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Photochemical Cycloaddition of Phenanthrene-Fused Lactones to (*E*)-Anethole. Structural Effects and Dual Collapse Processes of an Exciplex Leading to Cycloadducts

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On irradiation with (*E*)-anethole in benzene 10-hydroxymethyl-9-phenanthrenecarboxylic acid lactone (*s-trans* lactone, STL) gave an intermolecular [2+2] cycloadduct, a cyclobutane derivative, while 8-hydroxymethyl-9-phenanthrenecarboxylic acid lactone (*s-cis* lactone, SCL) afforded a cyclobutane derivative and an olefinic product derived from an oxetane precursor, the carbonyl adduct. The formation of cycloadducts of highly different structures in SCL was ascribed to competitive collapse of the involved exciplex to the products. The features of intermolecular cycloaddition of the phenanthrene derivatives are discussed on the basis of results obtained from molecular orbital calculations.

Photochemical [2+2] cycloaddition is one of the most important and well-studied reactions.[1—5] Exciplexes are intermediates in this cycloaddition, and the products formed are those of maximum overlap of the chromophores at the transition state for the reaction.[1—3] On excitation of methyl 9-phenanthrenecarboxylate (9MCP) with (*E*)-anethole [(*E*)-1-(*p*-methoxyphenyl)-1-propene, (*E*)-AN], only a cyclobutane derivative, the head-to-head cycloadduct, was obtained, but incorporation of the two chromophores in one molecule separated by a polymethylene chain brought about a new aspect of the competitive cycloaddition of intramolecular exciplexes involving carbonyl addition.[6] This can be ascribed to a change of the photochemical properties of the respective chromophores by imposing conformational constraints on intramolecular processes.

In order to get further insight into the structural factors controlling the carbonyl addition we have studied on behavior of *intermolecular* exciplexes arising from rigid planar phenanthrene-fused lactones and (*E*)-AN. For 9-phenanthrenecarboxylates, a conformation in which the 9-10 bond of the phenanthrene ring and the carbonyl bond are *s-trans* is assumed to be preferable, and this is the case for 4-methoxyphenylalkenyl 9-phenanthrenecarboxylates which show the competitive intramolecular cycloadditions.[6,7] Esters in general strongly prefer a conformation for the C–O single bond in which the alkyl group and carbonyl group are *s-cis*, and the carbonyl and *O*-alkyl bonds are coplanar.[8]

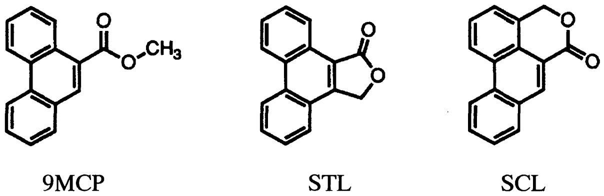


Chart 1.

As rigid planar substrates, 10-hydroxymethyl-9-phenanthrenecarboxylic acid lactone (STL) and 8-hydroxymethyl-9-phenanthrenecarboxylic acid lactone (SCL) were prepared; STL and SCL have conformations where the 9-10 bond and carbonyl bond are *s-trans* and *s-cis*, respectively, and the *O*-alkyl moiety and carbonyl group are fixed to be *s-trans* (Chart 1). In this paper we describe a new aspect in photochemical intermolecular cycloaddition of the rigid substrates with (*E*)-anethole; only in the case of SCL the carbonyl addition as well as the cyclobutane formation proceeded efficiently. This was ascribed to competitive collapse of an exciplex intermediate to the products, and structural effects of phenanthrenecarboxylic acid derivatives on the cycloadditions were discussed on the basis of results obtained from molecular orbital calculations.[9]

Experimental

General. Proton NMR 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 with a Hewlett Packard 5890A mass spectrometer. Infrared spectra (IR) were obtained with 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 purified by column chromatography (SiO_2, hexane) followed by distillation under reduced pressure. All other chemicals used were reagent grade and were recrystallized or distilled if necessary.

Methyl 10-Methyl-9-phenanthrenecarboxylate (10M9MCP). 9-Methylphenanthrene was prepared according to the literature[10] from 9-bromophenanthrene (12.0 g, 47 mmol), butyllithium (31.8 ml, 15 wt% in hexane, 1.1 equiv), and methyl iodide (3.2 ml, 1.1 equiv) (7.6 g, 85%); mp 91—91.5°C (MeOH).

Bromination of 9-methylphenanthrene (17.3 g, 90 mmol) with PBr_5 (46.4 g, 1.2 equiv) in benzene gave 9-bromo-10-methylphenanthrene (16.1 g, 66%); mp 116—118°C (hexane).

The bromide (10.0 g, 37 mmol) was treated with butyllithium, and then with methyl chloroformate (4.6 ml, 1.6 equiv) to afford methyl 10-methyl-9-phenanthrenecarboxylate (4.9 g, 53%); mp 61—62°C (EtOH) (lit, 61—62°C);[11] UV (PhH) $\lambda_{\max}$ 301 nm (ε 10200), 352 (140).

Phenanthro[9,10-*c*]furan-1(3*H*)-one (10-Hydroxymethyl-9-phenanthrenecarboxylic Acid Lactone, STL). Bromination[11] of 10M9MCP (1.55 g, 6.2 mmol) by *N*-bromosuccinimide (NBS, 1.2 equiv) in CCl_4 (40 ml) containing a catalytic amount of dibenzoyl peroxide gave methyl 10-bromomethyl-9-phenanthrenecarboxylate (1.37 g, 73%); mp 154.5—155.5°C (EtOH) (lit, 152—153°C).[11]

Reflux of the bromide (9.0 g, 30 mmol) with KOH (2.4 equiv) in methanol[12] afforded methyl 10-methoxymethyl-9-phenanthrenecarboxylate (4.8 g, 57%); yellow oil; ^{1}H NMR ($CDCl_3$) δ=3.4 (s, 3H, CH_3O), 4.0 (s, 3H, CH_3OCO), 4.9 (s, 2H, OCH_2), 7.2—7.8 (m, 8H, ArH).

The ester was refluxed in acetic anhydride (4 equiv) with a catalytic amount of $ZnCl_2$, and then refluxed with KOH in 1 : 1 ethanol-benzene.[13] The hydrolysate was refluxed with *p*-toluenesulfonic acid in benzene to give phenanthro[9,10-*c*]furan-1(3*H*)-one,[14] The crude product was purified by column chromatography (SiO_2, $CHCl_3$) and recrystallization from benzene (1.1 g, 15% from methyl 10-bromomethyl-9-phenanthrenecarboxylate); mp 258.5—259°C (PhH) (lit, 259°C).[15] UV (PhH) $\lambda_{\max}$ 304 nm (ε 8400), 315 (7500), 354 (740).

Methyl 8-Methylphenanthrene-9-carboxylate (8M9MCP).[16] 2-(*o*-Methylphenyl)-3-(*o*-nitrophenyl)-2-propenoic acid was obtained by refluxing[17] *o*-methylphenylacetic acid (6.0 g, 40 mmol) and *o*-nitrobenzaldehyde (5.3 g, 35 mmol) in acetic anhydride (15 cm^3) with K_2CO_3 (1.6 g, 14 mmol) (7.3 g, 74%); mp 165°C (MeOH) (lit, 168°C).[16]

The nitro acid was reduced with iron(II) sulfate ($FeSO_4 \cdot 7H_2O$, 30.0 g, 108 mmol) and ammonia (28%, 90 ml) to give 2-(*o*-methylphenyl)-3-(*o*-aminophenyl)-2-propenoic acid (2.1 g, 56%); mp 225°C (MeOH) (lit, 225°C).[16]

The amino acid (1.27 g, 5 mmol) was diazotized with sodium nitrite (0.4 g, 5.8 mmol) and hydrochloric acid, and the diazonium salt was treated with copper powder (0.32 g) at room temperature to afford 8-methyl-9-phenanthrenecarboxylic acid (0.85 g, 72%); mp 175—178°C (MeOH) (lit, 181—182°C).[16]

This acid was converted to the methyl ester (8M9MCP) through acid chloride (58%);[18] mp 94—95°C (MeOH) (lit, 92—94°C).[17] UV (PhH) $\lambda_{\max}$ 305 nm (ε 10800), 353 (200).

4*H*,6*H*-Phenanthro[1,10-*cd*]pyran-6-one (8-Hydroxymethyl-9-phenanthrenecarboxylic Acid Lactone, SCL). Reflux of 8M9MCP (1.0 g, 4 mmol) with NBS (1.2 equiv) in CCl_4 (50 cm^3) containing a catalytic amount of dibenzoyl peroxide afforded 4*H*,6*H*-phenanthro[1,10-*cd*]pyran-6-one.[11] The crude lactone was purified by column chromatography (SiO_2, 3 : 1 hexane-benzene) and recrystallization from benzene (0.25 g, 29%); mp 151°C (PhH); UV (PhH) $\lambda_{\max}$ 316 nm (ε 11700), 327 (10700), 364 (520). Calcd for $C_{16}H_{10}O_2$: C, 82.03; H, 4.30%. Found: C, 82.04; H, 4.44%

Irradiation of STL with (*E*)-Anethole ((*E*)-AN). A solution of STL (94 mg, 4×10^{-3} mol dm^{-3}) and (*E*)-AN (74 mg, 5×10^{-3} mol dm^{-3}) in benzene (100 cm^3) was irradiated for 5 h in a uranium glass tube with a 450-W high-pressure mercury lamp under nitrogen atmosphere at room temperature. After evaporation of the solvent, the residue was separated by preparative HPLC (SiO_2, 1 : 5 AcOEt-hexane) to give oily products. The products were identified to be a head-to-head adduct (CB1) of STL with (*E*)-AN [15% yield based on STL consumed (32%)] and *p*-methoxybenzaldehyde (10%) from their spectral data.

CB1: ^{1}H NMR ($CDCl_3$) δ=1.33 (d, 3H, CH_3), 3.23 (m, 1H, Me-CH), 3.68 (s, 3H, OCH_3), 3.72—3.83 (m, 3H, CH_2 and Ar-CH), 6.85 (m, 4H, phenyl H), 7.19—8.20 (m, 8H, phenanthryl H); IR ($CHCl_3$) 1780 cm^{-1} ($\nu_{C=O}$); Mass *m*/*z* 382 (M^+).

Irradiation of SCL with (*E*)-AN. A solution of SCL (70 mg, 3×10^{-3} mol dm^{-3}) and (*E*)-AN (45 mg, 3×10^{-3} mol dm^{-3}) in benzene (100 cm^3) was irradiated for 2 h in a similar way to that for STL. After evaporation of the solvent, the residue was separated by preparative HPLC (SiO_2, 1 : 5 AcOEt-hexane) to give two oily products with comparable yields. The products were identified to be a head-to-head adduct (CB2) of SCL with (*E*)-AN [19% based on SCL consumed (86%)] and an olefin (OL2, 23%) on the basis of their spectral data.

CB2: ^{1}H NMR ($CDCl_3$) δ=1.23 (d, 3H, CH_3), 2.45 (m, 1H, Me-CH), 3.67 (s, 3H, OCH_3), 3.67—4.10 (m, 2H, 10-H and Ar-CH), 4.52 (br. s, 2H, CH_2), 6.60 (m, 4H, phenyl H), 7.10—8.03 (m, 7H, phenanthryl H); IR ($CHCl_3$) 1730 cm^{-1} ($\nu_{C=O}$); Mass *m*/*z* 382 (M^+).

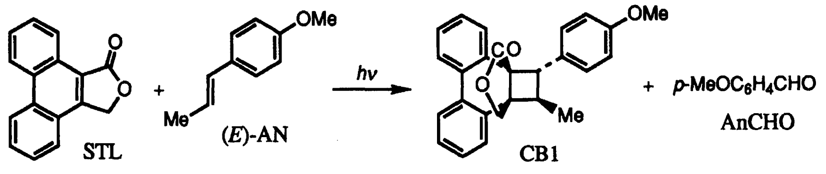
OL2: ^{1}H NMR ($CDCl_3$) δ=3.78 (s, 3H, OCH_3), 5.30 (s, 2H, CH_2), 6.62 (s, 1H, C=CH), 6.87—8.53 (m, 13H, aryl H); IR ($CHCl_3$) no carbonyl peak; Mass *m*/*z* 338 (M^+).

Photophysical Measurements. Ultraviolet absorption spectra (UV) were taken on a Hitachi 200-20 spectrophotometer. Fluorescence and phosphorescence spectra were obtained on a Hitachi F-4000 fluorescence spectrofluorometer. Fluorescence quantum yields (ϕ_f) were determined in benzene by comparing the corrected fluorescence spectra with that of phenanthrene (ϕ_f=0.13).[19] Fluorescence lifetimes (τ_f) were measured by single photon counting by using an Ortec/Applied Photophysics SP-3X system or a Horiba NAES-1100 time-resolved spectrofluorometer.

Methods of Calculations. Semiempirical molecular orbital calculations were carried out by AM1 method.[20] On optimization of conformations of methyl arenecarboxylates was assumed a structure that the methyl group and carbonyl group are cis for the C–O single bond, the carbonyl and *O*-alkyl bonds are coplanar, and the carbonyl group is directed to the peri-hydrogen for 9-phenanthrenecarboxylate. 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.

Results and Discussion

Photochemical and Photophysical Behavior of Lactones. On irradiation of STL at 366 nm in benzene in the presence of (*E*)-AN under nitrogen a cyclobutane (CB1) was produced in 15% yield together with *p*-methoxybenzaldehyde[21] (AnCHO, 10% yield) (Scheme 1). The structure of CB1 was determined on the basis of various spectral data, mainly ^{1}H NMR and similarity of the ^{1}H NMR spectrum to that of the photoadduct from 9MCP with (*E*)-AN.[6]



Scheme 1.

Similar irradiation of SCL with (*E*)-AN in benzene, however, gave both a cyclobutane (CB2, 19%) and an olefin (OL2, 23%) (Scheme 2). The structure of CB2 was also determined by comparing its spectral data with those of CB1 and the photoadduct from 9MCP with (*E*)-AN.⁶⁾ OL2 was identified on the basis of various spectral data.

Cyclobutanes CB1 and CB2 are [2+2] head-to-head cycloadducts at the 9-10 bond of the lactones, and OL2 is a secondary product which might be derived from the carbonyl adduct OX2 (Scheme 2) through elimination of acetaldehyde during the separation. Similar cleavage was observed for an oxetane, the intramolecular carbonyl adduct of (*E*)-3-(*p*-methoxyphenyl)-3-pentenyl 9-phenanthrenecarboxylate.6a) The attempted careful work-up to detect OX2 was unsuccessful.

The efficiency of reaction was very low for STL, but much higher for SCL; the limiting quantum yields for disappearance (ϕ_r) at infinite (*E*)-AN concentration were less than 10^{-3} for STL and 0.13 for SCL. The latter value is comparable to that for the photocycloaddition of 9MCP to (*E*)-AN. Similarity of STL in reaction mode to 9MCP could be ascribed to their analogous conformations in which the 9-10 and carbonyl bonds are *s-trans*.

The cycloadditions proceed through exciplexes formed from the lactone singlets. The lactones, STL and SCL, exhibited their fluorescence spectra in benzene in the wavelength region similar to that of 9MCP; that of STL appears in slightly shorter wavelengths. The fluorescence lifetime (τ_f) and quantum yield (ϕ_f) were also similar in the two lactones; $\tau_f = 22.0$ ns and $\phi_f = 0.26$ for STL and $\tau_f = 15.5$ ns and $\phi_f = 0.20$ for SCL in benzene. The fluorescence spectra of STL and SCL were efficiently quenched by (*E*)-AN in benzene ($k_q = 7.1\times10^9$ and 6.1×10^9 mol^{-1} dm^3 s^{-1}, respectively) with an isoemissive point (455 and 470 nm, respectively) and weak exciplex emissions were observed in the longer wavelength region (430—480 and 450—500 nm, respectively).²²⁾ There are no large differences in physical properties of the excited singlet state of STL, SCL, and 9MCP, and all the three substrates afford the head-to-head cycloadducts. Nevertheless, only SCL gives the oxetane in addition to the cyclobutane.

Molecular Orbital Considerations. The difference in photochemical behavior might arise from the structure of exciplexes involved and their collapse processes. In intermolecular cycloadditions the precursor exciplexes can generally take a conformation of maximum overlap of the chromophores at the transition state for the reaction.¹⁻³⁾ For STL and 9MCP⁶⁾ the cyclobutane derivatives are produced, though the efficiencies are very much different, through an exciplex having the most stable conformation, but the formation of oxetanes might require another exciplex possessing a less stable conformation. Thus, the latter process could not compete with the former.

Molecular orbital (MO) calculations also indicate that the formation of oxetane-type exciplexes is much less favorable than that of cyclobutane-type exciplexes in both 9MCP²³⁾ and the lactones. The perturbation theory²⁴,²⁵⁾ was applied to estimate the stability of 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.²³⁾

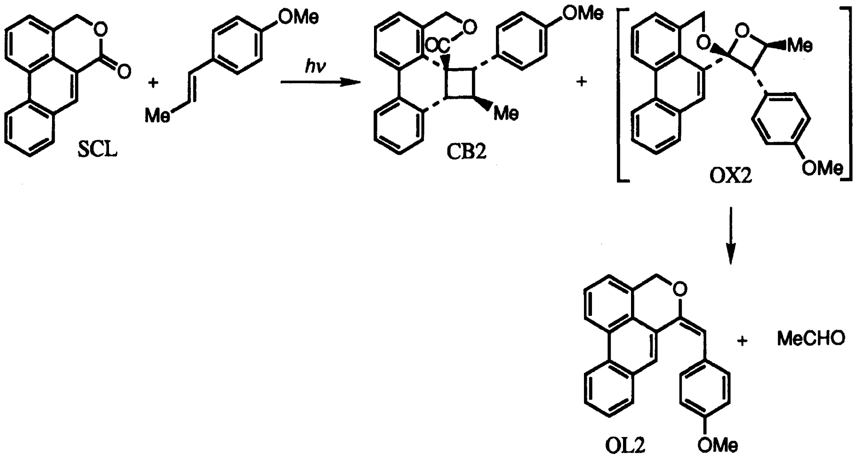
Thus, the total stabilization energies are estimated according to the following equation;

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

where α_i are the contribution factors of electronic configurations in the excited singlet state of an acceptor (^{1}A*), $C_{\mathrm{A}*}{}^{kr}$ and $C_{\mathrm{D}}{}^{ls}$ the coefficients of MO's k of ^{1}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 NHOMO of the lactones and their coefficients in the reactive states by AM1-CI calculations,²⁰⁾ and the results are shown in Fig. 1. In Fig. 2 are compared the energies of MO's of the lactones and some phenanthrene- and naphthalenecarboxylates,²³⁾ and the electronic configurations of their excited singlet states are summarized in Table 1.

The overlap interactions between the lowest L_b singlets of phenanthrene derivatives²⁶,²⁷⁾ and ground-state (*E*)-AN were estimated at a distance of 350 pm by using the interorbital interaction integrals²⁰,²⁸⁾ and the atomic orbital coefficients obtained from AM1-CI calculations for planar molecular geometries.²⁰⁾ Under the



Scheme 2.

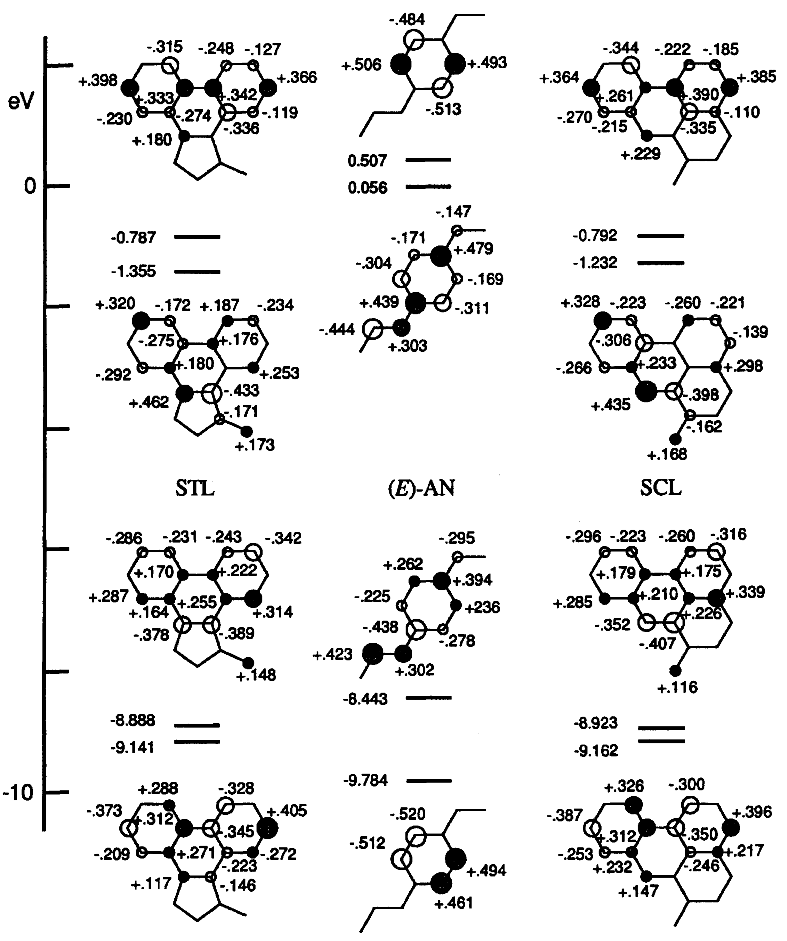


Fig. 1. Coefficients of NLUMO, LUMO, HOMO, and NHOMO of STL, (*E*)-AN, and SCL calculated by AM1-CI method.

above conditions, irradiation leads to the lowest singlet states of lactones. The estimated stabilization energies for formation of the exciplexes with a cyclobutane or oxetane structure are listed in Table 2, and their comparison show that the cyclobutane formation is much more favorable than the oxetane formation for STL and SCL as well as 9MCP. Estimation of dipole moments of the pair components also indicates that the exciplex formation with (*E*)-AN is favorable only in a cyclobutane structure and unfavorable in an oxetane structure, as shown in Fig. 3. Similar results for phenanthrene- and naphthalenecarboxylates were described elsewhere.[23]

Dual Collapse Processes Leading to Cycloadducts. For the intramolecularly linked bichro-

Table 1. Contribution Factors (α_i) of Electronic Configurations and Energies (E_S) for the Excited Singlet State of Some Phenanthrene and Naphthalene Derivatives [a)]

Compound	Electronic configuration a.b.c.d in (NHOMO)^a(HOMO)^b(LUMO)^c(NLUMO)^d 2.1.1.0	 2.1.0.1	 1.2.1.0	 1.2.0.1	E_S(calcd) kcal mol^{-1}	E_S(obsd) kcal mol^{-1}
STL	0.0003	0.3855	0.5741	0.0004	75.1	80.6
SCL	0.0137	0.4125	0.5304	0.0044	77.6	77.5
9MCP	0.0090	0.3766	0.5750	0.0040	77.3	77.9
9CNP	0.0048	0.4217	0.5358	0.0020	77.4	79.0
3MCP	0.0009	0.4498	0.5284	0.0025	79.9	80.3
2MCN	0.3822	0.2711	0.2061	0.1271	78.9	83.6
1MCN	0.7766	0.0069	0.0027	0.1988	80.8$^{b)}$	80.3

a) Four-electron configurations were employed by the AM1-CI method. b) S_2; the S_1 state (E_S 79.3 kcal mol^{-1}, L_b type) is assumed to overlap with the S_2 state.

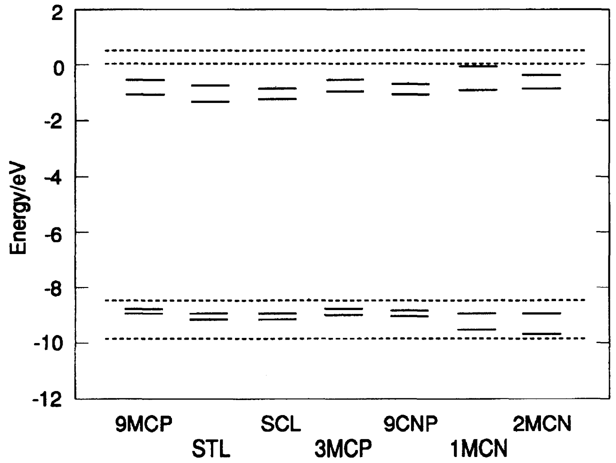
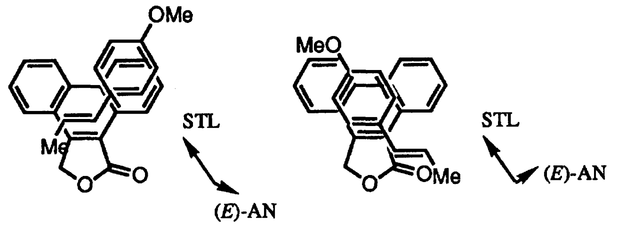
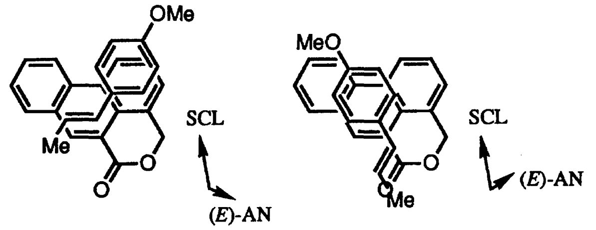


Fig. 2. Comparison of energies of NLUMO, LUMO, HOMO, and NHOMO for 9MCP, STL, SCL, methyl 3-phenanthrenecarboxylate (3MCP), 9-cyanophenanthrene (9CNP), methyl 1-naphthalenecarboxylate (1MCN), 2-naphthalenecarboxylate (2MCN) (real lines), and (*E*)-AN (dotted lines), calculated by AM1-CI method.



a) STL



b) SCL

Fig. 3. Conformations of intermediates favorable for formation of the cycloadducts in STL and SCL. Arrows show directions of dipole moments of the components.

mophoric esters, 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)] For the present intermolecular system, however, the conformational constraints are not the case. The results of molecular calculations definitely show that the oxetane-type exciplex formation is much less favorable than the cyclobutane-type exciplex formation.

The enhancement of reactivity in oxetane formation could be explained by a competitive collapse of a cyclobutane-type exciplex to the products. Dreiding models show that for STL the interconversion between the two conformations, one favorable for cyclobutane and the other favorable for oxetane formation, needs a rotation of 180° about the long molecular axis and a rotation of 60° about the axis perpendicular to the molecular plane of one of the partner molecules (Fig. 3a). Accordingly, only the exciplex leading to cyclobutane is essentially formed. For SCL, the conformations of maximum overlap resulting in cycloadducts (Fig. 3b) are in a similar situation to the case of STL; however, these two conformations might be located in shallow energy minima, and can be easily converted to each other by a 60° rotation of either component molecule about the axis

Table 2. Stabilization Energies (kcal mol^{-1}, Contribution/%) by Molecular Orbital Interaction between the Lactones and Other Phenanthrene Derivatives in the Excited Singlet State and Ground-State (*E*)-Anethole Calculated by AM1-CI Method[a]

Orbitals	STL	SCL	9MCP	9CNP
Cyclobutane type				
NLUMO–NLUMO	0.435 (7.7)	0.493 (9.8)	0.489 (7.8)	0.546 (11.1)
LUMO–LUMO	0.791 (14.0)	0.722 (14.4)	0.850 (13.6)	0.923 (18.7)
HOMO–HOMO	2.323 (41.3)	2.053 (40.7)	3.358 (53.9)	1.958 (39.6)
NHOMO–NHOMO	2.085 (37.0)	1.763 (35.1)	1.537 (24.7)	1.510 (30.6)
Total	5.634 (100)	5.031 (100)	6.234 (100)	4.937 (100)
Oxetance type				
NLUMO–NLUMO	0.497 (15.3)	0.537 (20.4)	0.608 (17.4)	
LUMO–LUMO	0.636 (19.5)	0.662 (25.2)	0.981 (28.0)	
HOMO–HOMO	0.777 (23.8)	0.698 (26.6)	1.099 (31.3)	
NHOMO–NHOMO	1.350 (41.4)	0.727 (27.8)	0.814 (23.3)	
Total	3.260 (100)	2.624 (100)	3.502 (100)	

a) The distance between the chromophores is assumed to be 350 pm.

perpendicular to the molecular plane while maintaining the parallel relation. Furthermore, the interorbital interaction integral (0.17 eV) between carbon and oxygen atoms, $-\Delta\beta_{\rm CO}$, is much lower at a long distance like 350 pm than that (0.47 eV) between carbon atoms, $-\Delta\beta_{\rm CC}$; however, at a very close distance like 150 pm, $-\Delta\beta_{\rm CO}$ (7.05 eV) exceeds $-\Delta\beta_{\rm CC}$ (6.97 eV).[20,28] This might affect the transition state of carbonyl addition.

Conclusion

In the intramolecular cases such as (*E*)-5-(*p*-methoxyphenyl)-4-pentenyl 9-phenanthrenecarboxylate, the exciplex affording a cyclobutane and that giving an oxetane are similar in energy due to the conformational constraints, and each product might arise from a particular exciplex; *the formation of exciplexes might be competitive.* In the present intermolecular case of the lactone, however, a sole exciplex contributes to the formation of both cycloadducts by *competitive exciplex→product collapse.*

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