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Photoreactivity of 1-Pyrenylmethyl Esters. Dependence on the Structure of the Carboxylic Acid Moieties and the Nature of the Excited States

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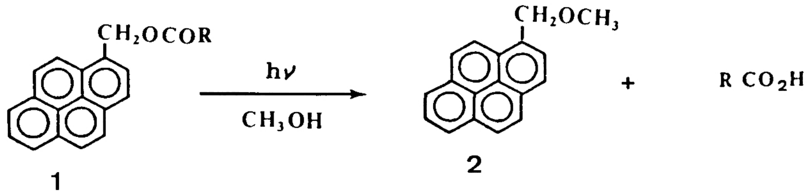
While the photolysis of 1-pyrenylmethyl phenylacetates in methanol gave the original phenylacetic acids, irradiation of the 1-naphthoate and 9-anthracenecarboxylate leads to the formation of the intramolecular exciplexes that are inert to the photolysis. The Φ_f and τ_f values of these esters have been determined.

The photolysis of the 1-pyrenylmethyl esters (**1**) of typical carboxylic acids in methanol leads to nearly complete recovery of the starting carboxylic acids along with formation of methyl 1-pyrenylmethyl ether (**2**) under mild and neutral conditions. Since these esters **1** are obtained by the reactions of 1-diazomethylpyrene (**3**) or 1-pyrenylmethanol (**4**) with carboxylic acids, the 1-pyrenylmethyl group is proposed to serve as one of the most useful protecting groups of carboxylic acids.[1)] We would like to report here more quantitative aspects of the reactions and structural dependences of the excited state properties of **1a** - **f**.

A 0.5 - 1.0 mmol dm^{-3} methanol solution of **1** was irradiated at 340 nm[2)] and the reaction mixture was analysed by HPLC at certain time intervals. Some results on the disappearance of **1** under similar conditions are shown in Fig. 1. Esters **1a** - **d** were photolysed up to 90% within 2 h giving the corresponding carboxylic acids and **2**. The alkaline extraction of the reaction mixtures gave 70 - 80% of the starting carboxylic acids. The rates of the photolysis are in the order: **1d** > **1c** > **1b** > **1a**. No appreciable decrease in the amounts of **1e** and **1f** was observed after the 2 h irradiation either at 340 nm or at 254 nm; **1e** and **1f** are inert to the photolysis under these conditions.

Both absorption and emission spectra of **1a** - **e** resemble each other without showing any meaningful shift of the maxima or the disappearance of the fine structure. **1f** has, however, absorptions at a longer wavelength region characteristic of the anthracene chromophore in addition to the ones similar to



R = a, CH_3

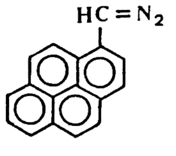
b, p-$CH_3C_6H_4$

c, $C_6H_5CH_2$

d, 1-Naphthylmethyl

e, 1-Naphthyl

f, 9-Anthryl



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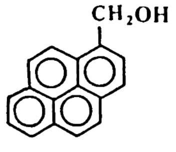

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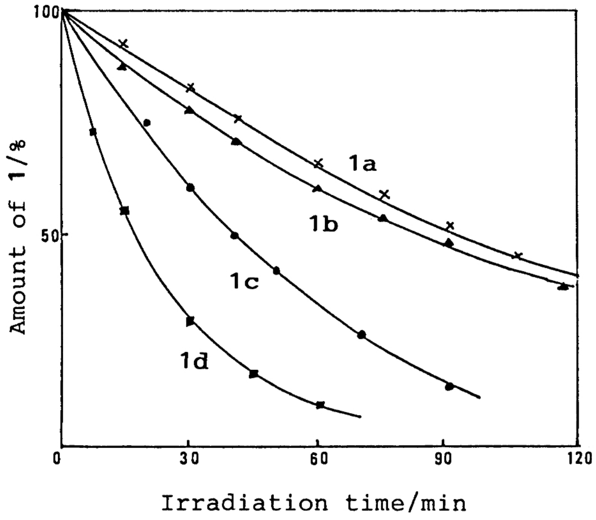

Fig. 1. Photochemical consumption of **1** by irradiation at 340 nm in methanol.

the spectra of **1a** - **e**. Figure 2 shows the absorption and emission spectra of **1e** and **1f**. Only **1f** has a broad structureless fluorescence band that is independent of concentration.[3] This band is characteristic of an intramolecular excimer or exciplex formation often observed for molecules with two aromatic chromophores isolated by three atoms.[4] The absence of the exciplex fluorescence in **1e** is rather strange since both **1e** and **1f** are inert to photolysis and have similar arrangements of the aromatic rings capable of formation of the intramolecular exciplexes with the pyrene ring. In order to explain this discrepancy, the fluorescence lifetime (τ_f) and quantum yield (Φ_f) of **1e** were determined in various solvents (Table 1). The presence of a non-radiative exciplex is suggested from large solvent effects on both τ_f and Φ_f, and explains the similar photochemical behavior of **1e** to that of **1f**. In Table 2 are collected the τ_f and Φ_f values of **1a** - **1e**. The relationship among the τ_f, Φ_f, and the photoreactivity can be summarized as follows.

1) The photo-reactive esters have long fluorescence lifetimes, τ_f >200 ns, in methanol, the only one exception being **1b** that has the τ_f value of 97 ns.

2) The Φ_f and τ_f values of the photo-resistant esters are order of magnitude smaller than those of the photo-reactive esters.
3) The esters with four connecting atoms between the pyrene ring and the other aromatic ring (**1c** and **1d**) show relatively small solvent effects both on Φ_f and τ_f similar to those of aliphatic carboxylate **1a**, indicating that there is no intramolecular exciplex formation.
4) The formation of both radiative and non-radiative exciplex interfere with the photolysis.
5) There is no linear relationship between the order of photoreactivity and the fluorescence lifetime.

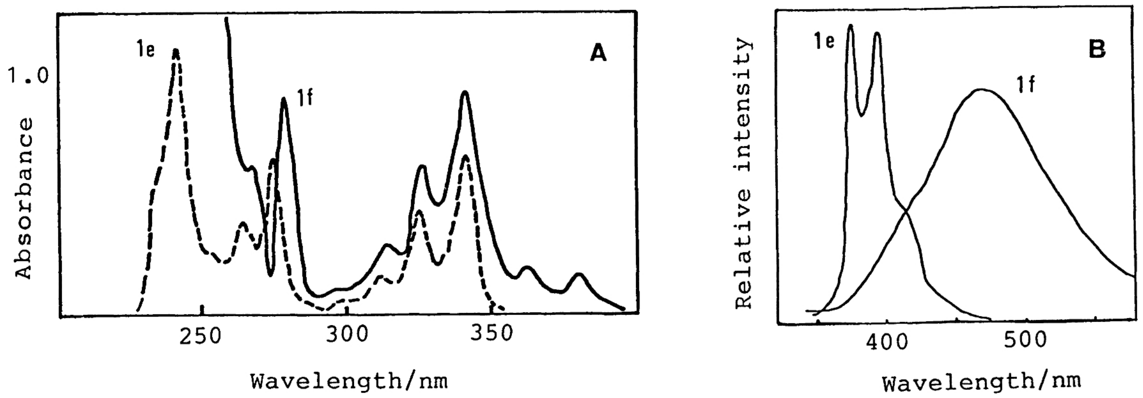

Fig. 2. Absorption (A) and fluorescence (B) spectra of **1e** and **1f** in methanol.

Table 1. Effects of the Solvents on Φ_f and τ_f of **1e** [5]

Solvent (Dielectric constant)	Φ_f	τ_f/ns
Methanol (32.6)	0.001	0.85
Isobutyl alcohol (17.5)	0.012	2.8
Tetrahydrofuran (7.6)	0.017	3.9
Di-isobutyl ether (3.1)	0.087	60
iso-Octane (2.1)	0.36	170

Lastly, we point out the possibility of the formation of weak non-radiative exciplexes in **1b**, since it has the "three connecting atoms" between the two aromatic rings and showed a medium τ_f value and a large solvent effect. More detailed studies are now in progress delineating the effects of the substituents on the phenyl group and the quantum yields of the photoreactions.

Table 2. Fluorescence Quantum Yields and Lifetimes of Esters **1**[5]

		1a	**1b**	**1c**	**1d**	**1e**	**1f**
Φ_f	in MeOH	0.57	0.22	0.31	0.14	0.001	0.01
	in iC_8H_{18}	0.81	0.34	0.38	0.65	0.36	0.12
τ_f/ns	in MeOH	246	97	246	235	0.85	<1
	in iC_8H_{18}	271	242	273	282	170	a)

a) Not determined.

References

1) M. Iwamura, T. Ishikawa, Y. Koyama, K. Sakuma, and H. Iwamura, Tetrahedron Lett., 28, 679 (1987)

2) A 500 W Xenon lamp with a monochrometer was used as a light source. At this wavelength, the pyrene chromophores absorb most of the incident light in **1a** - **e** and 90% light in **1f**.

3) This is the first example of the observation of the intramolecular exciplex formed between the pyrene and anthracene chromophores connected through the ester C(=O)-O-C bonds. A study of its photophysical features is in progress.

4) F. Hirayama, J. Chem. Phys., 42, 3163 (1965); F. C. De Schryver, N. Boens, and J. Put, Adv. Photochem., 10, 359 (1977); F. C. De Schryver, P. Collart, J. Vanderdriessche, R. Goedeweeck, A. Swinnen, and M. Van der Auweraer, Acc. Chem. Res., 20, 159 (1987).

5) Quantum yields were determined relative to that of pyrene on a Hitachi 850 spectrofluorometer with a single photon counting equipment. Lifetime measurements were carried out with the single photon technique on a Horiba NAES 1100 time-resolved spectrofluorometer.

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