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Steric Effects in Photochemical Cycloadditions of 9-Phenanthrenecarboxylates

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Synopsis. Efficiency of photochemical intramolecular and intermolecular cycloaddition of 9-phenanthrenecarboxylate-anethole systems is dependent on the structure of anethole moiety. Reduction in reactivity of the anethole moiety by steric effects is explained in terms of decrease in coefficients of frontier orbitals on the double bond due to twisting of the anisyl moiety.

Previously, we reported a competitive cycloaddition of intramolecular exciplexes involving carbonyl addition caused by linking the two chromophores with a molecular chain composed of an ester group.[1] Thus, in two series of bichromophoric phenanthrenecarboxylates with different linking sites, some afforded only oxetane adducts, whereas others gave both oxetane and head-to-head cyclobutane adducts.

A bichromophoric ester, (*E*)-4-(*p*-methoxyphenyl)-4-hexenyl 9-phenanthrenecarboxylate (*E*-B3), afforded, on irradiation in benzene, a cyclobutane (CB3x) and an oxetane derivative (OX3x); however, the corresponding *Z* isomer (*Z*-B3) was found to be much less reactive under similar reaction conditions. This finding prompted us to investigate steric effects of ground-state addends on the intermolecular cycloaddition.

In this paper we wish to describe photochemical and photophysical behavior of methyl 9-phenanthrenecarboxylate (9MCP) with four anethole derivatives.

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*)-1-(*p*-methoxyphenyl)-1-propene ((*E*)-anethole, (*E*)-AN) was purified by column chromatography (SiO_2, hexane) followed by distillation under reduced pressure; UV (hexane) λ_{max} 259 nm (ε 20800). Preparation and purification of methyl 9-phenanthrenecarboxylate (9MCP), (*E*)-4-(*p*-methoxyphenyl)-4-hexenyl 9-phenanthrenecarboxylate (*E*-B3), and (*Z*)-4-(*p*-methoxyphenyl)-4-hexenyl 9-phenanthrenecarboxylate (*Z*-B3) were described previously.[1]

(*Z*)-1-(*p*-Methoxyphenyl)-1-propene ((*Z*)-Anethole, (*Z*)-AN). After irradiation of (*E*)-AN with 2-acetylnaphthalene in benzene (*Z*)-AN was separated by preparative HPLC (SiO_2, hexane); ^{1}H NMR ($CDCl_3$) δ=1.84 (dd, 3H, *J*=7, 2 Hz, β-CH_3), 3.73 (s, 3H, CH_3O), 5.58 (dq, 1H, *J*=11, 7 Hz, β-H), 6.25 (dq, 1H, *J*=11, 2 Hz, α-H), 6.76—7.11 (m, 4H, anisyl H); UV (hexane) λ_{max} 253 nm (ε 17700).

(*E*)- and (*Z*)-3-(*p*-Methoxyphenyl)-2-pentene ((*E*)-EtAN and (*Z*)-EtAN, respectively).[2,3] *p*-Methoxypropiophenone (11.0 g, 0.067 mol) was treated in ether with ethylmagnesium bromide prepared from ethyl bromide (8.3 g, 0.076 mol) and Mg (1.8 g, 0.076 mol). The isolated 3-(*p*-methoxyphenyl)-3-pentanol was dehydrated by refluxing with *p*-toluenesulfonic acid in benzene. The obtained isomeric mixture of (*E*)-EtAN and (*Z*)-EtAN was separated by column chromatography (SiO_2, benzene : hexane=1 : 1).

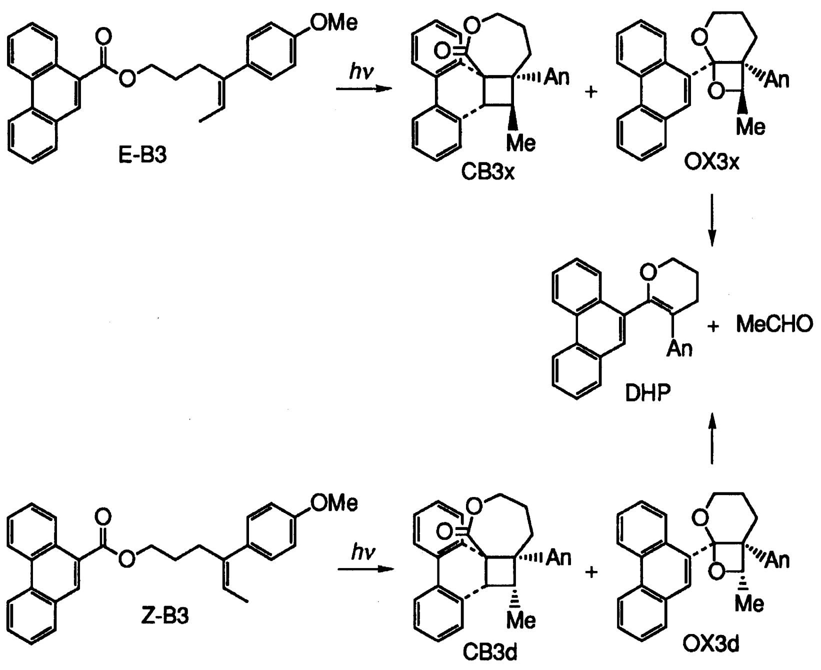
(*E*)-EtAN: 6.4 g (overall yield 54%); ^{1}H NMR ($CDCl_3$) δ=1.72 (d, 3H, *J*=7 Hz, β-CH_3), 0.94 (t, 3H, *J*=7 Hz, CH_2CH_3), 2.43 (q, 2H, *J*=7 Hz, CH_2CH_3), 3.68 (s, 3H, CH_3O), 5.57 (q, 1H, *J*=7 Hz, β-H), 6.64—7.25 (m, 4H, anisyl H); UV (hexane) λ_{max} 250 nm (ε 10700).

(*Z*)-EtAN: 3.7 g (overall yield 37%); ^{1}H NMR ($CDCl_3$) δ=1.52 (d, 3H, *J*=7 Hz, β-CH_3), 0.92 (t, 3H, *J*=7 Hz, CH_2CH_3), 2.30 (dq, 2H, *J*=1, 7 Hz, CH_2CH_3) 3.73 (s, 3H, CH_3O), 5.42 (tq, 1H, *J*=1, 7 Hz, β-H), 6.72—7.10 (m, 4H, anisyl H); UV (hexane) λ_{max} 235 nm (ε 9400).

Irradiation of Methyl 9-Phenanthrenecarboxylate (9MCP) with (*E*)-EtAN. A solution of 9MCP (62 mg, 0.022 mol dm^{-3}) and (*E*)-EtAN (46 mg, 0.022 mol dm^{-3}) in 9 : 1 benzene-isoprene (10 cm^3) was irradiated with a 450-W high-pressure mercury lamp through a Toshiba UVD-35 glass filter for 2.5 h under a 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 (CB1) of 9MCP and (*E*)-EtAN (64.5 mg, 60%). Crystallization from methanol gave colorless crystals; mp 180—182°C; ^{1}H NMR ($CDCl_3$) δ=0.66 (t, 3H, *J*=7 Hz, CH_2CH_3), 1.12 (d, 3H, *J*=6 Hz, $CHCH_3$(exo)), 2.36 (q, 2H, *J*=7 Hz, CH_2CH_3), 2.91 (m, 1H, $CHCHCH_3$), 3.62 (s, 3H, OCH_3), 3.73 (s, 3H, CO_2CH_3), 3.73—3.75 (probably d, 1H, $CHCHAr$), 6.63—7.83 (m, 12H, ArH); IR (KBr) 1720 cm^{-1} ($\nu_{C=O}$). Calcd for $C_{28}H_{28}O_3$: C, 81.52; H, 6.84%. Found: C, 81.23; H, 6.91%.

Irradiation of 9MCP with (*Z*)-EtAN. A solution of 9MCP (65 mg, 0.023 mol dm^{-3}) and (*Z*)-EtAN (48 mg, 0.023 mol dm^{-3}) in 1 : 9 isoprene-benzene (10 cm^3) was irradiated with a 450-W high-pressure mercury lamp through a Toshiba UVD-35 glass filter for 2.5 h under a nitrogen atmosphere at room temperature. No cyclobutane derivative was detected.

Irradiation of *E*-B3. A solution of *E*-B3 (97 mg, 3.4×10^{-4} mol dm^{-3}) in benzene (700 cm^3) was irradiated with a 450-W high-pressure mercury lamp through a uranium glass filter (λ>350 nm) for 30 min. TLC separation (SiO_2, PhH : Et_2O=205 : 15) of the reaction mixture gave two oily products together with recovered *E*-B3 (5 mg, 5%) and its isomer *Z*-B3 (25 mg, 26%).



Scheme 1.

The major product (36 mg, 42%) and the minor product (23 mg, 24%) were 5-(*p*-methoxyphenyl)-6-(9-phenanthryl)-3,4-dihydro-(2*H*)-pyran (DHP) and a [2+2] cycloadduct (CB3x), respectively, as identified previously.[1]

Irradiation of *Z*-B3. A solution of *Z*-B3 (98 mg, 3.4×10^{-4} mol dm^{-3}) in benzene (700 cm^3) was irradiated in a similar way to that in the case of *E*-B3. DHP (9 mg, 10%), CB3x (6 mg, 6%), and CB3d (5 mg, 5%) were isolated by TLC separation (SiO_2, PhH : Et_2O=205 : 15) together with recovered *Z*-B3 (71 mg, 72%) and isomerized *E*-B3 (9 mg, 9%). CB3d showed a characteristic peak at δ=0.12 (d, 3H, J=4 Hz, *endo*-CH_3), attributable to the anisotropic effect of the phenanthrene ring, in ^{1}H NMR spectrum.

A solution of *Z*-B3 (70 mg, 3.4×10^{-4} mol dm^{-3}) in 9 : 1 benzene-isoprene was irradiated similarly. DHP (3 mg, <3%) and CB3d (6 mg, 8%) was isolated together with recovered *Z*-B3 (66 mg, >90%). No *E*-B3 was detected.

Triplet Sensitized Irradiation of *E*-B3. A solution of *E*-B3 (55 mg, 3.4×10^{-4} mol dm^{-3}) and Michler's ketone (0.01 mol dm^{-3}) in benzene (400 cm^3) was irradiated under similar conditions, where most of light (>90%) was absorbed by the ketone. CB3x (5 mg, 9%), *E*-B3 (9 mg, 17%), and *Z*-B3 (32 mg, 59%) were isolated by TLC.

Quantum Yield Measurements. Quantum yields for disappearance (ϕ_{dis}) of phenanthrenecarboxylates were measured in degassed benzene with 366-nm light as relative values to that for 9MCP-(*E*)-AN reaction (ϕ_{dis}= 0.11).[1,4] The amounts of substrates were determined with an Otsuka Electronics HPLC with SiO_2 (eluent, AcOEt-hexane) and/or ODS (eluent, H_2O-MeOH or H_2O-MeCN) column.

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).[5] 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.

Cyclic Voltammetry. Cyclic voltammetry was carried out using a four-necked 10-cm^3 cell attached with a platinum disc (as a working electrode), a platinum wire (a counter electrode), an SCE (a reference electrode), and an argon inlet tube. A Hokuto HA-310 potentiostat/galvanostat and a Hokuto HB-104 function generator controlled the potentials. The current-voltage curves were recorded on a Rikadenki RW-21 XY recorder. The scan rate was 100 mV s^{-1}. Tetrabutylammonium perchlorate (polarographic grade) was used as a supporting electrolyte without further purification. Solvent acetonitrile (spectrograde) was distilled from calcium hydride before use.

Results and Discussion

Photochemical Behavior of *E*-B3 and *Z*-B3. As reported previously,[1] irradiation of *E*-B3 with 366-nm light in 9 : 1 benzene-isoprene under nitrogen gives a cyclobutane (CB3x, 28%) and a dihydropyran (DHP, 49%); DHP arises from the initially formed carbonyl adduct OX3x (Scheme 1). In the absence of triplet quencher, isoprene, isomerization of the styryl group

Table 1. Product Yields and Quantum Yields for Disappearance (ϕ_{dis}) of the Starting Material on Irradiation of *E*-B3 and *Z*-B3 in Benzene

Ester	Additive	ϕ_{dis}	Product yield/%				
			CB3x	CB3d	DHP	*E*-B3	*Z*-B3
E-B3	—	0.63	24	—	42	5	26
	Isoprene	0.52	28	—	49	6	10
Z-B3	—	0.12	6	5	10	9	72
	Isoprene	0.03	—	8	<3	—	>90

Table 2. Energies and Coefficients of the Frontier Molecular Orbitals of Anetholes Calculated by AM1 Method

Anethole	$\varphi/°$	HOMO			LUMO		
		Energy	Coefficients		Energy	Coefficients	
		eV	α-Carbon	β-Carbon	eV	α-Carbon	β-Carbon
(*E*)-AN	17	−8.454	+0.2952	+0.4130	−0.0799	+0.2981	−0.4362
(*Z*)-AN	30	−8.506	+0.2846	+0.3922	+0.1390	+0.2927	−0.4211
(*E*)-EtAN	30	−8.506	+0.2846	+0.3922	+0.1390	+0.2927	−0.4211
(*Z*)-EtAN	60	−8.702	+0.2096	+0.2742	+0.3580	+0.2347	−0.3163

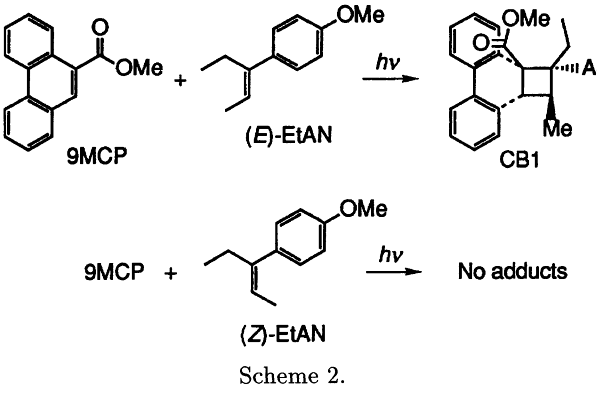
was increased (10%⟶26%); however, the yields of cycloadducts were not affected essentially (CB3x 24% and DHP 42%).

The *Z* isomer, *Z*-B3, showed a low reactivity in cycloadditions; in 9 : 1 benzene-isoprene *Z*-B3 afforded small amounts of DHP (<3%) and an isomeric cyclobutane, CB3d (8%). In the absence of triplet quencher, the isomerized *E*-B3 also reacted to give CB3x and DHP.

The quantum yields for disappearance of the starting material were measured in degassed benzene in the presence of isoprene (10 vol%) to be 0.52[1] for *E*-B3 and 0.03 for *Z*-B3 (Table 1).

Photochemistry of Methyl 9-Phenanthrenecarboxylate (9MCP) with (*E*)- ((*E*)- EtAN) and (*Z*)-3-(*p*-Methoxyphenyl)-2-pentene ((*Z*)-EtAN). As intermolecular models of the above reactions the photochemistry of 9MCP with (*E*)-EtAN and (*Z*)-EtAN was studied. Irradiation of 9MCP in 9 : 1 benzene-isoprene in the presence of (*E*)-EtAN with 366-nm light afforded a [2+2] cycloadduct, CB1 in 60% yield. The structure is the same as that of the [2+2] cycloadduct from 9MCP and (*E*)-AN[1] as determined on the basis of ^{1}H NMR spectrum. On the contrary, irradiation of 9MCP in the presence of (*Z*)-EtAN gave no cycloadducts under similar conditions. The limiting quantum yield for consumption (ϕ_{dis}) of 9MCP in the presence of (*E*)-EtAN was determined in deaerated benzene to be 0.09 in comparison with that for 9MCP-(*E*)-AN reaction.[1] These results show that the structure of styryl moiety plays an important role in the present reactions (Scheme 2).

Quenching Studies. The fluorescence lifetime (τ_{f}, 15.5 ns in deaerated benzene at room temperature) and quantum yield (ϕ_{f}, 0.26) of *Z*-B3 are very similar to those of 9MCP (τ_{f}=15.3 ns and ϕ_{f}=0.25)[1] in contrast to 7.2 ns and 0.09 of *E*-B3. This indicates that intramolecular singlet quenching is much more efficient in *E*-B3 than *Z*-B3, and is consistent with the aforementioned quantum yields for the reaction.



Scheme 2.

Quenching rate constants (k_{q}) of 9MCP fluorescence by anetholes and polymethoxybenzenes were measured in benzene. Figure 1 shows a Rehm-Weller plot[6] of the results, where the oxidation potentials of quenchers and the reduction potential of 9MCP (−1.98 V vs. SCE) were measured by cyclic voltammetry in acetonitrile. Figure 1 shows that the quenching rate constants for anetholes are generally lower than those of planar polymethoxybenzenes having the same oxidation potentials. This might be due to non-planar conformations of the anetholes.

Structural Factors of Anetholes in Photocycloaddition. As discussed by Michl[7] and Caldwell[8] by using PMO theory, the efficiency of cycloadduct formation depends on the relative stability of the exciplex. Important steric factors for the exciplex forma-

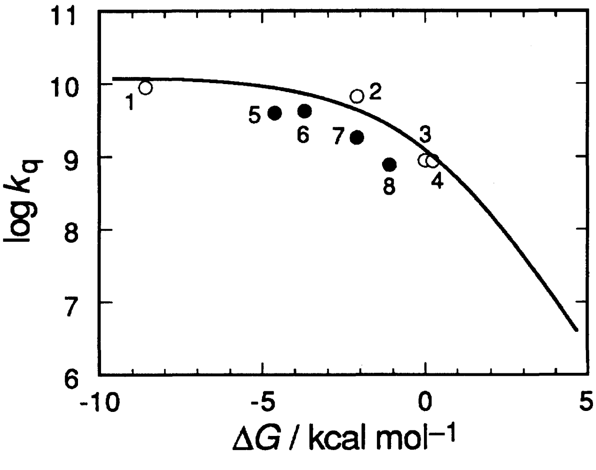


Fig. 1. Rehm-Weller correlation in quenching of 9MCP singlets by various electron donors, anetholes and polymethoxybenzenes; quenchers: 1, 1,2,4-trimethoxybenzene; 2, *p*-dimethoxybenzene; 3, *o*-dimethoxybenzene; 4, 1,2,3-trimethoxybenzene; 5, (*E*)-EtAN; 6, (*E*)-AN; 7, (*Z*)-AN; 8, (*Z*)-EtAN. The real line was obtained according to the equation, $k_{\mathrm{q}}=2\times10^{10}/(1+0.25[\exp(\Delta G^{\neq}/RT)+\exp(\Delta G/RT)])$, where $\Delta G^{\neq}$=2.4 kcal mol^{-1}.

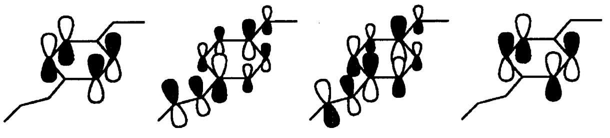


Fig. 2. Molecular orbitals of (*E*)-anethole.

tion might be reflected on the energy levels of frontier molecular orbitals and their coefficients at the reaction sites. We have evaluated these factors for the anetholes employed.

The twisted angles (φ) between the olefinic double bond and *p*-methoxyphenyl ring of anetholes were evaluated by comparing their absorption maximum wavelengths with those of *p*-methoxystyrene as a fully conjugated planar standard ($\varphi=0$) and anisole as a perpendicular model ($\varphi=90°$).9) Thus, the φ value for anetholes, (*E*)-AN, (*Z*)-AN, (*E*)-EtAN, and (*Z*)-EtAN, were estimated to be 11.6, 30.4, 37.4, and 61.6°, respectively. The reliability of these values is supported by CNDO/S calculations10) for substituted styrene derivatives.

For molecular orbital considerations, the energies and coefficients of the frontier molecular orbitals of the anetholes were calculated by AM1 method by assuming their twisting angles, φ, as 17° (AM1-optimized) for (*E*)-AN, 30° for (*Z*)-AN and (*E*)-EtAN, and 60° for (*Z*)-EtAN. In the photocycloaddition of the 9MCP excited singlets having L_b character, NHOMO and NLUMO as well as HOMO and LUMO should be taken into account; however, NHOMO and NLUMO have no significant coefficients at the olefinic sites of the anethole derivatives as shown in Fig. 2. The results are summarized in Table 2. With increasing twisting angle, the energy levels of frontier molecular orbitals approach each other (rising of LUMO and lowering of HOMO) and their coefficients are extremely diminished at the olefinic sites.

The results of the fluorescence quenching of 9MCP by the anetholes and the quantum yields for the reaction are in a parallel relationship with the aforementioned features of frontier molecular orbitals of the anetholes. Thus, the quenching rate constants are 4.2×10^9, 1.8×10^9, 3.9×10^9, and 0.8×10^9 $\mathrm{mol^{-1}\,dm^3\,s^{-1}}$ for (*E*)-AN, (*Z*)-AN, (*E*)-EtAN, and (*Z*)-EtAN, and the quantum yields for product formation are 0.11 and 0.09 for (*E*)-AN and (*E*)-EtAN; however, no adduct ($\phi=0.0$) was detected for (*Z*)-EtAN. Morrison pointed out that the molecular planarity should be a prerequisite for high efficiency in photophysical processes.11) Since compounds B3's are easily accessible to the maximum overlap conformations ($n=3$ rule),12) their photochemical behavior could be explained along the same line.

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