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The Intramolecular Interaction in the Excited State of 1-Pyrenylmethyl 9-Anthracenecarboxylate

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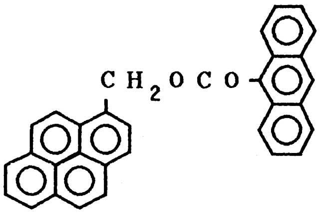
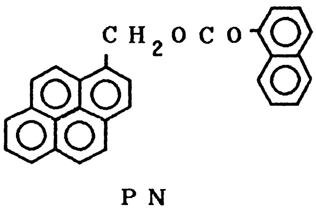
1-Pyrenylmethyl 9-anthracenecarboxylate exhibits an intramolecular exciplex emission. The electron transfer from the pyrene to the anthracenecarboxylate chromophore has been shown by the effects of solvent and temperature on the fluorescence spectra to drive the formation of the exciplex in spite of the unfavorable s-cis conformation of the carboxylate C-O bond.

The photoinduced electron transfer has received much attention in the areas of photophysics, organic synthesis and photobiology in the past ten years. In the course of our study on 1-diazomethylpyrenes as reagents for the fluorescent, photolabile protecting groups of carboxylic acids, we have found that some 1-pyrenylmethyl esters (**PA**, **PN**) are photostable.$^{1)}$ They showed fairly large solvent effects on the fluorescence quantum yields and lifetimes, indicating the existence of the intramolecular interaction in the excited states between the pyrene and carboxylate chromophores. Among these photostable esters, only 1-pyrenylmethyl 9-anthracenecarboxylate (**PA**) showed broad structureless emission bands in the longer wavelength region characteristic of the exciplex formation. In this communication, we wish to disclose some unique features of the exciplex of **PA**.

The absorption spectrum of **PA** in methanol is superimposable to that of a 1:1 mixture of ca. 10^{-5} M methanol solutions of 1-pyrenylmethanol and 9-anthracenecarboxylic acid. No solvent effect was observed either; the absorption spectrum of **PA** in isooctane is almost identical to that in methanol



PA



PN

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without any observable shift or change of the relative intensities of the absorption maxima. To the contrary, the shape and maximum wavelength of the emission spectra of **PA** consisting mostly of intramolecular exciplex showed marked solvent effects (vide infra). The 1:1 component mixture does not show any intermolecular exciplex emission at this concentration (Fig. 1), although 1-pyrenylmethanol (10^{-5}M) does form an exciplex having an emission maxima at 475 nm when the concentration of the acid is more than 10 times higher (>10^{-4} M).$^{2)}$ It is therefore concluded that the charge transfer interaction is not significant in the ground state but only in the excited state.

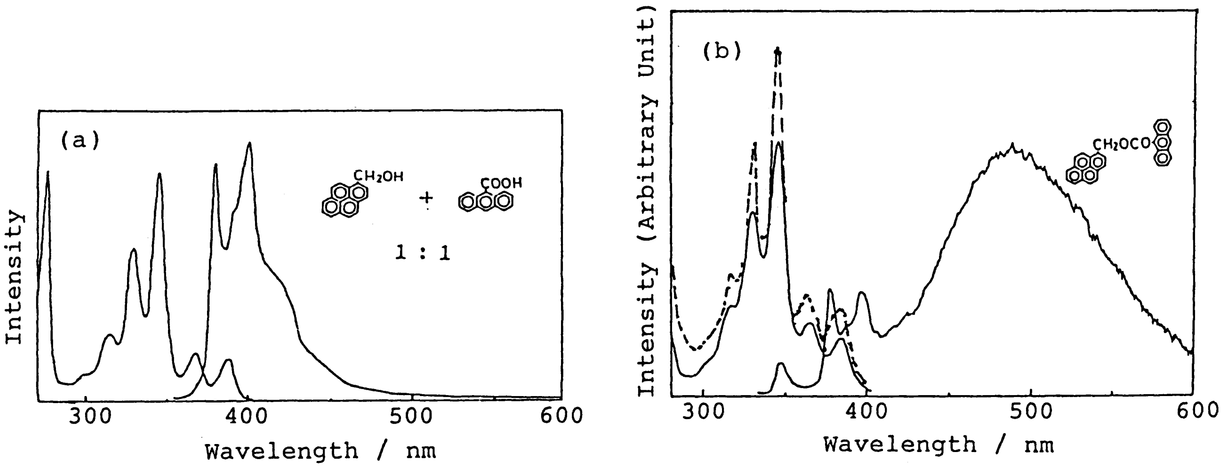

Fig. 1. Absorption and emission spectra at 20°C: (a) a 1:1 mixture of 1-pyrenylmethanol and 9-anthracenecarboxylic acid in methanol, and (b) **PA** in methanol (——) and isooctane (----).

The fluorescence spectra obtained by excitation at 313 nm in methanol or acetonitrile showed a weak emission (LE) due to the locally excited pyrene chromophore and a broad and strong emission band (EX) caused by the charge transfer from the pyrene to the anthracene part. When the anthracene part was selectively excited at 365 nm, the shape and emission maxima of EX band was the same as those obtained by excitation at 313 nm where more than 80% incident light was absorbed by the pyrene chromophore. As the polarity of the solvent was decreased, the fluorescence quantum yield increased. The LE emission was not observed in solvents with the dielectric constants smaller than that of tetrahydrofuran (ϵ = 7.6), probably due to the strong EX emission band overshadowing the relatively weak LE band. The fluorescence quantum yields, lifetimes and wavelengths of the emission maxima are listed in Table 1. The temperature dependence of the fluorescence spectra in methanol and isooctane is shown in Figs. 2a and 2b. The intensity ratio I_E/I_L of the exciplex emission to the locally excited emission increased continuously as the temperature was lowered. The similar spectra without any locally excited emission was observed when the spectra of a suddenly frozen dibutyl ether solution of **PA** was taken.

PA provides the first example in which an exciplex with a "sandwich-type structure" was observed between two hydrocarbon chromophores separated by a -C(O)-O-CH_2- bridge.$^{4)}$ It might be argued that the ester group is nothing but a

Table 1. Fluorescence Quantum Yields, Lifetimes and Emission Maxima of **PA** in Solvents of Different Polarities[3)]

Solvent	Quantum yield[a)]	Lifetime / ns[b)]		Emission maxima / nm
		at 20 °C	-70 °C	
Acetonitrile	0.013			477
Methanol	0.012	<1.0	2.0	487
Tetrahydrofuran	0.081	1.6		467
Dibutyl Ether	0.24	5.0(85) 10.9(15)	9.4(58) 19.8(42)	440, 457
Isooctane	0.61	5.0(33) 10.6(66)	6.0(22) 14.6(77)	437, 452

a) The sums of the quantum yields of LE and EX excited at 313 nm at 20 °C are given, since the separation of the low intensity LE from the strong EX was difficult.

b) The % ratios of the two lifetime components when excited at 362 nm are shown in parentheses.

n = 3 bridge, but it is totally different from a $-(CH_2)_3-$ bridge. The s-cis conformation necessary for the intramolecular exciplex formation is thermodynamically much less stable than s-trans conformation in esters. The rotation around the C-O bond of methyl acetate from s-trans to s-cis in the ground state requires an activation energy of 54 kJ/M.[4)] It could be possible to overcome this barrier for isomerization by a Coulombic attraction force between the two oppositely charged chromophores if the intramolecular charge transfer exists in the excited state. This seems to be the case with **PA**, since the preliminary result of a CARS (Coherent Anti-Stokes Raman Scatterings) study on **PA** showed the formation of the pyrene cation indicating the intramolecular CT state is formed in the excited state.[5)] Although this Coulombic attraction to form a "sandwich

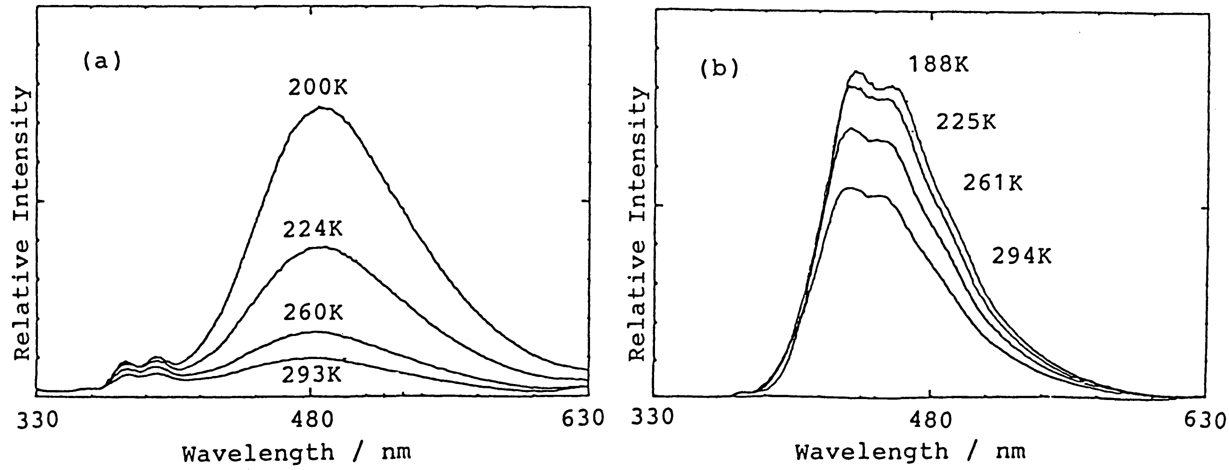

Fig. 2. The temperature dependence of the fluorescence spectra of **PA** excited at 313 nm in (a) methanol and (b) isooctane.

structure" is quite reasonable, there remains some difficulty in explaining the absence of LE emission and the presence of EX emission in the frozen **PA** solutionsince the rotation about the C-O bond might be difficult. The solvent dependency of the fluorescence quantum yields and the observation of the EX emission of the frozen sample indicate that the intramolecular interaction in **PA** is mainly through bonds rather than through space. The exciplex formation from a nearly s-trans conformation would account for the observation more readily. In order to elucidate these unique features of **PA**, more detailed photophysical studies and inspections of feasibility of the exciplex formation in the systems with longer methylene chains are now in progress in our laboratories.

References

1) M. Iwamura, T. Ishikawa, Y. Koyama, K. Sakuma, and H. Iwamura, Tetrahedron Lett., 28, 679(1987); M. Iwamura, K. Tokuda, N. Koga, and H. Iwamura, Chem. Lett., 1987 1729.

2) 1 M = 1 mol dm^{-3}.

PA was purified by several runs of flush column chromatography on silica gel and recrystallization. The absence of any impurity either fluorescent or non-fluorescent was confirmed by good agreement of the absorption and excitaion spectra and by HPLC equipped with a fluorescence detector. Sample solutions in concentrations of ca. 10^{-5}M were prepared and degassed by freeze-pump-thaw cycles. Absorption spectra were measured with a Hitachi UV/Vis spectrometer. Fluorescence spectra were measured on Hitachi 850 and Spex Fluorolog spectrometers. Fluorescence lifetime was obtained by a Horiba NAES 1100 time-resolved spectrophotometer.

3) The fluorescence decay curves could be fitted to sums of two exponentials over a temperature range between 25 °C to -70 °C in isooctane and dibutyl ether. In methanol the decay curves were fitted to a single exponential over the same temperature range, as they could no longer be resolved into two components. The lifetimes were nearly independent of the excitation wavelengths (313 nm and 362 nm) in any of the solvents used. The shape of the fluorescence spectra in isooctane also shows that there are at least two exciplex conformers. The structures of these conformers will be discussed elsewhere.

4) S. M. de B. Costa, M. J. Prieto,and R. S. Davidson, J. Photochem., 12, 1 (1980); P. Vanderauwere, F. C. DeShryver, A. Weller, M. A. Winnik, and K. A. Zachariasse, J. Phys. Chem., 88, 2964 (1984). They observed the intramolecular exciplex formation in ω-(dimethylamino)alkyl and ω-(N-methyl-N-phenylamino)alkyl 2- and 9-anthracenecarboxylates and 1-pyrenecarboxylate when the alkyl chains contained more than two carbon atoms, i.e., "n" > 4.

5) The s-trans vs. s-cis energy difference in methyl acetate, for example, is reported to be 35.5 ± 4.2 kJ/M; K. B. Wiberg and K. E. Laidig, J. Am. Chem. Soc., 109, 5935(1987).

6) Private communication from Prof. C. Hirose of Tokyo Institute of Technology.

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