Molecular Association and Electronic Spectra of Naphthoic Acids: Formation of an Excimer-like Complex in 1-Naphthoic Acid in Rigid-Glass Matrix

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Absorption and fluorescence spectra of 1- and 2-naphthoic acid (1- and 2-NA) have been studied in a hydrocarbon rigid-glass matrix at 77 K and in the crystal. Each of these acids is associated to form a hydrogen-bonded dimer. On increasing the concentration of 1- or 2-NA, the dimer is further associated to give a higher-order complex that may be assumed to be a tetramer. The fluorescence spectra of the monomer and dimer are in mirror-image relation to their respective absorption spectra in both 1- and 2-NA. When the tetramer of 1-NA is photoexcited, a broad structureless fluorescence emission appears, with the maximum at *ca.* 7000 cm^{-1} to the red from the 0–0 band of the dimer fluorescence. The structureless fluorescence spectrum, which has no mirror-image relation to the absorption spectrum of the tetramer, is supposed to originate from an "excimer-like tetramer" of 1-NA. Photo-excitation of the 2-NA tetramer results in a structured fluorescence emission which is considered to come from the simple excited state of the tetramer. The fluorescence lifetimes, quantum yields, and fluorescence-polarization spectra were measured for various molecular species of 1- and 2-NA. The natural fluorescence lifetime of the excimer-like tetramer of 1-NA is evaluated to be 320 nsec, which is 51 times as long as that of the dimer, and the fluorescence from the excimer-like tetramer is polarized mainly along the short molecular axis of the naphthalene nucleus. It is concluded from these observations that the excimer-like tetramer has a symmetrical configuration, with the planes of the constituent dimer molecules parallel to each other, and its fluorescence process is essentially symmetry forbidden.

In a previous paper,[1] we reported the emission spectra of benzoic acid in a hydrocarbon matrix at 77 K with particular regard to effects of dimer formation. As in the case of benzoic acid, 1-naphthoic acid (1-NA) and 2-naphthoic acid (2-NA) are each associated easily to form a dimer containing two O–H⋯O hydrogen bonds. The monomer of benzoic acid gives no fluorescence and only its dimer fluoresces, whereas both the monomer and dimer of the naphthoic acids are known to fluoresce.[2]

In the present study, absorption and fluorescence spectra of 1- and 2-NA have been examined in detail from the viewpoint of molecular association. It was found that, as the concentration of 1- or 2-NA in a hydrocarbon rigid-glass matrix is increased, the hydrogen-bonded dimer is associated further to form a tetramer. In 1-NA, the fluorescence was found to originate from an "excimer-like tetramer." The fluorescence spectra of crystal samples of the naphthoic acids were also obtained for the sake of comparison.

Experimental

1-Naphthoic acid (1-NA), G. R. grade, obtained from Wako Pure Chemical Industries, and 2-naphthoic acid (2-NA), G. R. grade, from Tokyo Kasei Industries were recrystallized from 95% ethyl alcohol and sublimed *in vacuo*. Isopentane, methylcyclohexane, and ethyl ether were purified by the same methods as described in the previous paper.[1] A mixture of isopentane and methylcyclohexane (6 : 1 by volume) was used as solvent, which is referred to as PM in this paper.

Absorption spectra were obtained at 77 K or at room temperature with a Hitachi EPS-3 spectrophotometer, and emission and excitation spectra with a Hitachi MPF-2A spectrophotometer or with an apparatus constructed in our laboratory.[3] Absorption measurements at 77 K were carried out on rigid-glass samples in a quartz cell of 10 mm or 1 mm path length placed in a glass Dewar vessel with quartz windows. Emission measurements at 77 K were made using a 10 mm square quartz cell and a quartz tube cell, 4 mm in diameter. The correction of emission and excitation spectra was made by the relative methods.[1]

Fluorescence decays were observed using 8-nsec exciting light pulses generated by electric discharges through the atmosphere, and the fluorescence lifetimes were obtained by the deconvolution method. Fluorescence quantum yields were determined according to the same procedure as described in Ref. 1.

The measurements of fluorescence polarization were made by the photoselection method.[3,4] The degree of polarization, P is defined as $P=(I_{\parallel}-I_{\perp})/(I_{\parallel}+I_{\perp})$, where $I_{\parallel}$ and $I_{\perp}$ are the intensities of the emitted light polarized, respectively, parallel and perpendicular to the exciting light, which is polarized with the electric vector perpendicular to the plane formed by the excitation and emission beams. The P values were corrected in the usual manner for instrumental and other factors.[3]

Absorption spectra of crystals were measured at room temperature and 77 K using crystal films prepared by evaporation. The crystal fluorescence and excitation spectra were obtained by the front-surface viewing method using crystal powder and crystal films.

The fluorescence spectrum of 1-NA in PM at 4.2 K was observed by immersing the sample cell (a 4-mm quartz tube) directly in liquid helium in a quartz Dewar vessel.

Results and Discussion

The naphthoic acids have large association constants in a hydrocarbon solvent. The monomer–dimer equilibrium constants, K, in PM at room temperature were determined through the procedure of Hosoya *et al.*[5] Since the solubilities of the acids

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1) H. Baba and M. Kitamura, *J. Mol. Spectry.*, **41**, 302 (1972).

2) R. M. Hochstrasser, *Can. J. Chem.*, **39**, 1776 (1961).

3) T. Takemura and H. Baba, This Bulletin, **42**, 2756 (1969).

4) F. Dörr, "Creation and Detection of the Excited State," Part A, ed. by A. A. Lamola, Marcel Dekker, New York (1971), pp. 53—122.

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are very poor in PM, the concentrations of the acids were of the order of 10^{-4} to 10^{-7} mol/l. The results are as follows:

1-naphthoic acid, $K=7.6\times 10^4$ l/mol
2-naphthoic acid, $K=3.4\times 10^4$ l/mol

Absorption Spectra. The absorption spectra at 77 K of 1- and 2-NA in PM are shown in Figs. 1(a) and 2. The K values obtained at room temperature, together with the large binding energies (~10 kcal/mol)[6] estimated for the formation of the dimer, indicate that virtually no monomeric species exists in PM at 77 K with the concentrations adopted in this study. As was reported,[1] the benzoic acid monomer exists in PM even at 77 K. It was confirmed that the naphthoic acids do not show such an unusual phenomenon. In Figs. 1(a) and 2, the absorption spectra in PM containing 5% ethyl ether by volume are regarded as representing approximately the spectra of the monomers.

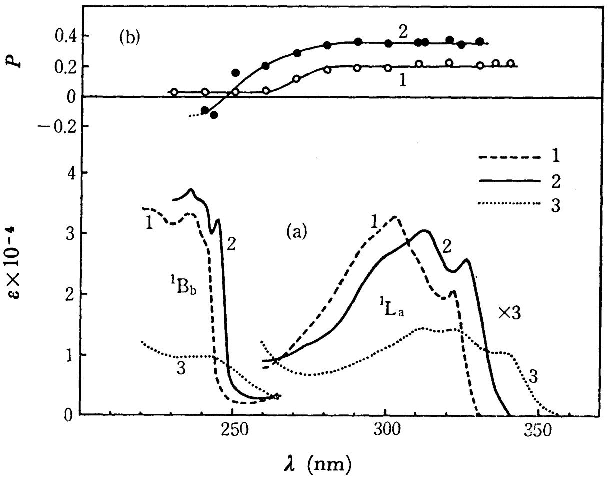

Fig. 1. (a) Absorption spectra of 1-naphthoic acid in PM at 77 K. (1) monomer (see text); (2) dimer (solute concentration, 1.0×10^{-5} mol/l); (3) a mixture of dimer and tetramer (1.0×10^{-4} mol/*l*).

(b) Excitation-polarization spectra of 1-naphthoic acid at 4.0×10^{-5} mol/*l*, obtained by monitoring the fluorescence at two wavelengths: (1) 440 nm (excimer-like tetramer fluorescence region); (2) 353 nm (dimer fluorescence region).

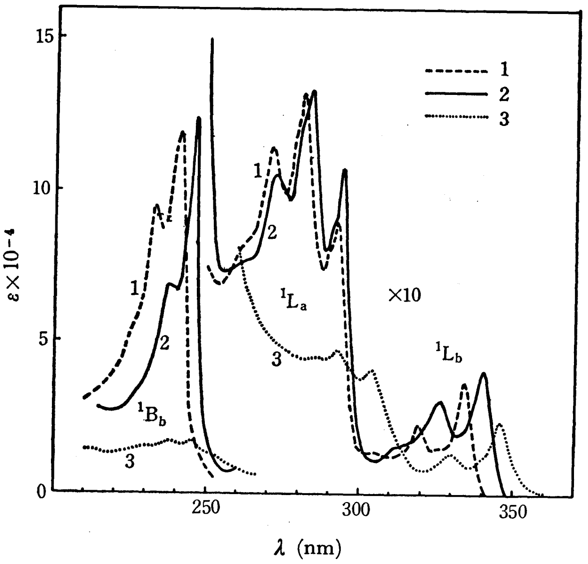

Fig. 2. Absorption spectra of 2-naphthoic acid in PM at 77 K. (1) monomer (see text); (2) dimer (solute concentration, 1.0×10^{-5} mol/l); (3) tetramer (1.0×10^{-4} mol/l).

When the concentration of 1- or 2-NA is 10^{-5} mol/l, only the spectrum of the dimer is obtained at 77 K. As the concentration is increased from 10^{-5} mol/l to 10^{-4} mol/l, new absorption grows up at somewhat longer wavelengths. The absorption spectra corresponding to different concentrations of the acid give an isosbestic point, indicating the existence of an equilibrium between the dimer and a new molecular complex. The new complex is assumed here to be a tetramer of 1- or 2-NA. In Fig. 1(a) or 2, the absorption spectrum represented by the dotted line is considered to be due to the tetramer, but in Fig. 1(a) the spectrum is attributed in part to the dimer. It is further assumed that the tetramer consists of two dimer molecules with their molecular planes parallel to each other; here the hydrogen-bonded dimer is regarded as planar. From the absorption-spectral data, the dimer–tetramer equilibrium constant was estimated to be *ca.* 2.5×10^4 l/mol for 1-NA. This value involves some uncertainty, because the amount of the tetramer produced varies according to the rate of cooling the solution.

In Figs. 1(a) and 2, the values for the molar extinction coefficients, ε, for the dimer and tetramer are defined as the values per monomer. It is evident that the ε values for the dimer defined in this way are comparable to those for the monomer, which fact shows that the π-electronic interaction between the unit monomer molecules is relatively weak in the dimer. This is consistent with the fact that the dimer is formed through the hydrogen bonds and is essentially planar as a whole.[7,8]

The ε values for the tetramer are considerably different from those for the monomer and dimer. This shows a strong π-electronic interaction to occur between the unit dimer molecules in the tetramer, and supports the preceding assumption concerning the configuration of the tetramer. However, inspection of the absorption spectra in Figs. 1(a) and 2 will lead to the following broad assignments of the electronic absorption bands, irrespective of the form of absorbing species (*i.e.*, monomer, dimer or tetramer). In 1-NA, the first absorption band is assigned to the $^1A\to{}^1L_a$ transition in the Platt notation, with the weak $^1A\to{}^1L_b$ transition being assumed to be hidden under the $^1A\to{}^1L_a$ (*vide infra*), and the second band is assigned to the $^1A\to{}^1B_b$ transition. In 2-NA, the first, second, and third absorption bands are assigned respectively to the $^1A\to{}^1L_b$, $\to{}^1L_a$, and $\to{}^1B_b$ transitions.

In Fig. 3 are shown the absorption spectra of crystal films of the naphthoic acids. These spectra are very broad and clearly different from the absorption spectra

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[6] G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freemann and Company, San Francisco (1960), pp. 351—353.

[7] J. Trotter, *Acta Crystallogr.*, **13**, 732 (1960).

[8] J. Trotter, *ibid.*, **14**, 101 (1961).

of the tetramers in solution (Figs. 1(a) and 2).

Fluorescence and Excitation Spectra. Figures 4(a) and 5(a) show the fluorescence spectra of 1- and 2-NA in PM solution and in the crystal at 77 K. The fluorescence spectra in PM containing 5% ethyl ether are attributed to the monomer as in the case of the absorption spectra.

The fluorescence spectrum at the solute concentration of 10^{-5} mol/l is due to the dimer. The fluorescence spectra of the monomer and dimer are in mirror-image relation to their respective absorption spectra. For 1-NA, on increasing the concentration, the intensity of the structured dimer fluorescence decreases and, at the same time, a new broad structureless fluorescence emission appears, its maximum being shifted to the red by about 7000 cm^{-1} from the 0–0 band of the dimer fluorescence. The new fluorescence spectrum has no mirror-image relation to the absorption spectrum of the tetramer. Only the broad spectrum with its maximum at 440 nm is observed upon excitation at 340 nm, where the tetramer alone is considered to be excited (*cf.* Fig. 1(a)). For 2-NA, the increase of the concentration results in a structured fluorescence which is red shifted by only 1700 cm^{-1} from the 0–0 band of the dimer fluorescence.

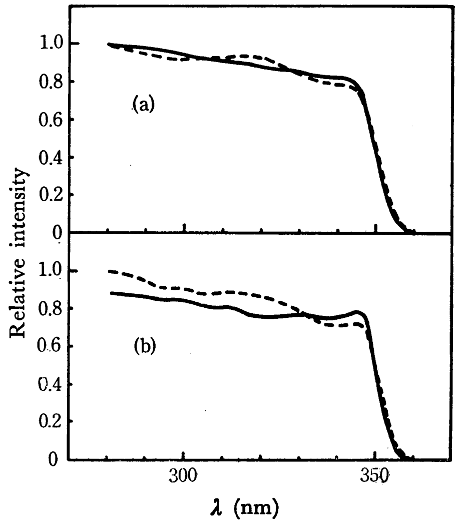

Fig. 3. Absorption spectra (——) and excitation spectra (----) in the crystal of 1-naphthoic acid (a) and 2-naphthoic acid (b) at 77 K.

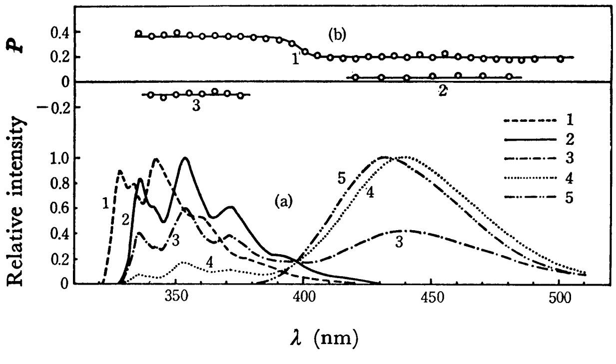

Fig. 4. (a) Fluorescence spectra of 1-naphthoic acid in PM and in crystal at 77 K. (1) monomer (see text); (2) dimer (solute concentration, 1.0×10^{-5} mol/l); (3) a mixture of dimer and excimer-like tetramer (4.0×10^{-5} mol/l); (4) a mixture of dimer and excimer-like tetramer (1.0×10^{-4} mol/*l*); (5) crystal.

(b) Fluorescence-polarization spectra of 1-naphthoic acid in PM at 4.0×10^{-5} mol/l, obtained by excitation at two wavelengths: (1) 310 nm, (2) and (3) 240 nm.

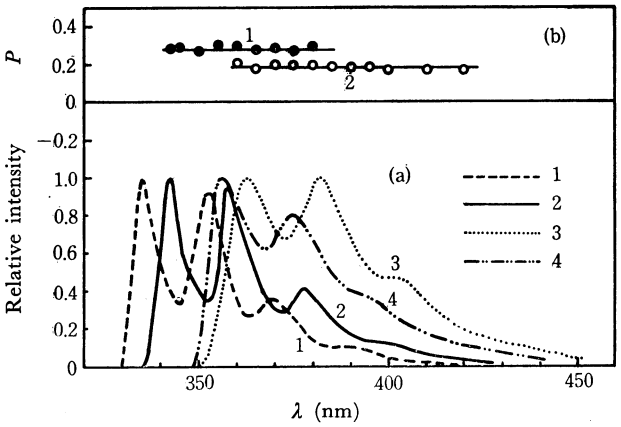

Fig. 5. (a) Fluorescence spectra of 2-naphthoic acid in PM and in crystal at 77 K. (1) monomer (see text); (2) dimer (solute concentration, 1.0×10^{-5} mol/l); (3) tetramer (1.0×10^{-4} mol/l); (4) crystal.

(b) Fluorescence-polarization spectra of 2-naphthoic acid dimer (1) and tetramer (2) in PM at 77 K, obtained by excitation in the region of the longest wavelength absorption (the ^1L_b band).

The new broad structureless fluorescence of 1-NA is considered to originate from an "excimer-like tetramer" in which the interplanar distance between the dimer molecules constituting the tetramer is definitely shortened as a result of the excitation of the tetramer. It should be noted that 1-NA dimer is here regarded as corresponding to the monomer in the ordinary excimer.[9–12] On the other hand, the new structured fluorescence of 2-NA is assigned to the simple tetramer.

In each of the monomer, dimer, and tetramer of the naphthoic acids, the corrected excitation spectrum related to the fluorescence was found to be in good agreement with the corresponding absorption spectrum.

The corrected excitation spectrum of the excimer-like tetramer of 1-NA is shown in Fig. 6 by a broken line. The excitation spectrum is similar to but somewhat different from the absorption spectrum for the 10^{-4} mol/l solution of 1-NA. Since in this solution the tetramer is considered to be largely responsible for the latter spectrum, it must be reasonable to assume that, actually, the excitation spectrum fully agrees with the absorption spectrum of the tetramer alone. The discrepancy between the excitation and absorption spectra for the 10^{-4} mol/l solution can then be at-

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10) J. B. Birks, "Photophysics of Aromatic Molecules," Wiley-Interscience, London (1970), pp. 301—371.

11) N. Mataga and T. Kubota, "Molecular Interactions and Electronic Spectra," Marcel Dekker, New York (1970). pp. 411—436.

12) S. P. McGlynn, A. T. Armstrong, and T. Azumi, "Modern Quantum Chemistry," Part III, ed. by O. Sinanoğlu, Academic Press, New York (1965), pp. 203—228.

Table 1. Fluorescence lifetimes and quantum yields for 1- and 2-naphthoic acids at 77 K

Compound		τ_f(nsec)	Φ_f	τ_f^0(nsec)	k_f(sec^{-1})
1-Naphthoic acid	Dimer	1.9	0.30	6.3	1.6×10^8
	Excimer-like tetramer	83.7	0.26	320	3.1×10^6
	Crystal	69.7			
2-Naphthoic acid	Dimer	23	0.54	43	2.3×10^7
	Tetramer	25	0.53	47	2.1×10^7
	Crystal	18			

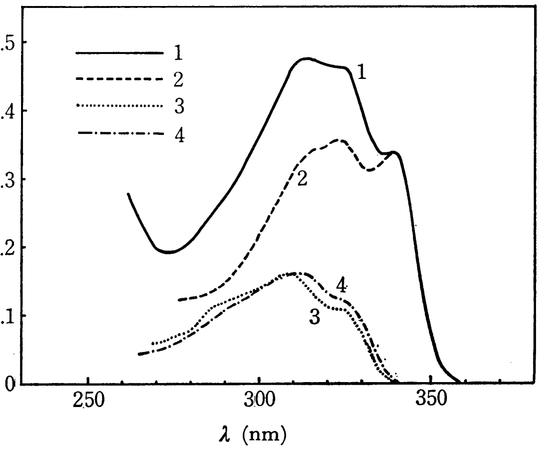

Fig. 6. Excitation spectrum related to the fluorescence from excimer-like tetramer and absorption spectra of 1-naphthoic acid. (1) absorption spectrum of a mixture of dimer and tetramer (solute concentration, 1.0×10^{-4} mol/l); (2) excitation spectrum of excimer-like tetramer; (3) subtracted spectrum (see text for the derivation of this spectral curve); (4) absorption spectrum of dimer (1.0×10^{-5} mol/l).

tributed to the fact that the absorption spectrum involves to some extent the contribution of the dimer. On the basis of the finding that the absorption band at 340 nm (Fig. 1(a)) is due to the tetramer alone, the excitation and absorption spectra are so drawn in Fig. 6 that the both spectra may have the same intensity at that wavelength. Under these conditions, subtraction of the excitation spectrum from the absorption spectrum for the 10^{-4} mol/l solution will yield the absorption spectrum for the dimer. This proves to be true, as is seen in Fig. 6. These considerations clearly indicate that the excimer-like tetramer of 1-NA is formed when the tetramer which exists already in the ground state is photo-excited.

The fluorescence spectra for the crystals of 1-NA and 2-NA are similar to those for the excimer-like tetramer of 1-NA and the simple tetramer of 2-NA, respectively, but the crystal spectra are slightly shifted to the blue (see Figs. 4(a) and 5(a)). The corrected excitation spectra associated with the crystal fluorescence emissions agree well with the crystal absorption spectra in both 1- and 2-NA (see Figs. 3(a) and 3(b)). It may be noted that the structureless excimeric fluorescence spectra of 1-NA in the crystal as well as in the rigid-glass matrix disappeared when a phosphoroscope (50 rps) was used.

Formation of the Excimer-like Tetramer. We are now in a position to examine in detail the excimer-like tetramer of 1-NA in comparison with the simple tetramer of 2-NA. To inquire into the mechanism of the formation of the excimer-like tetramer, it is desirable to know the nature of the excited states of the dimer. For this purpose we shall first consider the fluorescence lifetimes.

Table 1 shows observed fluorescence lifetimes, τ_f, and quantum yields, Φ_f, for 1- and 2-NA at 77 K. The τ_f value for the 1-NA dimer is 1.9 nsec, while that for the 2-NA dimer is 23 nsec. The natural lifetimes, τ_f^0, obtained by the use of the quantum yields are also shown in the table. The τ_f^0 values for the dimers of 1- and 2-NA are 6.3 and 43 nsec, respectively. This suggests that the lowest excited singlet state (fluorescent state), S_1, of the 1-NA dimer is the ^1L_a state and S_1 of the 2-NA dimer is the ^1L_b state. In fact, these values of τ_f^0 agree well with the ones calculated from the Strickler-Berg equation[13] on the basis of the above state assignments; the calculated values are 6.2 and 29.2 nsec, respectively, for the 1- and 2-NA dimers. In the 1-NA dimer the ^1L_a and ^1L_b absorption bands cannot be separated from each other, so that it is tentatively assumed here that the intensity of the ^1L_a absorption band is 80% of the whole absorption intensity in the region from 270 nm to 340 nm (see Fig. 1(a)). This assumption is based on the expectation that the ratio between the intensities of the ^1L_a and ^1L_b bands in the 1-NA dimer is not appreciably different from the corresponding ratios in other simpler naphthalene derivatives.[14-16]

In the 2-NA dimer, it follows from the absorption spectrum given in Fig. 2 that the ^1L_a state, which is the second excited singlet state, is located at an energy about 4600 cm^{-1} above the ^1L_b (S_1) state. It is generally known that the ^1L_a state is responsible for the formation of an excimer,[17,18] and that if the ^1L_a level is much higher than the ^1L_b, the excimer formation is hardly possible.[19] Thus, the difference in the tendency to form an excimer-like tetramer between 1- and 2-NA dimers seems to come from the difference in their electronic structure.

The potential curves illustrating the interaction of the two dimer molecules are shown schematically in Fig. 7. In 1-NA, the attractive force leading to the excimer-like tetramer may result from the inter-

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[14] L. S. Forster and K. Nishimoto, *J. Amer. Chem. Soc.*, **87**, 1459 (1965).

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[18] A. K. Chandra and E. C. Lim, *ibid.*, **48**, 2589 (1968).

[19] E. A. Chandross and H. T. Thomas, *J. Amer. Chem. Soc.*, **94**, 2421 (1972).

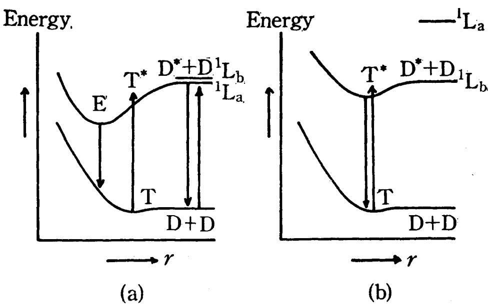

Fig. 7. Schematic potential energy curves showing the formation of excimer-like tetramer of 1-naphthoic acid (a) and tetramer of 2-naphthoic acid (b). r represents the interplanar distance.

action of the ^1L_a state and charge resonance states.[17] The excimer-like tetramer is thus formed along the potential curve for the excited state in Fig. 7(a).

As may be inferred from Fig. 7(b), the situation is different in the case of 2-NA, where the fluorescence is emitted from the simple excited state of the tetramer.

A broad structureless fluorescence emission to be assigned to the excimer-like tetramer was also observed at 4.2 K for 1-NA in PM. In this case, the fluorescence band maximum shows a slight blue shift of *ca.* 140 cm^{-1} compared with the fluorescence at 77 K. The probable increase of the matrix rigidity accompanying the temperature decrease will prevent the excimer-like tetramer from reaching its equilibrium state during its lifetime. This may result in the blue shift mentioned above.

Crystals of 1- and 2-NA are known to consist of nearly planar centrosymmetrical dimer molecules that are formed by the two O–H···O hydrogen bonds,[7,8] and the adjacent dimer molecules have their molecular planes parallel to each other. The difference in spectral behavior between the fluorescence emissions of the 1- and 2-NA crystals (Figs. 4(a) and 5(a)) may be interpreted, as before, in terms of the difference in the relative positions of the ^1L_a and ^1L_b levels. Furthermore, in 1-NA the crystal structure is more favorable for the strong π-electronic interaction to occur.[7,8]

Geometrical Configuration and Electronic Structure of the Excimer-like Tetramer. The geometrical configuration of excimers has been studied by means of intramolecular excimer fluorescence and excimer fluorescence in the crystal.[20,21] The results seem to indicate that a symmetrically overlapping configuration is favorable for the excimer formation. For such a configuration, theoretical considerations predict that the electronic transition associated with the excimer fluorescence should be symmetry forbidden.[11] However, the fact that most of the observed lifetimes of excimers in solution are relatively short is inconsistent with the above prediction.[9]

The lifetimes and quantum yields of the naphthoic acids are given in Table 1. It is seen that in 1-NA the excimer-like tetramer has a much longer natural lifetime $\tau_f{}^0$ than does the dimer. The radiative rate constants $k_f(=1/\tau_f{}^0)$ for the dimer, excimer-like tetramer, and tetramer will be denoted by k_f^D, k_f^E, and k_f^T, respectively. Then, from the data in Table 1 the following are obtained:

1-naphthoic acid, $k_f^D/k_f^E = 51$

2-naphthoic acid, $k_f^D/k_f^T = 1.1$

The results suggest that the fluorescence transition in the excimer-like tetramer is electronically forbidden.

The electronic structure of the excimer of naphthalene has attracted much attention.[12,18,22] McGlynn *et al.* showed that in a naphthalene excimer of relatively high symmetry, the transition between its fluorescent and ground states is forbidden.[12] In a similar manner it may be concluded that the excimer-like tetramer of 1-NA has a symmetrical configuration, with the planes of the constituent dimer molecules parallel to each other, and that its fluorescence process is essentially symmetry forbidden. Mataga *et al.* measured the fluorescence lifetimes of excimers of anthracene, perylene, and other aromatic hydrocarbons in cyclohexane matrix at 77 K,[23] and found that the lifetimes are of the order of 10^2 nsec and are longer than the fluorescence lifetimes of the corresponding monomers. Thus, with respect to the configuration and fluorescent state of the excimers, they reached a conclusion similar to the one we have just derived.

The question may then be raised why the "forbidden" fluorescence transition from the excimer-like tetramer of 1-NA has a relatively small but non-zero value of radiative rate constant ($k_f^E=3.1\times10^6\ \text{sec}^{-1}$). In general, an electronically-forbidden transition in a molecule may become allowed through vibronic interaction. Thus, for instance, in aromatic hydrocarbons like naphthalene, $k_f(^1L_a)/k_f(^1L_b)$ is of the order of 10 to 10^2,[11] where $k_f(^1L_a)$ and $k_f(^1L_b)$ are the radiative rate constants for the $^1L_a\to{}^1A$ and $^1L_b\to{}^1A$ transitions, respectively; the former transition is allowed, while the latter is essentially forbidden. As has been shown, $k_f^D/k_f^E=51$, so that it would be reasonable to consider that the "forbidden" fluorescence transition in the excimer-like tetramer steals a transition probability from other allowed transitions. Alternatively, we may suppose that the excimer-like tetramer deviates slightly from the symmetrical configuration, resulting in the non-zero value of the rate constant k_f^E.

Only a few studies have hitherto been made on the polarization of the excimer fluorescence because of experimental difficulties.[24–26] The excimer fluorescence has been observed not only in fluid solutions, but also in rigid matrices.[27,28] However, most of these matrices are opaque ones, *e.g.*, frozen cyclohexane and n-hexane, and are not suitable for the polarization measurement.

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We observed the fluorescence- and excitation-polarization spectra for the dimer and excimer-like tetramer of 1-NA in the transparent rigid-glass PM solution, together with the fluorescence-polarization spectra of the dimer and tetramer of 2-NA in the same solution. Figures 1(b) and 4(b) show respectively the excitation- and fluorescence-polarization spectra of 1-NA. Figure 4(b) is concerned with the fluorescence-polarization spectrum of 1–NA at the concentration of 4×10^{-5} mol/l, where both dimer and tetramer exist in the ground state. In the region of the excimer-like tetramer fluorescence (between 410 and 500 nm), the *P* values are 0.20 with respect to excitation at 310 nm (line 1), and 0.04 with respect to excitation at 240 nm (line 2). It may be noted that excitation at 340 nm, where only the tetramer is excited, leads to the same *P* values as excitation at 310 nm. In the region of the dimer fluorescence (between 335 and 380 nm), the *P* values are 0.36 for excitation at 310 nm (line 1) and −0.10 for excitation at 240 nm (line 3). The same results were also obtained at the 1-NA concentration of 10^{-5} mol/l, where only the dimer exists.

The fluorescence-polarization spectra of 2-NA are shown in Fig. 5(b). The polarization spectrum of the dimer was obtained at the 2-NA concentration of 1.0×10^{-5} mol/l, and that of the tetramer at 1.0×10^{-4} mol/l. The *P* values are 0.28 for the dimer (line 1) and 0.18 for the tetramer (line 2) with respect to the excitation in the region of the longest-wavelength absorption band.

In 1-NA, the $^1A\rightarrow{}^1L_a$ and $^1A\rightarrow{}^1B_b$ transitions are considered to be polarized largely along the short and long axes of the naphthalene nucleus, respectively.[29] Then, the polarization data for the 1-NA dimer (Figs. 1(b) and 4(b)) are reasonably explained by assuming that the dimer fluorescence has a transition moment parallel to the short axis. The fluorescence spectra of the dimer and tetramer of 2-NA are positively polarized with respect to the excitation into the ^1L_b state (Fig. 5(b)), so that the fluorescent state is regarded as the ^1L_b in either case. However, the *P* value is somewhat smaller for the tetramer, showing that the increase in the degree of molecular association is accompanied by a factor which leads to depolarization.

A comparison of the polarization data for the excimer-like tetramer of 1-NA with the corresponding data for the dimer (Figs. 1(b) and 4(b)) shows that depolarization occurs obviously in the fluorescence emission in passing from the dimer to the excimer-like tetramer. However, referring to the situation in 2-NA, one may say that the fluorescence emitted from the excimer-like tetramer is polarized essentially along the short axis, as in the case of the dimer fluorescence.

As has been mentioned, the "forbidden" transition associated with the fluorescence of the excimer-like tetramer may become partially allowed either by vibronic interaction or by deviation from the symmetrical configuration. Among the lower excited states of the excimer-like tetramer, there should exist an electronic state from which the transition to the ground state is symmetry allowed. The energy of this allowed transition must be higher than that of the forbidden transition, since the latter transition is related to the lowest excited state. According to the proposed mechanism of the formation of the excimer-like tetramer (*cf.* Fig. 7), the transition moment of the allowed transition in question should be parallel to the moment of the $^1A\rightarrow{}^1L_a$ transition in the dimer or simple tetramer of 1-NA. As regards the vibronic interaction, the forbidden transition will steal the transition probability efficiently from the allowed transition, because the energy difference between the two transitions concerned would not be large. On the other hand, the deviation from the symmetrical configuration, if it occurs at all, will result in a mixing of the allowed transition metioned above with the forbidden transition. These considerations account for the observed polarization of the fluorescence from the excimer-like tetramer.

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[29] S. Suzuki, T. Fujii, and H. Baba, *J. Mol. Spectry.*, in press.