Absorption and Fluorescence Spectra of Anthracenecarboxylic Acids. I. 9-Anthroic Acid and Formation of Excimer

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(Received December 8, 1977)

The absorption spectra of 9-anthroic acid (9-anthracenecarboxylic acid) in ethanol have been measured as a function of solute concentration. It was revealed that 9-anthroic acid forms a hydrogen-bonded dimer. The equilibrium constant for dimer formation was determined to be 6.6×10^4 mol^{-1} l in ethanol at 298 K. The fluorescence spectra of 9-anthroic acid have been investigated as a function of concentration and temperature in various solvents. An excimer mechanism was proposed for a broad fluorescence of 9-anthroic acid; the hydrogen-bonded dimer is excited and then associates with an unexcited hydrogen-bonded dimer to form an excited tetramer from which the broad fluorescence occurs.

The fluorescence spectrum of 9-anthroic acid (9-anthracenecarboxylic acid) in ethanol is strongly concentration-dependent. At a concentration below 10^{-5} mol/l the spectrum has an anthracene-like structure, while at a concentration above 10^{-3} mol/l it shifts to the red, turning into a broad structureless band. In order to elucidate this spectral change, Bazilevskaya and Cherkasov postulated that the linear-type dimers formed in the ground state rearrange themselves upon excitation into a characteristic excimer configuration, wherein the planes of anthracene rings are parallel.[1,2] On the other hand, Werner and Hercules explained the concentration dependence on the basis of an acid-base equilibrium, assigning the anthracene-like structured fluorescence to an ionized species.[3]

An excimer mechanism for the broad fluorescence of 9-anthroic acid is presented in this paper. In alcoholic solvents, 9-anthroic acid forms a hydrogen-bonded dimer in its ground state. The hydrogen-bonded dimer is excited and then associates with an unexcited hydrogen-bonded dimer to form an excited tetramer from which the broad fluorescence occurs. A discussion is given on an assumption of the excimer mechanism, validity of the assumption being made on the basis of experimental findings.

Experimental

9-Anthroic acid was purified by dissolution in base, precipitation with acid, and sublimation *in vacuo*. Ethanol (Wako Pure Chemical Industries, Inc., Super special grade) and propylene glycol (1,2-propanediol, Wako JIS S grade) were stored over molecular sieves 3A and then passed through a silica gel column. Toluene and methanol (Wako fluorometric grade) and acetonitrile (Wako spectrophotometric grade) were used. Hexane and isooctane (2,2,4-trimethylpentane) were purified in the usual way. The other solvents (JIS S grade) were used without further purification. The absorption spectra were recorded on a Hitachi EPS-3 recording spectrophotometer. The fluorescence and excitation spectra were obtained by means of a Hitachi MPF-2A fluorescence spectrophotometer and are given without corrections on quantum response of detecting and exciting systems and on reabsorption. The temperature was controlled with a metal cryostat (Torisha Laboratory, Ltd.).

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Results and Discussion

Absorption Spectra and Dimer Formation. The absorption spectrum of 9-anthroic acid in ethanol closely resembles that of anthracene. The lowest frequency band with a fine structure may reasonably be assigned to the ^1L_a transition and the intense band at higher frequencies to the ^1B_b transition. Figure 1 shows the concentration dependence of absorption spectra of 9-anthroic acid in ethanol. As the concentration of 9-anthroic acid increases, the ^1L_a band shifts to the blue and the fine structure becomes less sharp. The ^1B_b band also shows a blue shift. Several isosbestic points appear in the spectra. These observations indicate that a certain equilibrium is involved in the ground state of this system.

The most probable origin of the appearance of the isosbestic points in the absorption spectra of 9-anthroic acid is monomer-dimer equilibrium or proton dissociation. In the following, discussion is made as to which

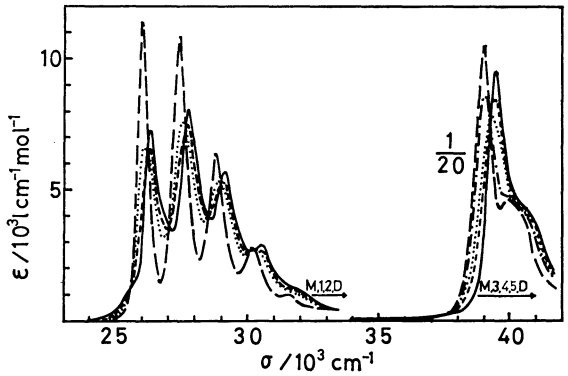

Fig. 1. The absorption spectra of 9-anthroic acid in ethanol at various concentrations and the estimated monomer and dimer absorption spectra. 1: 2.18×10^{-5} mol/l, 2: 1.09×10^{-4} mol/l, 3: 1.63×10^{-6} mol/l, 4: 1.63×10^{-5} mol/l, 5: 1.16×10^{-4} mol/l, M: the estimated monomer spectra, D: the estimated dimer spectra.

origin is valid on the basis of experimental evidence. Hereafter, the absorption band appearing at low concentrations in ethanol will be tentatively referred to as M absorption band, and the band at higher concentrations as D absorption band.

It has been well established that carboxylic acids have pK_a values in ethanol greater by about 5.8 than in water.[4,5] Since the reported pK_a value of 9-anthroic acid in water is 3.0[7] or 3.65,[6] it is estimated that that in ethanol is 8.8—9.4. If we assume that the concentration dependence of the absorption spectra in ethanol is attributed to proton dissociation, a pK_a value of 5.12 is obtained from the analysis of the observed concentration dependence of absorption spectra. This is too small to ascribe the concentration dependence of the absorption spectra to proton dissociation. From this point of view, proton dissociation is unfavorable as the origin of the spectral changes in this system.

When we ascribe the spectral changes to monomer-dimer equilibrium in this system, the equilibrium constant of dimer formation, K_D, can be determined by the usual procedure.[8] Thus, a K_D value of 6.6×10^4 mol^{-1} l was obtained for 9-anthroic acid in ethanol at 298 K. By using the observed spectral data at various concentrations and the K_D value, the monomer and dimer absorption spectra were determined. As shown in Fig. 1, the ^1L_a and ^1B_b bands become less sharp owing to dimer formation, which is consistent with general behavior of hydrogen bonding, but they show a blue shift. The origin of the unusual blue shift will be discussed later.

The formation of hydrogen-bonded dimers in aromatic carboxylic acids has been confirmed under various conditions for benzoic acid[8-11] and 1- and 2-naphthoic acids.[12] Besides the dimer formation, Kitamura and Baba reported that 1- and 2-naphthoic acid dimers further associate to give a higher-order complex which can be assumed to be a tetramer in a hydrocarbon rigid glass matrix at 77 K.[12] Similarly it is quite likely that 9-anthroic acid forms a hydrogen-bonded dimer under appropriate conditions. The monomer-dimer equilibrium constants for these acids are: 7.95×10^3 mol^{-1} l for benzoic acid in hexane,[8] 7.6×10^4 mol^{-1} l for 1-naphthoic acid, and 3.4×10^4 mol^{-1} l for 2-naphthoic acid in a mixture of isopentane and methylcyclohexane (6:1 by volume).[12] It appears that the equilibrium constants increases with increase in the number of benzene rings and then decrease in solubility. Since 9-anthroic acid is hardly soluble in hydrocarbons, there is little possibility that monomer-dimer equilibrium is involved in hydrocarbon solvents. The monomer-dimer equilibrium of 9-anthroic acid might be observed only when a solvent of higher solubility such as ethanol is used. It thus seems that the K_D value we obtained is reasonable. In conclusion, 9-anthroic acid in ethanol forms a hydrogen-bonded dimer in its ground state.

9-Anthroic acid is hardly soluble in isooctane ($<10^{-5}$ mol/l). The absorption spectra of 9-anthroic acid in isooctane show no concentration dependence in the concentration range 10^{-5}—10^{-7} mol/l. The spectral shape in isooctane closely resembles D absorption band in ethanol. This indicates that 9-anthroic acid dissolves in isooctane in dimer form. The carboxyl group is a typical hydrophilic group, while the anthryl group is a hydrophobic group. The hydrophilic character of the carboxyl group will be masked by the dimer formation, so that the dimer form will be stable in aprotic solvents as compared with the monomer form.

Fluorescence Spectra. The fluorescence spectrum of 9-anthroic acid in ethanol has an anthracene-like structure at a concentration below 10^{-5} mol/l. With increase in concentration the fluorescence spectrum shifts to the red, turning into a broad structureless emission (Fig. 2). The structured fluorescence can tentatively be assigned to a monomer fluorescence and the broad fluorescence to an excimer fluorescence. Hereafter, the structured fluorescence band is referred to as M fluorescence band and the broad fluorescence band as E fluorescence band. The solvents in which 9-anthroic acid emits the structured M fluorescence are: *N*-methylformamide, formamide, ethylene glycol, propylene glycol, glycerol, methanol, ethanol, isobutyl alcohol, *s*-butyl alcohol, and water.

Figure 3 shows the concentration dependence of fluorescence spectra of 9-anthroic acid in toluene. 9-Anthroic acid emits a broad fluorescence which has a shoulder, lying at higher frequency than that of E fluorescence. The fluorescence of 9-anthroic acid in toluene shows no substantial concentration dependence

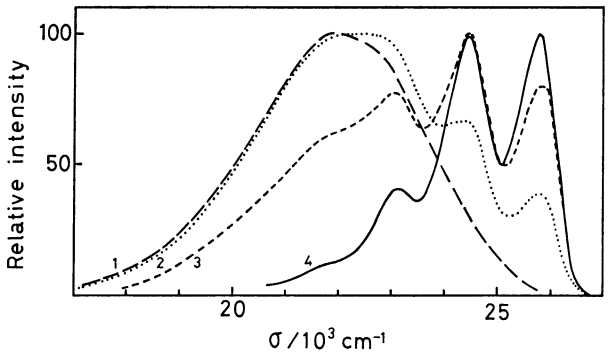

Fig. 2. The fluorescence spectra of 9-anthroic acid in ethanol at various concentrations. 1: 1.16×10^{-3} mol/l, 2: 1.29×10^{-4} mol/l, 3: 2.33×10^{-5} mol/l, 4: 1.16×10^{-6} mol/l. Methanol solution shows the analogous concentration dependence.

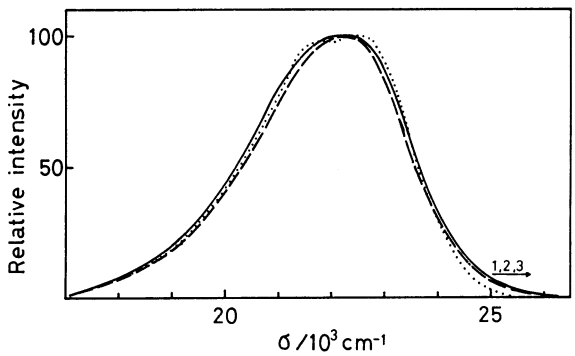

Fig. 3. The fluorescence spectra of 9-anthroic acid in toluene at various concentrations. 1: 1.2×10^{-3} mol/l, 2: 1.5×10^{-5} mol/l, 3: 3.0×10^{-7} mol/l.

down to 10^{-7} mol/l. These findings exclude the possibility of excimer emission for the broad fluorescence of 9-anthroic acid in toluene. The broad fluorescence band can be assigned to a dimer fluorescence and is hereafter referred to as D fluorescence band. The solvents in which 9-anthroic acid emits the broad D fluorescence only are: *N*,*N*-dimethylformamide, dimethyl sulfoxide, acetonitrile, acetone, 1,2-dichloroethane, tetrahydrofuran, methyl acetate, benzene, toluene, 1,4-dioxane, diethyl ether, hexane, isooctane, and *t*-butyl alcohol.

The spectral dependence of fluorescence spectra on the concentration of 9-anthroic acid in propylene glycol and isobutyl alcohol is given in Figs. 4 and 5. In propylene glycol, 9-anthroic acid emits M fluorescence only at lower concentrations. The fluorescence spectrum of 9-anthroic acid in isobutyl alcohol has M and D bands at 10^{-6} mol/l. The E band becomes obvious at concentration higher than 10^{-4} mol/l. Since 9-anthroic acid shows analogous spectral behavior both in ethanol and in propylene glycol, experimental studies on the temperature dependence of emission spectra were performed by using propylene glycol as a solvent instead of ethanol, because of experimental facility.

Figure 6 shows the excitation spectra of 9-anthroic acid at a concentration of 7.02×10^{-4} mol/l with observation at 410 and 540 nm. At this concentration,

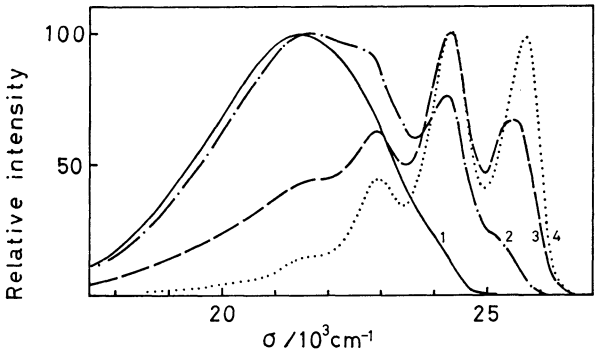

Fig. 4. The fluorescence spectra of 9-anthroic acid in propylene glycol at various concentrations. 1: 3.51×10^{-3} mol/l, 2: 7.02×10^{-4} mol/l, 3: 7.02×10^{-5} mol/l, 4: 1.01×10^{-5} mol/l.

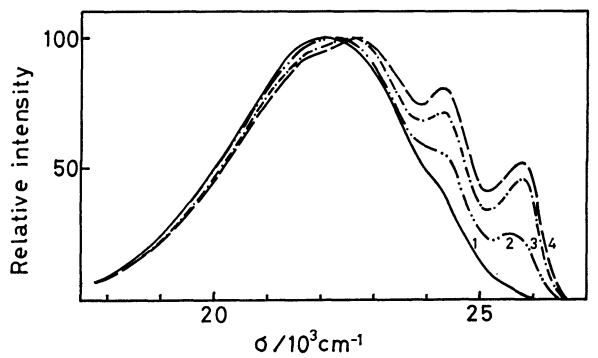

Fig. 5. The fluorescence spectra of 9-anthroic acid in isobutyl alcohol at various concentrations. 1: 10^{-3} mol/l, 2: 10^{-4} mol/l, 3: 10^{-5} mol/l, 4: 10^{-6} mol/l.

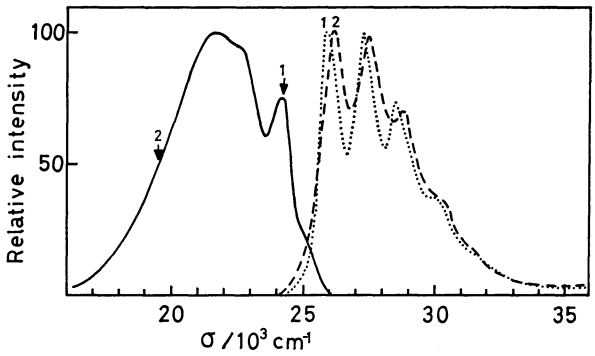

Fig. 6. The fluorescence and excitation spectra of 9-anthroic acid in propylene glycol at 299 K. Solute concentration: 7.02×10^{-4} mol/l. 1: observed at 410 nm, 2: observed at 540 nm.

the fluorescence has both structured and broad components. The excitation spectrum observed at the wavelength of the peak of M emission does not coincide with that observed at the wavelength of E emission. The former excitation spectrum corresponds to M absorption band, while the latter to D absorption band. It is therefore concluded that the broad E emission emerges only as a consequence of excitation of the species involved in solutions of higher concentrations.

As has been suggested by Werner and Hercules,[3] the most probable mechanism to account for a broad fluorescence is one involving rotation of the carboxyl group in the excited state into a position approaching coplanarity with the anthracene ring. A similar rotation may occur for the dimer molecules of 9-anthroic acid.

The results indicate that the use of a solvent having a hydroxyl or an imino group is essential for the appearance of M fluorescence, with exception of *t*-butyl alcohol. For instance, 9-anthroic acid emits M fluorescence in *N*-methylformamide, while it emits D fluorescence only in *N*,*N*-dimethylformamide. The solvents having a proton-accepting group only, such as acetone, 1,4-dioxane *etc.*, show no M fluorescence.

Werner and Hercules explained the concentration dependence of the fluorescence of 9-anthroic acid on the basis of an acid-base equilibrium.[3] For the molecular form of 9-anthroic acid a structureless fluorescence is observed. The large Stokes shift of the emission is a consequence of an excited state rotation of the carboxyl group into the plane of the anthracene ring. For the ionic form of 9-anthroic acid in protonic solvents, rotation is inhibited owing to strong ground-state solvation and an anthracene-like structured fluorescence is observed.

The simplest electrostatic theory based on Born's model predicts a linear relation between the medium effect on acid-base equilibria and the reciprocal of the dielectric constant of the solvents.[13] The experimental findings indicate that there is no correlation between the appearacne of the structured M fluorescence of 9-anthroic acid and the magnitude of dielectric constant of the solvent used. In view of the facts, we can rule out proton dissociation as the origin of M fluorescence for 9-anthroic acid.

Effect of Hydrogen Bonding. Figure 7 shows the effect of addition of acetic acid on absorption spectra of 9-anthroic acid in ethanol. Addition of acetic acid shifts the absorption spectra to the blue. As seen in Fig. 1, dimer formation also causes the blue shifts. These findings indicate that the blue shift caused by dimer formation is mainly attributed to hydrogen bonding between carboxyl groups rather than the exciton interaction between anthracene moieties.

A strong steric hindrance might exist between the carboxyl group and the peri-hydrogens, which would keep the carboxyl group from lying coplanar with the anthracene ring. It is likely that the hydrogen-bonded dimer in the ground state has a linear-type configuration in which two anthracene rings lie on the same plane and the plane of $-\overset{\diagup\!\!\diagdown}{\underset{\diagdown\!\!\diagup}{C}}-$ bridge is almost perpendicular to the plane of anthracene rings (Fig. 8). The anthracene-like structure of D absorption band supports this configuration for ground-state dimers, since the perpendicular configuration of the anthracene rings and $-\overset{\diagup\!\!\diagdown}{\underset{\diagdown\!\!\diagup}{C}}-$ group minimizes resonance interaction between these moieties.

Addition of a solvent having –OH or =NH group breaks the hydrogen bonds between a pair of 9-anthroic acid molecules and new hydrogen bonds are formed between "monomerized" acids and solvent molecules. The anthracene-like structure of M absorption band of 9-anthroic acid in ethanol supports the view that the hydrogen-bonded species with ethanol have a perpendicular configuration of the anthracene ring and the carboxyl group in the ground state.

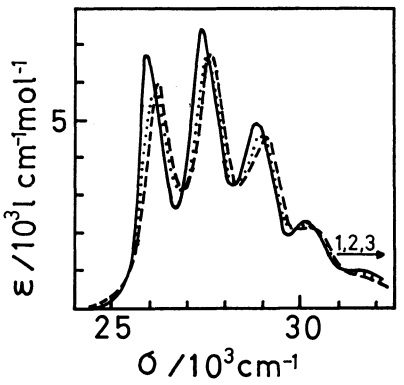

Fig. 7. The effect of addition of acetic acid on the absorption spectra of 9-anthroic acid in ethanol. Solute concentration: 8.05×10^{-6} mol/l. Acetic acid concentrations; 1: 0 mol/l, 2: 8.74×10^{-4} mol/l, 3: 8.74×10^{-2} mol/l.

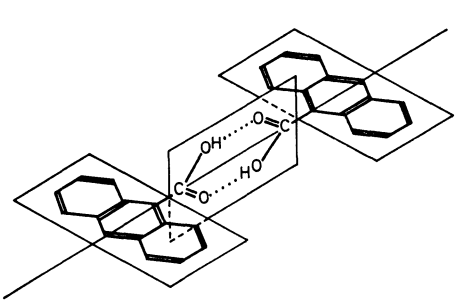

Fig. 8. The probable configuration of the hydrogen-bonded dimer of 9-anthroic acid.

9-Anthroic acid emits the structured fluorescence only when the solvent molecules have both proton-donating and accepting character such as –OH or =NH group. Such solvent molecules can self-associate through hydrogen bonding into a large variety of associated complex species (linear and cyclic polymers).[14,15] Fletcher studied the near-infrared absorption of decane solution of ethanol-*d* at 25 °C.[16] He found it to consist primarily of monomer, acyclic tetramer, and cyclic tetramer in ratios of 1:3.4:10.9, respectively. Kato and Fujiyama studied the local structures of a chloroform–ethanol system by light scattering.[17] They obtained the best fit between the calculated and observed concentration fluctuation by assuming that only an association of $(EtOH)_3CHCl_3$ can exist at 20 °C. The NMR study by Saunders and Hyne also confirmed that monomer-trimer and monomer-tetramer equilibria are dominant in ethanol–carbon tetrachloride system.[18] In the solvents in which 9-anthroic acid emits M fluorescence, the acid may associate with the solvent complex species through hydrogen bonding. This prevents the excited-state rotation of the carboxyl group, M fluorescence thus emerging. In *t*-butyl alcohol, 9-anthroic acid emits only a broad fluorescence. Probably, a bulky *t*-butyl group sterically hinders the formation of complex species, so that the excited-state rotation of a carboxyl group can not be prevented.

When a 9-anthroic acid molecule forms a dimer with another one in ethanol, the excited-state rotation of the carboxyl group will not be hindered because of the lack of the hydrogen-bonded linkages with solvent molecules. This leads to the excited-state rotation of $-\overset{\diagup\!\!\diagdown}{\underset{\diagdown\!\!\diagup}{C}}-$ group into the plane of anthracene rings, so that D fluorescence emerges. Thus, the appearance of the structured M fluorescence in ethanol may reasonably be interpreted within the framework of monomer-dimer equilibria.

The simplest exciton theory proposed by Kasha *et al.*[19,20] predicts the blue shift of the ^1B_b band and the red shift of the ^1L_a band, on the assumption that 9-anthroic acid dimer has the configuration shown in Fig. 8. Both the ^1B_b and ^1L_a bands of 9-anthroic acid show a blue shift (Fig. 1). The discrepancy on the shift of the ^1L_b band is due to the major contribution of the hydrogen-bonding effect on absorption spectra. This was confirmed experimentally as shown in Fig. 7. The hydrogen-bonded species with acetic acid show an absorption spectrum resembling D absorption band in ethanol. The contribution of exciton splitting is relatively small owing to the large distance of two anthracene rings separated by $-\overset{\diagup\!\!\diagdown}{\underset{\diagdown\!\!\diagup}{C}}-$ linkage

and to small oscillator strength of the ^1L_a transition. The blue shift of the ^1L_a band is mainly attributed to hydrogen bonding.

Temperature Dependence of Fluorescence. Figure 9 shows the temperature dependence of fluorescence spectra of 9-anthroic acid in propylene glycol at higher concentration. Lowering the temperature largely displaces the fluorescence to the blue, but no structured fluorescence appears. The fluorescence observed at lower temperatures lies at a position between E and M fluorescence, having a spectral shape resembling D fluorescence. The excitation spectrum monitored at the maximum of this emission corresponds to D absorption band. The fluorescence observed at low temperature can be assigned to the fluorescence of 9-anthroic acid dimers on the assumption of monomer-dimer equilibrium. The fact that E fluorescence disappears at low temperature suggests an excimer-type mechanism as the origin of the broad E fluorescence.

The temperature dependence of the fluorescence spectra of 9-anthroic acid in propylene glycol at lower concentrations is given in Fig. 10. Lowering of temperature causes no substantial spectral changes except for sharpening of the spectrum. Figure 11 shows the temperature dependence of fluorescence in 1:3 methylcyclohexane and isopentane mixtures. Lowering of temperature shifts the fluorescence to the red, further lowering of temperature shifting the fluorescence to the blue, in line with the general behavior of the temperature dependence of fluorescence.[21]

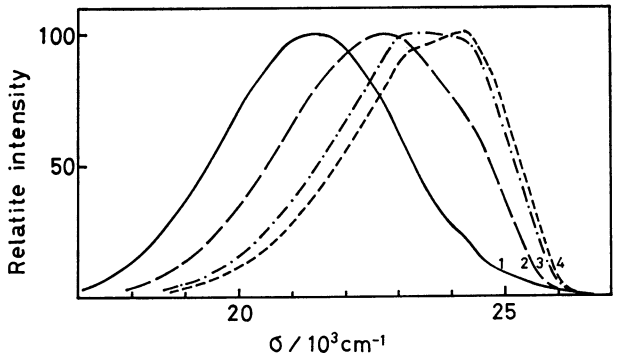

Fig. 9. The fluorescence spectra of 9-anthroic acid in propylene glycol at various temperatures. Solute concentration: 1.87×10^{-3} mol/l. Excitation wavelength: 362 nm. 1: 287 K, 2: 207 K, 3: 173 K, 4: 142 K.

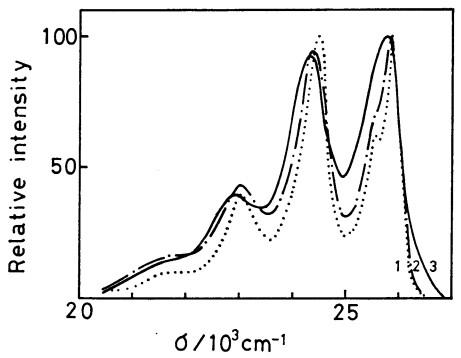

Fig. 10. The fluorescence spectra of 9-anthroic acid in propylene glycol at various temperatures. Solute concentration: 2.0×10^{-6} mol/l. Excitation wavelength: 362 nm. 1: 298 K, 2: 188 K, 3: 103 K.

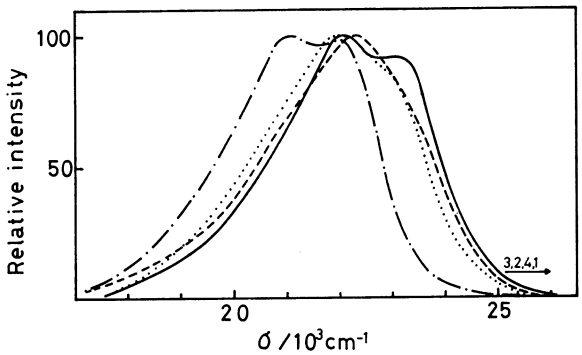

Fig. 11. The fluorescence spectra of 9-anthroic acid in 1:3 methylcyclohexane-isopentane mixture at various temperatures. Solute concentration: 9.6×10^{-6} mol/l. Excitation wavelength: 362 nm. 1: 286.5 K, 2: 260 K, 3: 140 K, 4: 77 K.

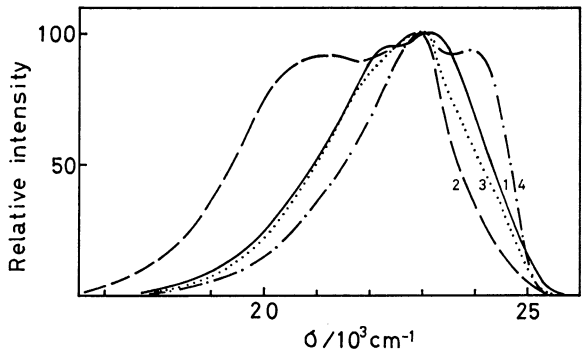

Fig. 12. The fluorescence spectra of 9-anthroic acid in diethyl ether at various temperatures. Solute concentration: 1.8×10^{-3} mol/l. Excitation wavelength: 362 nm. 1: 288 K, 2: 163 K, 3: 124 K, 4: 77 K.

The temperature dependence of fluorescence of 9-anthroic acid in diethyl ether at higher concentration is given in Fig. 12. At room temperature, 9-anthroic acid shows D fluorescence. On lowering the temperature, the component of E fluorescence appears in the spectrum. On further lowering of temperature, the emission shows blue shifts and E fluorescence disappears. Figure 13 gives the temperature dependence of 9-anthroic acid in diethyl ether at lower concentration. No component of E fluorescence appears in the whole temperature range at lower concentration. This indicates that excimer fluorescences can be observed in solvents other than alcohol, if appropriate conditions on concentration and temperature are fulfilled.

Figure 14 gives plots of $\log R$ *vs.* $1/T$ for 7.02×10^{-4} mol/l solution of 9-anthroic acid in propylene glycol. R is I_E/I_M, where I_E and I_M refer to the fluorescence intensity of E and M fluorescences, respectivley. The curve in Fig. 14 shows typical excimer behavior.[22,23] We can evaluate the binding energy of excimer, B, and the activation energy of excimer formation, W. On the assumption that the temperature dependence of the equilibrium constant is negligible within the limit-

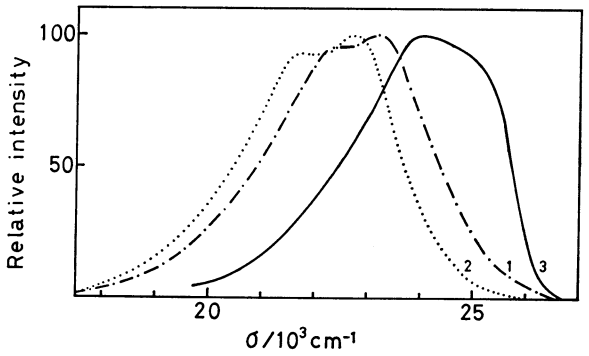

Fig. 13. The fluorescence spectra of 9-anthroic acid in diethyl ether at various temperatures. Solute concentration: 4.7×10^{-6} mol/l. Excitation wavelength: 362 nm. 1: 290 K, 2: 157 K, 3: 77 K.

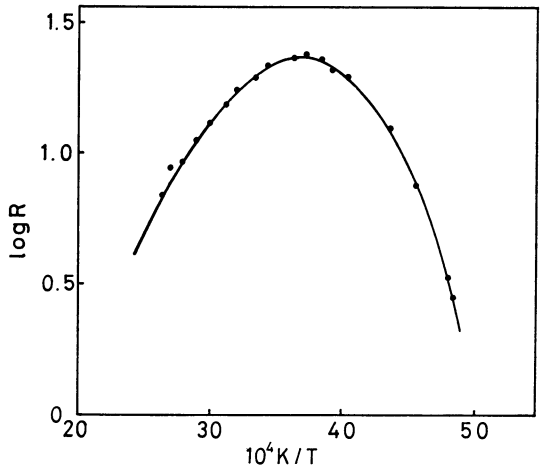

Fig. 14. The log R plot *vs.* $1/T$ for 7.02×10^{-4} mol/l solution of 9-anthroic acid in propylene glycol.

ed temperature range, $B=0.20$ eV was obtained from the slope at higher temperatures. The value of $W=0.36$ eV was also derived from the low-temperature slope of the curve. The values are in line with those obtained for other excimer-forming compounds. This indicates a "universal" type of excimer interaction on the dimer of 9-anthroic acid. Such behavior is unfavorable in the system involving proton dissociation. These findings support the excimer formation from the hydrogen-bonded dimers.

Kinetic Consideration. The ratio of the excimer fluorescence quantum yield to the monomer one is observed to be proportional to the monomer concentration in the case of usual excimer formation.[24] For 9-anthroic acid we propose the following scheme: A hydrogen-bonded dimer of 9-anthroic acid is excited and then associates with an unexcited dimer yielding an excited tetramer from which E emission occurs (Table 1). For steady excitation with light of intensity I_0, the rate equations for this scheme are

$$d[M^*]/dt = aI_0[M] - k_M[M^*],$$

$$d[D^*]/dt = bI_0[D] - (k_D + k_{ED}[D])[D^*] + k_{DE}[E^*],$$

$$d[E^*]/dt = k_{ED}[D][D^*] - (k_E+k_{DE})[E^*].$$

In the equations, the following supplementary parameters are defined:

Table 1. Reaction scheme

Process	Description	Rate parameter
$M^*\rightarrow M+h\nu_M$	fluorescence of M*	k_{FM}
$M^*\rightarrow M$	internal quenching of M*	k_{QM}
$D^*\rightarrow D+h\nu_D$	fluorescence of D*	k_{FD}
$D^*\rightarrow D$	internal quenching of D*	k_{QD}
$D^*+D\rightarrow E^*$	excimer formation	$k_{DE}[D]$
$E^*\rightarrow D^*+D$	regeneration of D* from dissociation of E*	k_{DE}
$E^*\rightarrow D+D+h\nu_E$	fluorescence of E*	k_{FE}
$E^*\rightarrow D+D$	internal quenching of E	k_{QE}

$$k_M = k_{FM} + k_{QM},$$

$$k_D = k_{FD} + k_{QD},$$

$$k_E = k_{FE} + k_{QE}.$$

M, D, and E refer to the monomer, hydrogen-bonded dimer, and excited tetramer, respectively. Under photostationary conditions $d[M^*]/dt=d[D^*]/dt=d[E^*]/dt=0$, and the following relations are obtained:

$$[D]/[M]^2 = K_D,$$

$$[E^*]/([D][D^*]) = K_E,$$

$$R = \frac{I_E}{I_M} = \frac{k_{FE}[E^*]}{k_{FM}[M^*]} \propto \frac{k_{FE}k_M K_E K_D^{1/2}}{k_{FM}} \frac{[D]^{3/2}}{k_D+(k_{ED}-k_{DE}K_E)[D]}.$$

The equation for R indicates that the ratio I_E/I_M is proportional to $[D]^{3/2}$ at low dimer concentrations.

The plot of log R *vs.* log [D] is given in Fig. 15. The I_M and I_E values are evaluated from the areas under the sharp and broad components, which are obtained by subtraction of the corrected M fluorescence spectrum, observed at the lowest concentration, from the corrected spectra observed at various concentrations. The broad component thus obtained closely resembles E fluorescence, indicating that the dimer fluorescence is not actually emitted in this system. It is seen from Fig. 15 that the slope of the plot for 9-anthroic acid

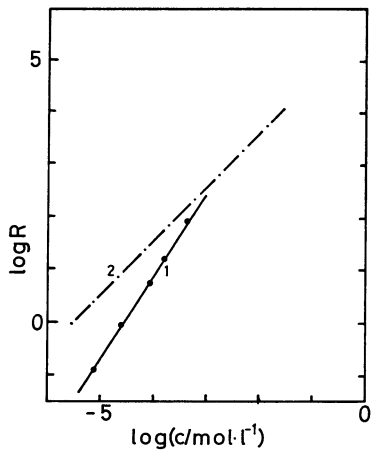

Fig. 15. The log R plot *vs.* log c. 1: The log R plot *vs.* log [D] for 9-anthroic acid in ethanol. 2: The log R plot *vs.* log [M] for 3-methylpyrene in cyclohexane.[23]

is 3/2. Figure 15 includes the plot of log R *vs.* log [M] for 3-methylpyrene, which forms a usual excimer. The slope of the plot is 1 as was expected. If we assume the reaction scheme according to Bazilevskaya and Cherkasov, the slope of the plot for log R *vs.* log [D] should be 1/2. On the other hand, the reaction scheme according to Werner and Hercules gives the slope of 1/2 *vs.* log [M]. We can therefore rule out the reaction scheme proposed by Bazilevskaya and Cherkasov and that by Werner and Hercules. If we assume that a hydrogen-bonded dimer molecule in the excited state associates with an unexcited monomer molecule, we can show that the slope of the plot for log R is 1 *vs.* log [D]. Kinetic consideration indicates the validity of the excited tetramer formed by the association of a hydrogen-bonded dimer in the excited state with a hydrogen-bonded dimer in the ground state.

Other Remarks and Conclusion. Cohen *et al.* gave a theoretical treatment on the general problem of the excimer emission from crystal, and applied it to the anthracene derivatives.[25] They suggested that 9-anthroic acid forms excimers in the head-to-head configurations in the crystal. Polarization study shows that the transition moment of the broad fluorescence has a component perpendicular to the dimer plane.[26] This observation also supports the conclusion stated above. The broad emission of 9-anthroic acid in alcoholic solvents originates from the excited tetramer formed by the association of an excited hydrogen-bonded dimer with an unexcited hydrogen-bonded dimer.

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