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Absorption and Fluorescence Spectra of Anthracenecarboxylic Acids. II. 1- and 2-Anthroic Acids

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The absorption and fluorescence spectra of 1- and 2-anthroic acids (1- and 2-anthracenecarboxylic acids) in alcoholic solvents have been observed as a function of solute concentration. It was revealed that 1- and 2-anthroic acids form hydrogen-bonded dimers in their ground states. The equilibrium constants for dimer formation are : 1.2×10^4 mol^{-1} l for 1-anthroic acid in methanol and 2.0×10^4 mol^{-1} l for 2-anthroic acid in ethanol. Owing to dimer formation, the lowest frequency absorption band of 1-anthroic acid was uniformly displaced to the red, while that of 2-anthroic acid was distinctly resolved into two bands. The band assignment was confirmed by the method of photoselection. No excimer-type fluorescence was observed in 1- and 2-anthroic acids. The lack of mirror-symmetry relationship between the absorption and fluorescence spectra of 1-anthroic acid is explained by the geometrical relaxation in its excited state.

The fluorescence spectrum of 9-anthroic acid (9-anthracenecarboxylic acid) in ethanol shows a remarkable concentration dependence. 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 largely shifts to the red, turning into a broad structureless band. Some attempts to elucidate the origin of this spectral change have been made.[1–5] In connection with this, the electronic spectra of 1- and 2-anthroic acids (1- and 2-anthracenecarboxylic acids) were also investigated.[6]

In the preceding paper[4] of this series, an excimer-type mechanism was presented for the broad fluorescence of 9-anthroic acid. 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 polarization study also supports the excimer mechanism.[5]

This paper presents the concentration and temperature dependence of the absorption and fluorescence spectra of 1- and 2-anthroic acids. In the ground state, 1- and 2-anthroic acids form hydrogen-bonded dimers as does 9-anthroic acid. They do not, however, show any excimer-type fluorescence in contrast to 9-anthroic acid.

Experimental

1-Anthroic acid was prepared from benzanthrone[7,8] and was purified by repeated recrystallization. 1-Anthroic acid from K & K Laboratories was purified by repeated recrystallization . Methanol (Wako fluorometric grade) was used without further purification. Ethanol (Wako super special grade) and propylene glycol (1,2-propanediol, Wako JIS S grade) were stored over molecular sieves 3A and passed through a silica gel column. 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 the quantum response of the detecting and exciting systems and on reabsorption. The degree of polarization, *P*, was measured by the method of photoselection.[9–12]

Results and Discussion

Absorption Spectra and Dimer Formation. The absorption spectra of 1-anthroic acid in methanol are shown in Fig. 1 as a function of concentration. The absorption spectrum of 1-anthroic acid has an anthracene-like structure at lower concentration. The spectra become less sharp on increasing the concentration. Several isosbestic points appear in the spectra. The most probable origin of the isosbestic points in the absorption specta of 1-anthroic acid may be monomer-dimer equilibrium in consideration of the results of 9-anthroic acid. When one ascribes the spectral changes to monomer-dimer equilibrium, the equilibrium constant of dimer formation, K_D, can be determined by the usual procedure.[13] The K_D of 1-anthroic acid was 1.2×10^4 mol^{-1} l in methanol at 290 K.

The concentration dependence of the absorption spectra of 2-anthroic acid in ethanol is given in Fig. 2. The absorption spectrum of 2-anthroic acid has four

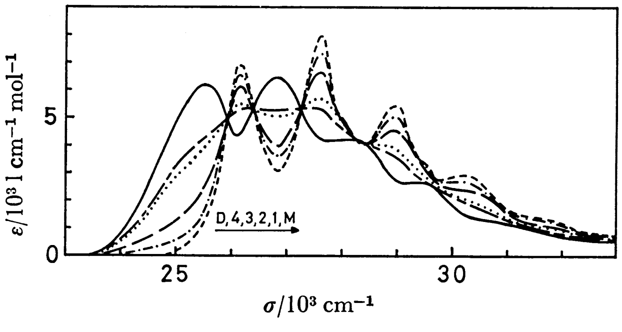

Fig. 1. The absorption spectra of 1-anthroic acid in methanol at various concentrations and the estimated monomer and dimer absorption spectra. 1 : 9.0×10^{-6} mol/l, 2 : 3.0×10^{-5} mol/l, 3 : 1.5×10^{-4} mol/l, 4 : 4.0×10^{-4} mol/l, M : the estimated monomer spectra, D : the estimated dimer spectra.

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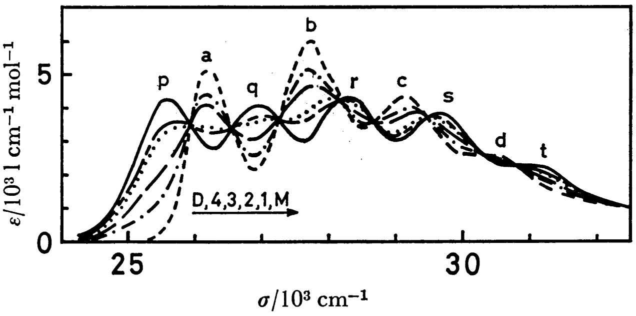


Fig. 2. The absorption spectra of 2-anthroic acid in ethanol at various concentrations and the estimated monomer and dimer absorption spectra. 1 : 2.0×10^{-5} mol/l, 2 : 4.0×10^{-5} mol/l, 3 : 9.9×10^{-5} mol/l, 4 : 2.0×10^{-4} mol/l, M : the estimated monomer spectra, D : the estimated dimer spectra.

vibrational peaks at lower concentration, while it has five vibrational peaks at higher concentration. From an analysis of the data on the concentration dependence of the absorption spectra, the K_D of 2-anthroic acid was determined to be 2.0×10^4 mol^{-1} l in ethanol. By using the observed spectral data at various concentrations and the K_D value, we can estimate the monomer and dimer absorption spectra.[13] The estimated monomer and dimer absorption spectra of 1- and 2-anthroic acids are included in Figs. 1 and 2.

Figure 1 shows that the monomer absorption spectrum of 1-anthroic acid has an anthracene-like progression spaced by 1400 cm^{-1}. The dimer absorption spectrum is displaced to the red with keeping the vibrational structure. The monomer absorption band of 1-anthroic acid in this region may safely be assigned to the ^1L_a transition.

The monomer absorption spectrum of 2-anthroic acid has four vibrational peaks in the region of the lowest-frequency absorption band, while the dimer absorption spectrum has five vibrational peaks. It has well been established that the ^1L_b and ^1L_a bands of 2-anthrol lie closely in this region.[14–16] The lowest-frequency absorption band of 2-anthrol was assigned to the ^1L_b transition and the next one to the ^1L_a transition. The ^1L_a band of 2-anthrol holds an anthracene-like vibrational structure which is characterized by equal spacings of about 1300 cm^{-1}. The ^1L_b band of 2-anthrol is greatly displaced to the red due to hydrogen bonding, while the ^1L_a band is slightly displaced to the blue. As a consequence of this, the ^1L_b and ^1L_a bands are resolved distinctly. The assignment of the absorption bands of 2-anthroic acid can be made as follows, by reference to that of 2-anthrol. Band b of the monomer absorption spectrum is composed of two vibrational bands, one of which belongs to the ^1L_b transition and the other to the ^1L_a transition. Owing to dimer formation, the ^1L_b band is greatly displaced to the red yielding Bands p and q, while the ^1L_a band is displaced to the blue yielding Bands r, s, and t. Band a and a part of Band b of the monomer absorption band may reasonably be assigned to the ^1L_b and a part of Band b and Bands c and d to the ^1L_a transition. This assignment was confirmed by the polarization study (see below).

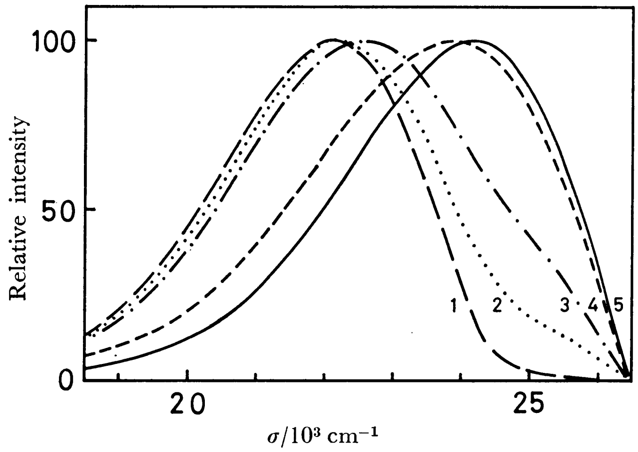


Fig. 3. The fluorescence spectra of 1-anthroic acid in methanol at various concentrations. 1 : 8.8×10^{-4} mol/l, 2 : 4.4×10^{-5} mol/l, 3 : 2.2×10^{-5} mol/l, 4 : 1.1×10^{-5} mol/l, 5 : 4.4×10^{-7} mol/l. Excitation wavelength : 360 nm.

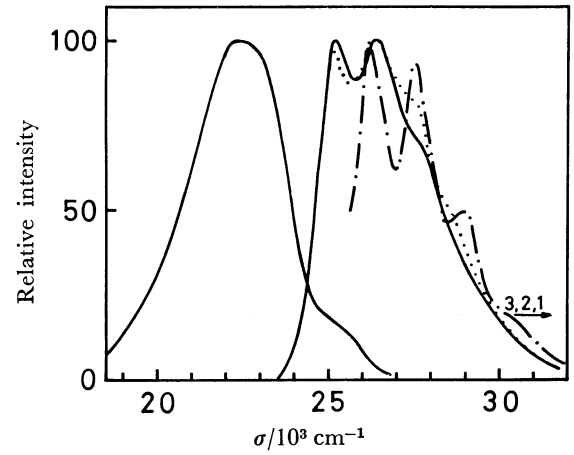


Fig. 4. The fluorescence and excitation spectra of 1-anthroic acid in methanol at 181 K. Solute concentration : 5.0×10^{-6} mol/l. 1 : Observed at 396 nm, 2 : observed at 440 nm, 3 : observed at 490 nm.

It has well been established that carboxylic acids have pK_a values in ethanol larger by about 5.8 than in water.[17–19] The reported pK_a's are 3.7[20] and 3.69[21] for 1-anthroic acid and 4.2[20] and 4.18[21] for 2-anthroic acid. The pK_a's of 1- and 2-anthroic acids in ethanol are estimated to be 9.5 and 10.0, respectively. Proton dissociation can, therefore, be ruled out as the origin of the spectral changes in these solvents.

Fluorescence Spectra. Figure 3 shows the concentration dependence of the fluorescence of 1-anthroic acid in methanol. The fluorescence of 1-anthroic acid exhibits no vibrational structure at lower concentration and the mirror-image relationship between the absorption and fluorescence spectra is lost. A large Stokes shift is observed on increasing the concentration.

The excitation spectra of 1-anthroic acid in methanol at 181 K are shown in Fig. 4. The excitation spectrum monitored at the maximum of the fluorescence band

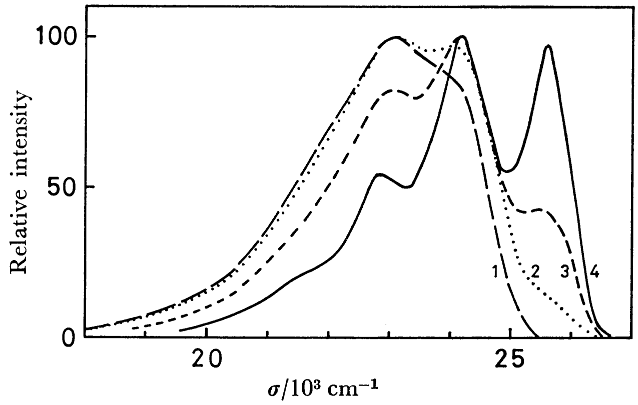


Fig. 5. The fluorescence spectra of 2-anthroic acid in ethanol at various concentrations. 1 : 4.0×10^{-4} mol/l, 2 : 9.9×10^{-5} mol/l, 3 : 4.0×10^{-5} mol/l, 4 : 4.0×10^{-6} mol/l. Excitation wavelength : 354 nm.

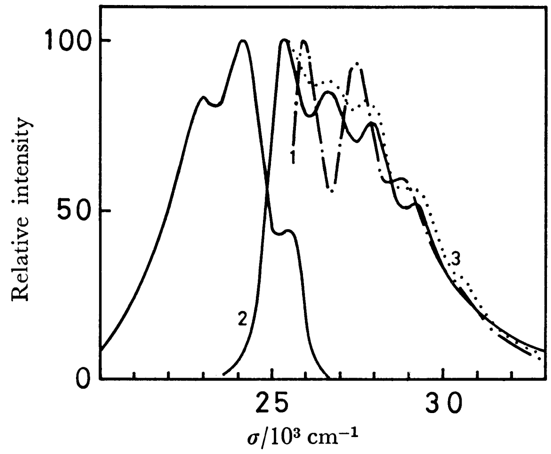


Fig. 6. The fluorescence and excitation spectra of 2-anthroic acid in ethanol at room temperature. Solute concentration : 4.0×10^{-5} mol/l. 1 : Observed at 395 nm, 2 : observed at 430 nm, 3 : observed at 460 nm.

corresponds to the dimer absorption spectrum. On the other hand, the excitation spectrum monitored at 396 nm corresponds to the monomer absorption spectrum. This indicates that the fluorescence observed at higher concentration is attributed to the dimer species.

The spectral dependence of the fluorescence of 2-anthroic acid on concentration is given in Fig. 5. The fluorescence of 2-anthroic acid has a vibrational structure at lower concentration. An approximate mirror-image relation of the fluorescence spectrum to the ^1L_b absorption band is observed. The fluorescence observed at lower concentration may therefore be assigned to the ^1L_b transition. On increasing the concentration, the fluorescence spectrum shifts to the red and becomes structureless. Figure 6 shows the excitation spectra of 2-anthroic acid in ethanol. The excitation spectrum corresponds to the monomer absorption band when monitored at 395 nm, while it corresponds to the dimer one when monitored at 430 nm. These findings indicate that the broad fluorescence can be assigned to the dimer fluorescence.

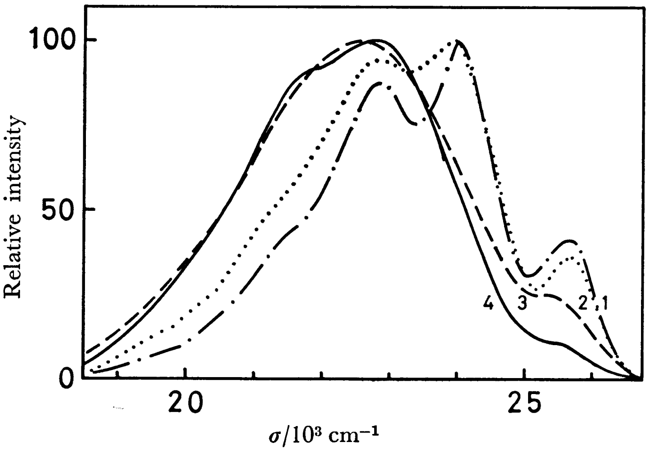


Fig. 7. The fluorescence spectra of 2-anthroic acid in ethanol at various temperatures. Solute concentration : 5.0×10^{-6} mol/l. Excitation wavelength : 360 nm. 1 : 293 K, 2 : 141 K, 3 : 109 K, 4 : 77 K.

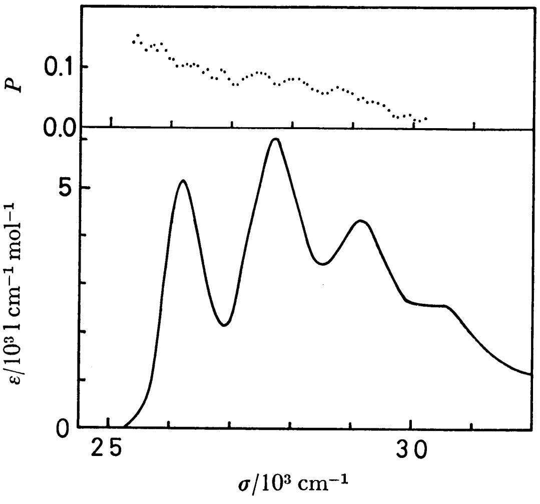


Fig. 8. The fluorescence excitation polarization spectra of 2-anthroic acid in ethanol at 152 K (upper) and the estimated monomer absorption spectrum (lower). Solute concentration : 6.8×10^{-6} mol/l. Observation wavelength : 420 nm.

Figure 7 shows the temperature dependence of the fluorescence of 1-anthroic acid in ethanol. Below the temperature at which the solvent freezes, the fluorescence of 1-anthroic acid has a vibrational structure. A mirror-image relationship between the absorption and fluorescence spectra is observed at lower temperature, although it is lost at room temperature. On the contrary to this, a mirror-image relation between the absorption and fluorescence spectra is observed in 2-anthroic acid at room temperature. These indicate that some geometrical relaxation occurs in 1-anthroic acid during its fluorescence lifetime.

X-Ray analysis of 1-naphthoic acid shows that the angle between the planes of the naphthalene ring and carboxyl group is 11°.[22] Steric hindrance in 1-anthroic acid to coplanarity of the carboxyl group and an aromatic ring should be similar to that of 1-naphthoic acid. An excited-state rotation of the carboxyl group into the plane of the anthracene ring may occur and

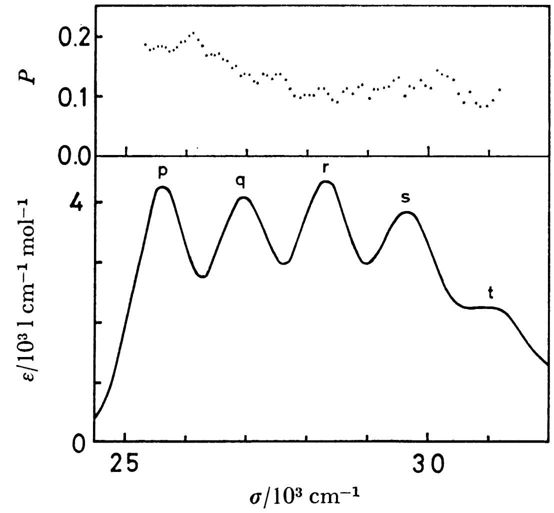


Fig. 9. The fluorescence excitation polarization spectra of 2-anthroic acid in ethanol at 156 K (upper) and the estimated dimer absorption spectrum (lower). Solute concentration : 4.7×10^{-5} mol/l. Observation wavelength : 480 nm.

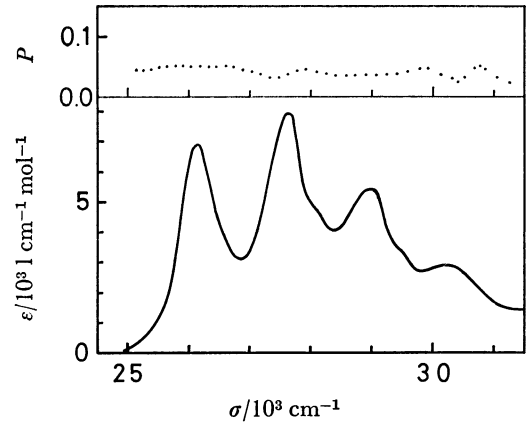


Fig. 10. The fluorescence excitation polarization spectra of 1-anthroic acid in methanol at 171 K (upper) and the estimated monomer absorption spectrum (lower). Solute concentration : 4.4×10^{-5} mol/l. Observation wavelength : 425 nm.

a structureless fluorescence is observed. Steric hindrance in 2-anthroic acid seems to be negligible and no geometrical relaxation upon excitation is expected to occur in 2-anthroic acid. Indeed, a mirror-symmetry relationship is observed in 2-anthroic acid even at room temperature. Any geometrical relaxation is impossible at sufficiently low temperature and, consequently, a mirror-symmetry relationship is observed in 1-anthroic acid at low temperature.

Figure 8 shows the fluorescence excitation polarization spectrum of 2-anthroic acid in ethanol at a concentration of 6.8×10^{-6} mol/l, together with the estimated monomer absorption spectrum. At such a low concentration, 2-anthroic acid exists substantially in the monomer form. The degree of polarization, P, decreases with increasing excitation energy. This suggests that two different electronic bands lie in this region. Figure 9 shows the fluorescence excitation spectrum of 2-anthroic acid at a concentration of 4.7×10^{-5} mol/l, together with the estimated dimer absorption spectrum. It appears from Fig. 2 that the 4.7×10^{-5} mol/l solution contains considerable amounts of dimer species. Furthermore, a 480-nm observation predominantly detects the fluorescence from dimer species. The polarization spectrum indicates that Bands p and q and Bands r, s, and t belong to different transitions.

The fluorescence excitation polarization spectrum of 1-anthroic acid in methanol is given in Fig. 10, together with the estimated monomer absorption spectrum. The concentration of the sample solution was 4.4×10^{-5} mol/l; 1-anthroic acid predominantly exists in monomer form. The value of P is relatively small, since the temperature is high compared with the freezing point of the solvent. The polarization spectrum has almost the same P values over the whole region of the lowest-frequency absorption band. The lowest-frequency absorption band appears to consist of a single electronic transition. The ^1L_a and ^1L_b bands of 1-derivatives of anthracene, in general, lie closely, the ^1L_b band being found at the lower energy side of the ^1L_a band.[13-15)] There is no evidence of the ^1L_b band lying under the ^1L_a band in 1-anthroic acid. The ^1L_b band of 1-anthroic acid seems to have a very small oscillator strength owing to the steric hindrance described above. The same situation was encountered in 9-anthroic acid.

Kinetic Consideration. An excimer mechanism has been presented for the pronounced concentration dependence of 9-anthroic acid in alcoholic solvents.[4)] 9-Anthroic acid forms a hydrogen-bonded dimer in its ground state. The monomer species show the structured fluorescence. The red-shifted broad fluorescence was assigned to the excimer which is formed by the association of the excited and unexcited hydrogen bonded dimers. It was shown that the ratio of the intensity of the excimer fluorescence to that of the monomer fluorescence, $R=I_E/I_M$, is proportional to $[D]^{3/2}$ at low dimer concentrations, where I_E and I_M refer to the fluorescence intensity of the excimer and the monomer, respectively.[4)] When the broad fluorescence is attributed to the dimer, on the other hand, it can easily be shown that the ratio R is proportional to [D].

The corrected fluorescence spectra at various concentrations were divided into the monomer and dimer components, the spectral shapes of which are assumed to be the same as the corrected fluorescence spectra observed at the lowest and the highest concentration. Figure 11 gives the log R plots *vs.* log [D] for 1- and 2-anthroic acids. It is seen from the figures that the slope of the plots is 1 for both 1- and 2- anthroic acids. These observations indicate that no excimer-type fluorescence is observed in 1- and 2-anthroic acids in contrast to 9-anthroic acid.

The sufficient overlap of the two anthracene rings constituting the hydrogen-bonded dimers is essential to the formation of stable excimers. The hydrogen-bonded dimers of 1- and 2-anthroic acids may have two types of conformations which are *cis-* and *trans-*

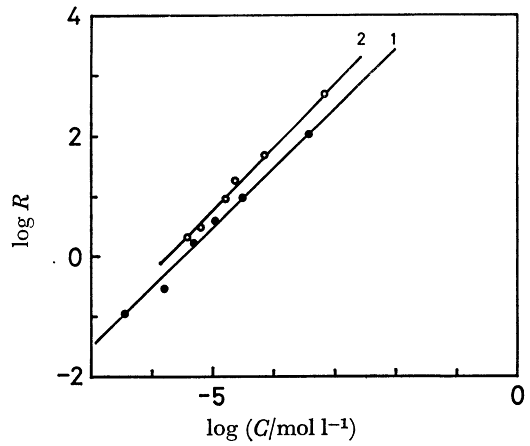


Fig. 11. The log R plots *vs*. log [D]. 1 : 1-Anthroic acid in methanol, 2 : 2-anthroic acid in ethanol.

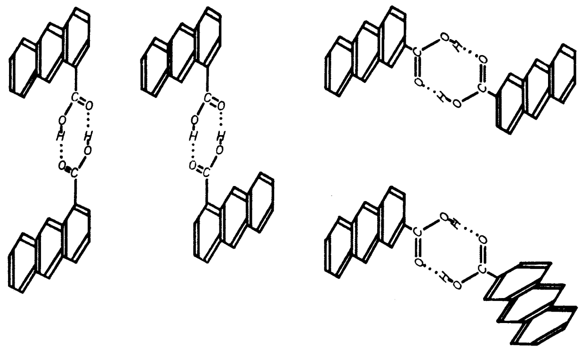
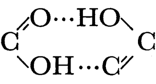


Fig. 12. The types of dimer conformations.

forms relative to  $-\mathrm{C}\begin{matrix}\nearrow\!\!\!\!\nearrow\mathrm{O}\cdots\mathrm{HO}\searrow\\ \searrow\mathrm{OH}\cdots\mathrm{C}\nearrow\!\!\!\!\nearrow\end{matrix}\mathrm{C}-$ linkages, while 9-anthroic acid forms a single type of dimers (see Fig. 12). This decreases the possibilities of excimer formation in 1- and 2-anthroic acids compared with 9-anthroic acid, because the presence of two types of dimer conformations decreases the possibility for encounter of the same type of dimers. Furthermore, the molecular rotation necessary for the two pairs of anthracene rings to overlap sufficiently is generally greater in 1- and 2-anthroic acids than in 9-anthroic acid. For example, when the planes of two dimers are parallel, the complete overlap of two anthracene rings can be realized by the in-plane rotation less than 45° with respect to the other in 9-anthroic acid. In the case of 1- and 2-anthroic acids, on the other hand, the complete overlap is not always realized by the in-plane rotation; sometimes it is necessary to reverse one dimer molecule with respect to the other. This further decreases the possibility of excimer formation in 1- and 2-anthroic acids than in 9-anthroic acid.

The ground-state dimer formation in alcoholic solvents is confirmed in 1- and 2-anthroic acids as well as in 9-anthroic acid. No excimer-type fluorescence is observed in 1- and 2-anthroic acids in contrast to 9-anthroic acid. This is interpreted by the variety of dimer conformations in 1- and 2-anthroic acids. The lack of mirror-symmetry relationship between the absorption and fluorescence spectra of 1-anthroic acid is explained by the geometrical relaxation in its excited state.

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