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Solvent Effects on the Fluorescence Quantum Yields and Lifetimes of 1- and 2-Acetyl- or Benzoylanthracenes

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The fluorescence quantum yields and lifetimes of 1- and 2-acetyl- or benzoylanthracenes were measured in various degassed solvents at room temperature. The natural fluorescence lifetime was evaluated to be 30—40 ns, depending a little on the compounds, but little on the solvent. This strongly supports the recent finding that the lowest excited singlet state of the acylanthracenes is of a $\pi\pi^*$ character. On the basis of triplet-yield measurements, it was also confirmed that the low fluorescence yield in nonpolar solvents is due to an efficient intersystem crossing to an upper triplet state.

It is well established that an intersystem crossing (ISC) is the dominant nonradiative decay pathway for the lowest excited singlet state (S_1) of aromatic hydrocarbons. In the case of anthracene, the lowest triplet state (T_1) lies much lower in energy than S_1, so that the direct ISC to T_1 is incapable of competing with rapid fluorescence. Instead, the ISC to an upper triplet state (T_x) lying slightly below S_1 is favored.[1] On the other hand, it has been widely accepted for 9-methyl-, phenyl-, or haloanthracene that the ISC occurs dominantly from a thermally activated level of S_1 into T_X lying above S_1.[2] This temperature-dependent ISC well explains the considerable fluorescence variation with the temperature.[3-6]

The fluorescence of 1- or 2-acetylanthracenes is significantly dependent on the solvent. As a general trend, the fluorescence yield increases, with a concomitant red-shift of the peak maximum, as the solvent polarity increases.[7,8] The possible mechanisms for this solvent variation in the fluorescence yield are as follows; (I) a change in the thermal barrier of the temperature-dependent ISC due to the displacement of the S_1 level, and (II) an inversion of the excited electronic configuration from $n\pi^*$ to $\pi\pi^*$, as in the case of 3-pyrenecarbaldehyde.[9] Recently, Hirayama has pointed out that the S_1 of acylanthracenes has a $\pi\pi^*$ electronic configuration.[10] His conclusion was supported for 9-acylanthracenes by the external-pressure effect on the fluorescence.[11] If this is so also for 1- or 2-acylanthracenes, the (II) mechanism can be excluded.

This paper will describe the results of the fluorescence-quantum-yield, lifetime, and triplet-yield measurements for 1- and 2-acetyl- or benzoylanthracenes in various degassed solvents at room temperature, these findings are consistent with the (I) mechanism.

Experimental

1-Acetyl- (**1A**), 1-benzoylanthracene (**1B**), and their 2-isomers (**2A** and **2B** respectively) were the same as those used before.[8] The cyclohexane (Cy), dipropyl ether (DPE), tetrahydrofuran (THF), 1,2-dichloroethane (DCE), acetone (AC), acetonitrile (ACN), *t*-butyl alcohol (*t*-BuOH), 2-propanol (*i*-PrOH), ethanol (EtOH), and methanol (MeOH) were GR- or Spectro-grade reagents. For all optical measurements except for that of phosphorescence, the sample solutions were degassed by the freeze-thaw method ($<5\times10^{-5}$ Torr; 1 Torr$\approx$133.32 Pa).

The corrected fluorescence spectra were measured by using a Hitachi MPF 4 spectrofluorometer, and the observed spectra on the wavelength scale were transformed into those on the wave-number scale. The fluorescence spectra of the samples were independent of the excitation wavelength. The fluorescence intensities calculated from the trapezoid rule were corrected for the refractive index of the solvent and for the sample absorbance at the exciting wavelength (385 nm for **1A** and **1B** and 360 nm for **2A** and **2B**). The fluorescence quantum yields were based on that of 9,10-diphenylanthracene in EtOH (0.76[12]).

The fluorescence lifetime measurements were done using an Ortec SP-3 nanosecond fluorometer. A nanosecond flash lamp filled with 0.5 atm of air was operated at 5 kV at a frequency of 100 kHz, the half-bandwidth of the light pulse being 6 ns. A band-pass filter (Corning 3-73) was inserted between the flash lamp and the sample cell in order to excite the sample by nitrogen-line outputs at 300—400 nm effectively. The monitoring wavelengths were selected by means of a monochrometor; 430 nm for aprotic solutions and 500 nm for alcoholic solutions.

The analogous technique developed by Grinvald and Steinberg[13] was applied to the deconvolution of the fluorescence time evolution $\{f(t)\}$, which has this form:

$$f(t) = \int_0^t g(t-s)i(s)\mathrm{d}s,$$

where $g(t)$ is the response of the detection system to the excitation flash and where $i(t)$ is the required fluorescence decay function. $g(t)$ was experimentally determined after Wahl *et al.*[14] by using 2,5-bis[5-*t*-butylbenzoxazol-2-yl]thiophene (BBOT) as a fluorophore. $i(t)$ was assumed to be mono- and biexponential; thus:

$$i(t) = \sum_{j}^{1,2} C_j \exp(-\lambda_j t),$$

where C_j and λ_j are unknown parameters. The convolution product of $i(t)$ with $g(t)$ was iteratively calculated by Marquardt's least-squares method[15] to fit the decay curves observed. The calculation was terminated whenever

$\Delta C_j/C_j \leq 0.001$ and $\Delta\lambda_j/\lambda_j \leq 0.001$ for all j,

where ΔC_j and $\Delta\lambda_j$ are the increments in the parameters at the last iteration. In order to judge whether or not the curve smoothing is good, the autocorrelation function and the residuals between observed and calculated curves were calculated.[13] If theobserved decay data scatter randomly about the calculated curve, the autocorrelation function fluctuates near the zero line with a high frequency and a low amplitude.[13] A typical example of the computer-simulated decay curve is shown in Fig. 1.

The triplet-triplet absorption measurements were done using a Ushio UFP-105 microsecond flash apparatus. The sample concentrations were prepared to be $1—2\times10^{-4}$ mol

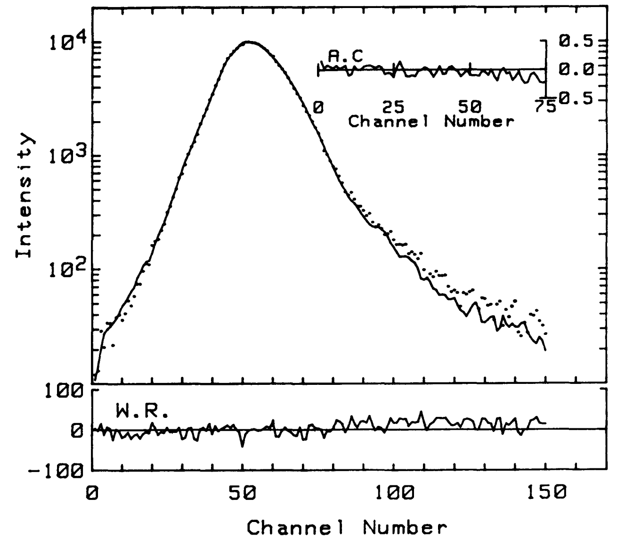


Fig. 1. Observed and simulated fluorescence decay curves of 2-acetylanthracene in cyclohexane.
W. R.: Weighted residual, A. C.: autocorrelation function.

dm^{-3}, so that the samples absorbed almost all the incident light selected by a Corning 3-73 filter. The relative triplet yields were determined from the initial absorbances of the maximum band lying at 485 nm for **1A**, at 437 nm for **2A**, at 422 nm for **1B**, and at 450 nm for **2B**, since the absorption spectra were little dependent on the solvent. The phosphorescence measurements were done in rigid methylcyclohexane glasses at 77 K.

Results

The absorption and fluorescence spectra of **1A** and **2A** in Cy are shown in Figs. 2a and 2b respectively. The general forms of the absorption and fluorescence spectra are little dependent on the substituent (acetyl and benzoyl) groups, but on the C-position of an anthryl ring, at which the substitution occurs. The fluorescence spectra of all the compounds examined are remarkably dependent on the solvent, while the absorption spectra undergo no corresponding change.[8] As the solvent polarity increases, the fluorescence spectra become more structureless and the peak maxima move to lower energies. Concomitantly, significant variations in the fluorescence quantum yield (ϕ_f) and the actual lifetime (τ_f) are observed. These values for **1A** and **2A** in several aprotic and alcoholic solvents, together with the energy of the fluorescence maxima ($\tilde{\nu}_f$), are listed in Table 1. In aprotic solvents, ϕ_f increases with an increase in the solvent polarity, but such a simple relation breaks in alcohols. From *t*-BuOH through MeOH, the ϕ_f value for **1A** increases, remains practically the same for **2A**, and considerably decreases for **1B** and **2B**. The observed solvent dependence of τ_f is similar to that of ϕ_f. Table 1 also shows the values of the radiative and nonradiative rate constants (k_f and k_{nr} respectively) evaluated from the observed ϕ_f and τ_f values for **1A** and **2A**.

It should be noted that the best fit to the fluorescence decay curves observed for **1B** and **2B** in alcohols was obtained by taking the biexponential function as $i(t)$; this is in contrast with the other cases, for which the observed decay curves were satisfactorily simulated with the monoexponential. The C_j and λ_j values for **2B**, together with the observed $\tilde{\nu}_f$ and ϕ_f values, are

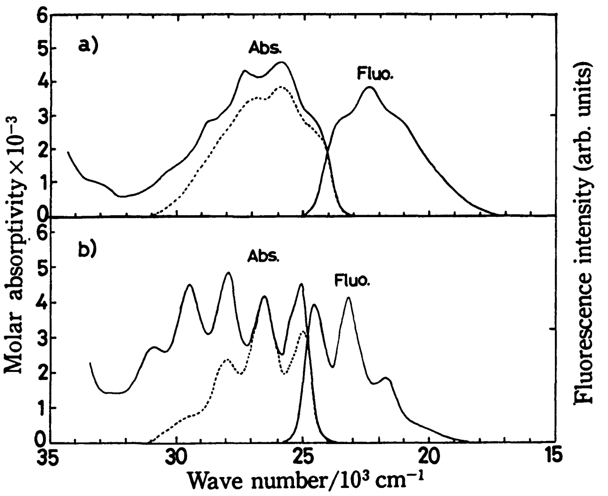


Fig. 2. Absorption and fluorescence spectra in cyclohexane.
a) 1-Acetylanthracene, b) 2-acetylanthracene. The broken curves are the mirror reflection of the fluorescence spectrum.

TABLE 1. FLUORESCENCE MAXIMA ($\tilde{\nu}_f$), QUANTUM YIELDS (ϕ_f), LIFETIMES (τ_f), RADIATIVE RATE CONSTANTS (k_f), AND NONRADIATIVE RATE CONSTANTS (k_{nr}) OF 1- AND 2-ACETYLANTHRACENES IN VARIOUS DEGASSED SOLVENTS

Solvents	1-Acetylanthracene					2-Acetylanthracene				
	$\tilde{\nu}_f$/cm^{-1}	ϕ_f	τ_f/ns	$k_f/10^7$ s^{-1}	$k_{nr}/10^7$ s^{-1}	$\tilde{\nu}_f$/cm^{-1}	ϕ_f	τ_f/ns	$k_f/10^7$ s^{-1}	$k_{nr}/10^7$ s^{-1}
Cy	21978	0.002	0.2	1.0	500	23419	0.035	1.6	2.2	59
DPE	21739	0.003	0.4	0.8	250	23095	0.073	3.2	2.3	29
THF	21413	0.014	0.6	2.3	160	22779	0.24	8.7	2.7	8.8
DCE	20964	0.046	1.9	2.5	51	22523	0.43	15	2.8	3.7
AC	20921	0.028	1.2	2.3	81	22676	0.36	13	2.8	4.9
ACN	20790	0.055	2.5	2.2	38	22472	0.49	18	2.7	2.9
t-BuOH	20243	0.35	9.1	3.9	7.1	21459	0.78	22	3.5	0.97
i-PrOH	19881	0.45	12	3.7	4.4	20661	0.82	22	3.8	0.81
EtOH	19531	0.50	13	3.8	3.9	20284	0.76	22	3.5	1.1
MeOH	19120	0.54	15	3.7	3.1	19802	0.77	23	3.4	0.99

TABLE 2. FLUORESCENCE MAXIMA ($\tilde{\nu}_f$), QUANTUM YIELDS (ϕ_f), C_j, AND λ_j FOR 2-BENZOYLANTHRACENE IN SEVERAL DEGASSED ALCOHOLS

Solvents	$\tilde{\nu}_f$/cm^{-1}	ϕ_f	$C_1/10^7$	$C_2/10^7$	$\lambda_1/10^7$ s^{-1}	$\lambda_2/10^7$ s^{-1}
t-BuOH	19920	0.63	6.9	6.9	4.8	4.8
i-PrOH	19268	0.57	9.2	5.7	7.4	4.1
EtOH	18553	0.37	9.0	9.7	18	6.0
MeOH	18051	0.10	29	1.3	24	5.9

TABLE 3. RELATIVE TRIPLET YIELDS (ϕ_T)

Solvents	ϕ_T[a]			
	1A	**2A**	**1B**	**2B**
Cy	1.0	1.0	1.0	1.0
THF	1.0	0.6		0.7
ACN	0.6	0.3	0.8	0.2
t-BuOH	0.6	0.03		0.1
MeOH	0.04	0.01	0.01	0.01

a) Relative to the triplet yield in cyclohexane.

listed in Table 2. Since the apparent lifetime of **1B** was very short, the C_j and λ_j values obtained were less reproducible.

The relative triplet yields (ϕ_T) in several solvents are listed in Table 3. An inverse relationship is observed between ϕ_T and ϕ_f as the solvent polarity increases in going from Cy through *t*-BuOH. It appears likely that the ϕ_T values in MeOH are too low to cover all of the nonradiative decay probability. This is of particular interest in the case of **1B** and **2B**, since the ϕ_f values of these compounds are also very low in the same solvent. On the other hand, the triplet lifetime was observed to be 0.2—0.4 ms, slightly dependent on the compound, but less sensitive to the solvent. The phosphorescence was detected except for **2A** (λ_{max}=684, 680, and 675 nm for **1A**, **1B**, and **2B** respectively).

Discussion

Red Shift of the Fluorescence Peak Maxima. The solvent dependence of $\tilde{\nu}_f$, as listed in Table 1, can be interpreted in terms of the nonspecific and specific solvent-solute interactions. In aprotic solvents, $\tilde{\nu}_f$ is well correlated with the macroscopic solvent polarity, which is itself associated with the dielectric constant and the refractive index.[8] This may suggest that the higher the solvent polarity, the greater the contribution of the charge-transfer (CT) resonance form in the excited state, in which positive and negative charges are localized in the anthryl and acyl moieties respectively. In reality, the excited-state dipole moments in polar solvents were measured to be 7D for **1A** and **1B** and 10D for **2A** and **2B**.[8] On the other hand, the red shift of $\tilde{\nu}_f$ in alcohols is extraordinarily larger than that to be expected from the solvent polarity. For example, $\tilde{\nu}_f$ in MeOH is lower in energy by *ca.* 2000 cm^{-1} than that in ACN, though these two solvents have quite similar polarities. The excess of the red shift in MeOH agrees with the stabilization energy due to the specific formation of hydrogen-bonded complex(es) in a hexane–MeOH mixture solution.[16]

Electronic Configuration of S_1 and ISC to the Upper Triplet State. As is shown in Table 1, k_f is little dependent on the solvent, whereas k_{nr} undergoes significant variation with the solvent. The k_f values observed in all solvents used are in an order of 2—3 × 10^7 s^{-1},[17] suggesting that the electronic configuration of the compounds concerned in the S_1 state is of the $\pi\pi^*$ type, even in a very nonpolar solvent (Cy) where ϕ_f is quite low. The result is consistent with a recent conclusion.[10] The $\pi\pi^*$ nature of the fluorescence can be further confirmed by a comparison of the observed k_f value with that alternatively calculated from the observed absorption and fluorescence spectra. Unfortunately, the two $\pi\pi^*$ transition bands ascribed to ^1L_a and ^1L_b are largely overlapping in the long-wavelength absorption spectra of the compounds concerned,[8] and no mirror-symmetry relation is seen between the absorption and fluorescence spectra, as is shown in Fig. 2. Therefore, the calculation of k_f was done using the long-end absorption band obtained from the mirror-symmetry reflection of the fluorescence spectrum according to this equation:

$$\varepsilon(\tilde{\nu})/\tilde{\nu} = F(2\tilde{\nu}_0 - \tilde{\nu})/(2\tilde{\nu}_0 - \tilde{\nu})^3, \qquad (1)$$

where $\varepsilon(\tilde{\nu})$ and $F(2\tilde{\nu}_0 - \tilde{\nu})$ are the molar absorptivity and the fluorescence intensity as a function of the wave number respectively, and where $\tilde{\nu}_0$ is the mirror-symmetry frequency.[18] The transition band thus assumed for **1A** and **2A** is shown in Fig. 2. In such cases, k_f can be calculated from the following equation:[18]

$$k_f = 2.88 \times 10^9 n^2 \int \varepsilon(\tilde{\nu})(2\tilde{\nu}_0 - \tilde{\nu})^3/\tilde{\nu}\,d\tilde{\nu}, \qquad (2)$$

where n is the refractive index of the solvent. The value of k_f was obtained as 4 × 10^7 s^{-1} for **1A** and as 3 × 10^7 s^{-1} for **2A**. These values are rather close to those experimentally determined from ϕ_f and τ_f, in spite of the rough estimation of $\varepsilon(\tilde{\nu})$.

Clearly, the solvent variation in both ϕ_f and τ_f in aprotic solvents is predominantly due to the solvent variation in k_{nr}. From the inverse relation between ϕ_f and ϕ_T, it appears probable that the ISC plays an important role in the nonradiative deactivation. Furthermore, it is shown that k_{nr} decreases with a decrease in the $\tilde{\nu}_f$ value. The plot of log k_{nr} *vs.* $\tilde{\nu}_f$ for **2A** is shown in Fig. 3. A linear relation is observed between

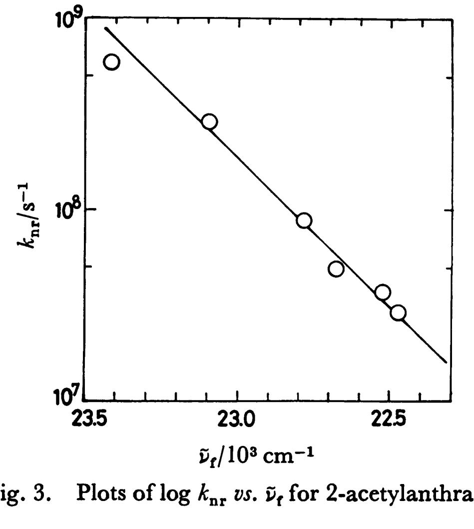
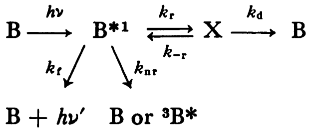


Fig. 3. Plots of log k_{nr} *vs.* $\tilde{\nu}_f$ for 2-acetylanthracene.

them. This striking relation may most reasonably be explained in terms of the (I) mechanism describing the validity of the thermally activated ISC, as in the cases of 9-haloanthracene derivatives, for which a direct correlation has been shown between the activation energy of the ISC and the solvent shift of S_1.[6] The situation is common to all the compounds examined, but it appears likely that not only the thermally activated ISC, but also the temperature-independent ISC, is operative for **1A**, **1B**, and **2B**, since these compounds exhibit the phosphorescence at 77 K, where the former ISC is inhibited. On the other hand, the temperature-independent ISC may be less important for **2A**, which emits no phosphorescence.

It was suggested for acylanthracenes that the triplet states of both $\pi\pi^*$ (T_2) and $n\pi^*$ ($T_{n\pi^*}$) are lying near S_1 and that, on the basis of the photoreduction and oxetane formation reaction, the reactive $T_{n\pi^*}$ lies above the nonreactive T_2 for the photostable derivatives.[10] The compounds concerned in this study are just like this. Combining these results with our data, the relative energy levels of relevant excited states in such noninteracting solvents as Cy may be deduced as follows; $T_{n\pi^*} > T_2 > S_1$ for **2A** and $T_{n\pi^*} > S_1 \geqslant T_2$ for **1A**, **1B**, and **2B**. Thus, the temperature-independent ISC to T_2 occurs only in the latter cases, but the temperature-dependent ISC to $T_{n\pi^*}$ occurs commonly in both cases.

Nonradiative Decay Pathways in Alcohols. It is clear that the fluorescence of the acylanthracenes in alcohols is perturbed by the hydrogen-bond interaction with the solvent. The very low ϕ_T values in such powerful hydrogen-donating solvents as MeOH may be due to the fact that a solvent-induced internal conversion pathway replaces ISC as the major nonradiative decay pathway.[19] However, the anomaly of the fluorescence decay kinetics observed for **1B** and **2B** cannot be explained by this mechanism alone. An explanation is, however, given by the following reaction scheme:



where the k's are the rate constants, where B, $^1B^*$, and $^3B^*$ are the aromatic carbonyl compounds in the ground, excited singlet, and triplet states respectively, and where it is assumed that $^1B^*$ is reversibly converted into a nonfluorescent X. The identification of X remains ambiguous at this stage of our investigation. In this respect, it was suggested that the nonradiative decay due to intramolecular charge sepearation is responsible for the observed decrease in ϕ_f.[8] The decrease in the delocalization interaction between the anthryl and benzoyl moieties may be associated with a noncoplanar geometry between the anthryl and phenyl rings. If so, the torsional isomer appears a likely possible model for X.

The reaction scheme leads to the following equations;

$$C_1 = (\lambda_2 - Z)(C_1 + C_2)/(\lambda_2 - \lambda_1), \tag{3}$$

$$C_2 = (Z - \lambda_1)(C_1 + C_2)/(\lambda_2 - \lambda_1), \tag{4}$$

Table 4. Rate parameters for 2-benzoylanthracene

Solvents	$k_f/10^7\ s^{-1}$	$(k_f+k_{nr}+k_r)$ $/10^7\ s^{-1}$	$(k_{-r}+k_d)$ $/10^7\ s^{-1}$
t-BuOH	3.0	4.8	4.8
i-PrOH	3.2	6.2	5.4
EtOH	3.3	12	12
MeOH	2.1	24	6.6

$$Z = k_f + k_{nr} + k_r, \tag{5}$$

$$\lambda_1 + \lambda_2 = k_f + k_{nr} + k_r + k_{-r} + k_d, \tag{6}$$

$$\lambda_1\lambda_2 = (k_f + k_{nr})(k_{-r} + k_d) + k_r k_d. \tag{7}$$

In the photostationary state, ϕ_f is given in the form:

$$\phi_f = k_f\,(k_{-r} + k_d)/\lambda_1\lambda_2. \tag{8}$$

By using the values of C_j, λ_j, and ϕ_f observed experimentally, the values of $k_f+k_{nr}+k_r$, $k_{-r}+k_d$, and k_f can be evaluated from Eqs. 3 or 4, 6, and 8 respectively. The results for **2B** are listed in Table 4. It is noteworthy that the k_f values thus obtained are of a similar magnitude with those observed in polar aprotic solvents ($k_f \simeq 3\times10^7\ s^{-1}$). This result may support the validity of the reaction scheme postulated. It is observed that either k_{nr} or k_r, or both, increases in going from *t*-BuOH to MeOH, while the sum of k_{-r} and k_d is less variant. It appears likely that the nonradiative decay due to the solvent-induced geometry change as well as to the solvent-induced internal conversion is important for **1B** and **2B** in polar protic solvents.

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17) The reproducibility for the τ_f values of **1A** in Cy and DPE is doubtful, since they are very short. This may affect the reliability of the k_f and k_{nr} values. We believe, however, that the k_f values for these solvents are of the same magnitude as that of the k_f values for the other solvents.

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