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Photochemical and Photophysical Behavior of *p*-Methoxyphenylalkenyl Phenanthrenecarboxylates. I. Structure and Competitive Formation of Intramolecular Cycloaddition Products

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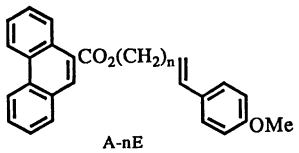
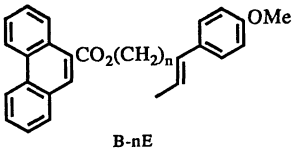
Irradiation of (*E*)-3-(*p*-methoxyphenyl)-3-pentenyl, (*E*)-4-(*p*-methoxyphenyl)-4-hexenyl, and (*E*)-5-(*p*-methoxyphenyl)-5-heptenyl 9-phenanthrenecarboxylates (B-2E, B-3E, and B-4E, respectively) in benzene gave intramolecular [2+2] cycloadducts, cyclobutane derivatives (CB-2, CB-3, and CB-4, respectively) possessing the same conformation as an intermolecular [2+2] cycloadduct (CB-0) between methyl 9-phenanthrenecarboxylate (9-MCP) and *trans*-anethole (*t*-AN), and oxetane derivatives (OX-2, OX-3, and OX-4, respectively) arising from intramolecular cycloaddition between the carbonyl group and the olefinic double bond. However, (*E*)-4-(*p*-methoxyphenyl)-3-butenyl and (*E*)-5-(*p*-methoxyphenyl)-4-pentenyl 9-phenanthrenecarboxylates (A-2E and A-3E, respectively) afforded only products derived from oxetane precursors.

Exciplexes are intermediates in [2+2] photocycloadditions, and the products formed are those of maximum "sandwich" overlap of the chromophores at the transition state for the reaction.[1-3] Incorporation of two chromophores in one molecule separated by a certain number of atoms changes the photochemical properties of the respective chromophores by imposing new restrictions on intramolecular processes.[4,5]

On excitation of 9-cyanophenanthrene with *trans*-anethole (*t*-AN, *trans*-1-(*p*-methoxyphenyl)propene), only a "head-to-head" product was obtained, but substituents in some cases caused the formation of "head-to-tail" products.[1b] For studying the effects of conformational constraints on the phenanthrene–styrene reaction, we have prepared two series (A-*n*E and B-*n*E) of bichromophoric esters with different linking sites and chain lengths, and compared their photochemical and photophysical behavior.



A-nE
n = 1 - 4



B-nE
n = 1 - 4

Among esters A-*n*E (*n*=1—4) and B-*n*E (*n*=1—4), several compounds showed much lower fluorescence intensities and much shorter fluorescence lifetimes compared with those of an unlinked model, methyl 9-phenanthrenecarboxylate, and some of them exhibited longer wavelength emissions due to intramolecular exciplexes.[6] In photochemistry the esters also provided a novel aspect caused by conformational constraints, a competitive addition of intramolecular exciplexes involving carbonyl addition. In this paper we compare photochemical behavior of intramolecular exciplexes; some of A series esters afford only oxetane adducts, whereas some of B series esters give both of oxetane and head-to-head cyclobutane adducts. In the accompanying paper[7] we describe efficiency of intramolecular quenching of the phenanthrene singlet by the styrene moiety on the basis of measurements of fluorescence lifetimes and quantum yields.

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). Tetramethylsilane (TMS, δ 0.0) was used as an internal standard for ^{1}H NMR. The spectra are reported as follows: chemical shift, multiplicity, number of protons, coupling constant (when measured), and assignment (if known). Carbon 13 NMR spectra were recorded on a JEOL FX-100 spectrometer (100 MHz). Chloroform (δ 77.7) was used as an internal reference for ^{13}C NMR. Infrared spectra (IR) were obtained on a Hitachi 215 spectrophotometer, and ultraviolet absorption spectra (UV) were taken on a Hitachi 200-20 spectrophotometer. Fluorescence spectra were obtained on a Hitachi MPF4 fluorescence spectrofluorimeter.

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]

Materials. Benzene was distilled from calcium hydride before use. Isoprene was purified by distillation. *trans*-Anethole was distilled under reduced pressure before use.

Methyl 9-Phenanthrenecarboxylate (9-MCP). 9-Phenanthrenecarboxylic acid was converted to the acid chloride with thionyl chloride; mp 102—104 °C (lit,[9] 103—104 °C).

The acid chloride was reacted with methanol in benzene containing pyridine. The product was crystallized from methanol; mp 115—116 °C (lit,[10] 115.5—116 °C); UV (PhH) λ_{max} 306 nm (ε 10500), 358 (480).

(*E*)-3-(*p*-Methoxyphenyl)-2-propenyl 9-Phenanthrenecarboxylate (A-1E). Ethyl (*E*)-3-(*p*-methoxyphenyl)propenoate was prepared according to the literature[11] from *p*-methoxybenzaldehyde and ethyl acetate in the presence of sodium ethoxide (64%); bp 125—129 °C/1 mmHg (lit,[11] 132 °C/1 mmHg) (1 mmHg=133.32 Pa).

The ester was treated with $LiAlH_4$ in ether to give (*E*)-3-(*p*-methoxyphenyl)-2-propen-1-ol (65%); mp 74—77 °C (lit,[12] 76—78 °C).

The propenol was reacted with 9-phenanthrenecarbonyl chloride in benzene containing pyridine to give A-1E (46%). The product was crystallized from 1 : 1 benzene-hexane; mp 134—135 °C; ^{1}H NMR ($CDCl_3$) δ=3.69 (s, 3H, CH_3O), 5.01 (d, 2H, *J*=6 Hz, CH_2), 6.32 (d. t, 1H, *J*=15, 6 Hz, C=CH), 6.72 (d, 1H, *J*=15 Hz, C=CH), 6.72—7.31 (m, 4H, ArH), 7.44—9.04 (m, 9H, ArH); UV (PhH) λ_{max} 299 nm (ε 14100), 358 (470). Calcd for $C_{25}H_{20}O_3$: C, 81.52; H, 5.43%. Found: C, 81.15; H, 5.43%.

(*E*)-4-(*p*-Methoxyphenyl)-3-butenyl 9-Phenanthrenecarboxylate (A-2E). A solution of 2,3-dichlorotetrahydrofuran (28.2 g, 0.20 mol) in ether (30 cm^3) was slowly added to the Grignard solution prepared from magnesium (8.0 g, 0.33 mol) and *p*-bromoanisole (56.1 g, 0.30 mol) in ether (50 cm^3).[13] The solution was refluxed for 2 h and quenched with cold dil H_2SO_4. The solvent was evaporated and the residue was distilled under reduced pressure to give a pale yellow oil of 2-(*p*-methoxyphenyl)-3-chlorotetrahydrofuran (6.4 g, 43%); bp 122—126 °C/2.5 mmHg.

To sodium particles (1.42 g, 0.062 mol) in ether (50 cm^3) was added a solution of 2-(*p*-methoxyphenyl)-3-chlorotetrahydrofuran (6.0 g, 0.028 mol) in ether (50 cm^3) in a period of 3 h with stirring.[14] The solution was refluxed for 3 h and treated with ice. The solvent was evaporated and the residue was column chromatographed (SiO_2, 2 : 3 $CHCl_3$-ether) to give a pale yellow oil of *trans*-4-(*p*-methoxyphenyl)-3-buten-1-ol (1.5 g, 30%).

The butenol was reacted with 9-phenanthrenecarbonyl chloride in benzene containing pyridine to give A-2E (0.85 g, 50%). The product was crystallized from 1 : 1 benzene-hexane; mp 96—97.5 °C; ^{1}H NMR ($CDCl_3$) δ=2.62 (d.t, 2H, *J*=6, 6 Hz, C=C-CH_2), 3.63 (s, 3H, CH_3O), 4.46 (t, 2H, *J*=6 Hz, OCH_2), 6.05 (d.t, 1H, *J*=16, 6 Hz, C=CH), 6.40 (d, 1H, *J*=16 Hz, C=CH), 6.65—7.27 (m, 4H, ArH), 7.35—9.06 (m, 9H, ArH); UV (PhH) λ_{max} 301 nm (ε 13400), 358 (470). Calcd for $C_{26}H_{22}O_3$: C, 81.65; H, 5.80%. Found: C, 81.53; H, 5.82%.

(*E*)-5-(*p*-Methoxyphenyl)-4-pentenyl 9-Phenanthrenecarboxylate (A-3E). Ethyl hydrogen pentanedioate was prepared according to the literature[15] from pentanedioic anhydride with ethanol (63%), and converted to ethyl 4-(chloroformyl)butanoate with thionyl chloride (68%); bp 116.5—118 °C/24 mmHg (lit,[16] 102.5—103.5 °C/10 mmHg).

The acid chloride (16.6 g, 0.093 mol) was slowly added to a stirred mixture of anisole (11.1 g, 0.10 mol) and $AlCl_3$ (24.8 g, 0.19 mol) in $(CHCl_2)_2$ (100 cm^3) cooled at 0 °C.[17] The mixture was stirred at 0 °C for 3 h and quenched with cold dil H_2SO_4. The solvent was evaporated and the residue was crystallized from hexane to give colorless crystals of ethyl 4-(*p*-methoxybenzoyl)butanoate (6.1 g, 26%); mp 58.5—59 °C.

The keto ester (3 g, 0.012 mol) was reduced with $NaBH_4$ (0.45 g, 0.012 mol) in ethanol (50 cm^3) to give ethyl 5-hydroxy-5-(*p*-methoxyphenyl)pentanoate (2.7 g, 90%).

After reflux of the hydroxy ester (2.7 g, 0.011 mol) in benzene with *p*-toluenesulfonic acid (0.8 g) (300 cm^3) for 30 min, the product was treated with SiO_2 column (benzene) to give a colorless oil of ethyl (*E*)-5-(*p*-methoxyphenyl)-4-pentenoate (1.5 g, 66%).

Treatment of the pentenoate with $LiAlH_4$ in ether gave (*E*)-5-(*p*-methoxyphenyl)-4-penten-1-ol (1.6 g, 86%); mp 72—73.5 °C.

The pentenol was reacted with 9-phenanthrenecarbonyl chloride in benzene containing pyridine to give A-3E (0.96 g, 48%); mp 59—60.5 °C; ^{1}H NMR ($CDCl_3$) δ=2.05 (t.t, 2H, *J*=6, 6 Hz, O-C-CH_2), 2.33 (d.t, 2H, *J*=6, 5 Hz, C=C-CH_2), 3.66 (s, 3H, CH_3O), 4.40 (t, 2H, *J*=6 Hz, OCH_2), 6.08 (d.t, 1H, *J*=16, 5 Hz, C=CH), 6.38 (d, 1H, *J*=16 Hz, CH=C), 6.66—7.27 (m, 4H, ArH), 7.45—9.04 (m, 9H, ArH); UV (PhH) λ_{max} 301 nm (ε 13300), 358 (480). Calcd for $C_{27}H_{24}O_3$: C, 81.79; H, 6.10%. Found: C, 81.88; H, 6.05%.

(*E*)-6-(*p*-Methoxyphenyl)-5-hexenyl 9-Phenanthrenecarboxylate (A-4E). Ethyl hydrogen hexanedioate was prepared according to the literature[18] by refluxing a mixture of hexanedioic acid and diethyl hexanedioate in ethanol in the presence of HCl (60%), and converted to ethyl 5-(chloroformyl)pentanoate with thionyl chloride (89%); bp 95 °C/10 mmHg (lit,[19] 120 °C/15 mmHg).

The acid chloride was reacted with anisole in $(CHCl_2)_2$ in the presence of $AlCl_3$ to give ethyl 5-(*p*-methoxybenzoyl)-pentanoate (50%); mp 52—54 °C. Treatment of the keto ester with $NaBH_4$ in ethanol gave ethyl 6-(*p*-methoxyphenyl)-6-hydroxyhexanoate (quantitative).

The hydroxy ester was converted to ethyl (*E*)-6-(*p*-methoxyphenyl)-5-pentenoate by refluxing with *p*-toluenesulfonic acid in benzene (quantitative).

The pentenoate was treated with $LiAlH_4$ in ether to give (*E*)-6-(*p*-methoxyphenyl)-5-penten-1-ol (69%).

The pentenol was reacted with 9-phenanthrenecarbonyl chloride in benzene containing pyridine to give A-4E (45%); mp 42.5—44 °C; ^{1}H NMR ($CDCl_3$) δ=1.36—1.92 (m, 4H, C-CH_2CH_2-C), 2.11 (d.t, 2H, *J*=6, 6 Hz, C=C-CH_2), 3.60 (s, 3H, CH_3O), 4.27 (t, 2H, *J*=6 Hz, OCH_2), 5.94 (d.t, 1H, *J*=15, 6 Hz, C=CH), 6.24 (d, 1H, *J*=6 Hz, C=CH), 6.60—7.12 (m, 4H, ArH), 7.29—8.96 (m, 9H, ArH): UV (PhH) λ_{max} 301 nm (ε 11000), 358 (410). Calcd for $C_{28}H_{26}O_3$: C, 81.92; H, 6.38%. Found: C, 81.81; H, 6.39%.

(*E*)-2-(*p*-Methoxyphenyl)-2-butenyl 9-Phenanthrenecarboxylate (B-1E). *p*-Methoxyphenacyl bromide was prepared by bromination[20] of *p*-methoxyacetophenone (25.0 g, 0.17 mol) with bromine (26.6 g, 0.17 mol) in chloroform (70 cm^3) (24 g, 64%); mp 69—70 °C (lit,[20] 70—71 °C).

The bromide (11.5 g, 0.05 mol) was converted to *p*-methoxyphenacyl acetate by the reaction with acetic acid (26.3 g, 0.44 mol) in acetone (50 cm^3) in the presence of triethylamine (27.8 g, 0.28 mol)[21] (7.3 g, 70%); bp 140—141.5 °C/2.5 mmHg (lit,[22] 157—160 °C/15 mmHg).[22]

The acetate (9.5 g, 0.046 mol) was reacted with the Wittig reagent prepared from ethyltriphenylphosphonium bromide (18.6 g, 0.05 mol) and butyllithium (21.4 g, 0.05 mol) in ether (150 cm^3)[23] and stirred for 5 h. The usual work-up gave a mixture of (*E*)- and (*Z*)-2-(*p*-methoxyphenyl)-2-butenyl acetate (1.8 g, 18%).

The mixture of the acetate was treated with $LiAlH_4$ in ether to give a mixture of (*E*)- and (*Z*)-2-(*p*-methoxyphenyl)-

2-buten-1-ol (1.1 g, 76%).

The mixture of the butenol was reacted with 9-phenanthrenecarbonyl chloride in benzene containing pyridine to give a mixture of B-1E and B-1Z (1.5 g, 61%).

B-1E was separated by HPLC (SiO_2, 30 : 1 hexane–AcOEt) and crystallized from methanol to give colorless needles; mp 100—102 °C; ^{1}H NMR ($CDCl_3$) δ=1.96 (d, 3H, J=7 Hz, CH_3), 3.73 (s, 3H, CH_3O), 5.33 (s, 2H, CH_2), 6.01 (qr, 1H, J=7 Hz, C=CH), 6.74—7.43 (m, 4H, ArH), 7.42—8.77 (m, 9H, ArH); UV (PhH) λ_{max} 303 nm (ε 11400), 358 (460). Calcd for $C_{26}H_{22}O_3$: C, 81.65; H, 5.80%. Found: C, 81.77; H, 5.78%.

(*E*)-3-(*p*-Methoxyphenyl)-3-pentenyl 9-Phenanthrenecarboxylate (B-2E). To a suspension of zinc powder (6.9 g, 0.11 mol) in benzene (30 cm^3) was added a solution of ethyl bromoacetate (17.6 g, 0.11 mol) and *p*-methoxypropiophenone (17.3 g, 0.11 mol) in benzene (30 cm^3).[24] The mixture was refluxed for 3 h and quenched with 10% H_2SO_4. The solvent was evaporated and the residue was distilled under reduced pressure to give a yellow oil of ethyl 3-(*p*-methoxyphenyl)-3-hydroxypentanoate (17 g, 64%); bp 153—157 °C/3 mmHg.

The hydroxy ester was treated with $LiAlH_4$ in ether. Column chromatography (SiO_2, 1 : 3 $CHCl_3$–ether) of the product gave 3-(*p*-methoxyphenyl)-1,4-pentanediol (4.7 g, 78%).

Distillation of the diol under reduced pressure gave (*E*)-3-(*p*-methoxyphenyl)-3-penten-1-ol (3.2 g, 50%); bp 142—144 °C/3 mmHg.

The pentenol was reacted with 9-phenanthrenecarbonyl chloride in benzene containing pyridine to give B-2E (4.0 g, 83%); mp 84—85 °C (1 : 1 benzene–hexane); ^{1}H NMR ($CDCl_3$) δ=1.85 (d, 3H, J=7 Hz, CH_3), 2.97 (t, 2H, J=7 Hz, C=C-CH_2), 3.66 (s, 3H, CH_3O), 4.06 (t, 2H, J=7 Hz, OCH_2), 5.74 (qr, 1H, J=7 Hz, C=CH), 6.70—7.29 (m, 4H, ArH), 7.34—8.96 (m, 9H, ArH); UV (PhH) λ_{max} 304 nm (ε 11200), 358 (490). Calcd for $C_{27}H_{24}O_3$: C, 81.79; H, 6.10%. Found: C, 81.66; H, 6.14%.

(*E*)- and (*Z*)-4-(*p*-Methoxyphenyl)-4-hexenyl 9-Phenanthrenecarboxylate (B-3E and B-3Z, Respectively). Ethyl 3-(*p*-methoxybenzoyl)propanoate was prepared from butanedioic anhydride by similar procedures to those employed for preparation of ethyl 4-(*p*-methoxybenzoyl)-butanoate; mp 51—53 °C.

The keto ester (9.9 g, 0.046 mol) was reacted with the Wittig reagent prepared from ethyltriphenylphosphonium bromide (17.1 g, 0.046 mol) and butyllithium (15 wt% in hexane, 28.4 cm^3, 0.046 mol) in ether (150 cm^3).[23] The mixture was stirred for 5 h at room temperature. The usual work-up gave a mixture of (*E*)- and (*Z*)-isomers of ethyl 4-(*p*-methoxyphenyl)-4-hexenoate (1.7 g, 16%).

The mixture of the hexenoate was treated with $LiAlH_4$ in ether to give a mixture of (*E*)- and (*Z*)-4-(*p*-methoxyphenyl)-4-hexen-1-ol (quantitative).

The mixture of the hexenol was reacted with 9-phenanthrenecarbonyl chloride in benzene containing pyridine to give a mixture of B-3Z and B-3E (2.0 g, 72%). Each isomer was separated by HPLC (SiO_2, 30 : 1 hexane–AcOEt).

B-3E: mp 71—73 °C; ^{1}H NMR ($CDCl_3$) δ=1.81 (d, 3H, J=7 Hz, CH_3), 1.90 (t.t, 2H, J=8, 7 Hz, O-C-CH_2), 2.73 (t, 2H, J=8 Hz, C=C-CH_2), 3.74 (s, 3H, CH_3O), 4.40 (t, 2H, J=7 Hz, OCH_2), 5.73 (qr, 1H, J=7 Hz, C=CH), 6.72—7.35 (m, 4H, ArH), 7.47—9.09 (m, 9H, ArH); UV (PhH) λ_{max} 305 nm (ε 10700), 358 (430). Calcd for $C_{28}H_{26}O_3$: C, 81.92; H, 6.38%. Found: C, 81.67; H, 6.37%.

B-3Z: mp 73—76 °C; ^{1}H NMR ($CDCl_3$) δ=1.58 (d, 3H, J=7 Hz, CH_3), 1.86 (t.t, 2H, J=7, 7 Hz, O-C-CH_2), 2.54 (t, 2H, J=7 Hz, C=C-CH_2), 3.75 (s, 3H, CH_3O), 4.37 (t, 2H, J=7 Hz, OCH_2), 5.57 (qr, 1H, J=7 Hz, C=CH), 6.74—7.17 (m, 4H, ArH), 7.47—9.01 (m, 9H, ArH); UV (PhH) λ_{max} 307 nm (ε 11800), 358 (500). Calcd for $C_{28}H_{26}O_3$: C, 81.92; H, 6.38%. Found: C, 81.74; H, 6.33%.

(*E*)- and (*Z*)-5-(*p*-Methoxyphenyl)-5-heptenyl 9-Phenanthrenecarboxylate (B-4E and B-4Z, Respectively). Ethyl 4-(*p*-methoxybenzoyl)butanoate was reacted with the Wittig reagent obtained from ethyltriphenylphosphonium bromide and butyllithium in ether[23] to give a mixture of (*E*)- and (*Z*)-isomers of ethyl 5-(*p*-methoxyphenyl)-5-heptenoate (18%).

The mixture of the heptenoate was treated with $LiAlH_4$ in ether to give a mixture of (*E*)- and (*Z*)-5-(*p*-methoxyphenyl)-5-hepten-1-ol (91%).

The mixture of the heptenol was reacted with 9-phenanthrenecarbonyl chloride in benzene containing pyridine to give a mixture of the corresponding ester (43%). The (*E*)-(B-4E) and (*Z*)-isomer (B-4Z) of the ester were separated by HPLC (SiO_2, 50 : 1 hexane–AcOEt).

B-4E: oil; ^{1}H NMR ($CDCl_3$) δ=1.79 (d, 3H, J=7 Hz, CH_3), 1.64 (m, 4H, C-CH_2CH_2-C), 2.59 (t, 2H, J=7 Hz, C=C-CH_2), 3.69 (s, 3H, CH_3O), 4.37 (t, 2H, J=6 Hz, OCH_2), 5.64 (qr, 1H, J=7 Hz, C=CH), 6.63—7.27 (m, 4H, ArH), 7.46—8.92 (m, 9H, ArH); UV (PhH) λ_{max} 304 nm (ε 10700), 357 (460). Calcd for $C_{29}H_{28}O_3$: C, 82.04; H, 6.64%. Found: C, 81.75; H, 6.65%.

B-4Z: oil; ^{1}H NMR ($CDCl_3$) δ=1.54 (d, 3H, J=7 Hz, CH_3), 1.62 (m, 4H, C-CH_2CH_2-C), 2.41 (t, 2H, J=7 Hz, C=C-CH_2), 3.69 (s, 3H, CH_3O), 4.36 (t, 2H, J=6 Hz, OCH_2), 5.49 (qr, 1H, J=7 Hz, C=CH), 6.66—7.10 (m, 4H, ArH), 7.46—8.92 (m, 9H, ArH); UV (PhH) λ_{max} 306 nm (ε 9600), 357 (410). Calcd for $C_{29}H_{28}O_3$: C, 82.04; H, 6.64%. Found: C, 82.05; H, 6.58%.

Irradiation of Methyl 9-Phenanthrenecarboxylate (9-MCP) with *trans*-Anethole (*t*-AN). A solution of 9-MCP (119 mg, 0.020 mol dm^{-3}) and *t*-AN (122 mg, 0.033 mol dm^{-3}) in 9 : 1 benzene–isoprene (25 cm^3) was irradiated with a 450-W high-pressure mercury lamp through a Pyrex wall for 2.5 h under nitrogen atmosphere at room temperature. After evaporation of the solvent, the residue was separated with TLC (SiO_2, 7 : 3 benzene–hexane) to give a colorless solid of the head-to-head adduct (CB-0) of 9-MCP and *t*-AN (149 mg, 77%). Crystallization from methanol gave colorless crystals: mp 135—137 °C; ^{1}H NMR ($CDCl_3$) δ=1.10 (d, 3H, J=6 Hz, CHC*H*$_3$ (exo)), 2.51 (m, 1H, C*H*CH$_3$), 3.34 (d, 1H, J=8 Hz, C*H*Ar), 3.50 (s, 3H, OCH_3), 3.67 (s, 3H, CO_2CH_3), 3.94 (d, 1H, J=10 Hz, CH), 6.24 (d.d, 1H, J=8, 2 Hz, ArH), 6.72—7.21 (m, 4H, ArH), 6.50—7.94 (m, 7H, ArH); ^{13}C NMR ($CDCl_3$) δ=57.3, 55.1, 52.5, 52.1, 47.4, 39.2, 17.8; IR (KBr) 1720 cm^{-1} ($\nu_{C=O}$). Calcd for $C_{26}H_{24}O_3$: C, 81.25; H, 6.25%. Found: C, 81.43; H, 6.37%.

Irradiation of A-2E. A solution of A-2E (197 mg, 4.1×10^{-4} mol dm^{-3}) in benzene (1.25 dm^3) was irradiated with a 450-W high-pressure mercury lamp through a Pyrex wall for 40 min under nitrogen atmosphere at room temperature. After evaporation of the solvent, the residue was separated by TLC (SiO_2, 3 : 1 $CHCl_3$–ether) to give a colorless solid of 3-(*p*-methoxyphenyl)-2-(9-phenanthryl)-oxacyclohex-2-en-4-ol (DHPL, 107 mg, 54%). Crystalliza-

tion from benzene-hexane gave colorless crystals; mp 145—150 °C; ^{1}H NMR ($CDCl_3$) δ=2.00 (s, 1H, OH), 2.20 (t.d, 2H, J=6, 3 Hz, 5-CH_2), 3.52 (s, 3H, OCH_3), 4.37 (t, 2H, J=6 Hz, 6-CH_2), 4.79 (t, 2H, J=3 Hz, 4-CH), 6.50—7.02 (m, 4H, ArH), 7.39—8.71 (m, 9H, ArH); ^{13}C NMR ($CDCl_3$) δ=31.33 (5-C), 54.86 (OCH_3), 61.97 (6-C), 63.69 (4-C); IR (KBr) 3450 cm^{-1} (ν_{O-H}), 1650 ($\nu_{C=C}$). Calcd for $C_{26}H_{22}O_3$: M, 382.1563, Found: m/z 382.1565.

Irradiation of A-3E. A solution of A-3E (191 mg, 4.0×10^{-4} mol dm^{-3}) in benzene (1.2 dm^3) was irradiated similarly with a 450-W high-pressure mercury lamp through a Pyrex wall for 15 min. TLC separation (SiO_2, 3 : 2 $CHCl_3$-benzene) of the reaction mixture gave a colorless oil of 3-(*p*-methoxyphenyl)-2-(9-phenanthryl)oxacyclohepta-2,4-diene (DHO, 87 mg, 57%); ^{1}H NMR ($CDCl_3$) δ=2.71 (d.t, 2H, J=5, 4 Hz, 6-CH_2), 3.41 (s, 3H, OCH_3), 4.48 (t, 2H, J=5 Hz, 7-CH_2), 5.90 (d.t, 1H, J=12, 4 Hz, 5-CH=), 6.08 (d, 1H, J=12 Hz, 4-CH=), 6.36—6.93 (m, 4H, ArH), 7.33—8.61 (m, 9H, ArH).

Irradiation of A-4E. A solution of A-4E (98.6 mg, 3.4×10^{-4} mol dm^{-3}) in 9 : 1 benzene-isoprene (700 cm^3) was irradiated for 30 min with a 400 W high-pressure mercury lamp through a Toshiba UVD-35 glass filter. TLC separation of the reaction mixture gave the cis isomer (A-4Z, 36%) and recovered the trans isomer (30%). A-4Z: ^{1}H NMR ($CDCl_3$) δ=3.62 (s, 3H, OCH_3), 5.50 (d.t, 1H, J=11.7 Hz, C=CH).

Irradiation of B-2E. A solution of B-2E (203 mg, 4.3×10^{-4} mol dm^{-3}) in benzene (1.2 dm^3) was irradiated with a 450 W high-pressure mercury lamp through a Pyrex wall for 30 min under nitrogen atmosphere at room temperature. After evaporation of the solvent, the residue was separated by TLC (SiO_2, 7 : 3 benzene-$CHCl_3$). Two oily products were obtained; R_f 0.36 (130 mg, 65%) and 0.07 (30 mg, 15%).

The minor product was identified as a [2+2] cycloadduct (CB-2) of a structure analogous to CB-0 from 9-MCP and *t*-AN; ^{1}H NMR ($CDCl_3$) δ=1.05 (d, 3H, J=7 Hz, CHCH_3 (exo)), 2.58—3.03 (t+m, 3H, CO_2C-CH_2, CHCH_3), 3.55—3.67 (m+s, 4H, CH, CH_3O), 6.15 (d.d, 1H, J=8, 2 Hz, ArH), 4.79 (t, 2H, CO_2CH_2), 6.63—7.18 (m, 4H, ArH), 6.42—8.03 (m, 7H, ArH); IR (KBr) 1720 cm^{-1} ($\nu_{C=O}$). Calcd for $C_{27}H_{24}O_3$: M, 396.1719, Found: m/z 396.1708.

Repeated TLC (SiO_2, 1 : 1 benzene-$CHCl_3$) of the major product gave a colorless oil of 3-(*p*-methoxyphenyl)-2-(9-phenanthryl)oxacyclopent-2-ene (DHF, 92 mg, 51%); ^{1}H NMR ($CDCl_3$) δ=3.24 (t, 2H, J=9 Hz, 4-CH_2), 3.52 (s, 3H, OCH_3), 4.57 (t, 2H, J=9 Hz, 5-CH_2), 6.48—6.87 (m, 4H, ArH), 7.44—8.72 (m, 9H, ArH); IR (KBr) 1660 cm^{-1} ($\nu_{C=C}$). Calcd for $C_{25}H_{20}O_2$: C, 85.20; H, 5.72%. Found: C, 85.10; H, 5.67%.

During NMR measurements in $CDCl_3$ of the major product the spectrum changed gradually by its decomposition giving acetaldehyde [δ=2.02 (d, 3H), 9.60 (qr, 1H)] and the oxacyclopentene. The residual signals were assigned to 5-(*p*-methoxyphenyl)-6-methyl-1-(9-phenanthryl)-2,7-dioxabicyclo[3.2.0]heptane (OX-2B); ^{1}H NMR ($CDCl_3$) δ=1.04 (d, 3H, J=7 Hz, 6-CHCH_3), 2.66 (t, 2H, J=6 Hz, 4-CH_2), 3.36 (s, 3H, OCH_3), 4.39—4.61 (m, 3H, 3-CH_2, 6-CHCH_3), 6.29—6.71 (m, 4H, ArH), 7.22—8.57 (m, 9H, ArH).

Irradiation of B-3E. A solution of B-3E (69 mg, 3.4×10^{-4} mol dm^{-3}) in 9 : 1 benzene-isoprene (500 cm^3) was similarly irradiated with a 450 W high-pressure mercury lamp for 30 min. TLC separation (SiO_2, PhH : Et_2O=205 : 15) of the reaction mixture gave two oily products together with recovered B-3E (4 mg, 6%) and its isomer B-3Z (7 mg, 10%).

The major product (30 mg, 49%) was identified as 3-(*p*-methoxyphenyl)-2-(9-phenanthryl)oxacyclohex-2-ene (DHP); mp 164.5—165.5 °C; ^{1}H NMR ($CDCl_3$) δ=2.20 (qr, 2H, J=6 Hz, 5-CH_2), 2.59 (t, 2H, J=6 Hz, 4-CH_2), 3.47 (s, 3H, OCH_3), 4.23 (t, 2H, 6-CH_2), 6.40—6.88 (m, 4H, ArH), 7.43—8.67 (m, 9H, ArH); IR (KBr) 1640 cm^{-1} ($\nu_{C=C}$). Calcd for $C_{26}H_{22}O_2$: C, 85.21; H, 6.05%. Found: C, 85.21; H, 6.05%.

The minor product (19 mg, 28%) was identified as a [2+2] cycloadduct (CB-3) of a structure analogous to CB-2 from B-2E; ^{1}H NMR ($CDCl_3$) δ=0.86 (d, 3H, J=7 Hz, CHCH_3 (exo)), 2.38 (m, 5H, CH_2CH_2, CHCH_3), 3.62 (s, 3H, OCH_3), 3.77 (d, 1H, CH), 4.29 (m, 2H, CO_2CH_2), 6.41 (d.d, 1H, J=6, 2 Hz, ArH), 6.54—7.10 (m, 4H, ArH), 7.10—8.09 (m, 7H, ArH).

Irradiation of B-4E. A solution of B-4E (107 mg, 3.2×10^{-4} mol dm^{-3}) in 9 : 1 benzene-isoprene (800 cm^3) was similarly irradiated for 30 min. TLC separation gave two oily products together with recovered B-4E (21 mg, 20%) and its isomer B-4Z (33 mg, 31%).

The major product (19 mg, 20%) was identified as 3-(*p*-methoxyphenyl)-2-(9-phenanthryl)oxacyclohept-2-ene (THO); ^{1}H NMR ($CDCl_3$) δ=2.03 (m, 4H, 5,6-$(CH_2)_2$), 2.78 (t, 2H, 4-CH_2), 3.53 (s, 3H, CH_3O), 4.13 (t, 2H, 7-CH_2), 6.41—6.89 (m, 4H, ArH), 7.25—8.67 (m, 9H, ArH).

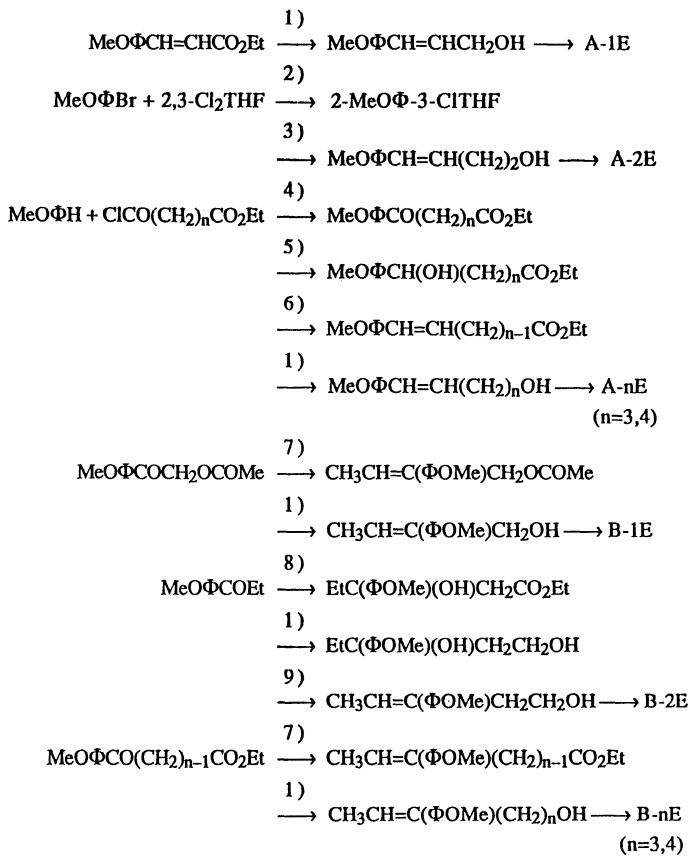
The minor product (16 mg, 15%) was identified as a [2+2] cycloadduct (CB-4) of the structure as that from B-2E; ^{1}H NMR ($CDCl_3$) δ=1.07 (d, 3H, J=7 Hz, CHCH_3), 2.10 (m, 8H, $(CH_2)_3$, CHCH_3, CH), 3.70 (s, 3H, OCH_3), 4.47 (m, 2H, CO_2CH_2), 6.3—8.50 (m, 11H, ArH).

Results and Discussion

Preparation of Bichromophoric Esters. Two series of the bichromophoric esters, 9-phenanthrenecarboxylates with a straight chain, A-*n*E (n=1—4), and those with a branched chain, B-*n*E (n=1—4), were prepared from 9-phenanthrenecarbonyl chloride and the corresponding alcohols, which were obtained by the routes shown in Scheme 1, where MeOΦ means a *p*-methoxyphenyl group. Series A esters are all in trans geometry, and with series B esters (*E*)- and (*Z*)-isomers were separated by TLC (cf. Experimental).

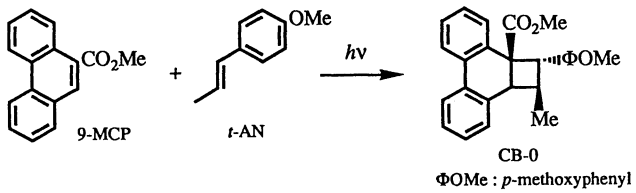
Photoreaction of Methyl 9-Phenanthrenecarboxylate (9-MCP) with *trans*-Anethole (*t*-AN). The photochemical cycloaddition of 9-MCP to *t*-AN afforded a head-to-head adduct of the expected[1b] stereochemistry. Irradiation of 9-MCP (0.02 mol dm^{-3}) with *t*-AN (0.033 mol dm^{-3}) at ambient temperature in benzene containing 10 vol% isoprene as a triplet quencher with a high-pressure mercury lamp through a Pyrex wall gave the head-to-head adduct (CB-0) in 77% yield (Scheme 2). The structure was determined on the basis of various spectral data, mainly ^{1}H and ^{13}C NMR and similarity of the ^{1}H NMR spectrum to that of the photoadduct of 9-cyanophenanthrene and *t*-AN.[1b]

The reaction is a singlet process. We observed a Stern-Volmer constant $k_q\tau$=46 dm^3 mol^{-1} for quenching of 9-MCP fluorescence by *t*-AN in benzene at ambient temperature. Weak exciplex emission with λ_{max} at 450 nm was observed. The limiting quantum



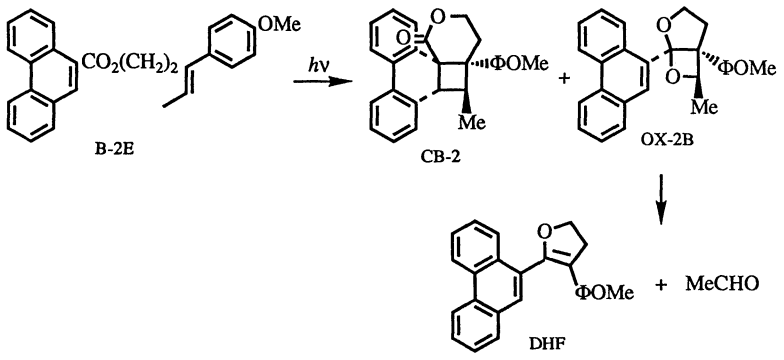
Scheme 1. 1) $LiAlH_4$, 2) Mg, 3) Na, 4) $AlCl_3$, 5) $NaBH_4$, 6) H^+, 7) $Ph_3P{=}CHCH_3$, 8) $BrCH_2CO_2Et/Zn$, 9) Distillation.

yield, the fraction of the quenched excited 9-MCP resulting in product formation, was estimated to be 0.11 from *t*-AN concentration dependence of the product formation. These results confirm that 9-MCP behaves similarly to 9-cyanophenanthrene.

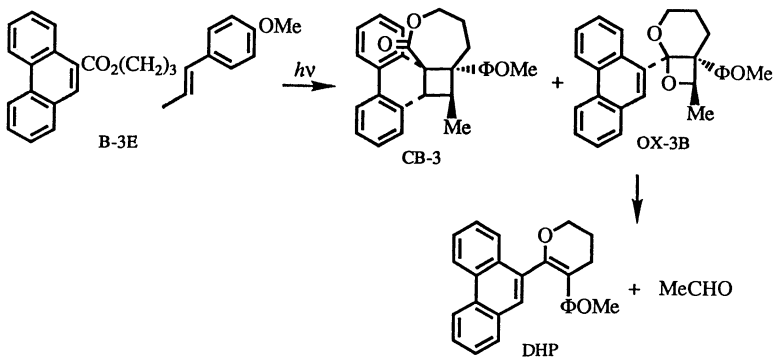


Scheme 2.

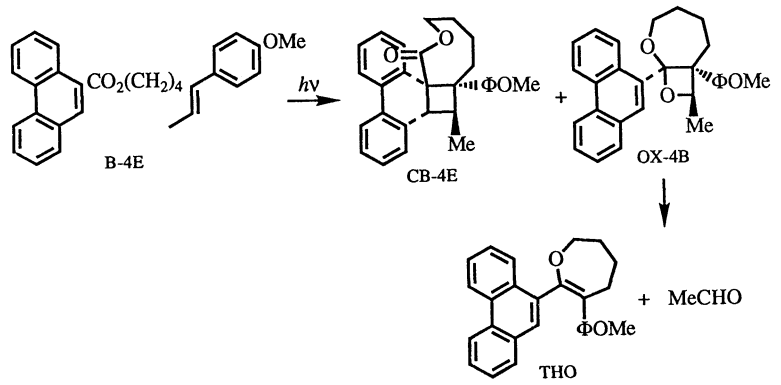
Photoreaction of B-2E and B-3E. Irradiation of B-2E (4.3×10^{-4} mol dm^{-3}) in benzene with a high-pressure mercury lamp through a Pyrex wall afforded a cyclobutane (CB-2, 15% yield) and a bicyclic acetal (OX-2B, 65%) (Scheme 3). The structure of CB-2 is analogous to that of CB-0 obtained from 9-MCP and *t*-AN as demonstrated by comparison of their NMR spectra. Acetal OX-2B is a [2+2] cycloadduct between the carbonyl group and the olefinic double bond.[25-28] During the measurement of an NMR spectrum in $CDCl_3$, OX-2B was slowly decomposed to a dihydrofuran (DHF)



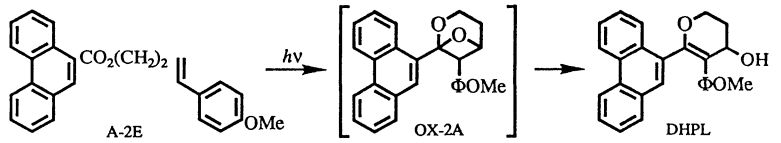
Scheme 3.



Scheme 4.



Scheme 5.



Scheme 6.

and acetaldehyde as revealed by the spectrum. Repeated chromatography of OX-2B on silica gel with $CHCl_3$ gave DHF (51% yield based on B-2E consumed).[29]

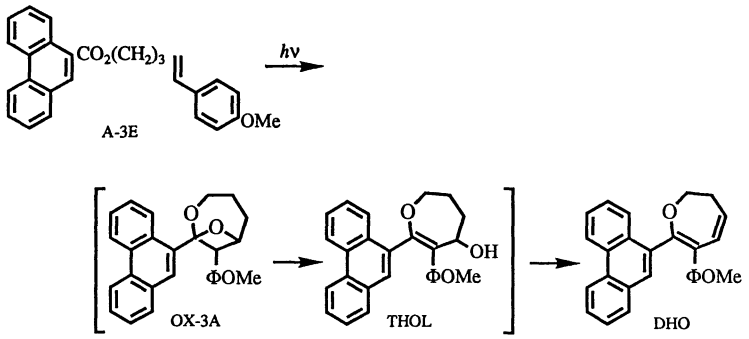
A similar irradiation of B-3E (3.4×10^{-4} mol dm^{-3}) in 9:1 benzene-isoprene afforded a dihydropyran (DHP, 49%) and a cyclobutane (CB-3, 28%) (Scheme 4). The product DHP can be rationalized by the initial formation of a carbonyl adduct (OX-3B), analogous to B-2E→OX-2B reaction, followed by loss of acetaldehyde. The structure of CB-3 was similar to CB-2 as demonstrated by comparison of their NMR spectra. Isomerization of the olefinic double bond (formation of the corresponding (*Z*) isomer, B-3Z, 10%) was also observed in this case.

Irradiation of B-1E and B-4E was carried out under similar conditions. No cycloaddition products were detected and only isomerized and dimeric products were obtained in the case of B-1E; however, B-4E (3.2×10^{-4} mol dm^{-3}) afforded a cyclobutane (CB-4, 15%) with a similar structure to CB-3 and a tetrahydrooxepin (THO, 20%) arising from loss of acetaldehyde from a carbonyl adduct (Scheme 5).

Photoreaction of A-2E and A-3E. Irradiation of esters A-2E (4.1×10^{-4} mol dm^{-3}) and A-3E (4.0×10^{-4} mol dm^{-3}) in benzene with a high-pressure mercury lamp through a Pyrex wall gave a dihydropyranol (DHPL, 54%) and a dihydrooxepine (DHO, 57%), respectively (Schemes 6 and 7). There was no spot in the TLC of either reaction mixture that could be ascribed to a cyclobutane adduct. The only unidentified spots showed $r_f\approx0$ and corresponded to small amounts of material. The products DHPL and DHO can be rationalized by the initial formation of acetals, OX-2A and OX-3A, respectively, analogous to the B-2E→OX-2B reaction, followed by obvious polar rearrangements and dehydration for DHO. That DHPL and DHO are not primary products is shown by their absence in TLC of reaction mixtures.

Irradiation of A-1E and A-4E was carried out under similar conditions; however, no cycloaddition products were detected, and only isomerized and dimeric products were obtained.

Intermediacy of Exciplexes in the Photocycloaddition. Fluorescence spectra of phenanthrenecarbox-



Scheme 7.

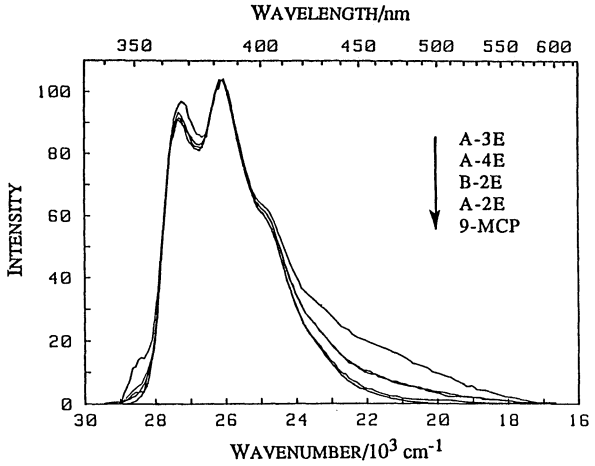


Fig. 1. Emission spectra of bichromophoric esters.

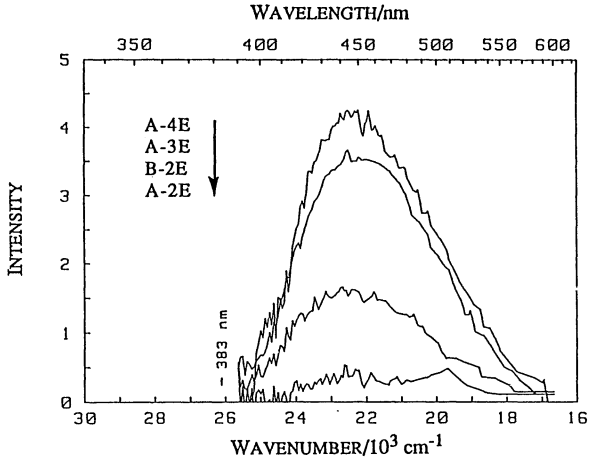


Fig. 2. Difference spectra of bichromophoric esters normalized at 383 nm.

ylates, 9-MCP, A-*n*E (*n*=1—4,), and B-*n*E (*n*=1—4) were measured in benzene at ambient temperature. All the bichromophoric esters exhibited similar fluorescence spectra to that of 9-MCP with emission maxima at 367 and 383 nm, and, except A-1E and A-2E, showed emission tailing in the longer wavelength regions (Fig. 1). Normalization of the spectra 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 (Fig. 2). These spectra can be assigned to intramolecular exciplexes.

Disappearance quantum yields measured by irradiating benzene solutions of the substrates with 366-nm light are as follows: B-2E, 0.70; B-3E, 0.63; B-4E, 0.15; A-2E, 0.36; A-3E, 0.61 (Table 1).[7] As will be reported in the accompanying paper, the much lower fluorescence quantum yields and much shorter singlet lifetimes of these esters compared to 9-MCP clearly demonstrate dominant intramolecular singlet interaction between chromophores, and the high disappearance quantum yields confirm its ultimate chemical nature. That exciplexes are indeed intermediates in at least the formation of the oxetanes from A-2E and A-3E is strongly suggested by a 10—20% greater quenching of product formation than of the phenanthrenecarboxylate fluorescence by molecular oxygen.[30,31] The efficiency of cycloadduct formation from the exciplexes will be discussed in detail in the accompanying paper.

Conformations of Intramolecular Exciplexes. That structures so different as cyclobutanes CB-2, CB-3, and CB-4 and oxetanes OX-2B and OX-3B arise from exciplexes with identical fluorescence maxima suggests that the energies of these exciplexes are rather insensitive to their geometries. The intramolecular cycloaddition of McCullough behave analogously.[5] Various photophysical measurements for intramolecular exciplexes[32] afford the same conclusion.

We believe that the strong preference for oxetane rather than cyclobutane formation from the esters employed arises from the conformational constraints of the aroyl ester group.[33-37] Esters in general strongly prefer 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.[33-37] In all such conformations, the formation of cyclobutane is precluded as can readily be seen from Dreiding models. That CB-2, CB-3, and CB-4 form at all is evidence that these conformations are not absolutely enforced. It is also possible that restricted rotation around the phenanthrene-carbonyl bond

Table 1. Disappearance Quantum Yields and Exciplex Emission Maxima

Compound	ϕ(disapp)[a]	λ_{max}(exciplex)/nm[b]
A-2E	0.36	450
A-3E	0.61	450
B-2E	0.70	450
B-3E	0.52	450
B-4E	0.15	450
9-MCP	0.11[c]	450

a) In benzene at 366 nm vs. potassium tris(oxalato)-ferrate(III). Substrate concentration 5×10^{-4} mol dm^{-3}. b) Obtained by subtraction of the fluorescence spectrum of 9-MCP after normalization. Results are identical for normalization at 367 (0,0) or 383 nm (λ_{max}). c) Extrapolated to infinite *t*-AN concentration.

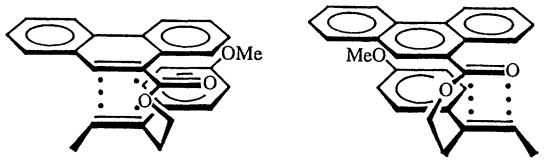


Fig. 3. Conformations of exciplexes leading to cycloadducts.

contributes to the disfavoring of cyclobutane formation, since models show that such rotation is probably necessary for close approach of the C=C double bonds. Although apparently undocumented for esters, the analogous restriction for benzaldehydes and acetophenones is well-known,[34,35] as is its relevance to aryl ketone photochemistry.[38,39] Finally, the models show that access of the carbonyl oxygen to the β-position of the *p*-methoxystyryl moiety, which leads to all the oxetanes, can be accomplished in the favored conformation of the ester C–O single bond without serious difficulty (Fig. 3).

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