Structural Effects on Photochemical Cycloaddition of Phenanthrene- and Naphthalenecarboxylic Esters.
Enhancement of Reactivity of an Ester Carbonyl Group by Interchromophoric Links

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On irradiation in benzene, (*E*)-5-(*p*-methoxyphenyl)-4-pentenyl 3-, 9-phenanthrenecarboxylate, 1-, and 2-naphthalenecarboxylate gave novel olefinic aldehydes presumably derived from oxetane precursors, the intramolecular carbonyl adducts. Intermolecular carbonyl addition was not detected between the corresponding ester and olefinic chromophores. Enhancement of reactivity of the ester carbonyl group in the linked systems is discussed on the basis of experimental and theoretical studies.

Synthetic applications of photochemical reactions have accepted a great deal of interest.[1] However, the ester carbonyl group has not attracted much attention as cycloaddend because of its low reactivity in photochemical cycloadditions.[2] Previously, we reported a novel aspect in the phenanthrene-styrene reaction brought about by interchromophoric links with the ester group, an oxetane formation through a carbonyl addition.[3] This might be of synthetic utility since it shows high regioselectivity and stereoselectivity. The ester group can play such useful roles in photochemical reactions as an electron-accepting substituent, a part of the addend in the π, π^* excited state through conjugation with aromatic moieties, and a linking chain of reactive chromophores.

Here we wish to report photochemical and photophysical studies on newly prepared (*E*)-5-(*p*-methoxyphenyl)-4-pentenyl 3-phenanthrenecarboxylate (3PC), 1-, and 2-naphthalenecarboxylate (1NC and 2NC, respectively), in addition to the previously reported 9-phenanthrenecarboxylate (9PC), as a basis of synthetic applications of the carbonyl addition.

Experimental

General. Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on a Hitachi R-24B (60 MHz) and a JEOL JNM-MH-100 spectrometer (100 MHz). Carbon 13 NMR spectra were recorded on a JEOL FX-100 spectrometer (25 MHz). Mass spectra were obtained on a Hewlett Packard 5890A mass spectrometer. Infrared spectra (IR) were obtained on a Hitachi 215 spectrophotometer.

Materials. Benzene was distilled from calcium hydride before use. Isoprene (2-methyl-1,3-butadiene) was purified by distillation. (*E*)-Anethole [(*E*)-1-(*p*-methoxyphenyl)-1-propene] was distilled under reduced pressure before use.

Methyl 9-Phenanthrenecarboxylate (9MCP). The ester was crystallized from methanol; mp 115—116°C;[3b] UV (PhH) $\lambda_{\max}$ 306 nm (ε 10500), 358 (480).

Methyl 3-Phenanthrenecarboxylate (3MCP), 1-Naphthalenecarboxylate (1MCN), and 2-Naphthalenecarboxylate (2MCN). These esters were prepared in a similar way to that of 9MCP through a reaction of methanol with the corresponding acid chloride in benzene containing pyridine.

3MCP: mp 95—96°C (2:1 hexane-AcOEt) (lit, 94.5—95°C);[4] UV (PhH) $\lambda_{\max}$ 304 nm (ε 12900), 315 (13000), 338 (1210), 354 (520).

1MCN: bp 120°C/2 mmHg (1 mmHg=133.32 Pa) (lit, 165—166°C/17 mmHg);[5] UV (PhH) $\lambda_{\max}$ 300 nm (ε 6500).

2MCN: mp 77—78°C (MeOH) (lit, 77°C);[5] UV (PhH) $\lambda_{\max}$ 320 nm (ε 1300), 335 (1740).

(*E*)-5-(*p*-Methoxyphenyl)-4-pentenyl 9-Phenanthrenecarboxylate (9PC). The preparative procedures of this ester was previously described;[3b] mp 59—60.5°C (1:1 hexane-benzene); UV (PhH) $\lambda_{\max}$ 301 nm (ε 13300), 358 (480).

(*E*)-5-(*p*-Methoxyphenyl)-4-pentenyl 3-Phenanthrenecarboxylate (3PC), 1-Naphthalenecarboxylate (1NC), and 2-Naphthalenecarboxylate (2NC). These esters were prepared in a similar way to that of 9PC[3b] through a reaction of (*E*)-5-(*p*-methoxyphenyl)-4-pentenol with the corresponding acid chloride in benzene containing pyridine.

3PC: mp 87—88.5°C (5:1 hexane-benzene); ^{1}H NMR ($CDCl_3$) δ=2.10 (tt, 2H, J=6, 6 Hz, O–C–CH_2), 2.33 (td, 2H, J=6, 5 Hz, C=C–CH_2), 3.68 (s, 3H, CH_3O), 4.42 (t, 2H, J=6 Hz, OCH_2), 6.02 (dt, 1H, J=16, 5 Hz, C=CH), 6.30 (d, 1H, J=16 Hz, CH=C), 6.68—7.14 (m, 4H, phenyl H), 7.42—9.30 (m, 9H, phenanthryl H); UV (PhH) $\lambda_{\max}$ 303 nm (ε 14800), 338 (1210), 354 (490). Calcd for $C_{27}H_{24}O_3$: C, 81.79; H, 6.10%. Found: C, 81.54; H, 6.17%.

1NC: mp 58—60°C (5:1 hexane-benzene); ^{1}H NMR ($CDCl_3$) δ=2.00 (tt, 2H, J=6, 6 Hz, O–C–CH_2), 2.37 (td, 2H, J=6, 5 Hz, C=C–CH_2), 3.70 (s, 3H, CH_3O), 4.39 (t, 2H, J=6 Hz, OCH_2), 6.00 (dt, 1H, J=16, 5 Hz, C=CH), 6.29 (d, 1H, J=16 Hz, CH=C), 6.77—7.19 (m, 4H, phenyl H), 7.33—8.91 (m, 7H, naphthyl H); UV (PhH) $\lambda_{\max}$ 295 nm (ε 9500). Calcd for $C_{23}H_{22}O_3$: C 79.74; H, 6.40%. Found: C, 79.65; H, 6.50%.

2NC: mp 59—61°C (5:1 hexane-benzene); ^{1}H NMR ($CDCl_3$) δ=2.00 (tt, 2H, J=6, 6 Hz, O–C–CH_2), 2.33 (td, 2H, J=6, 5 Hz, C=C–CH_2), 3.72 (s, 3H, CH_3O), 4.37 (t, 2H, J=6 Hz, OCH_2), 6.03 (dt, 1H, J=16, 5 Hz, C=CH), 6.31 (d, 1H, J=16 Hz, CH=C), 6.70—7.15 (m, 4H, phenyl H), 7.33—8.48 (m, 7H, naphthyl H): UV (PhH) $\lambda_{\max}$ 320 nm (ε 1360), 335 (1690). Calcd for $C_{23}H_{22}O_3$: C, 79.74; H, 6.40%.

Found: C, 79.45; H, 6.43%.

Irradiation of 3PC and 9PC. A solution of 3PC (202 mg, 3.4×10^{-4} mol dm^{-3}) in benzene-isoprene (9 : 1 by volume, 1.5 dm^3) was irradiated in a uranium tube (transmission wavelength > 350 nm) with a 450-W high-pressure mercury lamp for 60 min under argon atmosphere at 15±1°C. After evaporation of the solvent, the residue was separated by HPLC (SiO_2, 19 : 1—3 : 1 hexane–ethyl acetate) to give a colorless oil of 4-[(*E*)-2-(*p*-methoxyphenyl)-1-(3-phenanthryl)ethenyloxy]butanal (3PA, 40 mg, 39% yield based on 3PC consumed) and recovered starting material (cis+trans, 100 mg, 51% conversion).

3PA: ^{1}H NMR ($CDCl_3$) $\delta=2.18$ (m, 2H, CH_2), 2.65 (t, 2H, $J=6$ Hz, CH_2CO), 3.62 (s, 3H, OCH_3), 3.97 (t, 2H, $J=6$ Hz, OCH_2), 5.85 (s, 1H, C=CH), 6.44—6.83 (m, 4H, phenyl H), 7.30—8.62 (m, 9H, phenanthryl H), 9.73 (t, 1H, $J=2$ Hz, CHO); IR (neat) 1720 cm^{-1} ($\nu_{C=O}$); Mass, *m/z* 326 (100%), 396 (M^+, 26%).

A solution of 9PC (135 mg, 3.4×10^{-4} mol dm^{-3}) in 9 : 1 benzene-isoprene (1 dm^3) was similarly irradiated for 30 min. HPLC separation gave 4-[(*E*)-2-(*p*-methoxyphenyl)-1-(9-phenanthryl)ethenyloxy]butanal (9PA, 85 mg, 63% yield).

9PA: ^{1}H NMR ($CDCl_3$) $\delta=2.07$ (m, 2H, CH_2), 2.50 (t, 2H, $J=6$ Hz, CH_2CO), 3.53 (s, 3H, OCH_3), 3.95 (t, 2H, $J=6$ Hz, CH_2O), 6.07 (s, 1H, C=CH), 6.27—6.73 (m, 4H, phenyl H), 7.40—8.73 (m, 9H, phenanthryl H), 9.60 (t, 1H, $J=2$ Hz, CHO); IR (neat) 1720 cm^{-1} ($\nu_{C=O}$); Mass, *m/z* 326 (100%), 396 (M^+, 37%).

Irradiation of 1NC and 2NC. A solution of 1NC (177 mg, 3.4×10^{-4} mol dm^{-3}) in benzene-isoprene (9 : 1 by volume, 1.5 dm^3) was irradiated in a uranium tube (transmission wavelength > 310 nm) with a 450-W high-pressure mercury lamp for 90 min under argon atmosphere at 15±1°C. After evaporation of the solvent, the residue was separated by HPLC (SiO_2, 19 : 1 hexane–ethyl acetate) to give a colorless oil of 4-[(*E*)-2-(*p*-methoxyphenyl)-1-(1-naphthyl)ethenyloxy]butanal (1NA, 19 mg, 39% yield based on 1NC consumed) and recovered starting material (127 mg, 28% conversion).

1NA: ^{1}H NMR ($CDCl_3$) $\delta=2.08$ (m, 2H, CH_2), 2.54 (t, 2H, $J=6$ Hz, CH_2CO), 3.56 (s, 3H, OCH_3), 3.91 (t, 2H, $J=6$ Hz, CH_2O), 6.03 (s, 1H, C=CH), 6.30—6.67 (m, 4H, phenyl H), 7.27—7.94 (m, 7H, naphthyl H), 9.65 (t, 1H, $J=2$ Hz, CHO); IR (neat) 1720 cm^{-1} ($\nu_{C=O}$); Mass, *m/z* 276 (100%), 346 (M^+, 18%).

A solution of 2NC (177 mg, 3.4×10^{-4} mol dm^{-3}) in 9 : 1 benzene-isoprene (1.5 dm^3) was similarly irradiated for 60 min. HPLC separation gave 4-[(*E*)-2-(*p*-methoxyphenyl)-1-(2-naphthyl)ethenyloxy]butanal (2NA, 31 mg, 40% yield based on 2NC consumed) and recovered starting material (101 mg, 43% conversion).

2NA: ^{1}H NMR ($CDCl_3$) $\delta=2.08$ (m, 2H, CH_2), (t, 2H, $J=6$ Hz, CH_2CO), 3.63 (s, 3H, OCH_3), 3.89 (t, 2H, $J=6$ Hz, CH_2O), 5.78 (s, 1H, C=CH), 6.43—6.87 (m, 4H, phenyl H), 7.36—7.92 (m, 7H, naphthyl H), 9.70 (t, 1H, $J=2$ Hz, CHO); IR (neat) 1720 cm^{-1} ($\nu_{C=O}$); Mass, *m/z* 276 (100%), 346 (M^+, 18%).

Quantum Yield Measurements. Quantum yields for disappearance of substrates were measured by irradiating their deaerated benzene–isoprene (9 : 1 by volume) solutions (3.4×10^{-4} mol dm^{-3}, 20-min argon bubbling) with 366- (for 3PC and 9PC) or 313-nm light (for 1NC and 2NC) isolated from a 450-W high-pressure mercury lamp through a uranium glass wall ($\lambda>350$ nm) or through a uranium glass wall ($\lambda>310$ nm) and a $K_2CrO_4+Na_2CO_3$ solution filter. Consumption of the reactants was quantitatively determined on a Kusano HPLC with an SiO_2 column (30 cm; hexane : ethyl acetate=19 : 1). The quantum yields were determined in comparison with the previously reported values for intramolecular cycloaddition of (*E*)-4-(*p*-methoxyphenyl)-4-hexenyl 9-phenanthrenecarboxylate (0.52)[3] and for ring closure of a flugide, (*E*)-2-(2,5-dimethyl-3-furylethylidene)-3-isopropylidenebutanedioic acid anhydride (0.20 at 313 and 366 nm).[6]

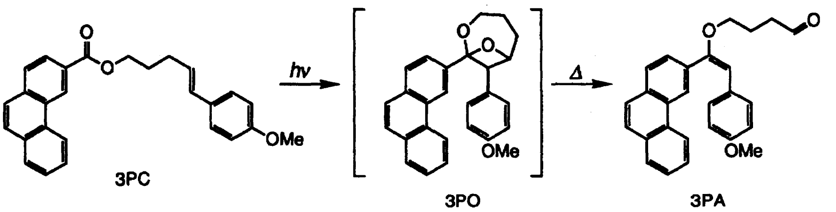
Photophysical Measurements. Ultraviolet absorption spectra (UV) were taken on a Hitachi 200-20 spectrophotometer. Fluorescence spectra were obtained on an F-4000 fluorescence spectrofluorometer. Fluorescence quantum yields were determined in benzene by comparing corrected fluorescence spectra with that of phenanthrene, of which the fluorescence quantum yield is reported, $\phi_f=0.13$.[7] The fluorescence quantum yields of the phenanthrene and naphthalene moieties of bichromophoric esters were determined by comparing the peak height at the 0,0 band of their corrected spectra with those of the corresponding methyl esters. The fluorescence quantum yields of intramolecular exciplexes were determined for the residual emissions. Fluorescence lifetimes were determined with a Horiba NAES-1100 time-resolved fluorescence spectrophotometer (single photon counting). Phosphorescence spectra were obtained with a Hitachi F-4000 spectrofluorometer with phosphorescence accessories.

Methods of Calculations. Semiempirical molecular orbital calculations were carried out by AM1 method.[8] On optimization of conformations of methyl arenecarboxylates was assumed a structure that the alkenyl group and carbonyl group are cis for the C–O single bond, the carbonyl and *O*-alkyl bonds are coplanar, and, for 9-phenanthrenecarboxylate and 1-naphthalenecarboxylate, the carbonyl group is directed to the peri-hydrogen. Validity of the results were checked by a good correlation between the calculated energy levels of LUMO (or HOMO) and reduction (or oxidation) potentials obtained by cyclic voltammetry.

Conformational analysis of propyl acetate was performed by MM2 calculations.[9]

Results and Discussion

Photochemical Intramolecular Carbonyl Addition in Phenanthrene- and Naphthalenecarboxylates. When (*E*)-5-(*p*-methoxyphenyl)-4-pentenyl 3-phenanthrenecarboxylate (3PC) was irradiated in 9 : 1 benzene-isoprene under nitrogen with 366-nm light from a 450-W high-pressure mercury lamp through a uranium glass wall, an olefinic aldehyde (3PA) was produced in 39% yield (based on 3PC consumed) at 51% conversion (Scheme 1). The reaction is assumed to proceed from 3PC singlets through intramolecular cycloaddition of the ester carbonyl group to the styryl double bond followed by thermal cleavage of the resulting oxetane. Similar cleavage was observed for an oxetane, the intramolecular carbonyl adduct of (*E*)-3-(*p*-methoxy-



Scheme 1.

phenyl)-3-pentenyl 9-phenanthrenecarboxylate.[3] The attempted careful work-up to detect the intermediate oxetane (3PO) was unsuccessful.

The corresponding 9-phenanthrenecarboxylate, 9PC, and naphthalenecarboxylates, 1NC and 2NC, were also irradiated with 366- (for 9PC) or 313-nm light (for NC's) under otherwise the same conditions to afford the corresponding olefinic aldehydes (yield: 63, 39, and 40% for 9PC, 1NC, and 2NC, respectively) of a similar structure to 3PA (Schemes 2 and 3). In the previous paper[3] 9PC was reported to give 3-(*p*-methoxyphenyl)-2-(9-phenanthryl)oxacyclohepta-2,4-diene on TLC separation (SiO_2, 3 : 2 chloroform–benzene) of the reaction mixture. Use of chloroform as eluent and a prolonged contact time on an SiO_2 plate for TLC separation induced an rearrangement of the oxetane precursor.

The corresponding methyl esters afforded no cycloadducts on irradiation with (*E*)-anethole ((*E*)-1-(*p*-methoxyphenyl)-1-propene, (*E*)-AN) under similar conditions though methyl 9-phenanthrenecarboxylate (9MCP) gave a cyclobutane, the [2+2] cycloadduct across the 9—10 bond and the styryl double bond.[3]

Disappearance quantum yields (ϕ_r) of the starting esters were measured by irradiating benzene–isoprene solutions of the substrates with 313- or 366-nm light as summarized in Table 1.

Photophysical Properties and Rates for Exciplex Formation. All the bichromophoric esters exhibited fluorescence in benzene and showed emission tailing assignable to intramolecular exciplexes in the longer wavelength regions (Table 2). Tables 1 and 2 summarize photophysical properties of the bichromophoric esters and the corresponding methyl esters, as determined by steady and time-resolved fluorescence spectroscopy.

When the fluorescence (k_{mf}) and nonradiative deactivation (k_{md}) rate constants of the arenecarboxylate chromophore ($^1A^*$) are assumed to be independent of the structure and identical with those of the monofunctional system, the corresponding methyl phenanthrenecarboxylate (MCP) or naphthalenecarboxylate (MCN), the decrease in singlet lifetime of bifunctional systems ($^1A^*$-D) can be ascribed to intramolecular quenching, and thus the total quenching rate constant (k_q) for $^1A^*$-D interaction in the excited singlet state can be estimated by using $k_q=1/\tau_S-(k_{mf}+k_{md})$, where τ_S is the fluorescence lifetime (Scheme 4). Also, k_{mf} was estimated from ϕ_{mf} and τ_S of the monofunctional system according to $k_{mf}=\phi_{mf}/\tau_S$. The estimated k_q values for PC's and NC's are in the range of 1.1—5.5×10^8 s^{-1}. Because of high quantum yields of substrate disappearance and a single exponential decay nature of $^1A^*$ fluorescence in A-D a return process from exciplex to local excited state $[^1(A\text{–}D)^* \longrightarrow {}^1A^*\text{–}D]$ was neglected.

Table 1. Kinetic Parameters for the Excited Singlet State of Arenecarboxylates

Ester	ϕ_r a)	ϕ_{mf} b)	ϕ_q c)	ϕ_{ef} b)	ϕ_r/ϕ_q
3MCP	—d,e)	0.18	—	—	—
9MCPf)	0.11e,g)	0.25	—	—	—
1MCN	—d,e)	0.12	—	—	—
2MCN	—d,e)	0.46	—	—	—
3PC	0.32	0.04	0.77	0.01	0.42
9PCf)	0.61	0.04	0.80	0.01	0.76
1NC	0.15	0.05	0.35	0.004	0.43
2NC	0.44	0.09	0.83	0.02	0.53

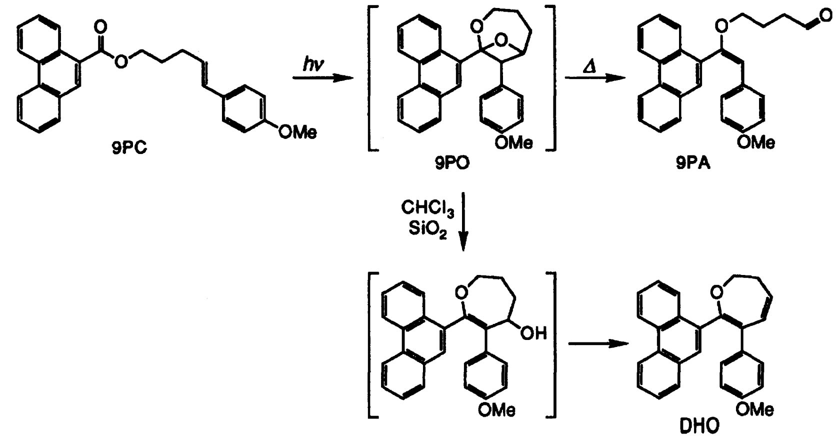
a) Disappearance quantum yields, 3×10^{-4} mol dm^{-3} in benzene at room temperature; irradiation at 313 (for naphthalenecarboxylates) of 366 nm (for phenanthrenecarboxylates). b) Fluorescence quantum yields for the phenanthrene or naphthalene moieties (ϕ_{mf}) and exciplexes (ϕ_{ef}), 10^{-5} mol dm^{-3} in benzene at room temperature; excitation wavelength, 324 nm. c) Quantum yields for intramolecular quenching. d) No adducts were detected. e) With (*E*)-AN. f) Ref. 3. g) Extrapolated to infinite (*E*)-AN concentration.

Table 2. Absorption and Emission Spectra of Arenecarboxylates

Ester	λ_{max}/nm (ε/M^{-1} cm^{-1})a)	λ^m_{max}/nm b)	τ_S/ns c)	λ^e_{max}/nm d)
3MCP	354(520)	356	30.6	430e)
9MCPf)	358(480)	367	15.3	450e)
1MCN	300(6520)	356	0.94	450e)
2MCN	335(1740)	342	13.8	430e)
3PC	354(490)	357	6.9	420
9PCf)	358(480)	367	3.2	450
1NC	295(9480)	358	0.63	440
2NC	335(1690)	342	2.1	420

a) Wavelengths of absorption maxima (molar extinction coefficients). b) Wavelengths of fluorescence maxima for the phenanthrene or naphthalene moiety. c) Fluorescence lifetimes of the phenanthrene or naphthalene moiety. d) Wavelengths of exciplex emission maxima. e) With (*E*)-AN. f) Ref. 3.

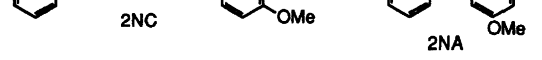
The ϕ_r values for 2NC and 3PC are comparable with that of 9PC,[3] but that for 1NC is lower than the others. Among the esters employed, 1-naphthalenecar-



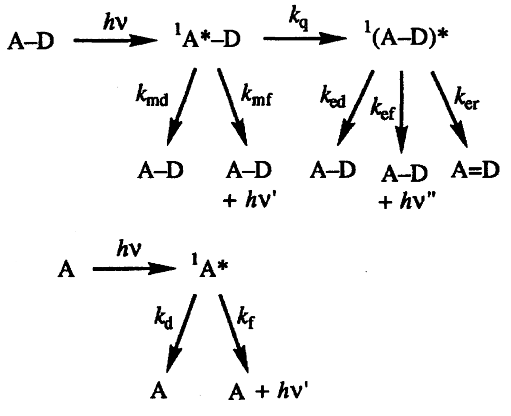
Scheme 2.

boxylates (1MCN and 1NC) have an L_a character of the lowest excited singlet state and the others an L_b character.[7] This is reflected in the fluorescence lifetime as shown in Table 2, and the lower ϕ_r value for 1NC can be ascribed to the lower intramolecular quenching efficiency (ϕ_q) due to the short singlet lifetime. Comparison of ϕ_r with ϕ_q shows that the localized singlet is efficiently quenched by the styrene moiety and the exciplex thus formed affords the cycloadduct quite efficiently, the exciplex⟶product probabilities being 0.42—0.76 (Table 1).

All the methyl esters employed afforded no carbonyl adducts with (*E*)-AN though their excited singlet states were efficiently quenched by (*E*)-AN (Table 3). However, all the employed bichromophoric esters, irrespective of a great structural difference, produced the olefinic aldehydes in good chemical and quantum yields through carbonyl addition. The difference in photochemical behavior between the inter- and intramolecular systems might arise from a change of the photochemical properties of the respective chromophores by imposing conformational constraints of intramolecular processes. No intramolecular interaction between the two chromophores in the ground state was detected by optical absorption spectrum and NMR spectrum. Thus, the olefinic protons and methoxyl protons exhibited essentially identical chemical shifts among 3PC, 9PC, 1NC, and 2NC. Also, the ^{13}C chemical shifts of the ester carbonyl group showed no significant difference among ethyl, (*E*)-3-(*p*-methoxyphenyl)-2-propenyl, (*E*)-4-(*p*-methoxyphenyl)-3-butenyl, and (*E*)-5-(*p*-methoxyphenyl)-4-pentenyl 9-phenanthrenecarboxylate (9PC).



Scheme 3.



Scheme 4.

Molecular Orbital Considerations. Caldwell[10] proposed a method for prediction of reactivity of photochemical cycloadditions on the basis of perturbation energies. Application of this method to possible intermolecular cycloadditions (cyclobutane formation and oxetane formation) of MCP's and MCN's with (*E*)-AN indicates that the cyclobutane formation is much more favorable than the oxetane formation, though the cy-

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

Ester	k_{mf}/s^{-1}	k_{md}/s^{-1}	k_q
3MCP	5.9×10^6	2.7×10^7	1.1×10^{9} a)
9MCP c)	1.6×10^7	4.9×10^7	4.1×10^{9} a)
1MCN	1.3×10^8	9.4×10^8	1.0×10^{10} a)
2MCN	3.3×10^7	3.9×10^7	9.9×10^{9} a)
3PC	5.5×10^6		1.1×10^{8} b)
9PC c)	1.3×10^7		2.5×10^{8} b)
1NC	7.7×10^7		5.5×10^{8} b)
2NC	4.3×10^7		4.0×10^{8} b)

a) In mol^{-1} dm^3 s^{-1}. b) In s^{-1}. c) Ref. 3.

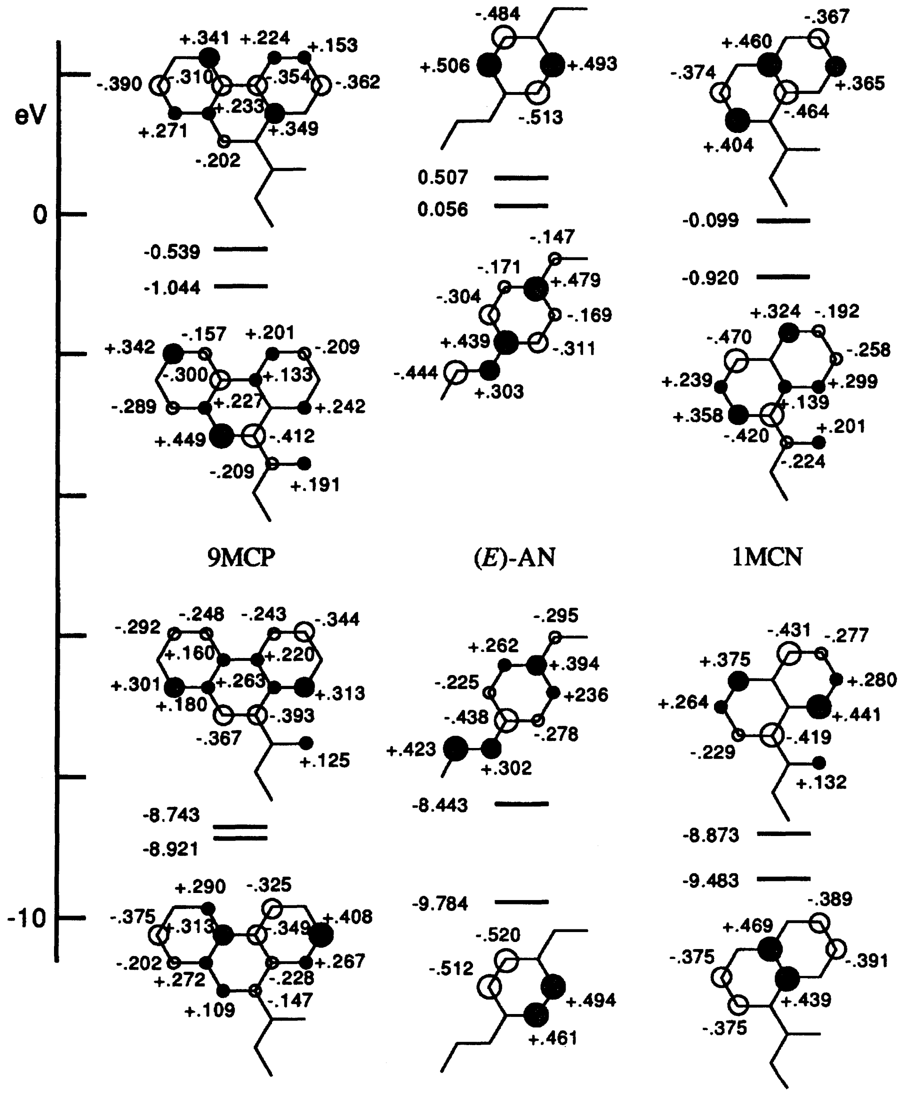


Fig. 1. Energies and Coefficients of NLUMO, LUMO, HOMO, and NHOMO of 9MCP, (*E*)-AN, and 1MCN Calculated by AM1-CI Method.

clobutane formation is not always a favorable process. Thus, we estimated the sum of products of coefficients (Σc^2) between frontier molecular orbitals (FMO's) at the reactive sites for the optimized triplet-state geometries of (*E*)-AN and the arenecarboxylates by means of AM1 calculations. Substitution of the Σc^2 values, the triplet (E_T) and singlet excitation energies (E_S)[11—14] of the addends into the following equation[10] gives $\gamma(r_\mathrm{c})$ values (resonance integrals for end-on interaction of 2p orbitals at distance r) in the range of 30—36 kcal mol^{-1} for cyclobutane formation and of 65—150 kcal mol^{-1} for oxetane formation.[15]

$$\gamma(r_\mathrm{c}) = \left(E_\mathrm{T}^\mathrm{A} + E_\mathrm{T}^\mathrm{B} - E_\mathrm{S}^\mathrm{A}\right)/\Sigma c^2$$

We also applied the perturbation theory[16,17] to estimate the stabilization energies for the cycloadduct formation. The total stabilization energies were estimated according to the following equation for exciplex conformations leading to cyclobutanes and oxetanes by calculating overlap interactions of molecular orbitals involved in bond formation in the conformations with an appropriate distance between the chromophores;

$$\Delta E_\mathrm{Tot} = \sum_i \alpha_i \frac{\left(\sum C_{\mathrm{A}^*}^{kr} C_\mathrm{D}^{ls} \gamma_\mathrm{xy}\right)^2}{\Delta E_{kl}}$$

where α_i are the contribution factors of electronic configurations in the excited singlet state of an acceptor ($^1\mathrm{A}^*$), $C_{\mathrm{A}^*}{}^{kr}$ and $C_\mathrm{D}{}^{ls}$ the coefficients of MO's k of $^1\mathrm{A}^*$ and l of a donor (D) at the reaction sites r and s, respectively, γ_xy the overlap integrals of atoms x and y, and ΔE_{kl} the energy gaps between the MO's k and l.

Actually, the total stabilization energies are obtained as the sum of NHOMO–NHOMO, HOMO–HOMO, LUMO–LUMO, and NLUMO–NLUMO interactions between the excited singlet state of an acceptor and a ground-state donor multiplied with the corresponding contribution factors of electronic configurations. We estimated the energies of NLUMO, LUMO, HOMO, and

Table 4. Stabilization Energies (kcal mol^{-1}) by Molecular Orbital Interaction between the Esters in the Excited Singlet State and Ground-State (*E*)-Anethole Calculated by AM1-CI Method[a)]

Orbitals	3MCP	9MCP	1MCN	2MCN
Cyclobutane type				
NLUMO–NLUMO	0.885(12.9)	0.489(7.8)	0.276(6.5)	0.952(15.6)
LUMO–LUMO	1.679(24.4)	0.850(13.6)	0.749(17.7)	1.809(29.7)
HOMO–HOMO	3.076(44.7)	3.358(53.9)	2.488(58.8)	1.575(25.8)
NHOMO–NHOMO	1.237(18.0)	1.537(24.7)	0.721(17.0)	1.760(28.9)
Total	6.877(100)	6.234(100)	4.234(100)	6.096(100)
Oxetane type				
NLUMO–NLUMO	0.874(20.4)	0.608(17.4)	1.203(16.2)	0.760(20.9)
LUMO–LUMO	0.962(22.5)	0.981(28.0)	2.030(27.3)	0.988(27.2)
HOMO–HOMO	1.247(29.2)	1.099(31.3)	1.901(25.6)	0.430(11.8)
NHOMO–NHOMO	1.194(27.9)	0.814(23.3)	2.295(30.9)	1.456(40.1)
Total	4.277(100)	3.502(100)	7.429(100)	3.634(100)

a) The distance between the chromophores is assumed to be 350 pm. Contribution (%) of each interaction is in the parentheses.

NHOMO of the esters and their coefficients in the reactive states by AM1-CI calculations,[8)] and the results are shown in Fig. 1 and Table 4.[18)] The estimated stabilization energies for formation of the exciplexes with a cyclobutane or oxetane structure show the same reactivity prediction as obtained from Caldwell's method; the cyclobutane formation is predicted to be much more favorable than the oxetane formation except for the case of 1MCN.

A remarkable result from estimation by AM1 calculations of dipole moments of the pair components is that the exciplex formation with (*E*)-AN is favorable only for 9MCP, 1MCN, and 2MCN in a cyclobutane structure and unfavorable for all the four arenecarboxylates in an oxetane structure.

Calculation by Molecular Mechanics for Carbonyl Addition. Treatment of Dreiding models shows that the conformation preferable for carbonyl addition can be easily achieved as shown in Fig. 2. Microwave measurements,[19)] molecular mechanics (MM2),[20)] and other data indicate that the ester group takes a conformation for the C–O single bond in which the alkyl group and carbonyl group are cis, and the carbonyl and *O*-alkyl bonds are coplanar.[21)] The steric constraints forced by the intervening spacer were estimated by conformational analysis of propyl acetate by the MM2 calculations.[22)] Table 5 summarizes the estimated heats of formation for several conformations of propyl acetate. This table shows that conformer E, which is the most preferable conformer for the present intramolecular carbonyl addition, is expected to be facilely attained by bond rotations from the most stable conformer, A ($\Delta\Delta H$=0.71 kcal mol^{-1}).

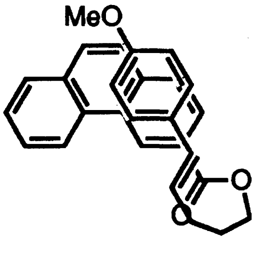
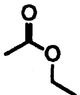
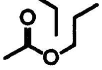
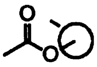
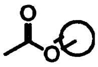
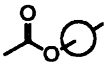
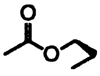
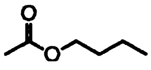


Fig. 2.

Table 5. Heat of Formation (ΔH) of Various Conformations of Propyl Acetate Estimated by MM2 Calculations

Conformer		ΔH/kcal mol^{-1}	$\Delta\Delta H$/kcal mol^{-1}
	H	10.00	4.04
	G	8.86	2.90
	F	6.92	0.71
	E	6.92	0.71
	D	6.44	0.48
	C	6.21	0.25
	B	6.19	0.23
	A	5.96	0.00

Conclusion

In intermolecular systems the exciplexes can generally take a conformation of maximum overlap of the chromophores, and the products might arise from such a transition state for the reaction. In the present case, however, the intermolecular interaction could not lead to a conformation preferable for carbonyl addition. The conformational constraints resulting from the link of two interacting chromophores might destabilize the exciplexes with conformations achieved in the intermolecular systems, and the exciplexes preferable for carbonyl addition might be of similar stability to, or of higher stability than, those with other conformations though less stabilized than the intermolecular exciplexes.[23)]

In this situation the carbonyl addition becomes a main process in the present systems. It should be noted that the interorbital interaction integral between carbon and oxygen atoms, $\Delta\beta_{CO}$, exceeds that between carbon atoms, $\Delta\beta_{CC}$, at a very close distance like 150 pm,[24)] as described elsewhere.[18,25)] The present results suggest that the intramolecular carbonyl addition could be of synthetic utility and applied to various aromatic esters of a similar structure.

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