The Absorption and Fluorescence Spectra of 2-Methyl-1-aceanthrenone and Its Cation. A Comparison with 9-Anthracenecarboxaldehyde

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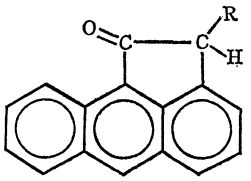
The fluorescence and absorption spectra of 2-methyl-1-aceanthrenone (I) and its cation were investigated. The spectra showed well-defined vibrational structures in a wide variety of solvents, but not in ethyl alcohol and acetic acid. The existence of the ^1L_b absorption band on the shorter-wavelength side of the ^1L_a band was strongly supported by the different solvent effects of these bands. In non-polar solvents, (I) formed a strongly fluorescent, 1 : 1, hydrogen-bonded complex with a trichloroacetic acid molecule. The formation constant in *n*-hexane was determined spectrophotometrically as 3.1×10^2 M^{-1} at 20 °C. In acidic solutions, pK_a and pK_a^*, were determined as −5.1 and 1.3 for the ground and first excited singlet states respectively. These values are the same as the corresponding values of 9-anthracenecarboxaldehyde (9-CHO-A), reflecting a marked resemblance in the electronic nature of the carbonyl groups of the two compounds. The broad absorption spectra of 9-CHO-A, in contrast to the highly structured spectra of (I), are due to a feasible torsional motion of the carbonyl group of the former compound.

The photochemical and photophysical processes of the carbonyl derivatives of anthracene have long attracted our attention, and several new features have been revealed by the present author and his co-workers.[1–4]

In spectroscopic studies of the carbonyl derivatives, an unavoidable complexity is met in elucidating the electronic nature of the excited states, because all these compounds have $n\rightarrow\pi^*$ states in addition to $\pi\rightarrow\pi^*$ states in the energy region attainable by usual photo-excitation. Before any detailed discussion of the photochemical and photophysical behavior of these compounds, threfore, it is necessary not only to determine the energy levels of four states—$S_{1\pi\pi^*}$, $S_{n\pi^*}$, $T_{1\pi\pi^*}$, and $T_{n\pi^*}$—at least, but also to elucidate the principal pathways of the internal conversion and intersystem crossing processes between any two states chosen from these states and the ground state. Actually, however, it is quite rare for all the above-mentioned matters to be made sufficiently clear. In this sense, 9-anthracenecarboxaldehyde (9-CHO-A) is a typical compound; its unusual photochemical reactivity has long been the subject of dispute, but no unambiguous conclusion has yet been obtained as to its reactive excited state. Several investigators, including Yang,[5–8] have proposed that the reactive excited states are the upper triplet $n\rightarrow\pi^*$ and/or the singlet $n\rightarrow\pi^*$ states. On the contrary, Suppan recently asserted that the reactive excited state was the lowest excited singlet $\pi\rightarrow\pi^*$ state.[9] The reason for this discrepancy can be ascribed to the shortage of useful spectroscopic data because of the broadness of the absorption and fluorescence spectra of 9-CHO-A.

A few studies of the molecular structure of 9-CHO-A have revealed that the angle between the anthracene ring and the plane containing the aldehyde group is approximately 25 °,[10] whereas for the other 9-carbonyl derivatives of anthracene this angle is believed to be close to 90 ° as a result of the large steric effect of the peri hydrogen atom.[11] Therefore, except for a characteristic non-fluorescent property common to these carbonyl derivatives,[1,2,12] they hardly differ from the 9-alkyl substituted anthracenes in UV absorption spectrum. Thus, the unusual photochemical reactivity and the broadness in the absorption and fluorescence spectra of 9-CHO-A may be supposed to arise from the approximate co-planarity of the anthracene ring and the plane of the aldehyde group.



(I): R=CH_3

(II): R=H

In 2-methyl-1-aceanthrenone (I) and 1-aceanthrenone (II), which are the main photo-products of 9-α-bromopropionylanthracene[13] and 9-ω-bromoacetylanthracene[4] respectively, it is quite evident that the planes of the carbonyl groups lie on the same plane as the anthracene ring. Considering the approximate co-planarity seen in both (I) and 9-CHO-A, we may expect a very similar behavior of these two compounds in various points. Therefore, detailed investigations of the spectroscopic properties and photochemical reactions of (I) or (II) should aid in clarifying the unusual photochemistry of 9-CHO-A.

The intention of this paper is to report for the first time on the fluorescence and absorption spectra of (I) and its cation and to discuss the results in comparison with the spectroscopic properties of 9-CHO-A as reported by Schulman and Young.[14]

Experimental

Materials. Compound (I) was obtained as the main product of the photolysis of 9-α-bromopropionylanthracene.[13] It was purified by column chromatography and then sublimated twice *in vacuo*. Obviously, (I) and (II) are quite similar in their structural and spectroscopic properties. (I) was employed in this paper simply because it was readily available.

9-CHO-A was prepared according to the well-known method[15] and was recrystallized from acetic acid and purified by sublimation *in vacuo*.

Among the solvents used for the spectroscopic measurements, *n*-hexane and cyclohexane were of a spectro grade (Nakarai Chem. Co., Ltd.). The other solvents (guaranteed

grade) were either distilled before use on a 1-ft Widmar column or were used as received. Tetrahydrofuran, *n*-hexane, and methylenedichloride employed to study the effect of a small amount of oxygen or moisture on the spectra were distilled from a Widmar column and then dried over sodium-potassium amalgam. All these solvents were transferred into an optical cell *in vacuo*. Sulfuric acid (s.g. 1.86) and trichloroacetic acid obtained from the Nakarai Chem. Co., Ltd., were used without further purification. Deionized and distilled water was used.

Optical Measurements. The absorption spectra at room temperature were taken on a Hitachi 124 Spectrophotometer. The fluorescence and excitation spectra were recorded on a Shimadzu Corrected Spectrofluorophotometer, RF 502. To produce corrected spectra, the time- and wavelength-dependent variation in the irradiation-source intensity was corrected automatically by using a rhodamine B quantum counter, while the response of the monochromator-photomultiplier combination was calibrated by means of the manufacturer's electrical compensator. The correctness of the calibration was checked with a dilute standard solution of quinie bisulfate (5×10^{-5} M in 0.5 M sulfuric acid). To record the fluorescence spectra at 77 K, a Dewar vessel and a sample cell made for ordinary ESR measurements at 77 K were used after a slight modification; the Dewar vessel was set in the cell holder of the spectrofluorophotometer, RF 502. Therefore the fluorescence spectra obtained thus at 77 K were uncorrected. The absorption spectra at low temperatures were taken by using a modified Beckman-type spectrophotometer equipped with an EMI 9558 QB photomultiplier. Constant low temperatures were obtained by circulating cold nitrogen gas.

Determination of the Acid Dissociation Constants. The acid dissociation constant, pK_a^*, of the first excited singlet state of (I) was determined by an approximate procedure, *i.e.*, by the fluorimetric pH titration in water-sulfuric acid mixed solvents and buffer solutions.[16] Sørensen's buffer solutions were used, and the pH measurements were made on a Takeda Riken pH-meter, Model HG-2. Sample solutions were prepared by adding a buffer or an acid solution to each 1.0 ml ethanol solution of (I) (*ca.* 10^{-4} M) in a 50 ml volumetric flask. The fluorescence intensities were measured at the wavelength where the fluorescence intensity of the neutral molecule reaches its maximum value.

The acid dissociation constant, pK_a, of the ground state of (I) was determined spectrophotometrically according to the method of Davis and Geissman.[17] The corrected Hammett acidity scale of Jorgenson and Hartter[18] was adopted here. To prepare the sample solutions, the solvent was removed from the 1.0 ml ethanol solution of (I) (*ca.* 1.2×10^{-2} M) in a 25 ml volumetric flask, and then an acidic solution of a known H_0 was poured into the flask until the volume reached 25 ml. The H_0 values were determined by weighing each solvent before mixing. Since, above $H_0=-5.3$, (I) became insoluble in water–sulfuric acid mixed solvents, a small amount of ethanol (2% by volume) was added. All the measurements were carried out at 20 °C.

Results

Neutral Molecule. In Fig. 1 are shown the absorption and fluorescence spectra of (I) observed at room temperature in *n*-hexane and ethanol. The fluorescence yield in *n*-hexane is so low that the spectrum in *n*-hexane is enlarged approximately 44 times. In relation to the photochemistry of 9-ω-bromoacetylanthracene, the absorption spectra of (II) in cyclohexane and ethanol have already been reported.[4] They are very similar to those of (I). In Fig. 2 the fluorescence and excitation spectra of (I) in EPA (5 : 5 : 2 by volume) at 77 K are shown. The fluorescence intensity is rather weak and does not increase very much when the temperature is lowered to 77 K.

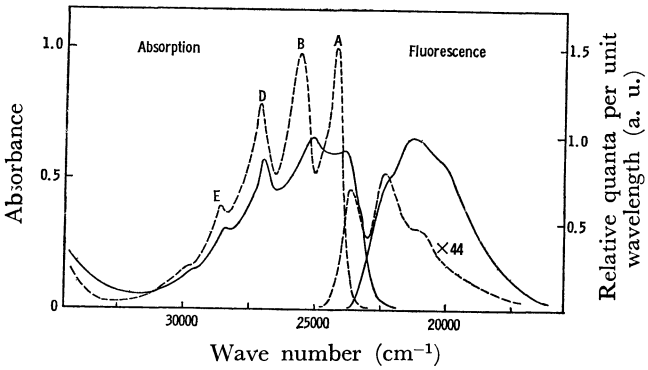


Fig. 1. Absorption and fluorescence spectra of (I) at room temperature.
——: ethanol (8.3×10^{-5} M),
----: *n*-hexane (1.0×10^{-4} M).
The fluorescence spectra were observed at the concentration of *ca.* 5×10^{-5} M in both media. The fluorescence intensity in *n*-hexane is enlarged approximately 44 times. The symbols A to E denote the vibrational band maxima (see also Table 1).

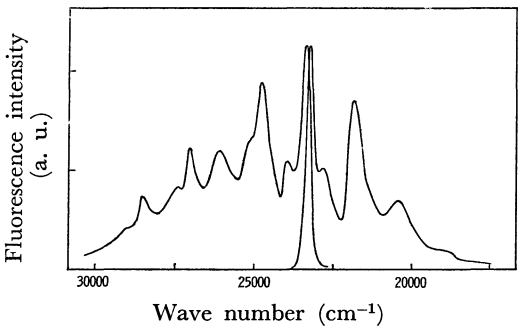


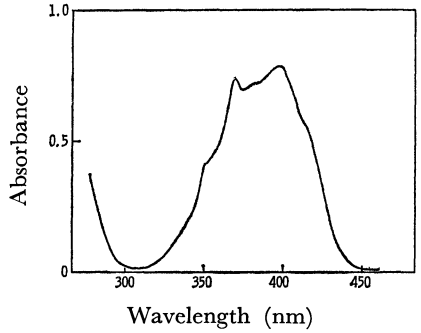
Fig. 2. Fluorescence and excitation spectra of (I) (*ca.* 5×10^{-5} M) in EPA at 77 K.
The excitation spectrum accords well with the absorption spectrum observed at 77 K in the same medium. Comparing the fluorescence and excitation spectra, the existence of the ^1L_b band with sharp band maxima at 351 and 369 nm is evident.

The absorption spectrum of 9-CHO-A in *n*-hexane is shown in Fig. 3 for the sake of comparison. Practically, 9-CHO-A is non-fluorescent in this solvent. The absorption spectrum of 9-CHO-A is inherently broad and does not differ much in a wide variety of solvents.[3] Its fluorescence spectrum at 77 K is also less structured than that of (I), and the fluorescence intensity varies little with the temperature. In contrast, the shape and the position of the absorption spectrum of (I) depend greatly on the solvents. The wave numbers of the absorption band maxima observed for (I) in various solvents are collected in Table 1 (see also Fig. 1). In such polar solvents as dimethylformamide and methylenedichloride, the red shifts were so large that the new absorption maxima (Band

Table 1. UV absorption band maxima of (I)

Solvent	^1L_a (cm^{-1})			^1L_b (cm^{-1})	
	A	B	C	D	E
n-Hexane	24270	25640	—	27170	28650
Triethylamine	24210	25580	—	27100	28570
Carbon tetrachloride	23920	25320	shoulder	27030	28490
Acetonitrile	23920	25250	flat	27170	28650
Benzene	23810	25190	26460	27100	28490
Methylenedichloride	23810	25130	26460	27030	28570
Dimethylformamide	23700	25000	26320	27100	28570
Pyridine	23640	24940	26250	27030	28490
Benzonitrile	23580	24940	26250	27030	28410
n-Hexane+*ca.* 1% trichloroacetic acid[a)]	23200	24390	25640	26880	28250

a) Absorption maxima for the hydrogen-bonded complex.



Eig. 3. Absorption spectrum of 9-CHO-A (1.2×10^{-4} M) in *n*-hexane.
The spectrum should be compared with that of (I) shown in Fig. 1. The shoulder observed at around 420 nm is attributed to the 0-0 band.

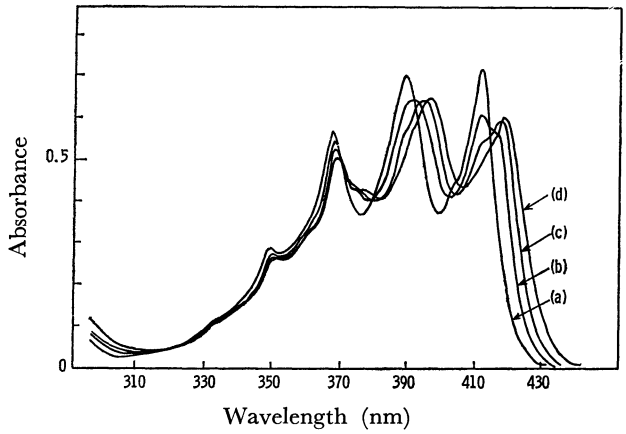


Fig. 4. Absorption spectrum change upon the addition of methylenedichloride to a *n*-hexane solution of (I). The concentrations of the additive by volume are; (a) 0%, (b) 9.1%, (c) 23.1%, (d) 50%. The concentration of (I) is the same (7.2×10^{-5} M) for (a) to (d).

C) appeared clearly between Bands B and D. Despite the large solvent effect in these solvents, the absorption spectra are highly structured and the band widths of A, B, and C are comparable to those obtained in non-polar solvents. It should also be noted that, in any of the solvents studied here, the band widths of D and E are narrower than those of A, B, and C.

On the basis of the different solvent effects on the two band groups, the A, B, and C absorption bands are considered to originate from a different electronic transition from that of the D and E bands. The former band group showed a larger red shift in polar solvents than did the latter band group. Furthermore, the energy separations between B and D, and between D and E, are not the same, so these bands are not considered to belong to the same vibrational manifold of the same excited singlet state. The A, B, and C bands could be assigned to the vibrational manifold of the ^1L_a band, and D and E, to that of ^1L_b. The fact that the fluorescence spectrum shown in Fig. 2 lacks the vibrational progression (corresponding to the bands at 28,490 and 27,100 cm^{-1}) seen in the excitation spectrum also supports this.

As an example of a large solvent effect on the absorption spectrum of (I), the absorption spectrum change in *n*-hexane–methylenedichloride mixed solvents is shown in Fig. 4. Although no clear isosbestic points can be seen, the spectrum changes as if (I) and methylenedichloride form a certain complex; two clear absorption peaks can be recognized at around 410 nm even at a high concentration of methylenedichloride. The fluorescence intensity was observed to increase as the fraction of methylenedichloride increased. In general, the fluorescence yield was larger in polar solvents than in non-polar solvents; *i.e.*, (I) showed a so-called fluorescence activation. Dissolved oxygen and moisture did not affect the fluorescence yield appreciably, as evidenced by a comparison of the fluorescence intensities observed in dry and degassed and aerated solvents.

Figure 5 shows the absorption spectrum change when a small amount of trichloroacetic acid is added to a *n*-hexane solution of (I). In this case, clear isosbestic points are seen at 415, 395.5, 377.5, 371, 355.5, and 352.5 nm, indicating the formation of a hydrogen-bonded complex. The detailed analysis of the spectra showed it to be a 1 : 1 complex with the formation constant of 3.1×10^2 M^{-1} at 20 °C.

Figure 6 shows how the fluorescence spectrum and its intensity change upon the addition of trichloroacetic acid. Compared with the fluorescence spectra shown in Fig. 1, the fluorescence spectra in Fig. 6

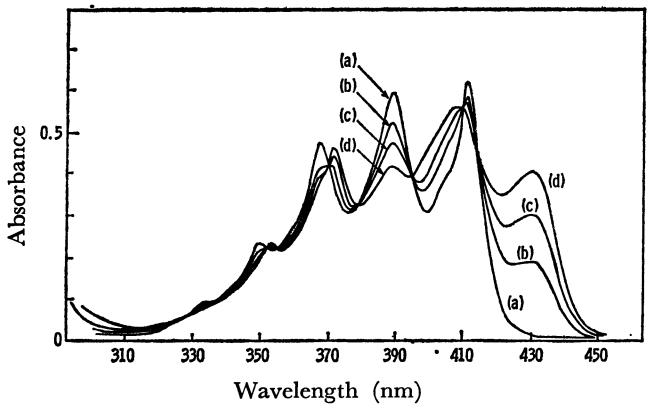


Fig. 5. Absorption spectrum change upon the addition of a small amount of trichloroacetic acid to a *n*-hexane solution of (I).
The concentrations of the additive are;
(a) 0 M, (b) 2.4×10^{-3} M, (c) 6.6×10^{-3} M, (d) 4.4×10^{-2} M.
The isosbestic points are seen at 415, 395.5, 377.5, 371, 355.5, and 352.5 nm, indicating the formation of the 1 : 1 hydrogen-bonded complex.

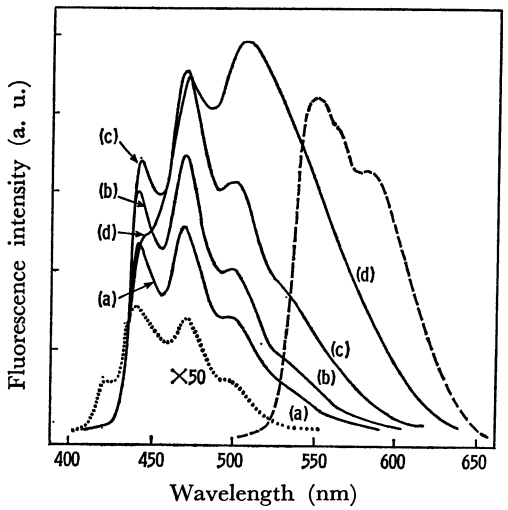


Fig. 6. Fluorescence spectra observed for the 1 : 1 hydrogen-bonded complex of (I).
The spectra denoted by (b) to (d) were observed for the solutions showing the absorption spectra represented by Fig. 5(b) to (d) respectively. The spectrum (a) was observed for the 1.2×10^{-3} M solution of trichloroacetic acid.
The excitation wavelength was 370±10 nm. The fluorescence at the longer wavelength is emitted from the cation. In a much more concentrated solution of trichloroacetic acid (*ca.* 0.5 M), the fluorescence band maximum lies at 532 nm. The broken line represents the fluorescnece spectrum of the cation in conc. sulfuric acid.
In a very dilute solution of trichloroacetic acid (*ca.* 10^{-6} M), fluorescences from the two species (hydrogen-bonded and non-hydrogen-bonded molecules) can be observed as shown by the dotted line.

differ in their position, intensity, and vibrational structure. Thus, the fluorescence spectrum observed in *n*-hexane with a small amount of trichloroacetic acid can be attributed to the hydrogen-bonded mole-

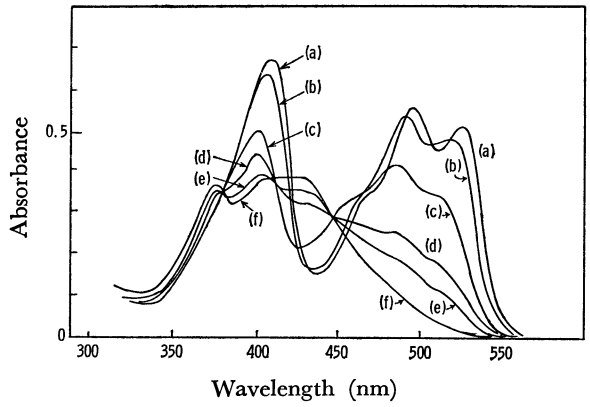


Fig. 7. Absorption spectra of (I) (5.7×10^{-5} M) in acidic solutions.
(a) conc. sulfuric acid, (b) $H_0=-7.74$, (c) $H_0=-5.32$, (d) $H_0=-4.45$, (e) $H_0=-4.23$, (f) $H_0=-4.03$.
In the $H_0\geqq-5.0$ range rather good isosbestic points are seen at 379 and 441 nm.

cule. A further increase in the concentration of trichloroacetic acid greatly shifted the fluorescence spectra to the red and caused the loss of a vibrational structure. A comparison with the fluorescence spectrum observed in sulfuric acid (broken line in Fig. 6) revealed that the fluorescence in a concentrated trichloroacetic acid solution was due to a fluorescence from the cation of (I).

Although 9-CHO-A behaved in a way analogous to (I) upon the addition of trichloroacetic acid, the observed spectra lacked a clear vibrational structure. Consequently, the spectroscopic discrimination of the existence of a non-hydrogen-bonded state and a hydrogen-bonded state is not so feasible as in the case of (I).

Cation. Figure 7 shows the absorption spectra of (I) observed in water-sulfuric acid mixed solvents. The cation formed in sulfuric acid emitted a fluorescence with a band maximum at 550 nm. Although the cation, which naturally showed no ESR signal, was comparatively stable, it could not be set aside for a long time. The absorption at around 520 nm gradually became broader, indicating a decomposition of (I).

Schulman and Young[14] have reported on the absorption and fluorescence spectra of 9-CHO-A under similar conditions; they obtained the values of the acid dissociation constants, pK_a and pK_a^*, as −5.1 and 1.3 for the ground and the lowest excited singlet states respectively. The cations of (I) and 9-CHO-A resemble each other in their absorption spectra, though the latter cation absorbs at wavelengths a little longer. Compared with the absorption spectra observed at high H_0 values, the bands at 410 nm and in the range from 450 to 550 nm in sulfuric acid are assigned to the ^1L_b band and the ^1L_a band respectively. It should be noted here that the ^1L_b band of the cation of (I) is structureless and is as broad as that of the cation of 9-CHO-A.

pK_a and pK_a^*. An approximate value of pK_a^*[16] was obtained by observing the fluorescence intensities of the neutral molecule at 495 nm (excitation: 420±10 nm) at various pH's. The fluorescence inten-

sity *vs.* pH curve gave 1.3 as the approximate value of pK_a^*. Since the fluorescence intensity depends on the kind of buffer solution used, the error in pK_a^* determination may be considerable.

The value of pK_a was determined spectrophotometrically according to the method of Davis and Geissman.[17] The difference in the absorbances at the wavelengths of the absorption peaks of the cation and the neutral molecule were plotted against H_0. The inflection point of this curve gave the value of pK_a as -5.1. As may be seen in Fig. 7, in a strict sense no isosbestic point was observed when H_0 was varied over a wide range; hence, the obtained value of pK_a may again have an appreciable error. In the $H_0 \geqq -5.0$ range, however, rather good isosbestic points were observed at 379 and 441 nm.

The obtained values of pK_a^* and pK_a are in good agreement with those of 9-CHO-A determined by Schulman and Young,[14] indicating a close similarity of the electronic natures of the two carbonyl groups.

Using the equation based on the Förster cycle: $pK_a^* = pK_a + (0.625/T)\,(\bar{\lambda}_N^{-1} - \bar{\lambda}_C^{-1})$, the difference $\Delta pK = pK_a^* - pK_a$ was calculated as 6.7; it showed good agreement with the experimental value of 6.4. The terms in the parentheses are the 0–0 frequencies (in cm^{-1}) estimated from the mean of the positions of the wavelengths of the absorption and fluorescence maxima for the neutral molecule and the cation respectively.

Photolysis of (I). Neither the photochemical reduction of (I) in isopropanol, dimethylaniline, and triethylamine nor the photocycloaddition reaction in 2-methylpentene was observed. That is, both photochemical reactions noted for 9-CHO-A[3,5-8] did not proceed. On the irradiation of (I), however, the absorbance of the p-band gradually decreased; this indicates the occurrence of photochemical reactions presumably including a photodimerization reaction.

Discussion

Similarity and Dissimilarity in the Spectroscopic Properties of (I) and 9-CHO-A. Both compounds bear a marked resemblance to each other in various properties, such as the basicity of the carbonyl groups (pK_a^* and pK_a), a large red shift of the ^1L_a band compared with those of the other 9-carbonyl derivatives of anthracene, fluorescence activation, and the ability of hydrogen-bonding. It is quite evident that the cause for this resemblance is attributable to the fact that the planes of the carbonyl groups and the anthracene ring are approximately coplanar; *i.e.*, the increased conjugation between the carbonyl groups and the anthracene ring endows these compounds with similar properties. This is also supported by the fact that it is impossible to find such a similarity among the other 9-carbonyl derivatives: 9-RCO-A (*e.g.*, R=CH_3–, CH_3CH_2–, $CH_3CH_2CH_2$–, ph–, CH_2=CH–, NH_2– CH_3O–, HO–,) where the carbonyl groups are supposed to make almost right angles with the anthracene ring at the ground states. From this resemblance between (I) and 9-CHO-A, it can also be said that the unusual spectroscopic behavior of 9-CHO-A can not necessarily be ascribed to the fact that its carbonyl group is aldehyde.

On the other hand, a distinct difference in the spectra of (I) and 9-CHO-A lies in the sharpness and the vibrational structure of the absorption and fluorescence bands. Schulman and Young[14] have attributed the lack of a vibrational structure in the absorption spectrum of 9-CHO-A to the loss of vibrational quantization in ^1L_a band. To explain the loss of quantization, they assumed that, since the $^1L_a \leftarrow {}^1A$ transition bore a CT character to some extent, the solvent-relaxation process and the functional rehybridization (the rotation of the aldehyde group) had to occur during the electronic transition, particularly in polar fluid solvents. In comparison with the absorption spectra of (I), however, we see that Schulman's proposal has several difficulties. First, (i) it is questionable whether the rotation of the carbonyl group of 9-CHO-A competes well with the electronic transition. Second, (ii) the broadening in the UV spectrum of 9-CHO-A should be strongly solvent-dependent if solvent relaxation process alters the vibrational sublevels of the Franck-Condon-excited state. On the contrary, though, the broadening is nearly insensitive to solvents. Third, (iii) if the CT character of the ^1L_a band is partly responsible for the broadening, a similar broadening should be observed for (I) and 9-CHO-A. Fourth, (iv) even if the rotation of the carbonyl group is forbidden as in (I), its absorption and fluorescence spectra are quite broad in alcohols. (This will be discussed in a later section.) Fifth, (v) the ^1L_b band of the cation of (I), for which a non-Franck-Condon electronic transition is not to be expected because of the structurally fixed carbonyl group, is also broad and vibrationally structureless, as has been observed for the cation of 9-CHO-A. Furthermore, it should be noted that the absorption spectrum of 9-CH_3OCO-A, whose substituent is supposed to rotate into a coplanar configuration at the excited state, has been reported by Werner and Hoffman[19] to retain an anthracene-like structure. Thus it seems inappropriate to interpret the spectrum broadening observed for 9-CHO-A in terms of a non-Franck-Condon transition to the ^1L_a state.

A comparison of the ^1H spectra of 9-CHO-A and (I) implies the occurrence of a torsional motion of the carbonyl group of 9-CHO-A in the ground state.[20] Therefore, in the present author's opinion, the breadth of the absorption spectrum of 9-CHO-A can be explained as follows, without introducing the concept of a non-Franck-Condon transition to the ^1L_a state. The transition energy changes as the extent of the conjugation of the substituent varies; *i.e.*, the transition energy is a function of the angle made by the carbonyl group and the anthracene ring. Hence, if the electronic transition is supposed to occur from the various ground states with respect to the angle, this will naturally lead to the spectrum broadening, which will be almost insensitive to solvents.

The sharpness of the ^1L_b bands of (I) and 9-CHO-A can also be understood when it is noted that the energy of the ^1L_b band, which is polarized to the long axis of the anthracene ring, is not appreciably affected by meso-substitution, so the transition energy does not

depend on the extent of conjugation of the carbonyl group. This is substantiated by the approximate invariance of the values of the $^1L_b \leftarrow ^1A$ transition energy observed for several 9-substituted anthracenes.[21]

Energy Levels. The electronic states of (I) are well defined. The A, B, and C bands belong to the ^1L_a band, and D and E, to the ^1L_b band, as has been described already. Since, in general, the ^1L_a band does not suffer significantly any substituent effect due to the 1- or 2-position, the large red shift of the 0–0 band of the ^1L_a band may be regarded as being due to the conjugation effect of the carbonyl group. Though the position of the 0–0 band of the ^1L_a band of 9-CHO-A is not clear, a comparison of the absorption spectra of (I) and 9-CHO-A implies that the shoulder observed at around 420 nm in Fig. 3 is due not to the $n \rightarrow \pi^*$ transition, but to the 0–0 band of the ^1L_a band. The lowest excited singlet state of (I) is undoubtedly the $\pi \rightarrow \pi^*$ state, as can be seen from Fig. 1, so the lowest excited singlet state of 9-CHO-A, which has long been in dispute, should also be the $\pi \rightarrow \pi^*$ state. Therefore, the phenomenon of fluorescence activation found for 9-CHO-A as well as for (I) should be explained by a mechanism other than the level inversion between $S_{1\pi\pi^*}$ and $S_{n\pi^*}$ states,[22] as has been suggested by the present author in a previous paper.[3] Instead, two triplet states, $T_{2\pi\pi^*}$ and more particularly, $T_{n\pi^*}$, seem to play an important role in the fluorescence activation phenomenon. However, it is impossible at present to determine the energy levels of these states experimentally. The best way to do so would be to estimate the energy levels from the spectroscopic data accumulated for various carbonyl derivatives of anthracene.[3] All we can say now, on the basis of the present results, is that the fluorescence activation process can more reasonably be explained in terms of the level inversion between $S_{1\pi\pi^*}$ and $T_{n\pi^*}$ states, which may be caused by the increased solvent polarity or by the formation of a hydrogen-bond with a solvent molecule. The fact that abnormal photo-reactivity was not found for (I) may reflect either an unsuitable energy level of the $T_{n\pi^*}$ state relative to the $T_{2\pi\pi^*}$ state (*i.e.*, the lifetime of $T_{n\pi^*}$ is too short for its state to participate in the reactions because of an efficient internal conversion to $T_{2\pi\pi^*}$) or a steric prohibition of the reactions.

Explanation of the Absorption Spectra of (I) in Alcoholic Solvents. The absorption and fluorescence spectra of (I) observed in alcoholic solvents differ much in their breadth from those in non-alcoholic polar solvents, such as dimethylformamide and acetonitrile. The non-hydrogen-bonded neutral molecule of (I) and also the hydrogen-bonded molecule show pronounced vibrational structures in both the fluorescence and absorption spectra, as is indicated in Figs. 1 and 6. The broadening observed in alcoholic solvents can not, therefore, be explained in terms of a simple solvent effect on the spectra. When the temperature was lowered to *ca.* −80 °C, the absorption band at 418 nm sharpened, became more pronounced, and shifted to 420 nm. At the same time, the new bands with peaks at 430 (shoulder), 412, and 388 nm, which correspond well with the absorption peaks observed for a hydrogen-bonded molecule, appeared. Since the band at 418 nm corresponds to the non-hydrogen-bonded molecule, the above-mentioned fact is indicative of the coexistence of at least two species. Thus, the apparent broadening in alcoholic solvents can be reasonably explained in terms of the coexistence of hydrogen-bonded and non-hydrogen-bonded molecules, which absorb light at slightly different wavelengths. A part of the broadening observed for 9-CHO-A may be attributed to such a coexistence, but an experimental proof is need. In order to confirm these things, further studies are now in progress.

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