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Temperature Effects on the Electronic Spectra of 2-Methyl-1-aceanthrenone

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The absorption, fluorescence, and excitation spectra of 2-methyl-1-aceanthrenone (I) were investigated in several solvents in the temperature range of 77—298 K. The results show that the hydrogen-bonded (fluorescent) and non-hydrogen-bonded (very weakly fluorescent) molecules of I coexist in ethanol to a comparable extent. This is the reason why its absorption spectra are very broad in alcoholic solvents. With a decrease in the temperature, the apparent fluorescence quantum yield in ethanol at first rises to a maximum (0.37) at 197 K and then decreases. Below *ca.* 113 K, a new fluorescence band due to the non-hydrogen-bonded molecule appears. In 2-methyltetrahydrofuran (MTHF), the temperature dependence of the fluorescence quantum yield of I is significant only at low temperatures. The yield varies monotonously from 0.014 at 132 K to 0.30 at 77 K. A behavior intermediate between those in ethanol and in MTHF is observed in EPA. The rise and fall of the fluorescence quantum yield in ethanol or in EPA may be interpreted in terms of the temperature-dependent concentration change in the hydrogen-bonded molecule. From the results in MTHF, the maximum rate constant of the intersystem crossing between the $S_{1\pi\pi^*}$ and $T_{n\pi^*}$ states is estimated to be of the order of 10^{13} s^{-1}.

The way to interprete the electronic spectra of 9-anthracenecarboxaldehyde (9-CHO-A), which is distinguished from the other 9-carbonyl derivatives of anthracene by its high photochemical reactivity, is not unique,[1,2] because the diffuse nature of the electronic spectra makes impossible any accurate location of electronic states. This ambiguity has often led to very different interpretations of experimental results.[3–5] Recently, however, the present author has noted that a comparison of the electronic spectra of 9-CHO-A with those of 2-methyl-1-aceanthrenone (I), which is very similar in molecular structure to 9-CHO-A but which shows well-defined electronic spectra in all of the non-hydrogen-bonded, hydrogen-bonded, and cation forms, has made it possible to elucidate the electronic nature of the excited states of 9-CHO-A.[6]

Although such a comparison is successful in some points, as has previously shown,[6] the spectroscopic data on I and 9-CHO-A have never been adequate enough. In this paper, therefore, prominent, newly found temperature effects on the electronic spectra and the fluorescence quantum yields of I will be reported. The results obtained will not only confirm the author's earlier interpretation as to the electronic nature of the excited states of 9-CHO-A and I,[6] but will also add important experimental facts on the radiationless transition processes of 9-carbonylanthracenes.[6–11] Furthermore, compound I may be expected to serve as a model compound in interpreting unestablished spectroscopic properties of the compounds whose carbonyl groups are co-planar or almost coplanar with the parent aromatic rings.[12] For instance, the present results will point out, as may be seen below, that the interpretation of the spectroscopic properties of pyrene-3-aldehyde (3-CHO-P) and 9-CHO-A given by Förster *et al.*[1] should be re-examined.

Experimental

Materials. Compound I, obtained as one of the main photo-products of 9-α-bromopropionylanthracene,[9] was purified by column chromatography and was then sublimated twice *in vacuo.* The 9-methylanthracene (9-Me-A) was synthesized according to the well-known method[13] and recrystallized from ethanol. The 9,10-diphenylanthracene (9,10-diph-A) was obtained from the Nakarai Chem. Co., Ltd., and was used as received.

Among the solvents employed for the spectroscopic measurements, *n*-hexane and ethanol were of a spectro grade. Acetonitrile (ACN), dimethylformamide (DMF), 2-methyltetrahydrofuran (MTHF), methylenedichloride (MDC), triethylamine (TEA), isopentane (IP), methylcyclohexane (MCH), and diethyl ether were of a guaranteed grade from the Nakarai Chem. Co., Ltd., and were distilled carefully before use.

Optical Measurements. The absorption spectra were taken on a Hitachi Dual-Beam Spectrophotometer 124. For low temperature measurements, a rectangular quartz cell (1×1×5 cm, with a glass pipe 30 cm long attached on the top of the cell to facilitate handling and evacuation), each corner of which was well-fused in order to avoid cracking due to sudden cooling or warming, was held by a block made of brass, and the whole was put into a transparent Dewar vessel. The same type of cell and Dewar vessel as described above was used as a reference-cell combination. Only the sample-cell combination was cooled.

The excitation and fluorescence spectra were recorded on a Shimadzu Corrected Spectrofluorophotometer, RF 502, whose spectral characteristics have been described elsewhere.[6] For measurements at low temperatures, a Dewar vessel and a sample cell described previously[6] were employed. Correction for the spectral response of its particular cell arrangement was carried out by using a quinine bisulfate solution (5×10^{-5} M in 0.5 M sulfuric acid[14]) and an ethanol solution of anthracene as standard solutions for the fluorescence and excitation spectral measurements respectively.

In every case, the temperature of the sample was controlled by boiling liquid nitrogen using a power resister and allowing cold nitrogen gas to enter the Dewar vessel. The temperature was monitored through a thermocouple immersed in the sample cell and was recorded on a Yokogawa recorder, Type 3046. After thermal equilibrium had been reached, all the measurements were performed.

Determination of the Fluorescence Quantum Yields. In order to determine the fluorescence quantum yields as a function of the temperature, it is necessary to correct for the absorbance change with the temperature, so the absorption spectra of I were measured in MTHF, ethanol, and EPA (ether, isopentane and ethanol 5 : 5 : 2 by volume) at various temperatures. Thus, a calibration curve of the absorbance change as a function of the temperature was obtained for each solvent. A similar correction was made at 77 K for 9-Me-A,[15] which was used as a fluorescence-quantum-yield standard of the unit yield at 77 K. The excitation of the fluorescence was performed at the 0–0 band of the $^{1}\mathrm{L}_{\mathrm{b}}\leftarrow{}^{1}\mathrm{A}$ transition of I[6] (370 nm, band pass, 5 nm), since this band showed little spectral shift upon a decrease in the temperature.

A comparison of the areas of the corrected fluorescence spectra of I taken at various temperatures with that of 9-Me-A obtained at 77 K gave the relative fluorescence quantum yields of I at the corresponding temperatures. In correcting the relative fluorescence quantum yield, allowance was not made for variation in the refractive indices of the solvents with the temperature, since appropriate data were not available.

The relative fluorescence quantum yields of I in various solvents at room temperature were determined in a similar manner except that 9,10-diph-A was used as the fluorescence quantum-yield standard of the unit yield.[15] The change in the refractive index with the solvent was taken into account in this case.[17]

Since oxygen did not affect the present results, all these experiments were carried out without degassing. The fluorescence intensity was always measured in a dilute solution (2—3×10^{-5} M).

Results

Figure 1 shows the temperature dependence of the absorption spectra of I in ethanol. A small peak at 418 nm seen at room temperature gradually sharpened as the temperature was decreased and eventually became the main absorption band, with a peak at 425 nm at 77 K. Corresponding to this, a shoulder at 425 nm at room temperature came to form a small but clearly resolved band with a peak at 433 nm. The position of the latter band agreed approximately with the 0–0 absorption band observed for the hydrogen-bonded molecule of I formed in *n*-hexane containing a small amount of trichloroacetic acid (abbreviated as IH hereafter).[6]

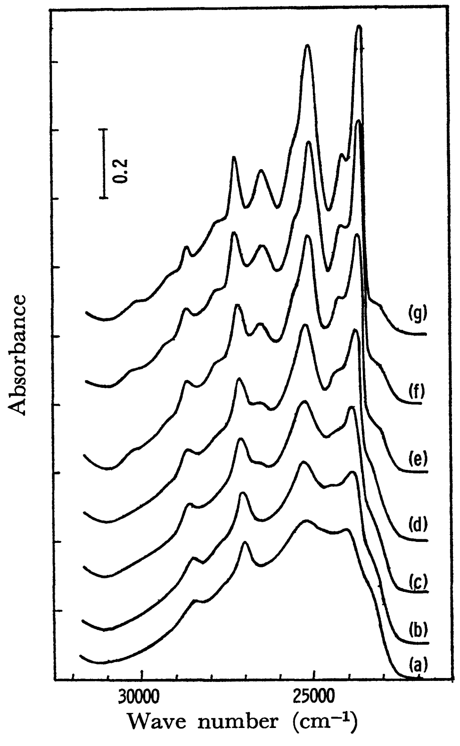

Fig. 1. Temperature effect on the absorption spectra of I (6.0×10^{-5} M) in ethanol.
(a) 290 K, (b) 250 K, (c) 233 K, (d) 190 K, (e) 160 K, (f) 125 K, (g) 77 K.
For the sake of clarity, the base line (right-hand side) of each spectrum is shifted by an appropriate amount of absorbance. The small peaks at 433 nm seen clearly in (e)—(g) are due to the hydrogen-bonded molecule of I. The decrease in the absorbance at 433 nm with a decrease in the temperature can be verified by a comparison of (d)—(g).

In non-polar solvents, such as MCH or IP, and aprotic polar solvents, such as MTHF, however, no peak corresponding to the one at 433 nm was found at any temperature. Consequently, the small absorption peak at 433 nm found in ethanol at low temperatures can be attributed to a hydrogen-bonded molecule.

From the (g) spectrum, approximately 5—10% of I is seen to exist in a hydrogen-bonded form, even at 77 K, if the hydrogen-bonded molecule of I in ethanol is assumed to have a molar extinction coefficient of a magnitude similar to that of IH.

Figure 2 shows the effect of the temperature on the fluorescence spectra of I in ethanol. At first the spectrum was diffuse, but it gradually became structured with a decrease in the temperature. At tem-

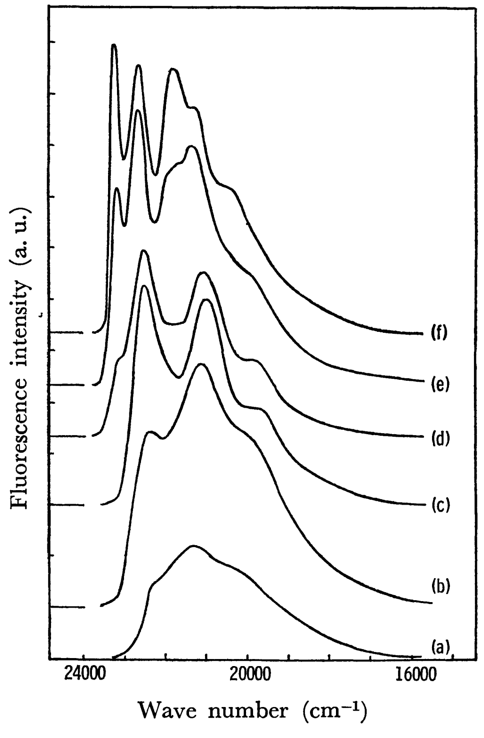

Fig. 2. Temperature effect on the fluorescence spectra of I (*ca.* 3×10^{-5} M) in ethanol.
(a) 256 K, (b) 185 K, (c) 134 K, (d) 103 K, (e) 89 K, (f) 77 K.
The excitation wavelength was 370 nm (band pass, 5 nm). The base line of emission intensity for each spectrum is shown by the solid line on the left-hand side. The fluorescence intensity of each spectrum is not parallel with the fluorescence quantum yield (for the exact value, see Fig. 5). Below *ca.* 110 K a new fluorescence band due to the non-hydrogen-bonded molecule appears on the shorter-wavelength side.

peratures near 134 K, the observed fluorescence spectrum closely resembles that of IH observed at room temperature.[6] It should be noted that the temperature effect on the shift of the fluorescence 0–0 band frequency (or the fluorescence-maximum frequency) is relatively small, reflecting a rigid molecular structure of I.[1] At temperatures below *ca.* 110 K, a new fluorescence band began to grow on the shorter-wavelength side; at 77 K this band surpassed the band at the longer wavelength.

The excitation spectra of the fluorescence of I in ethanol were also observed under similar conditions; the results are displayed in Fig. 3. In comparison with the absorption spectra shown in Fig. 1, it is quite evident that the main absorbing species is not the emitting species. The excitation spectra at low temperatures above *ca.* 110 K agreed well with those of IH, indicating that fluorescence is emitted by the hydrogen-bonded molecule. Below *ca.* 100 K, however, the excitation spectra changed significantly with the wavelength where fluorescence is observed, since, at these temperatures, two kinds of fluorescence are observable with a comparable intensity.

In Fig. 4 the fluorescence spectra of I in MTHF at low temperatures are shown. Contrary to the case in ethanol, the fluorescence spectrum in MTHF consists of only one component, which corresponds well to the component observed on the shorter-wavelength side in ethanol at very low temperatures. Evidently, the fluorescence observed in MTHF is due to a non-hydrogen-bonded molecule of I, so, of the two fluorescence components in ethanol, the one on the shorter-wavelength side can be attributed to the non-hydrogen-bonded molecule.

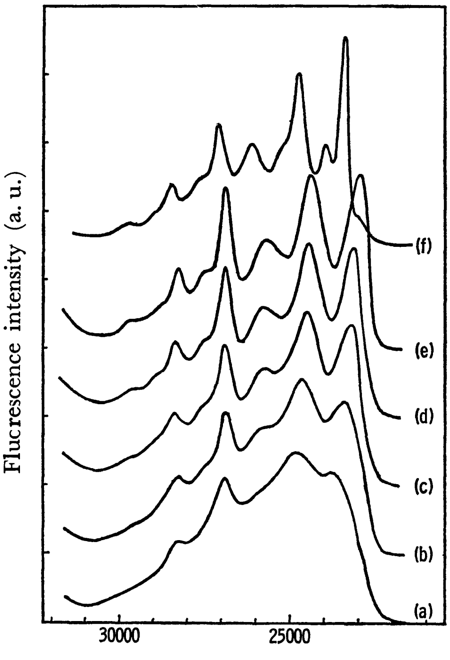

Fig. 3. Temperature effect on the excitation spectra of I (*ca.* 3×10^{-5} M) in ethanol.
(a) 290 K, (b) 236 K, (c) 185 K, (d) 148 K, (e) 106 K, (f) 77 K.
The fluorescence intensity was observed at 470 nm (the approximate fluorescence maximum of the hydrogen-bonded molecule of I) except in the case of (f), where the measurement was made at 460 nm (the approximate fluorescence maximum of the non-hydrogen-bonded molecule of I). In comparison with Fig. 1, it is evident that, except for 77 K, the excitation spectra do not accord with the absorption spectra. The coincidence of the spectra at 77 K is fortuitous.

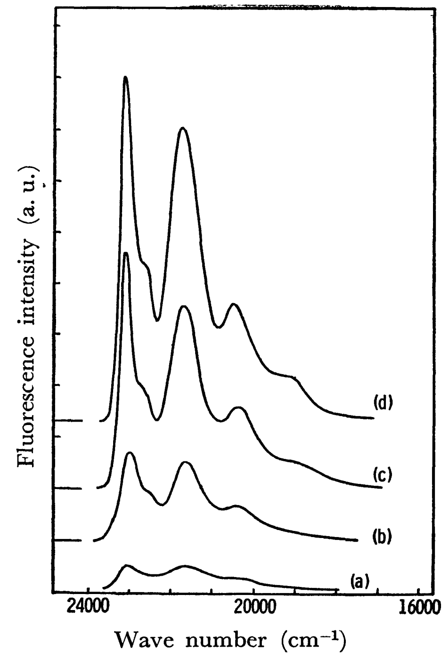

Fig. 4. Temperature effect on the fluorescence spectra of I (*ca.* 2×10^{-5} M) in MTHF.
(a) 128 K, (b) 111 K, (c) 98 K, (d) 92 K.
The excitation wavelength was 370 nm (band pass, 5 nm). The base line of the emission intensity for each spectrum is shown by the solid line on the left-hand side. The fluorescence intensity is not parallel with the fluorescence quantum yield (for the exact value, see Fig. 5). Below 92 K the fluorescence spectra are almost the same in shape.

In non-polar solvents such as MCH and IP, only a very weak fluorescence was observed. The fluorescence spectra in these solvents at 77 K were unresolved and shifted greatly to the red (λ_{max}=480 nm). In a frozen matrix of these solvents, diffuse emission spectra are frequently observed, probably because either of educed microcrystals or aggregated molecules of solutes. However, the absorption spectra of I observed in a mixed solvent of MCH and IP (3 : 1 by volume, abbreviated as MCHIP) down to temperatures as low as 77 K revealed that, at such a low concentration ($2-3\times10^{-5}$ M) as was used for the fluorescence measurements, the eduction of the solute was minute; hence, most of the solute must be dissolved homogeneously. Therefore, it may be presumed that the red-shifted weak emission observed in MCH or IP is due to educed microcrystals and that the temperature effect on the fluorescence yield of I is not appreciable in these non-polar solvents. The reason for this will be considered in a later section.

In Fig. 5 the temperature dependences of the fluores-

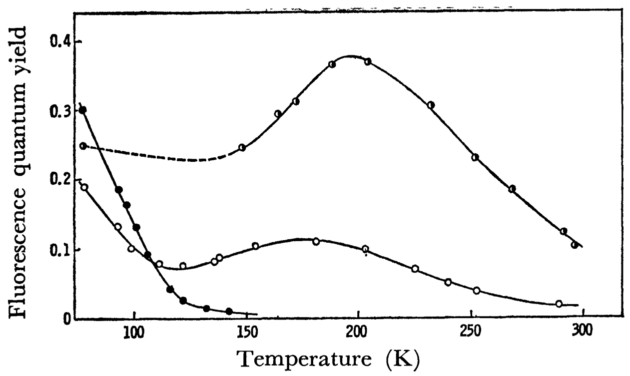

Fig. 5. Temperature dependence of the fluorescence quantum yields of I in ethanol, EPA, and MTHF. —◑—: ethanol, —○—: EPA, —●—: MTHF. Between 150 and 77 K a precise determination of the quantum yields in ethanol was difficult because of its unhomogeneous glassing.

cence yields of I in three media are depicted. In ethanol and EPA, the hydrogen-bonded and non-hydrogen-bonded molecules should coexist, so the obtained fluorescence yields in these media are sums of the apparent fluorescence yields from the two species. In MTHF, only at very low temperatures, the fluorescence became appreciable and the fluorescence quantum yield increased monotonously with a decrease in the temperature.

The behavior seen in EPA is intermediate between those in ethanol and in MTHF. The once-decreased fluorescence quantum yield begins rapidly to increase again near 113 K. Below this temperature, there was almost no fluorescence exhibited by the hydrogen-bonded molecule, and at 77 K no evidence for the existence of the hydrogen-bonded molecule was found in any of the absorption, excitation, and fluorescence spectra. Hence, the second increase in the apparent yield is attributable to the increase in the fluorescence quantum yield of the non-hydrogen-bonded molecule. This difference in temperature dependence between that in ethanol and that in EPA seems to reflect a difference in the hydrogen-bonding ability of these media toward I at low temperatures.

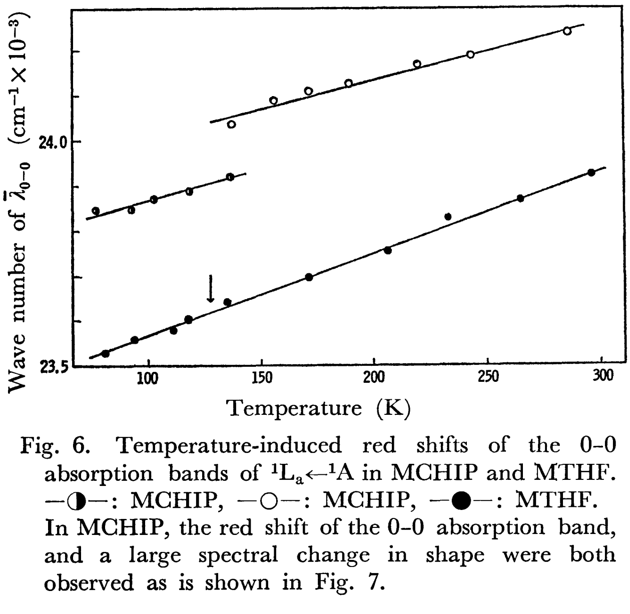

Fig. 6. Temperature-induced red shifts of the 0-0 absorption bands of $^1L_a \leftarrow {}^1A$ in MCHIP and MTHF. —◑—: MCHIP, —○—: MCHIP, —●—: MTHF. In MCHIP, the red shift of the 0-0 absorption band, and a large spectral change in shape were both observed as is shown in Fig. 7.

In Fig. 6 the frequencies of the 0–0 bands of the $^1L_a \leftarrow {}^1A$ transition observed in MTHF and MCHIP are plotted against the temperature. The red shift in MTHF is monotonous. In MCHIP not only the red shift but also the inversion of the absorption intensity was observed, as is represented in Fig. 7. As the temperature was lowered, a new band appeared on the longer-wavelength side of the band which was temporarily assigned as a 0–0 band at room temperature. A further decrease in the temperature inverted the absorption intensities of these two bands. In Fig. 6, therefore, the two frequencies of these two bands are plotted against the temperature. In either case, however, the magnitude of the red shift observed on cooling to 77 K is greater in MTHF than in MCHIP. Moreover, the value of $\bar{\lambda}_{0-0}$ in MTHF at the temperature where the fluorescence quantum yield of I begins to increase (indicated by the arrow in Fig. 6) is still smaller than the smallest $\bar{\lambda}_{0-0}$ (at 77 K) in MCHIP. These two facts are worth mentioning when we note that the lowering of the excited singlet-state energy is

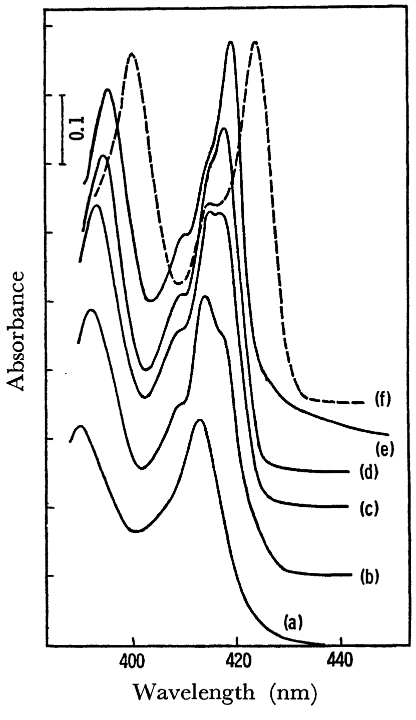

Fig. 7. Temperature effect on the absorption spectra of I (3.3×10^{-5} M) in MCHIP.
(a) 286 K, (b) 188 K, (c) 156 K, (d) 138 K, (e) 77 K, (f) 77 K (in EPA).
For the sake of clarity, the base line of each spectrum is shifted by an appropriate amount of absorbance. For comparison, the absorption spectrum in EPA (the broken line) is also shown. The broad tail seen for (e) is indicative of the existence of the educed microcrystals of I, which may be responsible for a broad weak fluorescence in this medium at 77 K. The other vibrational bands which belong to the ^1L_a or ^1L_b band did not show any marked change in shape as the temperature is lowered.

TABLE 1. FLUORESCENCE QUANTUM YIELDS OF I IN VARIOUS SOLVENTS

Solvent	Quantum yield[a]	Fluorescence maximum[b] ($10^{-3}\times$cm^{-1})
n-Hexane	<0.002	22.22
TEA	<0.002[c]	—
MDC	0.016	21.65
MTHF	0.006 (0.30)[d]	21.88
DMF	0.011	21.60
ACN	0.016	21.74
EPA	0.017 (0.19)[d]	21.65
Ethanol	0.12 (0.25)[d]	21.37
n-Hexane + a small amount of trichloroacetic acid	0.78[e]	21.28[e]

a) Values at *ca.* 18 °C with reference to 9,10-diph-A. For further details, see text. b) Data on the absorption spectra of I are given in Ref. 6. c) A strong fluorescence similar to the one in MTHF at 77 K was also observed in this solvent at 77 K. The 0–0 absorption band shifted much more to the red, compared with those in the other non-polar solvents. d) The quantum yields at 77 K, with reference to 9-Me-A. e) The values for IH.

indispensable for the appearance of the strong fluorescence of I, as will be discussed later.

Relative fluorescence quantum yields of I obtained in various solvents at room temperature are collected in Table 1. It is evident from Table 1 tends to show fluorescence activation.[1)] The comparatively high fluorescence quantum yield in ethanol is due to the coexisting hydrogen-bonded molecule.

Discussion

Temperature Effects on the Electronic Spectra. As is shown in Fig. 1, it is evident that, in ethanol at least, two forms of I, *i.e.*, the hydrogen-bonded and the non-hydrogen-bonded molecules, exist to a comparable extent. Thus, the present author's earlier supposition[6)] that the diffuse absorption spectra of I in ethanol and acetic acid must be partly due to the coexistence of the two species has been confirmed experimentally. It is the rigid molecular structure of I that makes such experimental confirmation feasible.

In contrast to the rather rapid sharpening in the shape of the absorption and excitation spectra, the fluorescence spectra become structured less rapidly with a decrease in the temperature. On the other hand, the fluorescence spectra of IH are considerably structured, even at room temperature. From these facts, it may be inferred that the hydrogen-bonded molecule of I in ethanol does not have a definite composition and structure, but rather a loose structure composed of several solvent molecules which may be deformable upon photo-excitation.[18)] Such a structure is appropriate to explain the absence of the hydrogen-bonded molecule in EPA at 77 K, in contrast to the case in ethanol.

The temperature effect on the absorption spectra of I in non-hydrogen-atom-donating polar solvents is merely a red shift. The magnitude of the red shift of I in MTHF between room temperature and 77 K (400 cm^{-1}) is larger than the corresponding values for 9-Me-A (240 cm^{-1}) and 9-propionylanthracene (9-CH_3CH_2CO-A, 200 cm^{-1}). (The latter compound shows an analogous temperature effect on the fluorescence intensity at temperatures near 77 K.) This is indicative of the greater increase in the dipole moment of the excited singlet state of I, compared with those of 9-Me-A and 9-CH_3CH_2CO-A, and also compatible with the great increase in the basicity of the carbonyl group of I at the first excited singlet state.[6)]

The cause of the anomalous temperature effect seen in the absorption spectrum of I in MCHIP is not yet clear. Dissolved oxygen and moisture did not affect the spectrum. A trace amount of impurities, if any, cannot explain such a large spectral change. Since the spectra observed at temperatures below *ca.* 140 K are quite close to those in MTHF except for the larger red shift in the latter solvent, the anomalous spectrum change may be related to a structural change in I, probably occurring in the slightly strained five-membered ring. Such a structural change brought about by lowering the temperature will affect the transition moments, resulting in the reversal of the absorption intensities.[19)]

Temperature Effects on the Fluorescence Quantum Yields. Since fluorescence in ethanol is emitted almost entirely from the hydrogen-bonded molecule except at very low temperatures, the rise or fall of the apparent fluorescence yield seen above 113 K must be determined by the variation in the fluorescence quantum yield of the hydrogen-bonded molecule and/or the variation in its concentration with the temperature. Since the fluorescence quantum yield of IH was determined to be close to unity (0.78), if a value with a similar magnitude is adopted for the fluorescence quantum yield of the hydrogen bonded molecule in ethanol[20)] its temperature-induced increase, if any, will be too small to account for the initial three-fold increase in the apparent fluorescence quantum yield.

On the other hand, the heat of formation of IH was calculated as −12.6 kcal mol^{-1} from the temperature dependence of its formation constant. Therefore, for the hydrogen-bonded molecule formed in ethanol, we can also expect at least a negative value for its heat of formation, though it may plausibly be larger than −12.6 because of the stronger interactions between ethanol molecules compared with those of *n*-hexane, in which the heat of formation of IH was determined. Moreover, as has been calculated from the 0–0 band frequencies of the absorption and fluorescence spectra by the use of the Förster cycle, the hydrogen-bond formation constant, K, in ethanol is larger at the first excited singlet state than at the ground state. The difference in log K for the excited singlet state between at 298 and 200 K is calculated to be greater than 0.5, corresponding to more than a three-fold increase in the concentration of the electronically excited hydrogen-bonded molecule on cooling to 200 K, if the hydrogen-bonding at the excited state is completely accomplished. Hence, the initial increase in the apparent fluorescence yield shown in Fig. 4 can most reasonably be interpreted in terms of the increase in the concentrations of the hydrogen-bonded molecules both at the ground and first excited singlet states.

At temperatures near the melting point of ethanol, however, the interactions of solvent molecules themselves come to predominate over interactions between I and ethanol molecules. As a result of this, a gradual decrease in the concentration of the hydrogen-bonded molecules, and hence a fall in the apparent fluorescence quantum yield shown in Fig. 4, are brought about. Although it may be difficult to verify quantitatively the initial increase in the concentration of the hydrogen-bonded molecule at the ground state from the absorption spectra shown in Fig. 1, the decrease in its concentration below *ca.* 190 K is definitely indicated by the absorption spectra.

In EPA, as is shown in Fig. 2 in Ref. 6, no evidence for the existence of the hydrogen-bonded molecule of I could be obtained at 77 K, indicating a prohibition of the hydrogen-bond formation at very low temperatures.[22)]

A similar phenomenon, *i.e.*, the appearance of a maximum in fluorescence quantum yields when the temperature is varied, has previously been noted for 3-CHO-P by Förster *et al.*[1)] It was inferred by these authors that the $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ excited singlet states ($S_{\pi\pi^*}$ and $S_{n\pi^*}$ respectively) are close-lying in this molecule and that a decrease in the temperature brings about a level inversion between fluorescent $S_{\pi\pi^*}$ and non-fluorescent $S_{n\pi^*}$ states, which is responsible for the rise and fall in the fluorescence quantum yield of 3-CHO-P as a function of the temperature. Although this concept is now widely accepted,[21)] strong evidence supporting their proposition has not yet been obtained. Particularly, the location of the $S_{n\pi^*}$ state has not yet been established experimentally. Considering the analogous spectroscopic behavior found in three compounds—I, 9-CHO-A, and 3-CHO-P,[1,6,23)] the interpretation given in the present paper for the temperature dependence of the fluorescence quantum yield of I seems also applicable to the case of 3-CHO-P.[23)] In this sense, the proposition given by Förster *et al.* should be re-examined, though the complex electronic spectra of 3-CHO-P may prevent the drawing of a definite conclusion.

Mechanism of the Intersystem Crossing. Based on the facts that a high radiative electronic transition probability is expected for I because of its large molar extinction coefficient[9b)] and that I does not suffer any significant photochemical reactions which affect the excitation energy dissipation processes,[6)] the very low fluorescence quantum yield inherent in I must be interpreted in terms of the existence of an efficient intersystem crossing process. In the other non-fluorescent 9-carbonylanthracenes, a similar circumstance has already been met with, and the two main factors which determine the efficiency of the intersystem crossing process have previously been proposed by the present author and his co-workers.[9)] One is the relative positions of the $S_{1\pi\pi^*}$ and $T_{n\pi^*}$ states, between which the intersystem crossing process is supposed to be dominant, while the other is the degree of the prohibition of the rotational motion of the carbonyl group upon photoexcitation.

Since the lowest excited singlet state of I is undoubtedly $S_{1\pi\pi^*}$, as has been discussed in Ref. 6, and since a significant structural change of I upon photo-excitation is unexpected in view of its structure, the temperature and solvent effects on the fluorescence quantum yield of I can be interpreted most reasonably in terms of these effects on the position of the $S_{1\pi\pi^*}$ state relative to that of the $T_{n\pi^*}$ state, which is expected to lie in the close vicinity of the $S_{1\pi\pi^*}$ state.[24)] If the energy of the $S_{1\pi\pi^*}$ state is lowered relative to that of the $T_{n\pi^*}$ state by some cause, fluorescence will come to be emitted. In this sense, it is noteworthy that the red shift of $\bar{\lambda}_{0-0}$ with a decrease in the temperature is larger in MTHF than in non-polar solvents, where temperature-induced fluorescence enhancement was not observed. In the former solvent, moreover, the energy of the $T_{n\pi^*}$ state must be higher than those in non-polar solvents. The increase in the energy of the $T_{n\pi^*}$ state will add to the energy gap between $S_{1\pi\pi^*}$ and $T_{n\pi^*}$ state by that amount. This is the reason for the presence of a rather strong fluorescence in MTHF at very low temperatures.

It will be instructive to apply our reasoning to the case of IH. The energy of the $S_{1\pi\pi^*}$ state of IH is lower by 630 cm^{-1} than that of I in *n*-hexane, while the $T_{n\pi^*}$ state of IH is expected to shift greatly in the higher-energy direction on account of the lowering of the energy of the n-orbital of oxygen. Because of these effects, the energy gap between the $S_{1\pi\pi^*}$ and $T_{n\pi^*}$ states of IH is far greater than the corresponding gap of the non-hydrogen-bonded molecule in polar solvents. As a result, the fluorescence quantum yield of IH is considered to take a high value, close to unity.

Analysis of the Temperature Dependence of the Fluorescence Quantum Yield. When the external quenching of the fluorescence is absent, the following three processes are considered to determine the fluorescence quantum yield of I: the radiative process, the temperature-independent intersystem crossing process, probably from the $S_{1\pi\pi^*}$ state to the $T_{2\pi\pi^*}$ state, and the temperature-dependent intersystem crossing process from the $S_{1\pi\pi^*}$ state to the $T_{n\pi^*}$ state. We will represent the rate constants of these processes by k_f, k_{is}, and k'_{is} with the activation energy of E_a respectively. Then the fluorescence quantum yield, $\phi_f(T)$, at the temperature, T K, can be given by Eq. (1):

$$\phi_f(T) = \frac{k_f}{k_f + k_{is} + k'_{is}\exp(-E_a/RT)} \tag{1}$$

where k_f is assumed to be independent of the temperature and where the rate constant of the internal conversion from the $S_{1\pi\pi^*}$ state is assumed to be negligibly small, as is frequently done for anthracene derivatives.[25)]

Equation (1) can also be rewritten as:

$$\ln\left(\frac{1}{\phi_f(T)} - 1 - \frac{k_{is}}{k_f}\right) = \ln\frac{k'_{is}}{k_f} - \frac{E_a}{RT} \tag{2}$$

The results in MTHF were analyzed by the use of Eq. (2). Since the value of k_{is}/k_f is not known in our case, by putting an appropriate value of k_{1s}/k_f into Eq. (2) the left-hand side of Eq. (2) was plotted against $1/T$. When $k_{1s}/k_f=2.2$, the most satisfactory straight line, with a correlation coefficient of 0.998, was obtained. From the slope of the line, the activation energy was calculated as 780 cm^{-1}. From the intercept, assuming $k_f=10^8\ \text{s}^{-1}$, $k'_{1s}\simeq10^{13}\ \text{s}^{-1}$ was also obtained. Then the limiting maximum fluorescence quantum yield calculated from these values becomes 0.313, very close to that found at 77 K in MTHF.[26]

The very large value of k'_{1s}, which is not unreasonably high for the rate constant of a transition between two excited states of different electronic natures, explains the very low fluorescence quantum yield of I, particularly in non-polar solvents. If a similar value can be adopted for the corresponding process of the other 9-carbonylanthracenes, its magnitude will be large enough to account for the absence of fluorescence in these compounds at the ambient temperature.[7–11]

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18) Since a stronger interaction between I and ethanol molecules was expected in non-polar solvents, the temperature effect on the absorption spectrum of I was investigated in IP containing 1—10% ethanol down to temperatures as low as 163 K. However, no marked spectral change indicative of a considerable amount of the hydrogen-bonded molecule was observed.

19) Such a structural change is assumed to be already occurring in MTHF.

20) To assume a high value for the fluorescence quantum yield of the hydrogen-bonded molecule in ethanol is reasonable when we take into account the apparent fluorescence quantum yield of 0.37 at 197 K, where the amount of the hydrogen-bonded molecule is estimated as 20—25%.

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22) To confirm whether or not this suppression of the hydrogen-bond formation in polar solvents at low temperatures is general, the temperature effects on the concentration change of IH were studied in MCHIP (trichloroacetic acid 1.4×10^{-3} M) and EPA (trichloroacetic acid *ca.* 0.2 M). In the former medium, as expected, the concentration of IH increased continuously with a decrease in the temperature, until almost all the molecules of I had been transformed into IH (and IH_n; $1:n$ complex). In the latter, however, in spite of the much higher concentration of trichloroacetic acid, the concentration of IH was low and decreased slightly at low temperatures with a decrease in the temperature. The amount of IH formed in other polar solvents, such as ACN, DMF, and MTHF, was also minute.

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