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Polar Fluorescent State of 1- and 2-Acylanthracenes. II.[1] The Perturbation of Protic Solvents

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The steady-state and time-resolved fluorescence spectra were measured for protic solutions of 1- and 2-acetyl- or 1- and 2-benzoylanthracenes at various temperatures. It has been demonstrated that the perturbation of protic solvents on the fluorescence spectra is caused by a combination of the orientational dipolar solvent-solute relaxation and the hydrogen bond interaction. Based on the time-dependent spectral shift and the temperature dependence of fluorescence polarization observed for 2-acylanthracene, the relaxation process of the excited solute has been supposed to involve the level inversion of dual fluorescent states, which respond differently to the solvation of the system.

The solvent perturbation on the solute emission has been subject of continuing interest in recent years.[2] The solvent dipole-solute dipole interaction is very important in the excited-state relaxation of a fluorescent solute which is electronically neutral in the ground state, but it led to a highly polar state upon photoexcitation. This solvent relaxation process occurs on the nanosecond time scale subsequent to a rapid ($>10^{-12}$ s) vibrational relaxation from the excited Franck-Condon (F.C.) state to the excited equilibrium (e.q.) state. In a fluid solution in which the solvent relaxation is much faster than the fluorescence decay, the excited e.q. state is eventually stabilized by the orientational relaxation of the surrounding solvent molecules. The fluorecsence spectrum becomes diffuse and red-shifted as a result of solvent reorientation, where as the absorption spectrum remains unchanged. The more polar the solvent, the greater the stabilization energy, leading to the larger red shift of the fluorescence maximum. As the solvent-relaxation time increases, *e.g.*, in a viscous solution at a low temperature, the time-dependent spectral shift of the fluorescence associated with the solvent relaxation becomes experimentally observable, for which time-resolved emission spectroscopy is promising.[3]

Some anthracene derivatives are known to reveal the related spectral shift in polar solvents.[4-7] Very recently, we have studied the solvent dependence of the fluorescence spectra of 1- (**1a**) and 2-acetyl- (**2a**) or 1- (**1b**) and 2-benzoylanthracene (**2b**) in aprotic solvents.[1] The structured spectra in nonpolar solvents have been found to become structureless and red-shifted in solvents with a higher polarity than ethyl ether. This solvent dependence was consistent with the well-established mechanism which involves orientational dipolar solvent-solute interaction. The dipole moment of the excited state has been estimated to be about 10 D for the compounds examined.

We wish now to report the perturbation of protic solvents on the fluorescence of these compounds. The steady-state and time-resolved fluorescence measurements indicate that the compounds are subjected to hydrogen bonding with the solvents in addition to the general orientational relaxation. Of particular interest is the observation concerning the time-dependent spectral shift for 2-acylanthracenes (**2a** and **2b**), because there is not only a peak shift, but also a significant change in the spectral shape. This finding is discussed in terms of the level inversion of the dual fluorescent states, which consist of the lowest excited state perturbed by the hydrogen bond and the excited CT state.

Experimental

The acylanthracenes (**1** and **2**) were the same as those used before.[1] The hexane, 1-propanol, and propylene glycol were spectro- or GR-grade reagents and were used without further purification. The ethanol was dried by refluxing over calcium hydride and distilled fractionally.

The steady-state fluorescence measurements were made using a Hitachi MPF 2A spectrofluorometer. The excitation wavelength was 390 nm. The time-resolved fluorescence and lifetime measurements were done using an Ortec SP-3X nanosecond spectrometer. The photoexcitation was done by means of the 337-nm light supplied by a 0.5-atm air-saturated flash lamp through a Corning 7-60 filter. The bandwidth of the monitoring wavelength was 2 nm for the time-resolved measurements and 5 nm for the lifetime measurements. The outputs from a multichannel analyser were displayed on an X-Y plotter (Hewlett-Packard). The fluorescence lifetime was determined from the slope of the decay curve drawn. The sample solutions were deoxygenated by the flushing of argon gas for 10 min prior to measurements. The sample absorbance in a 1-cm square quartz cell was made *ca.* 0.1 at the excitation wavelength, an optical density corresponding to the concentration of the order of 10^{-5} mol dm^{-3}. The measurements for the temperature dependence were carried out with sample cells placed in a cryostat (Oxford DN-704) combined with a temperature controller (Oxford DTC-2). The degree of fluorescence polarization (P) was measured by the ordinary method using the linearly polarized exciting radiation.[8] Since the instrument responded differently to the light quanta of the two polarized components, correction was done for the polarized fluorescence intensities ($I_{\parallel}$ and $I_{\perp}$) by measuring the corresponding fluorescence intensities ($I'_{\parallel}$ and $I'_{\perp}$) for a horizontally polarized exciting radiation, which can be expected to be the same. The value of P was calculated from this equation:

$$P = \frac{I_{\parallel} - I_{\perp}(I'_{\parallel}/I'_{\perp})}{I_{\parallel} + I_{\perp}(I'_{\parallel}/I'_{\perp})}$$

Results and Discussion

Hydrogen-bond Contribution. The fluorescence maxima of 1- and 2-acylanthracenes (**1** and **2**) in protic solvents move to lower frequencies than ex-

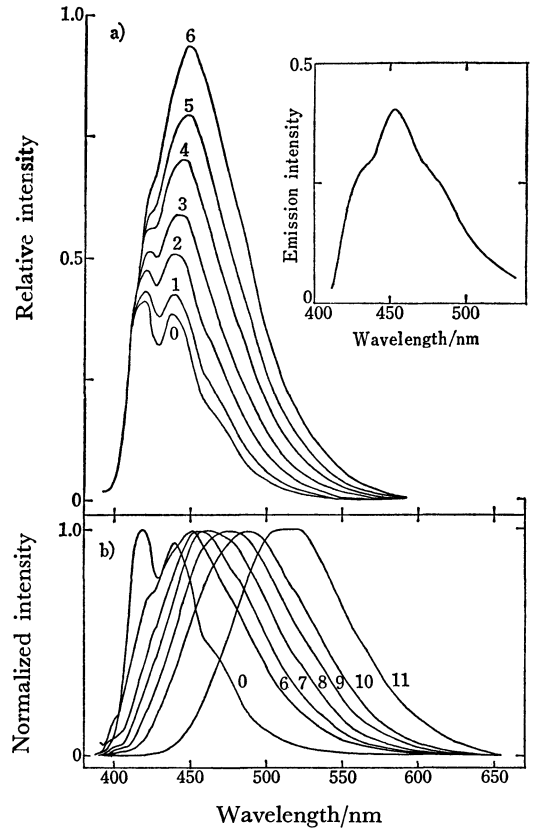


Fig. 1. Steady-state fluorescence spectra of 2-benzoylanthracene in hexane/1-propanol mixture. a) Normalized on the short wavelength side. Alcohol concentration: 0, pure hexane; 1, 0.013 mol dm^{-3}; 2, 0.027 mol dm^{-3}; 3, 0.04 mol dm^{-3}; 4, 0.054 mol dm^{-3}; 5, 0.067 mol dm^{-3}; 6, 0.081 mol dm^{-3}. Instert, hydrogen-bonded emission obtained by subtracting Spectrum 0 from Spectrum 4. b) Normalized at peak maxima. Alcohol concentration: 0, pure hexane; 6, 0.081 mol dm^{-3}; 7, 0.16 mol dm^{-3}; 8, 0.32 mol dm^{-3}; 9, 0.64 mol dm^{-3}; 10, 1.3 mol dm^{-3}; 11, pure 1-propanol.

pected from the properties of solvent polarity.[1] It appears probable that this extraordinary peak shift is attributable to hydrogen-bond formation, since these compounds have a carbonyl-type oxygen as a hydrogen-accepting site. Such protic solvent perturbation has been clearly demonstrated by the observation concerning the effect of very dilute concentrations of alcohols on the spectra of the compounds dissolved in a nonpolar solvent like hexane. As is shown in Fig. 1, the fluorescence spectra become structureless and red-shifted as the concentration of 1-propanol is increased. When perturbed by very small amounts of added alcohol (<0.01 M), which are insufficient to alter the absorption spectrum or the dielectric properties of the solvent, the spectrum does not only shift, but also broadens considerably (Fig. 1a). This suggests the appearance of new emission band(s). The emission spectra shown in Fig. 1a are normalized on the short-wavelength side, where the contribution of the new band is negligible. The subtraction of the unperturbed spectrum from the perturbed gives

Table 1. Peak positions of the fluorescence spectra of hydrogen-bonded 1- and 2-acylanthracenes

Compounds	λ_f/nm
1-Acetylanthracene (**1a**)	448
1-Benzoylanthracene (**1b**)	466
2-Acetylanthracene (**2a**)	420, 444
2-Benzoylanthracene (**2b**)	430, 454

rise to the emission band, presumably corresponding to a hydrogen-bonded species. The band peaks of all the compounds examined are listed in Table 1. On a further increase in the alcohol concentration, the fluorescence peak moves further to the red, the bandwidth remaining almost constant until the spectra coincide with that of the pure alcohol solution (Fig. 1b). This shift may be attributed to the general dipolar solvent-solute interaction. Thus, the protic solvent perturbation is due to a combination of the nonspecific dipolar and the specific hydrogen-bond interactions.

It can be noted that the hydrogen bond is facilitated in the excited state, because the photoexcitation leads to preferential electron migration from the anthryl group to the carbonyl group,[1] resulting in an increase in the carbonyl basity. Since the electron migration induces a resonance contribution to the π-electron conjugation of these two groups, a coplanar geometry of the molecular conformation is most likely to be attained, thus ensuring the delocalization of the π-electron.[9] The situation reported for methyl anthracenecarboxylate[6] is analogous to that in this study. It is of interest to mention the possibility of a change in geometry associated with photoexcitation, as was pointed out for methyl anthracenecarboxylate.[6] A difference in ground-state geometry appears among the three positional isomers of substituted anthracenes if the substituent lacks spherical or cylindrical symmetry.[10] Carbonyl-substituted anthracenes are just the same. It is known that the carbonyl group of the 9-isomer is perpendicularly torsional with respect to the plane of an anthryl ring because of the repulsive forces of two *peri*-hydrogen atoms.[10,11] Therefore, a significant geometry change is induced upon photoexcitation.[6a] On the other hand, the ground-state geometry of the 1- and 2-isomers stays rather coplanar because of these being less steric hindrance. This has been also confirmed for the compounds concerned by IR and UV absorption measurements. The carbonyl-stretching frequencies for **1a** and **2a** in $CHCl_3$ are 1675 cm^{-1} and 1678 cm^{-1} respectively, whereas the frequency for the 9-isomer is 1693 cm^{-1}. The lesser double-bond character of the carbonyl bond for the former compounds is consistent with a coplanar geometry.[10] The UV measurement indicates that all the acylanthracenes except the 9-isomer exhibit a fundamentally different spectrum from that of the parent substance, anthracene.[1] The observed spectral deformation can be explained as being due to an effective resonance contribution, which may lead to the same conclusion with respect to the ground-state geometry. In conclusion, the geometry change can be regarded as less

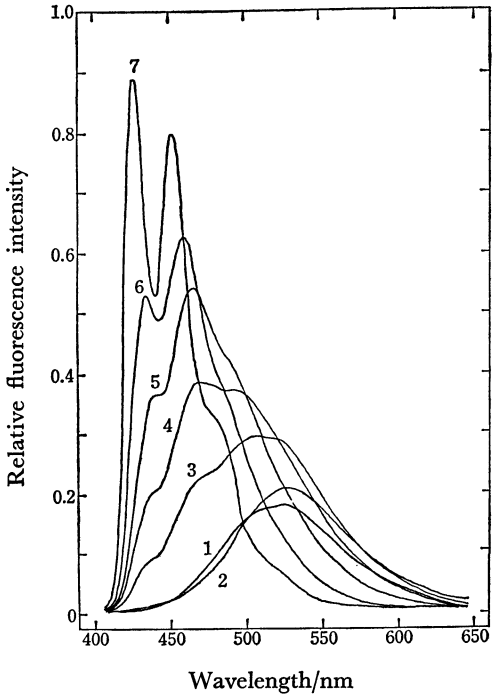


Fig. 2. Steady-state fluorescence spectra of 2-benzoylanthracene in ethanol. Temperature; 1, 20 °C; 2, −78 °C; 3, −117 °C; 4, −125 °C; 5, −135 °C; 6, −145 °C; 7, −175 °C.

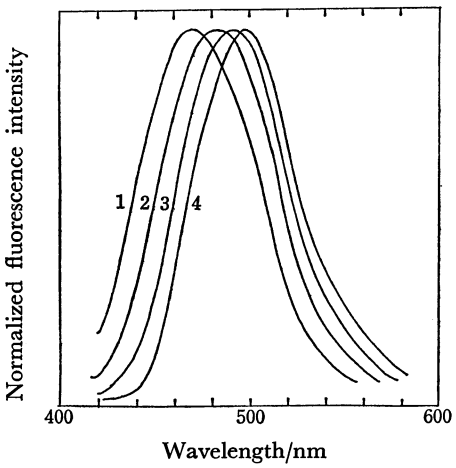


Fig. 3. Time-resolved fluorescence spectra of 1-benzoylanthracene in propylene glycol at −100 °C. 1, 5 ns; 2, 15 ns; 3, 20 ns; 4, 50 ns.

important in the cases we are studying than in the cases of methyl 1- and 2-anthracenecarboxylates.[6b]

Temperature and Time-dependent Spectral Shifts. The steady-state fluorescence spectra of **2b** in ethanol at various temperatures are shown in Fig. 2. At room temperature the spectrum is structureless and largely red-shifted, arising from a fully relaxed e.q. state. As the temperature is lowered, the spectra move to the blue and develop some structure, with a gradual increase in the emission intensity. At 77 K the spectrum is the same in both shape and peak position as that in a nonpolar solvent. No phosphorescence could be detected. The spectra of the other compounds (**1a**, **1b**, and **2a**) reveal a similar temperature dependence. In contrast with the emissive behavior, the absorption spectra show no corresponding change, except for the sharpening and slight intensifying of the bands at lower temperatures. The absence of the isoemissive point supports the view that the temperature-dependent spectral shift is due to solvent reorientation around the excited solute which is subjected to a hydrogen bond.

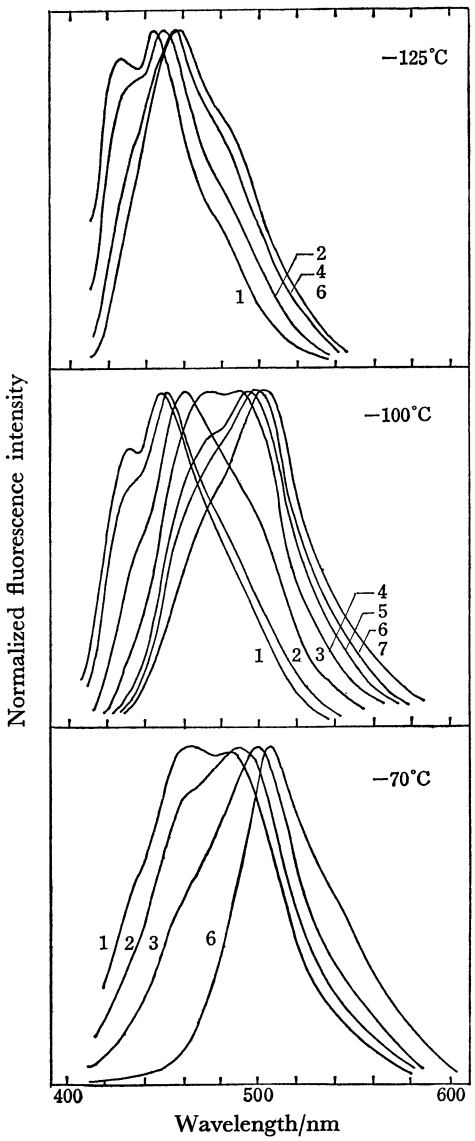


Fig. 4. Time-resolved fluorescence spectra of 2-benzoylanthracene in propylene glycol at the temperature indicated. 1, 5 ns; 2, 15 ns; 3, 20 ns; 4, 30 ns; 5, 40 ns; 6, 50 ns; 7, 70 ns.

The temperature-dependent spectral shift is, in fact, associated with the time-dependent spectral shift. The time dependence of the spectra is very intimate for each family of **1** or **2**. Some typical results for **1b** and **2b** in 1-propanol are shown in Figs. 3 and 4 respectively. Each spectrum is given at each delay time after the onset of a nanosecond flash lamp. The time-dependent spectral shifts amount to several tens of nanometers at −70 °C——100 °C. In this temperature range, the dielectric relaxation time of the solvent (τ_ρ=2.0—47×10^{-8} s[12]) is comparable in

order of magnitude to the fluorescence lifetime of $\tau_f \simeq 10^{-8}$ s. The wavelength span in which the spectra shift decreases on either further lowering or raising of the temperature, since the dielectric relaxation time becomes far from the fluorescence lifetime. At extreme temperatures, such as room temperature or 77 K, where the solvent relaxation is complete or totally inhibited, the spectrum is practically time-independent.

The wavelength region over which the spectral shift is observed moves to the blue with a decrease in the temperature. The extrapolation of the peak shift found at −125 °C to zero time provides the peak maxima of 450 nm for **1b** and 445 nm for **2b**. Although the dielectric relaxation at this temperature ($\tau_\rho \simeq 2 \times 10^{-5}$ s[12]) is much slower than the fluorescence decay, these peak positions lie about 20 nm to the red relative to the positions of the spectra at 77 K, which correspond nearly to the F.C. solvent configuration. This suggests that, even at −125 °C, the appreciable subnanosecond relaxation occurs. From the close resemblances of the zero-time spectra with the hydrogen perturbed spectra (Fig. 1a), it is clear that the hydrogen-bond interaction is responsible for this rapid relaxation.

The observed time-dependent spectral shifts are in many respects analogous for the systems of **1** and **2**. However, the difference between them is apparent at a glance in Figs. 3 and 4. While the spectra observed for **1b** retain, to a good approximation, their band width and shape during the progress of the peak shift (Fig. 3), it is striking that the spectra observed for **2b** exhibit a significant change in their structure (Fig. 4). In the latter case, there are at least two emissions with different solvent configurations. At −100 °C both emission spectra are observable: the one arises in the early stage of the delay time, and the other, in the later stage. The conversion of these two emissions occurs at an intermediate delay time of 30 ns. Each spectrum can be separately measured when the temperature is varied. At −125 °C only the early stage emission is predominant; it is attributed to the hydrogen bonded species. On the contrary, at −70 °C the later stage emission prevails, and it approaches the room-temperature spectrum. This temporal variation in the fluorescence spectra is very interesting, because it gives direct evidence of the solvent-induced change in the excited electronic structure.

At temperatures where there are time-dependent spectral shifts, the fluorescence lifetime is dependent on the excitation wavelength. For the system of 1-benzoylanthracene–propanol, which shows a continuous time-dependent spectral shift, the kinetics of the wavelength-dependent decay can be explained by the Bakhshiev formulation.[13] If the fluorescence quantum yield and the transition probability are time-independent, the decay law which describes the continuous orientational dipolar solvent-solute relaxation can be written as

$$I(\tilde{\nu}, t) = \text{const} \cdot \exp(-t/\lambda) \cdot f(\tilde{\nu}, t), \quad (1)$$

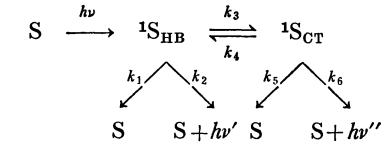
where $\exp(-t/\lambda)$ is a damping function which defines the electronic relaxation of the system and where $f(\tilde{\nu}, t)$ represents the effects of the time-dependent spectral shifts on the observed fluorescence decay. $f(\tilde{\nu}, t)$ can be estimated at a given wavelength from the normalized time-resolved spectra. The calculation of the decay time associated with $I(\tilde{\nu}, t)$ can be made assuming an appropriate value for λ. The values calculated for **1b** at various wavelengths are listed in Table 2. The agreement between the measured and calculated values is gratifying.

TABLE 2. OBSERVED AND CALCULATED FLUORESCENCE DECAY TIMES FOR 1-BENZOYLANTHRACENE IN PROPYLENE GLYCOL AT −100 °C, TAKING $\lambda = 10$ ns

Wavelength/nm	$\tau_{f,\,obsd}$/ns	$\tau_{f,\,calcd}$/ns
440	4.4	4.6
460	7.5	7.1
480	9.9	9.6
500	11	10
520	11	11
540	12	11

Excited-state Level Inversion. The temporal variation in the fluorescence spectra found for the 2-benzoylanthracene-propanol system indicates that this system involves at least two fluorescent species which are chemically the same, but electronically different. The acylanthracenes may be viewed as forming an intramolecular donor–acceptor system in which the anthryl group is a donor, and the carbonyl group, an acceptor. A previous study of the solvent dependence of the fluorescence suggests that the excited state in highly polar solvents has a character of charge transfer.[1] Consequently, the appearance of the two emissions may be interpreted in terms of two excited states, $^1S_{HB}$ (the lowest excited state perturbed by the hydrogen bond) and $^1S_{CT}$ (the excited CT state), which respond differently to the solvent relaxation. The conversion of $^1S_{HB}$ to $^1S_{CT}$ is an intramolecular electron-transfer reaction.

These considerations are summarized in the following reaction scheme:



The transient populations of $^1S_{HB}$ and $^1S_{CT}$ are given by the following equations:[3]

$$[^1S_{HB}] = C_1 \exp(-t/\lambda_1) + C_2 \exp(-t/\lambda_2), \quad (2)$$

$$[^1S_{CT}] = C_3\{\exp(-t/\lambda_1) - \exp(-t/\lambda_2)\}, \quad (3)$$

where

$$1/\lambda_1,\ 1/\lambda_2 = (1/2)[k_1+k_2+k_3+k_4+k_5+k_6 \mp \{(k_1+k_2+k_3-k_4-k_5-k_6)^2+4k_3k_4\}^{1/2}].$$

It is of interest to examine whether or not this reaction scheme is consistent with the wavelength-dependent kinetic behavior measured for the 2-benzoylanthracene–propanol system. In this respect, it was confirmed that the decay law of Eq. 1 in itself was no longer applicable to the observed time-dependent spectral

Table 3. Observed and calculated fluorescence decay times for 2-benzoylanthracene in propylene glycol at −100 °C, taking $\lambda_1=15$ ns and $\lambda_2=12$ ns

Wavelength/nm	$\tau_{f,obsd}$/ns	$\tau_{f,calcd}$/ns	
		$^1S_{HB}$	$^1S_{CT}$
430	5.6	5.6	
440	7.4	7.5	
460	11	10	
480	13	11	16
500	16	13	17
520	18		19
540	20		21
560	22		23

change (Fig. 4), apparently indicating that the fluorescence lifetime and/or the transition probability is time-dependent. We have analyzed the experimental results in ways similar to those presented above, but on the assumption that the damping function in Eq. 1 is biexponential, as is presented in Eq. 2 or 3. Since it was difficult to measure the rise in the curve of the $^1S_{CT}$ fluorescence, the calculation for this fluorescence has been done only for the decay time. We have also assumed, for the sake of simplicity, that the conversion of the two excited states is irreversible, *i.e.*, $k_3 \gg k_4 \simeq 0$, and therefore, $[^1S_{HB}]$ is represented only by the second term of Eq. 2. Table 3 shows the values calculated at various wavelengths, taking $\lambda_1=15$ ns and $\lambda_2=12$ ns together with the measured values. While it is to be expected that the calculated value deviates from the measured value in the wavelength region where the two emission spectra are greatly overlapping, these two values agree to a good precision at the other wavelengths. This supports the validity of the reaction scheme postulated.

Since the level inversion involves a change in the dipole moment, the photoselection technique is helpful to characterize the phenomenon. On the basis of this technique, Suzuki and his coworkers have extensively investigated the fluorescence level inversion of the dual fluorescence for indole and such 1-naphthyl derivatives as hydroxyl, cyano, or amino.[14] Similarly, we have measured the degree of the fluorescence polarization (P) for the compounds of **1** and **2** at various temperatures. In Fig. 5, the excitation polarization spectra for **1a** and **2a** in an ethanol glass at 77 K are compared with those in glycerol at room temperature. In the case of **1a**, the general shapes of the polarization spectra for the two temperatures are substantially the same, though the absolute value of P in ethanol at 77 K is larger than that in glycerol at room temperature. The increase in P at low temperatures is due to the depletion of the rotational depolarization, as is to be expected from the solvent viscosity. On the other hand, the two polarization spectra for **2a** are significantly different. It is noted that, while the spectra in the long wavelength region (>340 nm) have the ordinary temperature effect, the effect occurs in the opposite direction at the shorter wavelengths.

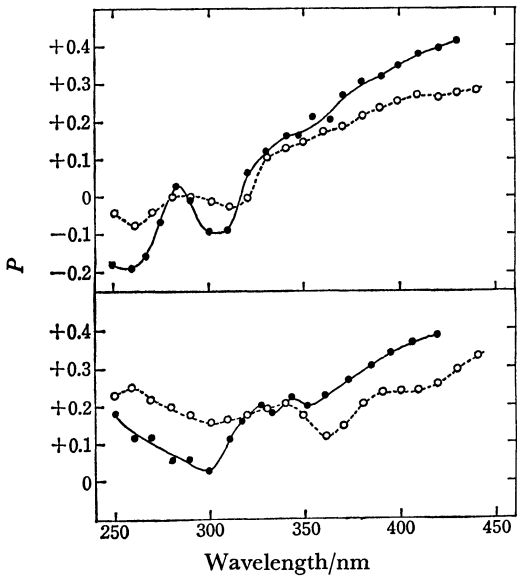


Fig. 5. Fluorescence excitation polarization spectra of 1-acetylanthracene (upper) and 2-acetlyanthracene (lower) in glycerol at 20 °C monitored at 510 nm (open circle) or in ethanol at 77 K monitored at 450 nm (closed circle).

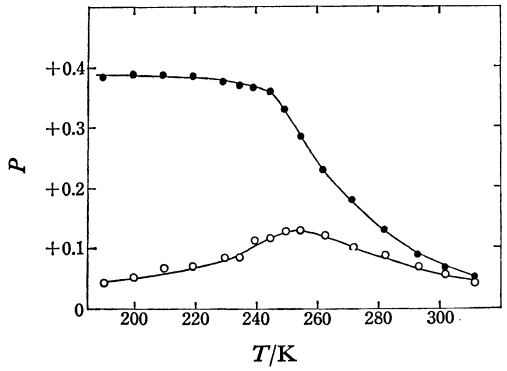


Fig. 6. Temperature dependence of the degree of fluorescence polarization of 2-acetylanthracene in propylene glycol monitored at 440 nm. The excitation wavelength was 400 nm (closed circle) and 300 nm (open circle).

The anomaly of the temperature effect is further evident from the measurement of P in propylene glycol by varying the temperature from 300 K to 200 K. As is shown in Fig. 6, when excited at 300 nm, the value of P first increases with a decrease in the temperature, reaching its maximum at about 250 K. On a further lowering in the temperature, though, it in turn decreases. This temperature dependence of P is in contrast with that for the excitation at a long wavelength, *e.g.*, 400 nm, which indicates a plateau in the values of P below 250 K. The decrease in P at low temperatures is characteristic of fluorescence-level inversion.[14]

There is an intense band near 300 nm in the absorption spectra of **2**. Since no corresponding band is present in the spectrum of the parent anthracene, this band may be identified as a CT transition band. However, it is reasonable that this CT band is too

high in energy to be ascribed to the emissive state in highly polar solvents at room temperature. An alternative band responsible for the polar fluorescence may subside in the longer-wavelength bands.

As has been demonstrated above, the temperature- and time-dependent spectral changes observed for **2** in protic solvents are partly due to the level inversion of dual fluorescence arising from the lowest excited singlet and excited CT states. Although the spectral shifts observed for **1** conform to a relaxation mechanism which involves the continuous orientational dipolar solvent-solute interaction, the possibility of a level inversion can not be excluded at this stage of the investigation. If the relevant energy levels are closely related, it appears unlikely that a drastic change in the fluorescence spectra is necessarily required.

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