Photochemical and Photophysical Behavior of *p*-Methoxyphenylalkenyl Phenanthrenecarboxylates. II. Kinetic Investigation of Intramolecular Cycloaddition

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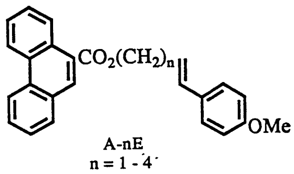
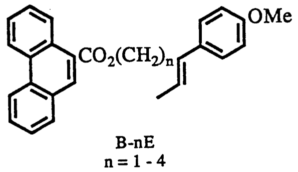
The efficiency of [2+2] photocycloadduct formation was examined by measuring fluorescence lifetimes and the quantum yields of fluorescence and product formation in two series of *p*-methoxyphenylalkenyl 9-phenanthrenecarboxylates (A-*n*E and B-*n*E). In (*E*)-3-(*p*-methoxyphenyl)-3-pentenyl, (*E*)-4-(*p*-methoxyphenyl)-4-hexenyl, and (*E*)-5-(*p*-methoxyphenyl)-5-heptenyl 9-phenanthrenecarboxylates (B-2E, B-3E, and B-4E, respectively) the intramolecular quenching leads to product (cyclobutane+oxetane) formation in almost unit efficiency, while in (*E*)-4-(*p*-methoxyphenyl)-3-butenyl and (*E*)-5-(*p*-methoxyphenyl)-4-pentenyl 9-phenanthrenecarboxylates (A-2E and A-3E, respectively) exciplex→product efficiency is a half to three quarters. Intermediacy of plural exciplex intermediates is suggested in the present bichromophoric systems on the basis of exciplex quenching results.

In the preceding paper[1)] we reported a novel aspect in the phenanthrene–styrene reaction[2,3)] brought about by interchromophoric links[4,5)] with an ester group, a competitive cycloaddition of intramolecular exciplexes involving carbonyl addition caused by conformational constraints.[6)] Thus, in two series (A-*n*E and B-*n*E, *n*=1—4) of bichromophoric phenanthrenecarboxylate esters with different linking sites and chain lengths, some of A series esters afforded only oxetane adducts, whereas some of B series esters gave both of oxetane and head-to-head cyclobutane adducts.

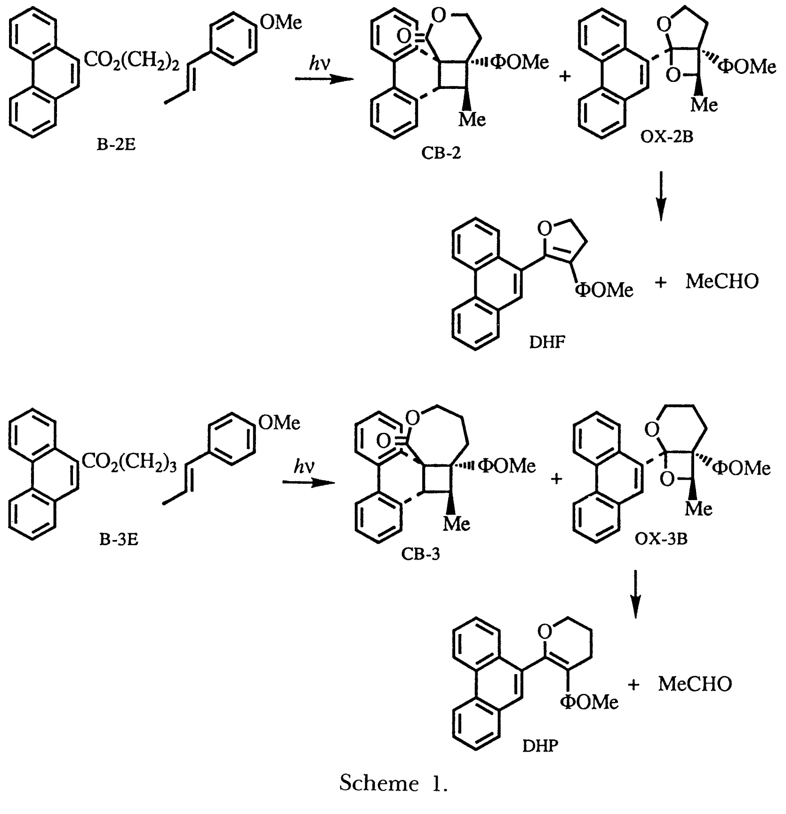


A-nE
n = 1 - 4

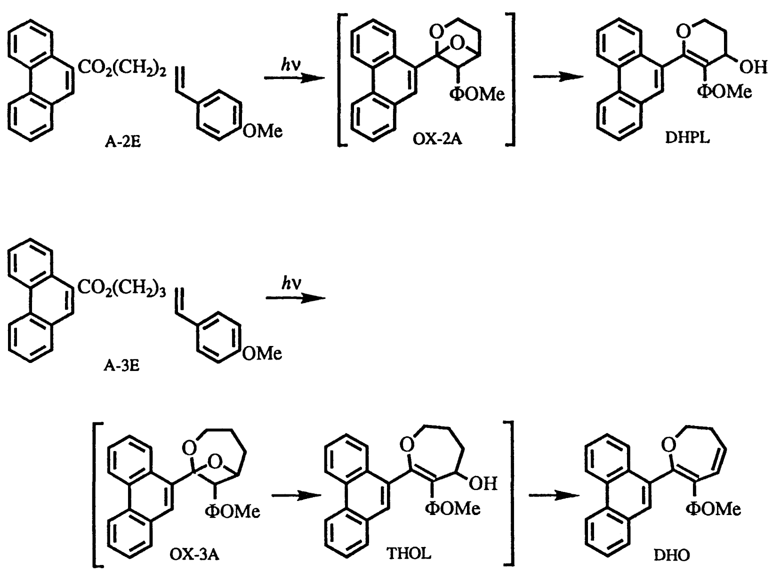


B-nE
n = 1 - 4

In this paper we compare photophysical and photochemical behavior of plural intramolecular exciplexes and discuss the efficiency of cycloadduct formation through intramolecular quenching of the phenanthrene singlet by the styrene moiety on the basis of



Scheme 1.



Scheme 2.

measurements of fluorescence lifetimes and quantum yields, and also of exciplex quenching results.

Experimental

Ultraviolet absorption spectra (UV) were taken on a Hitachi 200-20 spectrophotometer. Fluorescence spectra were recorded on a Hitachi MPF4 fluorescence spectrofluorimeter. The fluorescence quantum yield of methyl 9-phenanthrenecarboxylate (9-MCP) was determined in benzene by comparing its corrected fluorescence spectrum with that of phenanthrene, of which the fluorescence quantum yield is reported, $\phi_f=0.13$.[7] The fluorescence quantum yields of the phenanthrene moiety of bichromophoric esters were determined by comparing the peak height at the 0,0 band (367 nm) of their corrected spectra with that of 9-MCP. The fluorescence quantum yields of intramolecular exciplexes were determined for the residual emissions. Fluorescence lifetimes were measured by single photon counting by using an Ortec/Applied Photophysics SP-3X system.

Quantum yields for disappearance of substrates were measured by irradiating their degassed benzene solutions (5×10^{-5} mol dm^{-3}, three freeze-thaw cycles) with 366-nm light isolated from a 400-W high-pressure mercury lamp through a Toshiba UV-D36B glass filter. Product yields were determined on a Shimadzu LC-2 HPLC with a Zorbax-ODS column. Potassium tris(oxalato)ferrate(III) actinometry was used for determining light intensity.[8]

Benzene was distilled from CaH$_2$ before use. Isoprene was purified by distillation. *trans*-Anethole [*t*-AN, 1-(*p*-methoxyphenyl)propene] and dimethyl acetylenedicarboxylate (DMAD) were distilled under reduced pressure before use. Synthetic procedures for phenanthrenecarboxylates were described in the preceding paper.[1]

Results and Discussion

Fluorescence Spectra. All the bichromophoric esters exhibited similar fluorescence spectra to that of methyl 9-phenathrenecarboxylate (9-MCP) with emission maxima at 367 and 383 nm, and, except A-1E and B-1E, showed a weak emission in the longer wavelength regions (Fig. 1 in the preceding paper).[1] Normalization of the spectra at the 0,0 peak (367 nm) or at the emission maximum (383 nm) and subtraction of the 9-MCP spectrum from those of the esters gave residual emissions with a maximum around 450 nm due to intramolecular exciplexes (Fig. 2 in the preceding paper).[1] It is noteworthy that all the exciplex emissions show their maxima at 450 nm, indicating that intramolecular interaction is energetically very similar among the esters in spite of the difference in linking chain length and site. This is in contrast with the case of α,ω-dipyrenylalkanes,[9] in which the emission maximum is shifted with the chain length.

The quantum yields for fluorescence due to the phenanthrenecarboxylate chromophore and the intramolecular exciplexes (ϕ_{mf} and ϕ_{ef}, respectively) were determined in benzene relative to that of phenanthrene (0.13)[7] as summarized in Table 1.

The fluorescence lifetimes (τ_S) of 9-MCP and the bichromophoric esters were also measured in benzene by single photon counting techniques and are listed in Table 1. The phenanthrenecarboxylates affording photoadducts, i.e., A-2E, A-3E, B-2E, and B-3E, exhibit much lower fluorescence quantum yields and much shorter fluorescence lifetimes compared to 9-MCP, indicating that the reactions proceed from the phenanthrenecarboxylate singlets. The fluorescence quantum yields and lifetimes of A-1E and B-1E are also lower than those of 9-MCP; however, their low fluorescence efficiency may be due to intramolecular static quenching of phenanthrene singlets. No exciplex emission in these esters supports the static quenching.

For the intermolecular case of 9-MCP and *trans*-anethole (*t*-AN), the fluorescence of 9-MCP was

Table 1. Quantum Yields for Fluorescence (ϕ_{if}) and Disappearance (ϕ_r) of Phenanthrenecarboxylates[a)]

Compound	ϕ_{mf}[b)]	ϕ_{ef}[b)]	τ_S[c)]	λ_{max}[e d)]	ϕ_r
9-MCP	0.25	—	15.3	450[e)]	0.11[f)]
A-1E	0.10	—	10.7	No	—
A-2E	0.07	<0.001	3.9	450	0.36
A-3E	0.04	0.01	3.2	450	0.61
A-4E	0.15	0.02	12.1	450	0.05
B-1E	0.13	—	7.4	No	—
B-2E	0.06	0.005	5.2	450	0.70
B-3E	0.09	0.008	7.5	450	0.52
B-4E	0.15	0.01	14.4	450	0.15

a) 10^{-4} mol dm^{-3} in benzene at room temperature. b) Fluorescence quantum yields for the phenanthrene moiety (ϕ_{mf}) and exciplexes (ϕ_{ef}). c) Fluorescence lifetimes of the phenanthrene moiety. d) Wavelenghs of exciplex emission maxima. Results are identical for normalization at 367 (0,0) or 383 nm (λ_{max}). e) With *t*-AN. f) Extrapolated to infinite *t*-AN concentration.

quenched efficiently by *t*-AN, and a weak emission appeared in the 400—500 nm region (λ_{max} 450 nm). The quenching rate constant of 4.2×10^9 mol^{-1} dm^3 s^{-1} was obtained by dividing the Stern-Volmer constant (46 mol^{-1} dm^3) by 15.3 ns of the 9-MCP singlet lifetime determined above. Absorption spectrum measurements gave no evidence for a ground-state charge-transfer complex between 9-MCP and *t*-AN and also in the bichromophoric systems.

Quantum Yields for Reactions. For the esters affording products their disappearance quantum yields (ϕ_r) were measured at low conversion (<20%) by irradiating their benzene solutions with 366 nm light. The values obtained are listed in Table 1. As mentioned in the preceding paper,[1)] the four esters, B-2E, B-3E, A-2E, and A-3E, exhibit high disappearance quantum yields (0.36—0.70). For the intermolecular case the quantum yields were determined at various *t*-AN concentrations; the limiting quantum yield, the fraction of the quenched excited ester resulting in product formation was estimated to be 0.11 by extrapolating to infinite *t*-AN concentration (Table 1).

Exciplex Quenching. As described in the preceding paper,[1)] the oxetane formation was quenched by oxygen 10—20% more efficiently than phenanthrene fluorescence. More quantitative experiments were carried out by using other quenchers. The exciplex emission and cycloadduct formation from B-2E and A-3E were quenched by dimethyl acetylenedicarboxylate (DMAD).[10)] The fluorescence from the phenanthrene nucleus was scarcely quenched by DMAD. Table 2 lists the Stern-Volmer constants ($K_{SV}{}^e = k_{eq}\tau_e$) for the exciplex quenching in 9:1 benzene-isoprene, where k_{eq} and τ_e are the quenching rate constant by a quencher (Q) of the exciplex and its lifetime, respectively. The $K_{SV}{}^e$ values in Table 2 are different among the phenomena of each ester. If a common exciplex intermediate exhibited the emission and gave the cycloadducts, $K_{SV}{}^e$'s should be the same[10)] for the two (for A-3E) or three phenomena (for B-2E). The present results suggest that the exciplex emission, oxetane formation, and cyclobutane formation are ascribed to discrete exciplexes and these exciplexes might be formed directly from the locally excited singlet state, though involvement of the partial equilibrium among these exciplexes cannot be excluded.[11)] The above results are consistent with indications of the absence of serious geometrical restrictions for emissive intramolecular exciplex formation[12)] and with the observation that the exciplex emission is not significant in the intermolecular case of 9-MCP and *t*-AN giving the head-to-head cycloadduct.

Table 2. Stern-Volmer Constants for Exciplex Quenching

Phenomenon	$K_{SV}{}^e$/mol^{-1} dm^3 for Ester/DMAD	
	B-2E	A-3E
Exciplex emission[a)]	ca.10	ca.9
Oxetane formation	5.1	3.7
Cyclobutane formation	7.5	

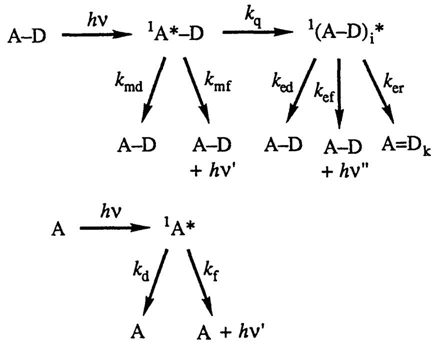
a) Exciplex emissions of B-2E and A-3E were too weak to allow determination of their lifetimes by single photon counting.

Estimation of Rates for Exciplex Formation and Exciplex→Product Probability. Combination of the disappearance quantum yields with the fluorescence data affords the exciplex→product probabilities. The processes concerning cycloadditions can be described as shown in Scheme 3, where A and D represent the phenanthrene and styrene moieties of a bichromophoric ester, respectively.

Because of high quantum yields of substrate disappearance and a single exponential decay nature of ^{1}A* fluorescence in A-D we neglected a return process from exciplex to local excited state [^{1}(A-D)*→^{1}A*-D]. Under this assumption, the lifetime of ^{1}A* (τ_S) and quantum yields for ^{1}A* fluorescence (ϕ_{mf}) and intramolecular quenching (ϕ_q) can be described by the following equations.

$$\tau_S = 1/(k_{mf}+k_{md}+k_q) \tag{1}$$

$$k_q = 1/\tau_S-(k_{mf}+k_{md}) \tag{2}$$



Scheme 3.

Table 3. Rate Constants for Fluorescence Emission (k_{mf}) and Intramolecular Quenching (k_q)

Compound	k_{mf}	k_{md}[a]	k_q	ϕ_q[b]	ϕ_r/ϕ_q
9-MCP	1.6×10^7	4.9×10^7			
A-1E	0.9×10^7		3.5×10^7	0.38	—
A-2E	1.8×10^7		1.9×10^8	0.74	0.49
A-3E	1.3×10^7		2.5×10^8	0.80	0.76
A-4E	1.2×10^7		2.2×10^7	0.26	0.19
B-1E	1.7×10^7		6.9×10^7	0.51	—
B-2E	1.2×10^7		1.3×10^8	0.69	1
B-3E	1.2×10^7		7.2×10^7	0.54	0.96
B-4E	1.0×10^7		1.0×10^7	0.15	1

a) A nonradiative decay rate constant of 9-MCP.
b) Quantum yields for intramolecular quenching.

$$\phi_{mf} = k_{mf}\tau_S \tag{3}$$

$$\phi_q = k_q\tau_S \tag{4}$$

When the fluorescence (k_{mf}) and nonradiative deactivation (k_{md}) rate constants of the phenanthrenecarboxylate chromophore are assumed to be independent of the structure and identical with those of the monofunctional system, 9-MCP, the decrease in the singlet lifetime of bifunctional systems can be ascribed to intramolecular quenching,[13] and thus we can estimate the total quenching rate (k_q) for $^1A^*$-D interaction in the excited singlet state by Eq. 2′. Also, k_{mf} was estimated from ϕ_{mf} and τ_S according to Eq. 4′. The estimated k_q, ϕ_q, and k_{mf} values are summarized in Table 3.

$$k_q = 1/\tau_S - (k_f + k_d) \tag{2'}$$

$$k_{mf} = \phi_{mf}/\tau_S \tag{4'}$$

The k_{mf} values are almost constant as expected and the k_q values for the reactive substrates are in the order of 10^8 s^{-1}, which is similar to the k_q values estimated for nonreactive substrates under a similar assumption, and highly reasonable for intramolecular singlet quenching.[13]

Comparison of the disappearance quantum yield with the efficiency of intramolecular quenching estimated from Eq. 4′ shows that for the reactive substrates the localized singlet is efficiently quenched by the styrene moiety and the exciplex thus formed affords the cycloadducts quite efficiently, especially for B-2E and B-3E the exciplex→product probability being almost unity. The high reactivity of the exciplexes and lower quenching rates for product formation than those for exciplex emission as well as insignificant exciplex emission in A-2E might reflect involvement of nonrelaxed exciplexes in the oxetane formation due to lack of conformational mobility in the linking chains.[14—16]

Caldwell[10] reported experimental evidence for the intermediacy of emissive exciplexes in the intermolecular photocycloaddition of 9-cyanophenanthrene-styrene systems. These systems take a conformation favorable for exciplex formation. As described above, however, in the case of the bichromophoric esters the conformational constraints by interchromophoric link brings about plural conformations in which the two chromophores can interact strongly enough to afford exciplexes;[17] some of them give specific products, and others undergo radiative decay.

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