)) on the singlet energy levels of the two components can be studied more easily with such compounds. In connection with the mixed T–T annihilation, quantitative investigations on the simple type T–T annihilation of the component compounds and on the delayed excimer fluorescence have been performed. The intensities of the mixed delayed excimer fluorescence (MDE-Fl) have been compared with those of

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[1] C. A. Parker, "Photoluminescence of Solutions," Elsevier, Amsterdam (1968), Chap. 2. D.

[2] J. B. Birks, "Photophysics of Aromatic Molecules," Wiley-Interscience, New York (1969), Chap. 8.

[3] C. A. Parker and C. G. Hatchard, *Proc. Chem. Soc.*, **1962**, 147.

[4] J. B. Birks, B. N. Srinivasan, and S. P. McGlynn, *J. Mol. Spectrosc.*, **27**, 266 (1968). G. F. Moore and I. H. Munro, *Spectrochim. Acta*, **23A**, 1291 (1967). J. B. Birks, *Chem. Phys. Letters*, **2**, 417 (1968).

[5] C. A. Parker, *Nature*, **200**, 331 (1963).

[6] C. A. Parker and C. G. Hatchard, *Proc. Chem. Soc.*, **1963**, 62.

[7] C. A. Parker, *Proc. Roy. Soc.* (London), **A276**, 125 (1963).

[8] C. A. Parker, C. G. Hatchard, and T. A. Joyce, *Nature*, **205**, 1282 (1965).

[9] K. Kikuchi, H. Kokubun, and M. Koizumi, *Z. Physik. Chem. N. F.*, **62**, 79 (1968).

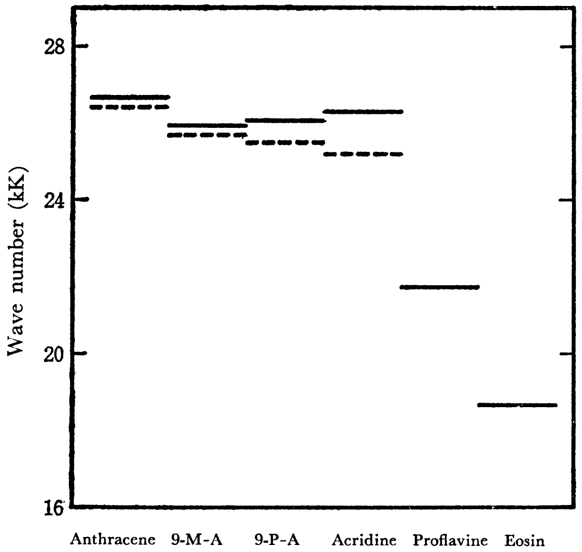

Fig. 1. 0-0 bands of absorption (solid line) and fluorescence (broken line).

the delayed excimer fluorescence (DE–Fl) of the components.

Figure 1 gives the energy levels of the lowest singlet excited states for the compounds studied, as evaluated from the 0–0 band of absorption and emission in ethanol.

Method of Analysis

Our method consists of the measurements of the time dependence of both T–T absorption and D–Fl under the same conditions by means of a flash apparatus.[10] For a solution containing a single component A or B which exhibits P-type D–Fl, the following relations

$$^3\mathrm{A} + {}^3\mathrm{A} \xrightarrow{p_\mathrm{A}k_\mathrm{TT}{}^\mathrm{A}} {}^1\mathrm{A}^* + \mathrm{A} \qquad \text{(i)}$$
$$\searrow \xrightarrow{q_\mathrm{A}k_\mathrm{TT}{}^\mathrm{A}} (\mathrm{AA})^* \qquad \text{(v)}$$

$$^3\mathrm{B} + {}^3\mathrm{B} \xrightarrow{p_\mathrm{B}k_\mathrm{TT}{}^\mathrm{B}} {}^1\mathrm{B}^* + \mathrm{B} \qquad \text{(ii)}$$
$$\searrow \xrightarrow{q_\mathrm{B}k_\mathrm{TT}{}^\mathrm{B}} (\mathrm{BB})^* \qquad \text{(vi)}$$

hold exactly between the measured D–Fl intensity I_DF and the measured optical density of the T–T absorption D_T.

$$I_\mathrm{DF}{}^\mathrm{A}(\mathrm{P},\ \lambda_1) = \alpha^\mathrm{A}(\lambda_1)\phi_\mathrm{F}{}^\mathrm{A}(p^\mathrm{A}k_\mathrm{TT}{}^\mathrm{A}[^3\mathrm{A}]^2)$$
$$= \alpha^\mathrm{A}(\lambda_1)\phi_\mathrm{F}{}^\mathrm{A}p^\mathrm{A}k_\mathrm{TT}{}^\mathrm{A}\left(\frac{D_\mathrm{T}{}^\mathrm{A}(\lambda_1')}{\varepsilon_\mathrm{T}{}^\mathrm{A}(\lambda_1')d}\right)^2 \qquad (1)$$

$$I_\mathrm{DF}{}^\mathrm{B}(\mathrm{P},\ \lambda_2) = \alpha^\mathrm{B}(\lambda_2)\phi_\mathrm{F}{}^\mathrm{B}(p^\mathrm{B}k_\mathrm{TT}{}^\mathrm{B}[^3\mathrm{B}]^2)$$
$$= \alpha^\mathrm{B}(\lambda_2)\phi_\mathrm{F}{}^\mathrm{B}pk_\mathrm{TT}{}^\mathrm{B}\left(\frac{D_\mathrm{T}{}^\mathrm{B}(\lambda_2')}{\varepsilon_\mathrm{T}{}^\mathrm{B}(\lambda_2')d}\right)^2 \qquad (2)$$

where k_TT and p are respectively the rate constant for the encounter of two triplet molecules and the efficiency of T–T annihilation, and α is a parameter depending on the spectral distribution of the fluorescence and on the experimental conditions. ϕ_F is a quantum yield of fluorescence and d, the cell length, is 10 cm. The wavelengths λ_1 and λ_2 are chosen in a suitable way as described below in the region where DE–Fl is negligible.

For a solution containing both A and B, the mixed T–T annihilation, should be taken into account. In

$$\nearrow \xrightarrow{p_\mathrm{M}{}^\mathrm{A}k_\mathrm{MT}} {}^1\mathrm{A}^* + \mathrm{B} \qquad \text{(iii)}$$
$$^3\mathrm{A} + {}^3\mathrm{B} \xrightarrow{p_\mathrm{M}{}^\mathrm{B}k_\mathrm{MT}} {}^1\mathrm{B}^* + \mathrm{A} \qquad \text{(iv)}$$
$$\searrow \xrightarrow{q_\mathrm{M}k_\mathrm{MT}} (\mathrm{AB})^* \qquad \text{(vii)}$$

this case D–Fl intensity of A (or B) at given triplet concentrations of A and B, is a sum of P-type D–Fl given by (1) (or (2)) and MD–Fl, (3) (or (4)).

$$I_\mathrm{DF}{}^\mathrm{A}(\mathrm{M},\ \lambda_1) = \alpha^\mathrm{A}(\lambda_1)\phi_\mathrm{F}{}^\mathrm{A}p_\mathrm{M}{}^\mathrm{A}k_\mathrm{MT}[^3\mathrm{A}][^3\mathrm{B}]$$
$$= \alpha^\mathrm{A}(\lambda_1)\phi_\mathrm{F}{}^\mathrm{A}p_\mathrm{M}{}^\mathrm{A}k_\mathrm{MT}\frac{D_\mathrm{T}{}^\mathrm{A}(\lambda_1')D_\mathrm{T}{}^\mathrm{B}(\lambda_2')}{\varepsilon_\mathrm{T}{}^\mathrm{A}(\lambda_1')\varepsilon_\mathrm{T}{}^\mathrm{B}(\lambda_2')d^2} \qquad (3)$$

$$I_\mathrm{DF}{}^\mathrm{B}(\mathrm{M},\ \lambda_2) = \alpha^\mathrm{A}(\lambda_2)\phi_\mathrm{F}{}^\mathrm{B}p_\mathrm{M}{}^\mathrm{B}k_\mathrm{MT}[^3\mathrm{A}][^3\mathrm{B}]$$
$$= \alpha^\mathrm{B}(\lambda_2)\phi_\mathrm{F}{}^\mathrm{B}p_\mathrm{M}{}^\mathrm{B}k_\mathrm{MT}\frac{D_\mathrm{T}{}^\mathrm{A}(\lambda_1')D_\mathrm{T}{}^\mathrm{B}(\lambda_2')}{\varepsilon_\mathrm{T}{}^\mathrm{A}(\lambda_1')\varepsilon_\mathrm{T}{}^\mathrm{B}(\lambda_2')d^2} \qquad (4)$$

In most systems, however, both D–Fl and the T–T absorption of the components overlap each other. The measured D–Fl intensity at λ_1, for example, consists of the components due to A and B species. Thus

$$I_\mathrm{DF}(\lambda_1) = I_\mathrm{DF}{}^\mathrm{A}(\mathrm{P},\ \lambda_1) + I_\mathrm{DF}{}^\mathrm{A}(\mathrm{M},\ \lambda_1)$$
$$+ I_\mathrm{DF}{}^\mathrm{B}(\mathrm{P},\ \lambda_1) + I_\mathrm{DF}{}^\mathrm{B}(\mathrm{M},\ \lambda_1) \qquad (5)$$

A similar equation holds for $I_\mathrm{DF}(\lambda_2)$. In an analogous way, the optical density for λ_1' is given by

$$D_\mathrm{T}(\lambda_1') = D_\mathrm{T}{}^\mathrm{A}(\lambda_1') + D_\mathrm{T}{}^\mathrm{B}(\lambda_1')$$
$$= \varepsilon_\mathrm{T}{}^\mathrm{A}(\lambda_1')[^3\mathrm{A}]d + \varepsilon_\mathrm{T}{}^\mathrm{B}(\lambda_1')[^3\mathrm{B}]d \qquad (6)$$

Hence we have to divide the measured quantity $I_\mathrm{DF}(\lambda_1)$ (or $I_\mathrm{DF}(\lambda_2)$) into the components $I_\mathrm{DF}{}^\mathrm{A}(\lambda_1)$ and $I_\mathrm{DF}{}^\mathrm{B}(\lambda_1)$ (or $I_\mathrm{DF}{}^\mathrm{A}(\lambda_2)$ and $I_\mathrm{DF}{}^\mathrm{B}(\lambda_2)$) and similarly $D_\mathrm{T}(\lambda_1')$ (or $D_\mathrm{T}(\lambda_2')$) into $D_\mathrm{T}{}^\mathrm{A}(\lambda_1')$ and $D_\mathrm{T}{}^\mathrm{B}(\lambda_1')$ (or $D_\mathrm{T}{}^\mathrm{A}(\lambda_2')$ and $D_\mathrm{T}{}^\mathrm{B}(\lambda_2')$). This is done successfully by means of the following equations, if λ_1, λ_2 and λ_1', λ_2' are chosen properly.

$$D_\mathrm{T}{}^\mathrm{A}(\lambda_2') = \{D_\mathrm{T}(\lambda_1') - [\varepsilon_\mathrm{T}{}^\mathrm{B}(\lambda_1')/\varepsilon_\mathrm{T}{}^\mathrm{B}(\lambda_2')] \times D_\mathrm{T}(\lambda_2')\}/$$
$$\{[\varepsilon_\mathrm{T}{}^\mathrm{A}(\lambda_1')/\varepsilon_\mathrm{T}{}^\mathrm{A}(\lambda_2')] - [\varepsilon_\mathrm{T}{}^\mathrm{B}(\lambda_1')/\varepsilon_\mathrm{T}{}^\mathrm{B}(\lambda_2')]\} \qquad (7)$$

$$D_\mathrm{T}{}^\mathrm{B}(\lambda_1') = \{D_\mathrm{T}(\lambda_2') - [\varepsilon_\mathrm{T}{}^\mathrm{A}(\lambda_2')/\varepsilon_\mathrm{T}{}^\mathrm{B}(\lambda_1')] \times D_\mathrm{T}(\lambda_1')\}/$$
$$\{[\varepsilon_\mathrm{T}{}^\mathrm{B}(\lambda_2')/\varepsilon_\mathrm{T}{}^\mathrm{B}(\lambda_1')] - [\varepsilon_\mathrm{T}{}^\mathrm{A}(\lambda_2')/\varepsilon_\mathrm{T}{}^\mathrm{A}(\lambda_1')]\} \qquad (8)$$

$$I_\mathrm{DF}{}^\mathrm{A}(\lambda_1) = \{I_\mathrm{DF}(\lambda_2) - [\alpha^\mathrm{B}(\lambda_2)/\alpha^\mathrm{B}(\lambda_1)] \times I_\mathrm{DF}(\lambda_1)\}/$$
$$\{[\alpha^\mathrm{A}(\lambda_2)/\alpha^\mathrm{A}(\lambda_1)] - [\alpha^\mathrm{B}(\lambda_2)/\alpha^\mathrm{B}(\lambda_1)]\} \qquad (9)$$

$$I_\mathrm{DF}{}^\mathrm{B}(\lambda_2) = \{I_\mathrm{DF}(\lambda_1) - [\alpha^\mathrm{A}(\lambda_1)/\alpha^\mathrm{A}(\lambda_2)] \times I_\mathrm{DF}(\lambda_2)\}/$$
$$\{\alpha^\mathrm{B}(\lambda_1)/\alpha^\mathrm{B}(\lambda_2) - \alpha^\mathrm{A}(\lambda_1)/\alpha^\mathrm{A}(\lambda_2)\} \qquad (10)$$

In order to carry out the above procedure, it is necessary to measure ε_T at various wavelengths and also to know the shape of the delayed fluorescence.

The above analysis enables us to compare the magnitude of $I_\mathrm{DF}{}^\mathrm{A}(\lambda_1)$ in the mixed system with that of $I_\mathrm{DF}{}^\mathrm{A}(\lambda_1)$ in the solution containing only A, both at various $D_\mathrm{T}{}^\mathrm{A}(\lambda_2')$ values; then the excess of the former is attributed to the mixed T–T annihilation given by Eqs. (3) and (4). A similar analysis can be applied to MDE–Fl, at least in principle. In this case the wavelengths of emission have to be chosen in the region of excimer fluorescence. In practice, however, the dif-

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[10] K. Kikuchi, H. Kokubun, and M. Koizumi, This Bulletin, **41**, 1545 (1968).

Table 1. Molar extinction coefficient of T–T absorption in ethanol

Compound	Molar extinction coefficients ($\times 10^4$ M^{-1} cm^{-1})							
	420 nm	421 nm	424 nm	426 nm	428 nm	440 nm	550 nm	580 nm
Anthracene	4.9	5.2	3.6	2.1		0.23		
9-Methylanthracene	2.4		4.3	3.7_4		0.28		
9-Phenylanthracene			1.2_5		1.3_5	0.9_1		
Acridine			0.8_9			1.8_5		
Eosin								0.9_4
Proflavine							1.1	

ficulty in obtaining the exact spectrum of DE–Fl prohibits a complete analysis of the data.

Experimeutal

Details of the apparatus and manipulation have been reported.[10] All the reagents were purified by standard methods. For the studies on the mixed T–T annihilation, β-acetonaphthone was used as a triplet energy sensitizer in order to produce a large quantity of the two species in the triplet state to be investigated. The scattering light longer than 400 nm was removed by means of a Hoya-U2 filter. Ethanol solutions were used. The concentrations of the solutes were usually chosen for a species with a higher T-level as 10^{-5} M and for the other, 10^{-6} M. The concentration of β-acetonaphthone was always 5×10^{-4} M. A set of five deaerated solutions were prepared simultaneously and two of them were used for the measurement of T–T absorption at two wavelengths and the remaining for the measurement of D–Fl at three wavelengths. It was confirmed that the fluctuation in the flash intensity was less than a few percent.

The molar absorption coefficient of T–T absorption at a certain wavelength was determined in the following way. Using eosin or proflavine as a T-energy donor, the optical density of T–T absorption of a given substance (acceptor) directly after flashing (energy donor only, excited) was measured under conditions of a complete energy transfer. The concentration of T-state was evaluated from the decrease of the ground state donor immediately after flashing in the absence of an acceptor, taking into consideration a correction factor determined from the ratio between the fluorescence intensities of a donor in the presence and absence of an acceptor. (In the presence of an acceptor, triplet donor quickly returns to the ground state and causes a corresponding increase in the absorption of light.) It was confirmed that the optical-densities taken at time t on the decay curves measured at various wavelengths remain constant in ratio with each other irrespective of the choice of t. This implies the non-participation of intermediates other than the triplet state. The molar absorption coefficients obtained are in satisfactory agreement with the data in literature. Some necessary data are listed in Table 1.

Results

Studies on the Delayed Fluorescence of a Solution Containing One Species. In order to analyse the data of the two component systems according to the method described above, it is necessary to prepare beforehand some data of the single component systems. Among them the p-values and the intensities of the excimer fluorescence of anthracene derivatives are considered to be of value since they have not yet been reported.

Measurement of D–Fl was made by using β-acetonaphthone as a sensitizer. The spectral shape was determined by plotting the intensities at the same time-points on the decay curves measured at various wave lengths. It was confirmed that the shape remains constant irrespective of the time points on the intensity decay curves. The spectral shapes for anthracene, 9-methylanthracene, 9-phenylanthracene, and acridine are given in Figs. 2, 3, 4, and 5. They were corrected for the instrumental factors. The intensities of D–Fl are weaker than those of normal fluorescence in the 0–0 band region due to the reabsorption but appreciably stronger in the longer wavelength region.

The latter result is attributed to DE–Fl which increases in the order, anthracene<9-methylanthracene<9-phenylanthracene. It is notable that the DE–Fl of acridine is apparent. The plots of $\sqrt{I_{\mathrm{DF}}(\lambda)}$

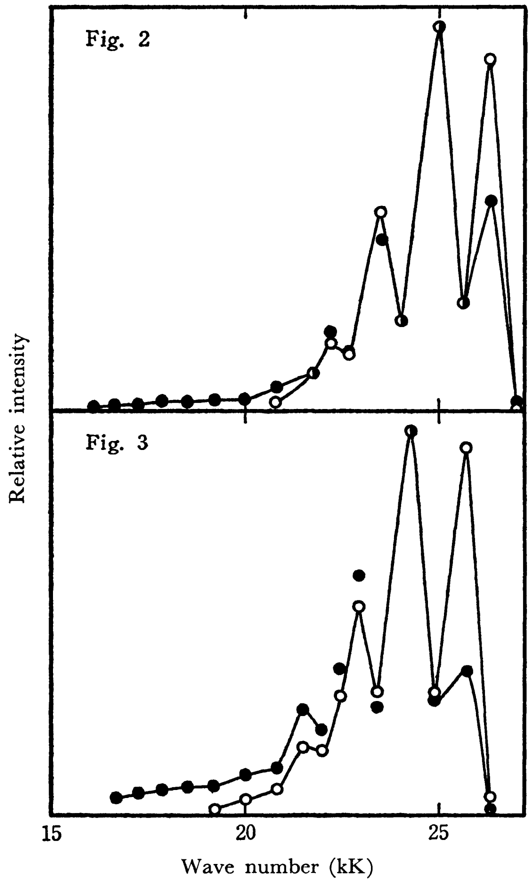


Fig. 2, 3. Normal fluorescence (○) and delayed fluorescence (●) spectra; Fig. 2, anthracene, Fig. 3, 9-methylanthracene.

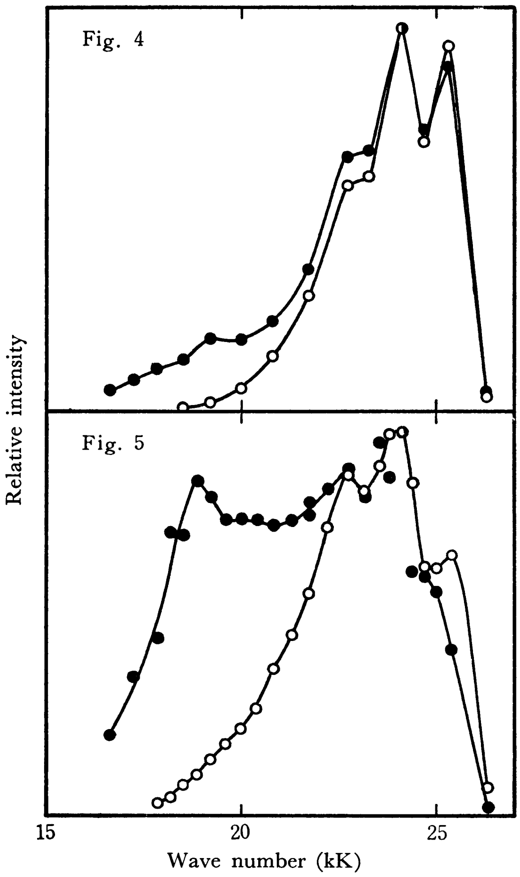


Fig. 4, 5. Normal fluorescence (○) and delayed fluorescence (●) spectra; Fig. 4, 9-Phenylanthracne, Fig. 5, acridine.

against D_{T} were found to be satisfactorily linear for anthracenes and acridine substantiating the view that the delayed fluorescence of these compounds are of P-type. These are the most important relations for the study of the mixed T–T annihilation. A few example for anthracene are shown in Fig. 6. The D–Fl spectra of eosin and proflavine both of E-type were not measured since the intensities were very weak. Some data necessary for the analysis of the mixed T–T annihilation are listed in Table 2.

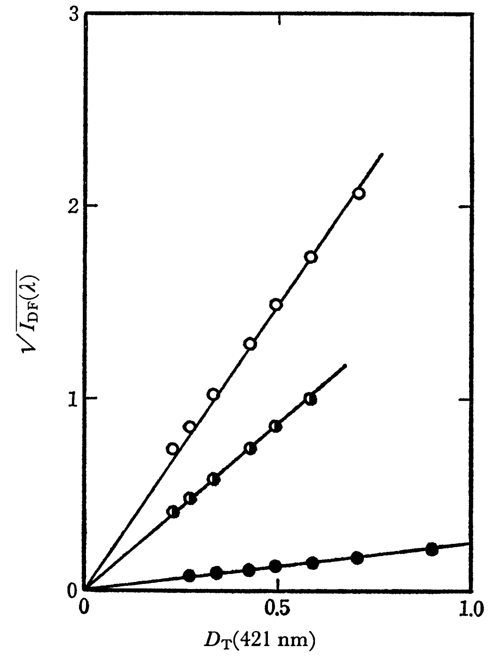


Fig. 6. The plots of $\sqrt{I_{\mathrm{DF}}(\lambda)}$ against $D_{\mathrm{T}}(421)$ for anthracene; ○ 400 nm, ◑ 412 nm, ● 540 nm.

From the results listed in Tables 1 and 2, we can evaluate the values of $\alpha(\lambda)\phi_{\mathrm{F}}pk_{\mathrm{TT}}$ by means of Eqs. (1) and (2). The values of p have been obtained by the method reported already.10) k_{TT}-values can be evaluated from the decay curves of T–T absorption and the ε_{T}-values listed in Table 1. The values of ϕ_{ST}, p, and k_{TT} for anthracene, 9-methyl- and 9-phenylanthracene, and acridine are compiled in Table 3.

A similar analysis can be carried out on the DE–Fl to the step of evaluating the $\beta\phi_{\mathrm{EF}}qk_{\mathrm{TT}}$ values, which are also listed in Table 3.

Studies on a Solution Dissolving Two Aromatic Compounds. In the studies of mixed T–T annihilation, it is most interesting to evaluate the $p_{\mathrm{M}}{}^{\mathrm{A}}$- and $p_{\mathrm{M}}{}^{\mathrm{B}}$-values (see processes (iii) and (iv)). The procedure both experimental and theoretical will be described in some detail for one system, anthracene (B) and 9-methylanthracene (A). For other systems, only significant findings will be described. All the data evaluated are listed in Table 4. A and B denote the species respectively with lower and higher 0–0 emission band. β-acetonaphthone was used as a sensitizer. For 9-methylanthracene(A)-anthracene(B), decays of T–T absorption were measured at 420 and 426 nm from 100 μsec after flashing because the triplet β-acetonaphthone was found to disappear almost completely during this time interval. The decays were analysed according to Eqs. (7) and (8).

Similarly the decays of D–Fl were measured at 400, 412, and 540 nm. The relation between D–Fl and T–T absorption for anthracene and for 9-methylanthracene obtained by the above analysis is shown in

Table 2. Relationship between delayed fluorescence and T–T absorption

Compound	Relation	Wavelength dependence of D-Fl intensity		
		400 nm	412 nm	540 nm
Anthracene	$\sqrt{I_{\mathrm{DF}}}(400)=3.0\times D_{\mathrm{T}}(421)$	1.00	0.32	0.0056
9-Methylanthracene	$\sqrt{I_{\mathrm{DF}}}(412)=4.6\times D_{\mathrm{T}}(424)$	0.33	1.00	0.018
9-Phenylanthracene	$\sqrt{I_{\mathrm{DF}}}(412)=13\times D_{\mathrm{T}}(424)$	0.76	1.00	0.042
Acridine	$\sqrt{I_{\mathrm{DF}}}(412)=1.9\times D_{\mathrm{T}}(440)$	0.75	1.00	0.18
Eosin	$I_{\mathrm{DF}}(570)=1.1\times D_{\mathrm{T}}(580)$*			
Proflavine	$I_{\mathrm{DF}}(500)=2.0\times D_{\mathrm{T}}(550)$*			

Table 3. Values of ϕ_{ST}, p, k_{TT}, and $\beta\phi_{EF}q$

	ϕ_{ST}	p	k_{TT} ($M^{-1}sec^{-1}$)	$\beta\phi_{EF}q$
Anthracene	0.070	0.77	2.9×10^9	2.6
9-Methylanthracene	0.65	0.05_3	2.4×10^9	$11._5$
9-Phenylanthracene	0.50	0.07_4	1.8×10^9	54
Acridine	$0.27^{a)}$	0.14	3.3×10^9	5.4

a) *cf.* This Bulletin, **43**, 3435 (1970).

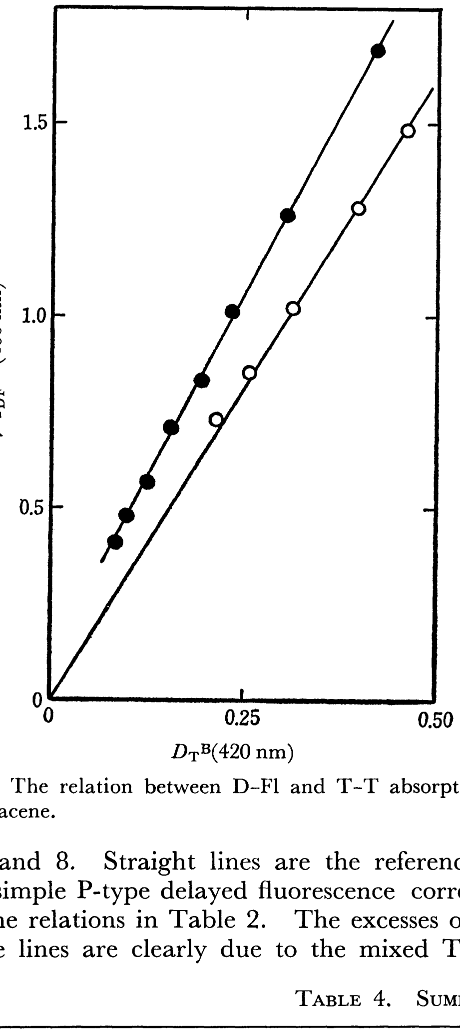


Fig. 7. The relation between D-Fl and T-T absorption for anthracene.

Figs. 7 and 8. Straight lines are the reference plots for the simple P-type delayed fluorescence corresponding to the relations in Table 2. The excesses over the reference lines are clearly due to the mixed T–T annihilation, I_{DF}^A(M, 412) and I_{DF}^B(M, 400). Figure 9 shows that these two quantities are in excellent proportionality to the product of D_T^B (420) and D_T^A (426) as is expected from Eqs. (3) and (4). Thus it is certain that the excess D–Fl is due to the mixed T–T annihilation. From the values of slope in Fig. 9 one can evaluate the value of $\alpha^B(400)\phi_F^B p_M^B k_{MT}/[\varepsilon_T^B(420)\varepsilon_T^A(426)d^2]$ and the corresponding value of A.

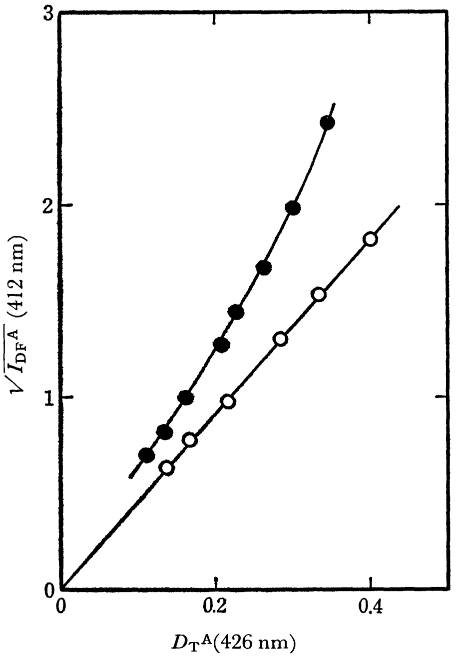


Fig. 8. The relation between D-Fl and T-T absorption for for 9-methylanthracene.

It is convenient to introduce a factor f defined as follows to compare the efficiency of the mixed type and pure P-type D-Fl.

$$f^A = p_M^A k_{MT}/p^A k_{TT}^A \qquad f^B = p_M^B k_{MT}/p^B k_{TT}^B \qquad (11)$$

By combining Eqs. (1), (2) and Eqs. (3), (4) one can easily evaluate the f^A and f^B values as well as the $p_M^A k_{MT}$ and $p_M^B k_{MT}$ values given in Table 4.

As seen in Fig. 2 and Fig. 3, DE–Fl of anthracene and 9-methylanthracene exists although very weak.

Table 4. Summary of mixed T-T annihilation

Compounds		f^A	f^B	$p_M^A k_{MT}$	$p_M^B k_{MT}$	$(p_M^A+p_M^B)k_{MT}$	p_M^A/p_M^B	$R_0^{B\to A}$	$R_0^{A\to B}$	$e^{-\Delta E/RT}$	$\beta_M(540)\times\phi_{EF}^M q^M k_{MT}$
A	B			($M^{-1}sec^{-1}$)				(Å)			
9-Methyl-anthracene	Anthracene	$1._4$	0.5_4	$1._7\times10^8$	$1._2\times10^8$	$2._9\times10^8$	$1._4$	14.5	7.4	0.028	0
9-Phenyl-anthracene	Anthracene	$2._3$	0.3_3	3×10^8	0.7×10^8	$3._7\times10^8$	$4._1$	15.0	7.6	0.009	4×10^{11}
9-Phenyl-anthracene	9-Methyl-anthracene	$1._6$	0.5_3	2×10^8	0.6×10^8	$2._6\times10^8$	$3._3$	13.8	13.8	0.32	2×10^{11}
Acridine	Anthracene	0.7_5	0.4_8	$3._5\times10^8$	$1._1\times10^8$	$4._6\times10^8$	$3._2$				2×10^{10}
Acridine	9-Methyl-anthracene	0.5	0.3_4	$2._3\times10^8$	0.4×10^8	$2._7\times10^8$	$5._7$				8×10^9
Acridine	9-Phenyl-anthracene	—	0.2_4	—	0.3×10^8	—	—				—
Eosin	Anthracene	—	0	$5._5\times10^8$	0	$5._5\times10^8$					—
Proflavine	Anthracene	—	0	$4._4\times10^8$	0	$4._4\times10^8$					—
Eosin	Acridine	—	0	$3._2\times10^8$	0	$3._2\times10^8$					—

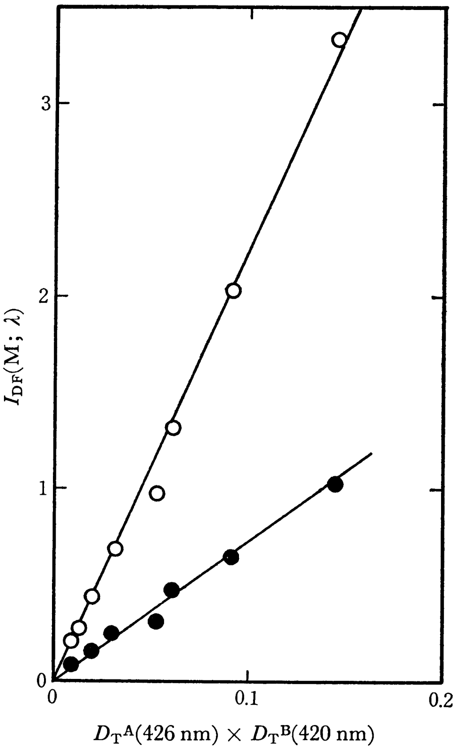


Fig. 9. The plots of $I_{DF}(M; \lambda)$ *vs.* $D_T^A(426) \times D_T^B(420)$ for 9-methylanthracene(A)-anthracene(B) system; ○ A at 412 nm, ● B at 400 nm.

Since D–Fl of monomer is negligible at 540 nm, D–Fl at this wavelength consists of the P-type and the mixed type DE–Fl, $I_{EF}(P, 540)$ and $I_{EF}(M, 540)$.

$$I_{DF}^A(P, 540) = I_{EF}^A(P, 540) + I_{EF}^A(M, 540)$$
$$= \beta^M \phi_{EF}^M q^M k_{MT} \frac{D_T^A(\lambda_1')D_T^B(\lambda_2')}{\varepsilon_T^A(\lambda_1')\varepsilon_T^B(\lambda_2')d^2} + \beta^A(540)\phi_{EF}^A q^A k_{TT}[D_T^A(\lambda)/\varepsilon_T^A(\lambda)d]^2 \qquad (12)$$

The analysis can be made as in the case of monomer D–Fl, but in this case it was found that MDE–Fl is negligible.

For anthracene(B)-9-phenylanthracene(A), Fig. 10 shows the relation between the MDE–Fl intensity I_{DF}^E at 540 nm and the product of $D_T^A(440)$ and $D_T^B(421)$, obtained as a result of the above analysis. Although the linearity is not very good, there is no doubt that MDE–Fl occurs in this system.

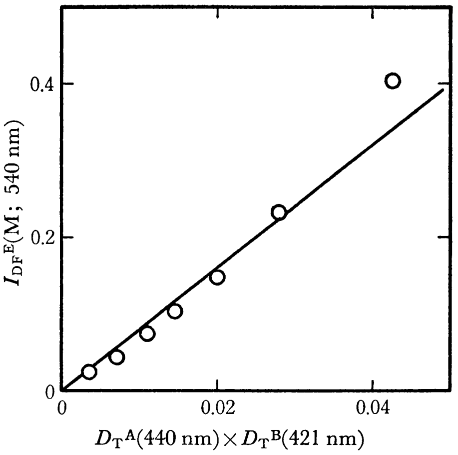


Fig. 10. The relation between $I_{DF}^E(M; 540)$ and $D_T^A(440) \times D_T^B(421)$ for anthracene(B)-9-phenylanthracene(A) system.

System, 9-phenylanthracene(A) and 9-methylanthracene(B) also gives MDE–Fl.

In acridine(A)-anthracene(B), the fluorescence yield of acridine is one order less than that of anthracene derivatives and the triplet lifetime is much smaller; hence the measurement and analysis could not be performed accurately. However, the analysis clearly showed that both components exhibit MD–Fl as shown in Fig. 11. There is scarcely any doubt that MDE–Fl also occurs as seen from Fig. 12. For acridine(A)-9-methylanthracene(B), the results are qualitatively similar to those of the above system.

In acridine(A)-9-phenylanthracene(B), D–Fl spectra of the two components greatly resemble each other and

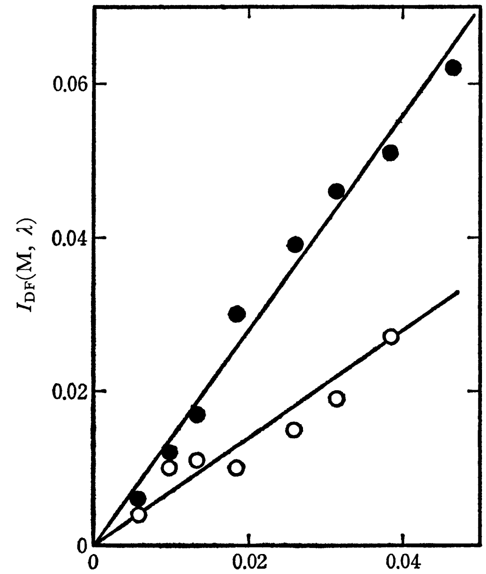


Fig. 11. The plots of $I_{DF}(M; \lambda)$ *vs.* $D_T^B(421) \times D_T^A(440)$ for acridine(A)-anthracene(B) system; ○ A at 400 nm, ● B at 412 nm.

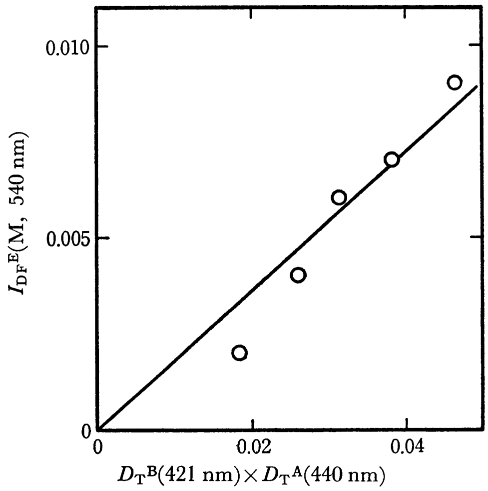


Fig. 12. The relation between $I_{DF}^E(M, 540)$ and $D_T^B(421) \times D_T^A(440)$ for acridine(A)-anthracene(B) system.

the fluorescence yield of the latter is considerably larger than that of the former. Therefore D–Fl could not be divided into two components. However, since D–Fl from acridine is very weak, the approximate values of f^B and $p_M{}^B k_{MT}$ could be estimated. The analysis at 540 nm also gave evidence for the occurrence of MDE–Fl.

Studies on Two Species with Quite Different Excited Singlet Levels. As is well known, D–Fl of eosin and of proflavine (both, A) is of E-type and is expressed by

$$I_{DF}{}^A(E,\lambda) = \alpha^A(\lambda)\phi_F{}^A k_T[{}^3A] \qquad (1')$$

of Eqs. (1) and (2). Accordingly, the expression for instead MD–Fl $I_{DF}(M,\lambda)$ has to be modified as follows.

$$I_{DF}{}^A(M,\lambda) = \alpha^A(\lambda)\phi_F{}^A p_M{}^A k_{MT}[{}^3A][{}^3B] + \alpha^A(\lambda)\phi_F{}^A k_T[{}^3A]$$

Apart from these two points, the method of analysis is essentially the same as in P-type D–Fl.[10] In eosin(A)-anthracene(B),[9] only D–Fl of eosin is increased remarkably by mixed T–T annihilation while that of anthracene scarcely shows any increase.

In proflavine(A)-anthracene(B), D–Fl of proflavine under ordinary conditions is of E-type and a similar analysis to that for the above system gave essentially the same result; D–Fl of proflavine largely increases by mixed T–T annihilation while that of anthracene is scarcely affected (Fig. 13).

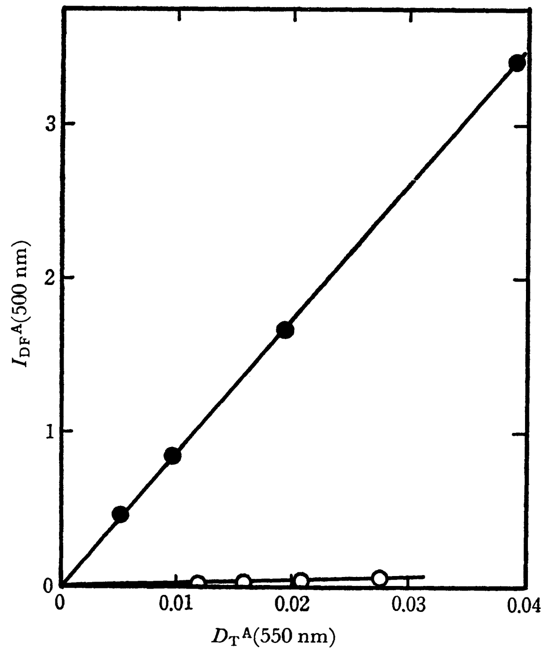


Fig. 13. The relation between $I_{DF}{}^A(500)$ and $D_T{}^A(550)$ for proflavine(A)-anthracene(B) system; ○[B] = 0 M, ●[B] = 2×10^{-6} M.

For eosin(A)-acridine(B), the results are similar to those of the above two systems.

For the last three systems MDE–Fl could not be investigated.

Discussion

In the present investigation, mixed T–T annihilation of anthracene derivatives have been studied quantitatively. Since the concentrations of both components are less than 10^{-5} M, no process in the initially excited singlet state participates, for instance, $A^*+B\rightarrow A+B^*$ and $A^*+B\rightarrow(AB)^*$, *etc.* Accordingly the present results are concerned only with T–T annihilation of various types. The method of analysis leaves nothing doubtful at least in principle. Although errors may become considerable in some cases owing to experimental difficulties, the following general conclusions can be drawn.

1) When the singlet excited levels of A and B differ a few times of kT, D–Fl of both components occur.

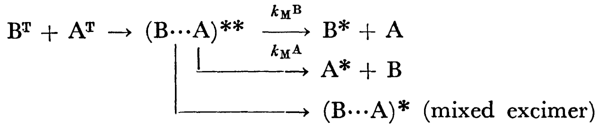
2) When the level differences largely exceed kT, only D–Fl of the component with a lower level occurs.

3) MD-Fl occurs generally in case 1).

4) The efficiency of MDE–Fl ($p_M{}^A + p_M{}^B$) is equal to that of P-type D–Fl (p^A or p^B) at least in the order of magnitude.

For the mixed excimer fluorescence Birks and Christophorous[11] in classifying two types, stated that it occurs with a diffusion controlled rate in the systems composed of like compounds such as anthracene and its derivatives, while it does not occur at all in a pair of molecules with different aromatic cores. It has been established that similar situations hold also in mixed T–T annihilation.

It is very interesting that the value of $p_M{}^A/p_M{}^B$ is always larger than unity, *i.e.*, the component with a lower singlet excited level emits more efficiently when the 0–0 band of fluorescence is adopted as an excited level. Since the mixed T–T annihilation at room temperature occurs according to the following scheme as has been well established,[4]



$$\begin{array}{l} B^T + A^T \rightarrow (B\cdots A)^{**} \xrightarrow{k_M{}^B} B^* + A \\ \qquad\qquad\qquad\qquad\quad \xrightarrow{k_M{}^A} A^* + B \\ \qquad\qquad\qquad\qquad\quad \longrightarrow (B\cdots A)^* \text{ (mixed excimer)} \end{array}$$

the value of $p_M{}^A/p_M{}^B$ is nothing but the ratio of the rate constants $k_M{}^A$ and $k_M{}^B$.

At present, the microscopic mechanism of a simple type delayed fluorescence as well as of a mixed one is unknown; $(B\cdots A)^{**}$ merely denotes an encounter state of unknown character. Birks suggested that the intermediate in the case of a simple type one may experience a quintet, triplet, or singlet state.[12] Such a change in spin states may occur in the early stage of encounter, but in mixed T–T annihilation, differing from the simple T–T annihilation, the two components A* and B or B* and A produced may still have a chance of transforming to each other. Thus it is necessary to take the following three possibilities into consideration as the molecular processes determining the $p_M{}^A/p_M{}^B$ value.

A) A^T and B^T approach close enough to interact and change their electronic states yielding ultimately (A^*+B) or (B^*+A) (bracket denotes that the two components still exist in the encounter state) in a certain proportion as determined by a specific electronic or vibronic interaction.

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[11] J. B. Birks and L. G. Christophorous, *Nature*, **196**, 33 (1962); p. 423 in Ref. 2.

[12] J. B. Birks, *Chem. Phys. Letters*, **1**, 561 (1968).

B) The possibility may exist that in the encounter state, the Boltzmann distribution is approached between A* and B* due to electronic exchange interaction.

C) During the diffusion apart, there is another possibility that a long range dipole-dipole interaction causes a mutual transformation. This is thought to be possible because the distance to which the two components separate during the lifetime of the excited state $\sim 10^{-8}$ sec is estimated to be 10—100 Å. If the R_0-value in Förster's theory[13] is suitable, then $A+B^* \rightleftharpoons B+A^*$ may occur during the lifetime.

From the above viewpoint, the values of the Boltzmann factor $e^{-\Delta E/RT}$ (ΔE, difference of 0–0 band of fluorescence) and of R_0 for $B^*+A \rightleftarrows B+A^*$ are added in Table 4. The values of $p_M{}^A/p_M{}^B$ change from 3 to 5 except for system (1). Putting aside the results for the systems involving acridine which are less reliable, only the $p_M{}^A/p_M{}^B$ values for (1), (2), and (3) will be discussed. It is evident that these values are not well related with either the values of R_0 or of $e^{-\Delta E/RT}$. It may be said from the R_0 values that the energy transfer due to Förster's mechanism does not occur so efficiently in the present systems. Although the value of $p_M{}^A/p_M{}^B$ for system (3) well agrees with the value of $e^{-\Delta E/RT}$, it may be judged that this is rather a mere coincidence in view of large discrepancies in (1) and (2). Thus in the present systems, it seems likely that the $p_M{}^A/p_M{}^B$ values are determined mainly by the ratio of the two processes $(A\cdots B)^{**} \rightarrow (A^*\cdots B)$ and $(A\cdots B^*)$. The two components in the encounter state may then separate quickly with any noticiable chance of transforming to each other. When the levels of A* and B* are far apart, it is reasonable to consider that only the emission of the lower component occurs.

A few remarks will be added to the DE–Fl of anthracene derivatives. Birks and Aladekomo[14] reported that anthracene does not exhibit the excimer fluorescence while 9-methylanthracene does. He states[15] that anthracene with a great tendency of forming a stable photodimer does not give excimer fluorescence, while 9-methylanthracene with less tendency of dimerization due to a little steric hindrance will emit the excimer fluorescence. He expects that 9-phenylanthracene which does not dimerize will be more liable of forming excimer. However, no experimental data were given for the latter two compounds. The present results have verified his argument for the first time. Thus the values of $\beta\phi_{EF}q$ measured at 540 nm listed in Table 3 increase five times from anthracene to 9-methylanthracene and also from 9-methylanthracene to 9-phenylanthracene. In spite of some uncertainty in β-value, there is scarcely any doubt that these great differences reflect the differences in their excimer formation tendencies.

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[13] Th. Förster, *Ann. Physik.*, **2**, 55 (1948).

[14] J. B. Birks and J. B. Aladekomo, *Photochem. Photobiol.*, **2**, 415 (1963).

[15] p. 321 in Ref. 2.