Intramolecular Photocycloaddition of (*E*)-3-(4-Methoxyphenyl)-3-pentenyl 6-Cyano-9-phenanthrenecarboxylate. Temperature and Solvent Effects

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(*E*)-3-(4-Methoxyphenyl)-3-pentenyl 6-cyano-9-phenanthrenecarboxylate as well as the corresponding 9-phenanthrenecarboxylate exhibited exciplex emission and gave [2+2] photocycloadducts of the double bond with the phenanthrene 9,10 bond (a cyclobutane) and with the ester carbonyl group (an oxetane). The involvement of plural exciplex intermediates for these phenomena was proposed on the basis of the temperature and solvent dependence of quantum efficiencies of fluorescence and cycloadditions as well as of the effects of quenchers of exciplex intermediates.

Conformational effects upon exciplex emission and product formation in the photochemistry of bichromophoric compounds have been the subject of much interest.[1—5] Previously, we reported competitive cycloadditions of the intramolecular exciplexes formed from bichromophoric esters with different linking sites and chain lengths.[6,7] Some of the esters afforded only oxetane adducts, whereas some others gave both of oxetane and head-to-head cyclobutane adducts. For example, (*E*)-3-(4-methoxyphenyl)-3-pentenyl 9-phenanthrenecarboxylate (9PC2αAn(*E*); Scheme 1) afforded a cyclobutane, 9PCB2, and an oxetane, 9POX2α. We suggested that each product arose from a particular exciplex.[6] However, the intensity of exciplex emission of 9PC2αAn(*E*) was too low to study the detailed behavior of discrete intramolecular exciplex intermediates. In order to get more insight into the behavior of exciplex intermediates we have studied the temperature and solvent dependence of quantum efficiencies of fluorescence and photocycloaddition of a novel bichromophoric ester, (*E*)-3-(4-methoxyphenyl)-3-pentenyl 6-cyano-9-phenanthrenecarboxylate (CN9PC2αAn(*E*)).

Experimental

General. Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on a JEOL JNM-MH-100 (100 MHz) or a Nicolet N360 (360 MHz) spectrometer. Infrared spectra (IR) were obtained on a Hitachi 215 spectrophotometer and ultraviolet absorption spectra (UV) were taken on a Hitachi 200-20 spectrophotometer.

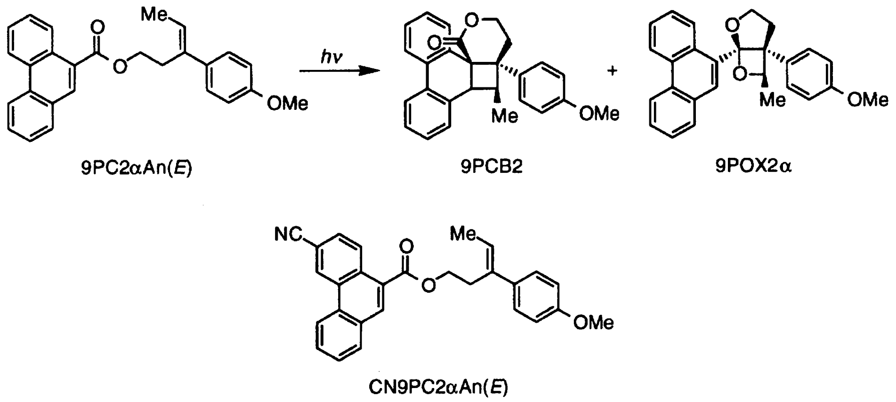
Materials. (*E*)-Anethole [(*E*)-1-(4-methoxyphenyl)-1-propene, (*E*)-AN], dimethyl acetylenedicarboxylate (DMAD), isoprene, and solvents, cyclohexane, benzene, chloroform, tetrahydrofuran, dichloromethane, and acetonitrile, were commercially available and distilled before use. Fumaronitrile (FN) was crystallized twice from hexane–benzene.

Methyl 6-Cyano-9-phenanthrenecarboxylate (CN9MCP). 4-Aminophenylacetic acid (22.7 g, 0.150 mol) prepared by reducing 4-nitrophenylacetic acid with hydrogen sulfide in aqueous ammonia[8] was diazotized and treated with copper(I) cyanide in a usual way[9] to give 4-cyanophenylacetic acid (13.7 g, 57 %). 4-Cyanophenylacetic acid (13.7 g, 0.085 mol) was allowed to react with benzaldehyde (11.6 g, 0.109 mol) in acetic anhydride containing pyridine[10] to give (*E*)-2-(4-cyanophenyl)-3-phenylpropenoic acid (14.7 g, 69 %). The propenoic acid (5.3 g, 0.021 mol) was converted to its methyl ester by sequential treatment with thionyl chloride and methanol[11] (4.5 g, 80 %).

The methyl ester (1.00 g, 3.86 mmol) was irradiated in chloroform (1 dm^3) under oxygen in the presence of iodine[12] with a 400-W high-pressure mercury lamp for 90 min. This process was repeated five times, and the collected product was crystallized from benzene to give CN9MCP (1.51 g, 31%); mp 180—182 °C; ^{1}H NMR (100 MHz) (CDCl$_3$) δ=4.00 (s, 3H, CH$_3$), 7.5—8.0 (m, 4H, ArH), 8.45 (bd, 1H, ArH), 8.49 (s, 1H, ArH), 8.80 (bs, 1H, ArH), 8.96 (d, 1H, ArH); UV (PhH) 309 nm (ε 14300), 318 (14900), 344 (540), 362 (290); IR (KBr) 1700 ($\nu_{\mathrm{C=O}}$), 2200 cm^{-1} ($\nu_{\mathrm{C\equiv N}}$); Mass *m*/*z* 261 (M$^+$, 90%), 230 (100%), 202 (60%). Anal. Calcd for C$_{17}$H$_{11}$NO$_2$: C, 78.14; H, 4.24; N, 5.36%. Found: C, 78.06; H, 4.26; N, 5.33%.

(*E*)-3-(4-Methoxyphenyl)-3-pentenyl 6-Cyano-9-phenanthrenecarboxylate (CN9PC2αAn(*E*)). Ethyl 3-(4-methoxyphenyl)-3-hydroxypentanoate was obtained from the Reformatsky reaction[13] of ethyl bromoacetate (22.6 g, 0.135 ml) with 1-(4-methoxyphenyl)-1-propanone (20.0 g, 0.135 mol) prepared from propionyl chloride and anisole in the presence of aluminum chloride in 1,1,2,2-tetrachloroethane (14.2 g, 42%). The pentanoate (8.2 g, 0.033 mol) was converted to 3-(4-methoxyphenyl)-1,3-pentanediol by reducing with LiAlH$_4$ (4.3 g, 62%). Dehydration of the diol (4.3 g, 0.020 mol) in the presence of *p*-toluenesulfonic acid in benzene gave (*E*)-3-(4-methoxyphenyl)-3-penten-1-ol (2.4 g, 62%).

CN9MCP (1.00 g, 3.83 mmol) was hydrolyzed with potassium hydroxide in aqueous alcohol and the resulting acid was treated with thionyl chloride. The obtained acid chloride was allowed to react with (*E*)-3-(4-methoxyphenyl)-3-penten-1-ol (0.83 g, 4.3 mmol) in benzene containing pyridine to give CN9PC2αAn(*E*). The product was crystallized from ethyl acetate (0.47 g, 29% from CN9MCP); mp 121—122 °C; ^{1}H NMR (100 MHz) (CDCl$_3$) δ=1.88 (d, 3H, CH$_3$–C=C), 3.07 (t, 2H, CH$_2$C=C), 3.75 (s, 3H, CH$_3$O), 4.47 (t, 2H, CH$_2$O), 5.58 (q, 1H, HC=C), 6.85 (d, 2H, ArH), 7.36 (d, 2H, ArH), 7.5—8.0 (m, 4H, ArH), 8.33 (s, 1H, ArH), 8.53 (bd, 1H, ArH), 8.92 (bs, 1H, ArH), 9.04 (d, 1H, ArH); UV (PhH) 309 nm (ε 10400), 318 (10600), 344 (520), 362 (250); IR (KBr) 1700 ($\nu_{\mathrm{C=O}}$), 2220 cm^{-1} ($\nu_{\mathrm{C\equiv N}}$). Anal. Calcd for C$_{28}$H$_{23}$NO$_3$: C, 79.78; H, 5.50; N, 3.32%. Found: C, 79.12;



Scheme 1.

H, 5.50; N, 3.19%.

Photophysical Measurements. Fluorescence spectra were obtained on a Hitachi MPF4 or a Hitachi F-4000 fluorescence spectrofluorimeter and fluorescence quantum yields were determined relative to that for phenanthrene (ϕ_f=0.13).[14] The fluorescence quantum yield of the phenanthrene moiety of the bichromophoric ester was determined by comparing the peak height at the 0,0 band of the corrected spectrum with that of the corresponding methyl ester. The fluorescence quantum yield of the intramolecular exciplex was determined for the residual emission. Fluorescence lifetimes were measured by single photon counting with an Ortec/Applied Photophysics SP-3X system (excitation at 334 nm for 6-cyano-9-phenanthrenecarboxylates).

Irradiation of Methyl 6-Cyano-9-phenanthrenecarboxylate (CN9MCP) with (*E*)-Anethole ((*E*)-AN). A solution of CN9MCP (173 mg, 5.5×10^{-3} mol dm^{-3}) and (*E*)-AN (107 mg, 6.0×10^{-3} mol dm^{-3}) in benzene (120 cm^3) was irradiated with a 400-W high-pressure mercury lamp through an acetone filter for 2.5 h under nitrogen atmosphere at room temperature. After evaporation of the solvent, the residue was separated with TLC (SiO_2, $CHCl_3$) to give a mixture of (*Z*)- and (*E*)-AN (R_f 0.67), CN9MCP (0.36), a mixture of head-to-head adducts (*exo*- and *endo*-Me adducts, CN9PCB0x and CN9PCB0d, respectively; 0.23—0.29) of CN9MCP with (*E*)-AN, and a small amount of a CN9MCP dimer (0.10). HPLC and NMR analyses showed that the ratio of CN9PCB0x, CN9PCB0d, and the dimer was 42 : 48 : 4.

The mixture of CN9PCB0x and CN9PCB0d: mp 78—85 °C; IR (KBr) 2227 cm^{-1} ($\nu_{C\equiv N}$), 1723 cm^{-1} ($\nu_{C=O}$).

CN9PCB0x: ^{1}H NMR (360 MHz, $CDCl_3$) δ=1.15 (d, 3H, J=6.4 Hz, *exo*-CH_3CH), 3.04—3.17 (m, 1H, C*H*CH$_3$), 3.64 (s, 3H, CH_3O), 3.79 (s, 3H, CO_2CH_3), 4.04 (d, 1H, J=11.1 Hz, C*H*Ar), 4.73 (d, 1H, J=9.4 Hz, C*H*Ar), 6.36 (d, 1H, J=8.0 Hz, ArH), 6.77 (d, 2H, J=8.8 Hz, ArH), 6.86 (d, 2H, J=8.8 Hz, ArH), 7.06 (bd, 1H, ArH), 7.20 (bd, 1H, ArH), 7.31—7.42 (m, 2H, ArH), 7.88 (bd, 1H, ArH), 8.23 (bs, 1H, ArH).

CN9PCB0d: ^{1}H NMR (360 MHz, $CDCl_3$) δ=0.78 (d, 3H, J=7.8 Hz, *endo*-CH_3CH), 2.47—2.63 (m, 1H, C*H*CH$_3$), 3.45 (d, 1H, J=9.4 Hz, C*H*Ar), 3.61 (s, 3H, CH_3O), 3.78 (s, 3H, CO_2CH_3), 4.32 (d, 1H, J=9.4 Hz, C*H*Ar), 6.43 (d, 1H, J=7.7 Hz, ArH), 6.72 (d, 2H, J=8.7 Hz, ArH), 6.82 (d, 2H, J=8.7 Hz, ArH), 7.12 (bd, 1H, ArH), 7.17 (bd, 1H, ArH), 7.31—7.42 (m, 2H, ArH), 7.84 (bd, 1H, ArH), 8.23 (bs, 1H, ArH).

Irradiation of CN9MCP with (*E*)-AN in the Presence of Isoprene. A Solution of CN9MCP (2.6×10^{-3} mol dm^{-3}) and (*E*)-AN (2.9×10^{-3} mol dm^{-3}) in isoprene–benzene (14 : 86 by volume, 120 cm^3) was irradiated with a 400-W high-pressure mercury lamp through a Toshiba UV-D36B glass filter for 3 h under nitrogen atmosphere at room temperature. The products were identified with HPLC.

Irradiation of (*E*)-3-(4-Methoxyphenyl)-3-pentenyl 6-Cyano-9-phenanthrenecarboxylate (CN9PC2αAn(*E*)) in the Presence of Isoprene. A solution of CN9PC2αAn(*E*) (202 mg, 3.2×10^{-4} mol dm^{-3}) in benzene (1.5 dm^3) was placed in 10 Pyrex tubes (100 cm^3 each+isoprene 10 cm^3) and irradiated with a 400-W high-pressure mercury lamp through a Pyrex wall for 10—15 min under nitrogen atmosphere at room temperature. After evaporation of the solvent, the residue was separated by TLC (SiO_2, $CHCl_3$). Two kinds of solid products were obtained as well as the starting material; R_f 0.66 (CN9PC2αAn(*E*)), 0.30 (70 mg, 35%), and 0.11 (79 mg, 39%).

The product of R_f 0.30 was identified as an oxetane derivative, 1-(6-cyano-9-phenanthryl)-5-(4-methoxyphenyl)-6-methyl-2,7-dioxabicyclo[3.2.0]heptane (CN9POX2α) of a structure analogous to 9POX2α from 9PC2αAn(*E*); mp 184—186 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ=1.12 (d, 3H, J=6.4 Hz, CH_3CH), 2.78—2.92 (m, 2H, 4-CH$_2$), 3.60 (s, 3H, CH_3O), 4.65—4.72 (m, 2H, 3-CH$_2$), 4.82 (q, 1H, J=6.4 Hz, C*H*CH$_3$), 6.44 (d, 2H, J=8.7 Hz, ArH), 6.80 (d, 2H, J=8.7 Hz, ArH), 7.41 (bd, 1H, ArH), 7.59 (d, 1H, ArH), 7.74 (bt, 1H, ArH), 7.79 (bt, 1H, ArH), 8.08 (bd, 1H, ArH), 8.61 (s, 1H, ArH), 8.63 (bd, 1H, ArH), 8.96 (bs, 1H, ArH); UV (PhH) λ_{max} 306 (ε 10900), 318 (11800), 339 (1050), 356 (360); IR (KBr) 2225 cm^{-1} ($\nu_{C\equiv N}$).

The product of R_f 0.11 was identified as an intramolecular [2+2] cycloadduct (CN9PCB2) of a structure analogous to 9PCB2 from 9PC2αAn(*E*); mp 204—206 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ=1.12 (d, 3H, J=6.9 Hz, *exo*-CH_3CH), 2.64—2.84 (m, 2H, OCH$_2$CH_2), 2.96—3.08 (m, 1H, C*H*CH$_3$), 3.72 (d, 1H, J=4.5 Hz, C*H*CHCH$_3$), 3.76 (s, 3H, CH_3O), 4.82—5.01 (m, 2H, OCH_2CH$_2$), 6.36 (d, 1H, ArH), 6.67 (d, 2H, J=8.9 Hz, ArH), 6.81 (d, 2H, J=8.9 Hz, ArH), 7.10 (bd, 1H, ArH), 7.12 (bd, 1H, ArH), 7.33 (bt, 1H, ArH), 7.37 (bt, 1H, ArH), 7.89 (bd, 1H, ArH), 8.24 (bs, 1H, ArH); IR (KBr) 2228 cm^{-1} ($\nu_{C\equiv N}$), 1715 cm^{-1} ($\nu_{C=O}$).

Irradiation of CN9PC2αAn(*E*) in the Absence of Isoprene. A solution of CN9PC2αAn(*E*) (1.7×10^{-4} mol dm^{-3}) in benzene was irradiated with a 400-W high-pressure mercury lamp in a uranium glass tube (transmission wavelength >350 nm) under nitrogen atmosphere at room temperature. The products were identified with HPLC.

Quantum-Yield Measurements. Quantum yields for disappearance of CN9PC2αAn(*E*) and formation of the products were measured by irradiating deaerated benzene solutions (2.8×10^{-4} mol dm^{-3}, argon bubbling) containing 10-vol% isoprene with 366-nm light isolated from a 400-W high-pressure mercury lamp through a Toshiba UV-D36B glass filter. Amounts of the starting material and product 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.[15]

Temperature Dependence. For studies at varying temperatures, fluorescence spectra were taken by utilizing the cell compartment of the spectrometer and quantum yield measurements were carried out by irradiating sample cells in a water bath of a merry-go-round irradiator. In both cases the temperature (12—40 °C) was maintained by circulating water from a Haake bath.

Results

Fluorescence Measurements. The fluorescence spectra in benzene of (*E*)-3-(4-methoxyphenyl)-3-pentenyl 6-cyano-9-phenanthrenecarboxylate (CN9PC2αAn(*E*)) and methyl 6-cyano-9-phenanthrenecarboxylate (CN9MCP, $\lambda_{\max}$ 387 nm) as a monochromophoric model of CN9PC2αAn(*E*) are shown in Fig. 1. In contrast to the corresponding 9-phenanthrenecarboxylate (9PC2αAn(*E*)) which exhibits a weak exciplex emission, CN9PC2αAn(*E*) shows a strong exciplex emission ($\lambda_{\max}{}^{e}$ 470 nm) of an almost equal intensity to that of the emission from the phenanthrene nucleus ($\lambda_{\max}$ 388 nm).

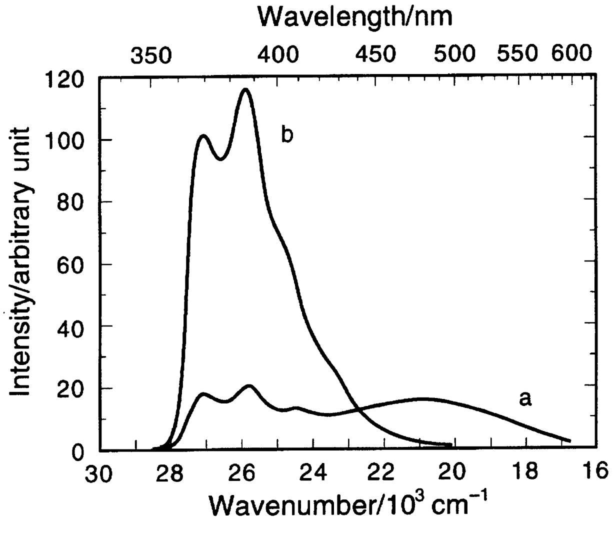


Fig. 1. Fluorescence spectra of CN9PC2αAn(*E*) (a) and CN9MCP (b) in benzene.

The fluorescence quantum yield (ϕ_f) of the phenanthrene moiety of CN9PC2αAn(*E*) was 0.012 as determined in benzene at ambient temperature (21 °C) by comparing the peak height at the 0,0 band of the corrected spectrum with that of CN9MCP; the latter value was obtained to be 0.19 with reference to that for phenanthrene ($\phi_f=0.13$).[14] The fluorescence quantum yield of the intramolecular exciplex was determined to be 0.014 for the residual emission. The fluorescence lifetimes (τ_f) were measured in benzene at ambient temperature. Those of CN9MCP, the phenanthrene moiety of CN9PC2αAn(*E*), and the intramolecular exciplex were determined to be 17.3, 2.7, and 6.6 ns, respectively, as monitored at each emission maximum.

Photoreaction of CN9MCP with (*E*)-AN. Irradiation of CN9MCP with (*E*)-AN in benzene at ambient temperature with 366-nm light gave head-to-head adducts, CN9PCB0x (*exo*-methyl, 42% yield) and CN9PCB0d (*endo*-methyl, 48%) (Scheme 2). The structure was determined on the basis of various spectral data, mainly ^{1}H NMR spectra and comparison of the spectra to that of the photocycloadduct of 9MCP and (*E*)-AN.[6] In the presence of isoprene as a triplet quencher, CN9PCB0x was predominantly formed (CN9PCB0x/CN9PCB0d=ca. 10).

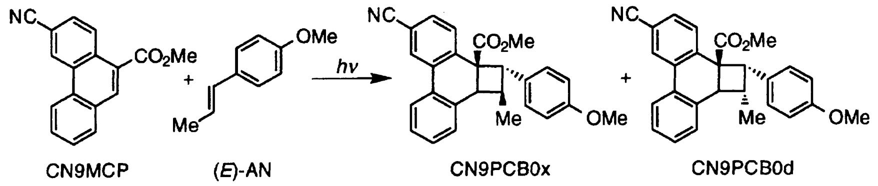
Photoreaction of CN9PC2αAn(*E*). Irradiation of CN9PC2αAn(*E*) (3.2×10^{-4} mol dm^{-3}) at room temperature (21 °C) in benzene containing 10% isoprene with 366-nm light afforded a cyclobutane (CN9PCB2, 39% yield) and a bicyclic acetal (CN9POX2α, 35%) as expected (Scheme 3).[6] On prolonged irradiation CN9POX2α completely disappeared, and only CN9PCB2 was afforded. Separate irradiation of pure CN9POX2α in benzene with 366-nm light gave CN9PC2αAn(*E*), its *Z* isomer (CN9PC2αAn(*Z*)), and CN9PCB2; these reactions were quenched by isoprene.

The quantum yields for disappearance (ϕ_{disap}) of CN9PC2αAn(*E*) and formation of CN9PCB2 (ϕ_{CB}) and CN9POX2α (ϕ_{OX}) were determined at 21 °C as 0.13, 0.063, and 0.058, respectively, by irradiating deaerated 9 : 1 benzene–isoprene solutions (2.8×10^{-4} mol dm^{-3}) with 366-nm light. The sum of ϕ_{CB} and ϕ_{OX} is in excellent agreement with ϕ_{disap}.

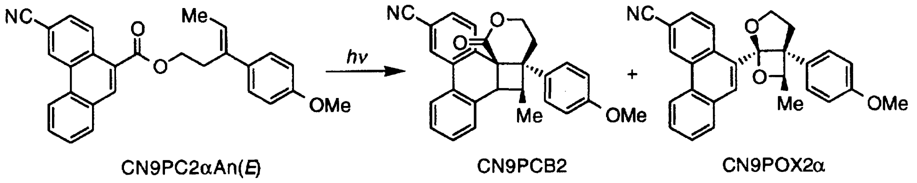
Temperature Dependence of Quantum Yields for Exciplex Emission and Reactions. Temperature dependence of the quantum yields for the photophysical and photochemical processes was examined for CN9PC2αAn(*E*) in the range of 12—40 °C in 9 : 1 benzene–isoprene, and is summarized in Table 1. With increasing temperature, the quantum yields for exciplex emission (ϕ_{ef}) and isomerization of the styryl moiety (ϕ_{Z}) decreased, whereas those for formation of CN9PCB2 (ϕ_{CB}) and CN9POX2α (ϕ_{OX}) increased.

The processes concerning cycloadditions can be described as shown in Scheme 4, where A and D represent the phenanthrene and styrene moieties of a bichromophoric ester, respectively.

Employing molecular oxygen as a quencher in



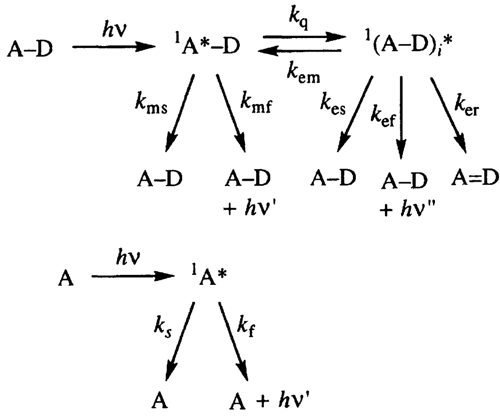
Scheme 2.



Scheme 3.

Table 1. Temperature Dependence of Quantum Yields

Temperature/°C	ϕ_{ef}	ϕ_{CB}	ϕ_{OX}	ϕ_{Z}
12	0.014	0.054	0.040	0.14
21	0.014	0.063	0.058	0.13
31	0.013	0.077	0.071	0.12
40	0.012	0.087	0.088	0.10



Scheme 4.

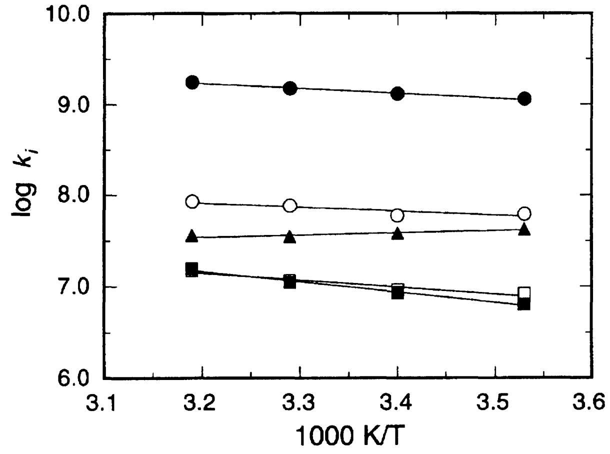


Fig. 2. Arrhenius plots for k_{q} (●), k_{D} (○), k_{ISC} (▲), k_{CB} (□), and k_{OX} (■).

Table 2. Activation Parameters

Process	$\Delta H^{\ddagger}/\mathrm{kJ\,mol^{-1}}$	$\Delta S^{\ddagger}/\mathrm{J\,mol^{-1}\,K^{-1}}$
k_{q}	8.8	−33
k_{D} [a]	0.4	−100
k_{ISC} [a]	−6.7	−113
k_{CB}	12	−59
k_{OX}	17	−33

a) Calculated for comparison purposes only. $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ have no meaning for processes involving transitions between electronic surfaces.

the steady-state kinetics developed by Klöpfer and Liptay[16] affords the total intramolecular quenching rate constants (k_{q}) and quantum yields (ϕ_{q}) for CN9PC2αAn(*E*), since the rate constants for fluorescence and non-radiative deactivation can be assumed to be identical in mono- and bifunctional systems. The reasonable assumption of temperature-independent fluorescence rate constant[17,18] and, furthermore, use of the exciplex emission lifetime as the average exciplex lifetime give the rate constants (k_{ei}) for the processes of intramolecular exciplexes, since the quantum yields (ϕ_{ei}) can be expressed by Eq. 1:

$$\phi_{\mathrm{ei}} = \frac{k_{\mathrm{q}}k_{\mathrm{ei}}}{k_{\mathrm{ed}}\left(k_{\mathrm{md}} + k_{\mathrm{q}}\right) + k_{\mathrm{em}}k_{\mathrm{md}}}, \qquad (1)$$

where $k_{\mathrm{ed}}=k_{\mathrm{ef}}+k_{\mathrm{es}}+k_{\mathrm{er}}$ and $k_{\mathrm{md}}=k_{\mathrm{mf}}+k_{\mathrm{ms}}$. The quantum yields for intersystem crossing of the singlet exciplex (ϕ_{ISC}) were taken as twice of ϕ_{Z},[17] and the non-radiative decay rate constant (k_{D}) was computed as $k_{\mathrm{es}}+k_{\mathrm{er}}=k_{\mathrm{D}}+k_{\mathrm{ISC}}+k_{\mathrm{OX}}+k_{\mathrm{CB}}$. The Arrhenius plot for each process (Fig. 2) afforded the activation parameters as listed in Table 2.

Exciplex Quenching. The exciplex emission and cycloadduct formation from CN9PC2αAn(*E*) were quenched not only by molecular oxygen but also by dimethyl acetylenedicarboxylate (DMAD) and fumaronitrile (FN). The fluorescence from the phenanthrene nucleus was scarcely and slightly quenched by DMAD and FN, respectively. Table 3 lists apparent Stern–Volmer constants ($K_{\mathrm{SV}}{}^{\mathrm{obsd}}$) obtained by plotting the ratios of observed quantum yields against quencher concentrations in 9 : 1 benzene–isoprene. The $K_{SV}{}^{obsd}$ values in Table 3 are different from each other for both quenchers.

Solvent Dependence of Exciplex Emission and Quantum Yields for Cycloadduct Formation. The exciplex emission was observed in nonpolar and moderately polar solvents, and the emission maximum ($\lambda_{max}{}^{e}$) was shifted to longer wavelengths with increasing polarity of the solvents as shown in Table 4; however, in a strongly polar solvent such as acetonitrile no exciplex emission was observed.

The quantum yields for cycloadduct formation (ϕ_{CB} and ϕ_{OX}) were measured in various solvents containing 10-vol% isoprene and are listed in Table 4. Nonpolar solvents such as cyclohexane and benzene afforded cycloadducts in higher quantum yields than did polar solvents, but THF and dichloromethane gave no cyclobutane derivative. Acetonitrile gave neither cyclobutane nor oxetane derivative. The efficiency of isomerization was also affected by solvents; the more polar the solvent (except acetonitrile), the more efficient the isomerization. In moderately polar solvents, the oxetane is composed of two isomers. One might be formed from CN9PC2αAn(*E*) and the other from CN9PC2αAn(*Z*) produced; the latter was major.

Discussion

The fluorescence spectrum of CN9MCP is very similar in shape and wavelength to that of 9MCP; however, the maximum of exciplex emission of CN9PC2αAn(*E*) is nearly 20 nm shifted to the longer wavelength region compared to 9PC2αAn(*E*). The photochemistry in 9 : 1 benzene–isoprene of CN9MCP and CN9PC2αAn(*E*) was quite similar to that of 9MCP and 9PC2αAn(*E*), respectively;[6] CN9MCP gave a head-to-head adduct CN9PCB0x of the expected stereochemistry[6,19] with (*E*)-anethole and CN9PC2αAn(*E*) gave a cyclobutane (CN9PCB2) and a bicyclic acetal (CN9POX2α) on irradiation of the phenanthrene moiety at 366 nm. However, the product ratio (CN9PCB2/CN9POX2α) is ca. 1.1 in contrast with 9PCB2/9POX2α=ca. 0.23.[6] Geometrical isomerization of the olefin moiety (CN9PC2αAn(*Z*) formation) was also observed even in the presence of the triplet quencher.

Introduction of a cyano group in the phenanthrene moiety of the ester led to increase in intramolecular quenching probability in the singlet state (0.96 vs. 0.69 for 9PC2αAn(*E*)),[6] relative increase in exciplex emission, decrease in reactivity for cycloaddition (quantum yield for disappearance 0.13 vs. 0.70 for 9PC2αAn(*E*)),[6] and relative increase in cyclobutane formation. These results indicate a stronger interaction between the intramolecularly linked chromophores and a higher stabilization of the intramolecular exciplex resulting in decrease in reactivity for cycloaddition in CN9PC2αAn(*E*) compared with 9PC2αAn(*E*).

Table 3. Stern–Volmer Constants for Exciplex Quenching by Dimethyl Acetylenedicarboxylate (DMAD) and Fumaronitrile (FN)

Phenomenon	$K_{SV}{}^{obsd}$/mol^{-1} dm^3 for quencher	
	DMAD	FN
Exciplex emission[a)]	12.1	42
Oxetane formation	9.1	31
Cyclobutane formation	5.8	11
Phenanthrene emission	—	6.5

a) Rate constants for quenching of the emissive exciplex of CN9PC2αAn(*E*) can be estimated as 2×10^9 and 6×10^9 mol^{-1} dm^3 s^{-1} for DMAD and FN, respectively.

Table 4. Solvent Dependence of Exciplex Emission and Quantum Yields for Cycloadduct Formation

Solvent	ϵ	$\lambda_{max}{}^{e}$/nm	ϕ_{CB}	ϕ_{OX}
Cyclohexane	2.02	425	0.068	0.073
Benzene	2.28	470	0.063	0.058
Chloroform	2.84	490	0.009	0.011
Tetrahydrofuran	7.58	510	—	0.008
Dichloromethane	7.77	510	—	0.007
Acetonitrile	37.5	—	—	—

The temperature effect[17,18,20)] and exciplex quenching[2,3,19)] are useful probes to determine behavior of exciplexes. The intersystem crossing and nonradiative decay are not affected significantly by temperature, whereas the cycloadditions apparently involve activated processes. As shown in Fig. 2 and Table 2, the intramolecular quenching (k_q) shows a small activation enthalpy and substantial negative activation entropy. The cycloadditions also show small activation enthalphies and substantial negative activation entropies. These features are quite similar to those reported for intermolecular cycloadditions of 9-cyanophenanthrene to styrenes[17)] and of phenanthrene to dimethyl fumarate.[18)]

If a common exciplex intermediate exhibited the emission and gave the cycloadducts, the quenching constants K_{SV}'s should be the same for the three phenomena. The results on exciplex quenching (Table 3) suggest that these phenomena are ascribed to discrete exciplexes and that each exciplex might be formed directly from the locally excited singlet state; involvement of the interconversion between the exciplexes cannot be excluded, however. This situation is consistent with indications on the absence of serious geometrical restrictions for emissive intramolecular exciplex formation[21)] and also with the observation that exciplex emission is not significant in the intermolecular case of CN9MCP with (*E*)-AN giving the head-to-head cycloadduct. The exciplex emission and cycloadditions of 9PC2αAn(*E*) and 5-(4-methoxyphenyl)-4-pentenyl 9-phenanthrenecarboxylate (oxetane formation) were also quenched by DMAD, and the Stern–Volmer plots exhibited different slopes among the phenomena for each ester.[6)]

The decrease of cycloadduct yields in polar solvents (Table 4) can be attributed to the stabilization of exciplexes diminishing the efficiency to overcome the activation barrier for cycloaddition of the exciplexes. In strongly polar solvents such as acetonitrile, the main process in the excited singlet state may be electron transfer from the styryl moiety to the phenanthrene moiety, leading to less effective isomerization and ineffective cycloadditions. The difference in solvent effect between the cycloadducts is also consistent with the involvement of discrete exciplex in each process.

The oxetane formation requires a less tight geometry (higher activation enthalpy and lower activation entropy) than does cyclobutane formation (Table 2). This is in accord with the previous observation that the oxetane formation is effective only in the intramolecular systems,[6,7] and also with the concept that the two cycloadducts arise from discrete exciplexes with different geometries;[17,18,20] the fluorescent exciplex may have a more loose geometry than those of the exciplexes giving the cycloadducts. The lower quenching rates for product formation than those for exciplex emission (Table 3) as well as insignificant exciplex emission in 9PC2αAn(*E*)[6] might reflect involvement of non-relaxed exciplexes in the oxetane formation due to limited conformational mobility in the linking chains.[1,4,5]

The excited singlet of the phenanthrene chromophore may interact with the styrene chromophore to give plural exciplexes competitively, which are presumably interconvertible (Fig. 3). The exciplex preferable for carbonyl addition may be similar in stability to that preferable for cyclobutane formation as discussed previously for 9PC2αAn(*E*).[7] The exciplexes emit fluorescence and cross over a small activation energy to the surfaces of biradicaloid species, respectively; the activation energies for two processes do not differ greatly. At the minimum of each energy surface the biradicaloid species cyclizes to the cyclobutane or oxetane, or decays to the starting substrate.

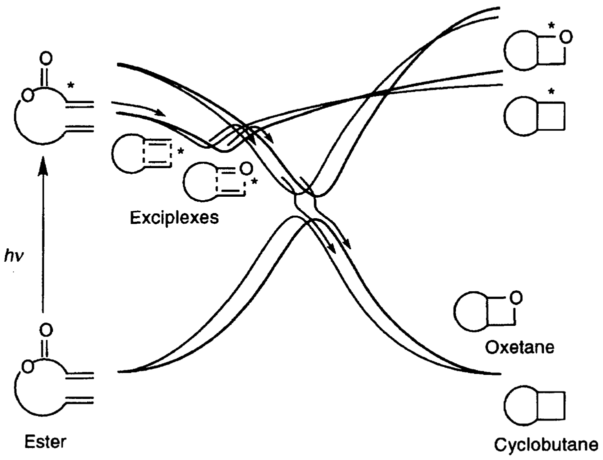


Fig. 3. Potential energy diagram for cycloadduct formation.

In contrast with the intermolecular systems where emissive exciplexes play an important role in the cycloaddition, in the intramolecular systems the conformational constraints by interchromophoric link brings about plural conformations in which the two chromophores can interact strongly enough to afford exciplexes;[22] some of them give specific products and others undergo radiative decay.

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References

1) F. C. De Schryver, N. Boens, and J. Put, *Adv. Photochem.*, **10**, 359 (1977).

2) F. C. De Schryver, N. Boens, J. Huybrechts, J. Daemen, and M. De Brackeleire, *Pure Appl. Chem.*, **49**, 237 (1977).

3) R. A. Caldwell and D. Creed, *Acc. Chem. Res.*, **13**, 45 (1980).

4) H. Bouas-Laurent, A. Castellan, and J. -P. Desvergne, *Pure Appl. Chem.*, **52**, 2633 (1980).

5) R. S. Davidson, *Adv. Phys. Org. Chem.*, **19**, 1 (1983).

6) H. Sakuragi, K. Tokumaru, H. Itoh, K. Terakawa, K. Kikuchi, R. A. Caldwell, and C.-C. Hsu, *J. Am. Chem. Soc.*, **104**, 6796 (1982); *Bull. Chem. Soc. Jpn.*, **63**, 1049 and 1058 (1990).

7) H. Itoh, M. Takada, F. Asano, Y. Senda, H. Sakuragi, and K. Tokumaru, *Bull. Chem. Soc. Jpn.*, **66**, 224 (1993).

8) G. R. Robertson, *Org. Synth.*, Coll. Vol. 1, 52 (1941).

9) R. Jeager and R. Robinson, *J. Chem. Soc.*, **1941**, 744.

10) R. E. Buckles and E. A. Hausman, *J. Am. Chem. Soc.*, **70**, 415 (1948).

11) E. B. Womack and J. McWhirter, *Org. Synth.*, Coll. Vol. 3, 714 (1955).

12) C. S. Wood and F. B. Mallory, *J. Org. Chem.*, **29**, 3373 (1964).

13) C. R. Hauser and D. S. Breslow, *Org. Synth.*, Coll. Vol. 3, 408 (1953).

14) I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York (1971), p. 376.

15) S. L. Murov, "Handbook of Photochemistry," Marcel Dekker, New York (1973), p. 111.

16) W. Klöpfer and W. Liptay, *Z. Naturforsch., A*, **25a**, 1091 (1970).

17) R. A. Caldwell and D. Creed, *J. Am. Chem. Soc.*, **100**, 2905 (1978).

18) R. A. Caldwell and D. Creed, *J. Am. Chem. Soc.*, **101**, 6960 (1979).

19) R. A. Caldwell, D. Creed, D. C. DeMarco, L. A. Melton, H. Ohta, and P. H. Wine, *J. Am. Chem. Soc.*, **102**, 2369 (1980).

20) F. D. Lewis and C. E. Hoyle, *J. Am. Chem. Soc.*, **99**, 3779 (1977).

21) N. Mataga and M. Ottolenghi, "Molecular Association," ed by R. Foster, Academic Press, London (1979) Vol. 2, pp. 1—78.

22) K. A. Zachariasse, G. Duveneck, and R. Busse, *J. Am. Chem. Soc.*, **106**, 1045 (1984).