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Intramolecular Through-Space Interaction in 2-(*p*-Methoxyphenyl)-2-butenyl 9-Phenanthrenecarboxylate as Evidenced by Their Isomerization Behavior

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Synopsis. Intramolecular quenching of the excited singlet state of a phenanthrene moiety was more efficient in (*E*)-2-(*p*-methoxyphenyl)-2-butenyl 9-phenanthrenecarboxylate (*E*-ABP) than in its *Z* isomer (*Z*-ABP) in benzene. The quenching is proposed to proceed in a through-space fashion on the basis of efficiencies of isomerization and photophysical processes as well as molecular orbital calculations.

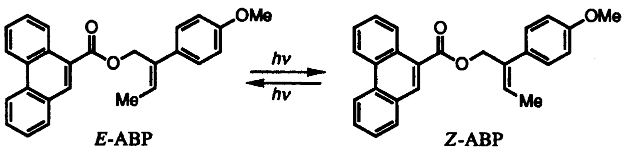


Chart 1.

Previously, we reported a novel aspect in phenanthrene–styrene photocycloadditions caused by linking the two chromophores with a molecular chain composed of an ester group; conformational constraints resulting from the linking brought about a competitive cycloaddition of intramolecular exciplexes involving carbonyl addition.[1] Thus, in two series of bichromophoric phenanthrenecarboxylic esters with different linking sites, some afforded only oxetane adducts, whereas others gave both of oxetane and head-to-head cyclobutane adducts. In these esters the exciplexes can take a so-called sandwich conformation leading to cycloadducts.

We also reported that bichromophoric phenanthrenecarboxylic esters with a short linking chain such as (*E*)-3-(*p*-methoxyphenyl)-2-propenyl 9-phenanthrenecarboxylate and (*E*)-2-(*p*-methoxyphenyl)-2-butenyl 9-phenanthrenecarboxyalte (*E*-ABP) give no cycloadducts but show a shorter singlet lifetime compared to a simple monochromophoric phenanthrenecarboxylate.[1] These bichromophores are regarded as substituted allyl esters with a (3-center-4π)*-CH$_2$-(2-center-2π) system, and photochemical work is rather rare for such a system in spite of much work on (2-center-2π)*-CH$_2$-(2-center-2π) systems such as di-π-methane.[2] Intramolecular triplet energy transfer in 2-cyclohexenyl benzoate has been reported to result in addition of acetic acid.[3]

In this paper we demonstrate that the two chromophores of *E*-ABP cannot take a sandwich conformation but can interact in a through-space fashion in the excited singlet state on the basis of photochemical and photophysical observations as well as molecular orbital calculations (Chart 1).

Experimental

Proton NMR spectra 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). Infrared spectra (IR) were obtained on a Hitachi 215 spectrophotometer.

Material. Synthetic procedures of (*E*)-2-(*p*-methoxyphenyl)-2-butenyl 9-phenanthrenecarboxylate (*E*-ABP) were described previously.[1]

E-ABP: mp 100—102 °C; UV (PhH) $\lambda_{\max}$ 303 nm (ε 11400), 358 (460).

(*Z*)-2-(*p*-Methoxyphenyl)-2-butenyl 9-phenanthrenecarboxylate (*Z*-ABP) was separated with HPLC (SiO$_2$, hexane : AcOEt=60 : 1) from an isomeric mixture of ABP;[1] mp 75—76 °C (benzene–hexane); ^{1}H NMR (CDCl$_3$) δ=1.72 (d, 3H, *J*=7 Hz, CH$_3$), 3.80 (s, 3H, OCH$_3$), 5.15 (s, 2H, OCH$_2$), 6.02 (q, 1H, *J*=7 Hz, CH=C), 6.89—7.32 (m, 4H, phenyl H), 7.41—8.76 (m, 9H, phenanthryl H); UV (PhH) $\lambda_{\max}$ 305 nm (ε 10700), 357 (430). Calcd for $C_{26}H_{22}O_3$: C, 81.65; H 5.80%. Found: C, 81.48; H, 5.82%.

p-Methoxybenzyl and 2-(*p*-methoxyphenyl)ethyl 9-phenanthrenecarboxylates (S1 and S2, respectively) were prepared in quantitative yields from the corresponding alcohol and acid chloride.

p-Methoxybenzyl 9-phenanthrenecarboxylate (S1); mp 124—125 °C; UV (PhH) $\lambda_{\max}$ 306 nm (ε 10000), 358 (470). Calcd for $C_{23}H_{18}O_3$: C, 80.68; H, 5.30%. Found: C, 80.93; H, 5.41%.

2-(*p*-Methoxyphenyl)ethyl 9-phenanthrenecarboxylate (S2); mp 84—86 °C; UV (PhH) $\lambda_{\max}$ 305 nm (ε 11000), 357 (470). Calcd for $C_{24}H_{20}O_3$: C, 80.88; H, 5.66%. Found: C, 80.93; H, 5.78%.

Benzene, isoprene (2-methyl-1,3-butadiene), and (*E*)-anethole [(*E*)-1-(*p*-methoxyphenyl)-1-propene] were purified as described previously.[4]

Photochemical Reactions. Bichromophoric esters, *E*-ABP, *Z*-ABP, and S2, in the concentration range of 1—4×10^{-4} mol dm^{-3} were irradiated in argon-purged benzene in the absence and in the presence of a triplet quencher (isoprene) at room temperature with a 450-W high-pressure mercury lamp through a UV-D35 filter or uranium wall. The reaction mixtures were analyzed with HPLC (ODS, MeOH–H$_2$O; or SiO$_2$, CHCl$_3$–benzene or AcOEt–hexane) to monitor disappearance of the starting materials and formation of products.

Isomerization quantum yields were measured by irradiating the sample solutions with 366-nm light from a 450-W high-pressure mercury lamp through a Toshiba UV-D36B glass filter. Light intensity was determined by potassium tris(oxalate)ferrate(III) actinometry.[5]

Photophysical Measurements. Ultraviolet absorption (UV) spectra were taken on a Hitachi 200-20 spectrophotometer. Fluorescence and phosphorescence spectra were obtained on a Hitachi F-4000 spectrofluorometer. Fluorescence quantum yields (ϕ_f) were determined in benzene by comparing the corrected fluorescence spectrum with that of phenanthrene (ϕ=0.13).[6] Fluorescence lifetimes (τ_s) were measured by means of the single photon counting method using an Ortec/Applied Photophysics SP-3X system or a Horiba NAES-1100 time-resolved spectrofluorometer.

The quantum yield for intersystem crossing (ϕ_{isc}) of methyl 9-phenanthrenecarboxylate (9MCP) was determined in argon-bubbled toluene by an emission-absorption technique[7] with reference to anthracene (ϕ_{isc}=0.73)[8] using a JASCO laser photolysis system with a Lambda Physik EMG-101 excimer laser (XeCl 150 mJ/pulse, 10-ns fwhm).[9] The laser power was controlled by combined ND filters.

Laser power dependence of fluorescence intensity at 450 or 480 nm and T–T absorption intensity at 395 nm were determined on pulsed laser excitation at 308 nm of toluene solutions of 9MCP, anthracene (reference compound), and a mixture of 9MCP as substrate and anthracene as quencher. Transient absorption spectra were also measured by the same laser flash photolysis system.

Results and Discussion

Photoreactions of Bichromophores. Irradiation of *E*-ABP in a low concentration of 1×10^{-4} mol dm^{-3} in benzene with 366-nm light resulted in isomerization of the substrate to its *Z* isomer (*Z*-ABP); for example, 10-min irradiation afforded a mixture of [*E*-ABP]/[*Z*-ABP]=23/77, and after 30-min irradiation the ratio was [*E*-ABP]/[*Z*-ABP]=13/87.[10,11] Prolonged irradiation gave a mixture of dimerization products of the phenanthrene moiety in low yields.

The quantum yields for isomerization of *E*-ABP and *Z*-ABP were determined to be $\phi_{E\rightarrow Z}=0.43$ and $\phi_{Z\rightarrow E}=0.10$ at low conversion (<20%) under similar conditions. Isoprene (2-methyl-1,3-butadiene), a triplet quencher, quenched the isomerization.[12] Thus, use of 10 vol% isoprene as co-solvent reduced $\phi_{E\rightarrow Z}$ and $\phi_{Z\rightarrow E}$ to 0.03 and ca. 0, respectively. Also, no $E\rightarrow Z$ isomerization was detected in use of 20 vol% isoprene.

Since the 366-nm light excites only the phenanthrene moiety of ABP, the isomerization of the methoxystyrene moiety takes place in its triplet state generated through intramolecular interactions, exciplex formation or triplet energy transfer. However, no emission ascribable to intramolecular exciplexes was detected.

Photophysical Behavior of Bichromophores. In order to get insight into the intramolecular interaction of the phenanthrene bichromophores, their photophysical behavior was examined and compared with that of some reference compounds. Esters *E*-ABP and *Z*-ABP exhibited similar UV absorption and fluorescence spectra, which were also similar to those of methyl 9-phenanthrenecarboxylate (9MCP), respectively; however, fluorescence quantum yields (ϕ_f) and lifetimes (τ_s) were markedly different; ϕ_f=0.13 and 0.19, and τ_s=7.4 and 15.3 ns for *E*-ABP and *Z*-ABP, respectively. Table 1 summarizes photochemical and photophysical data obtained for these and other phenanthrenecarboxylates. Table 1 shows that ϕ_f and τ_s values of *E*-ABP are significantly reduced compared with those of 9MCP. These observations indicate a strong interaction in the excited singlet state between the two chromophores in *E*-ABP.

Table 1. Photochemical and Photophysical Parameters of Phenanthrenecarboxylates[a]

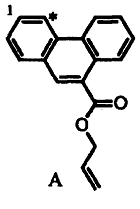
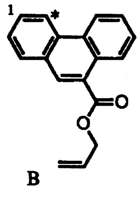
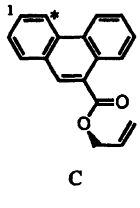
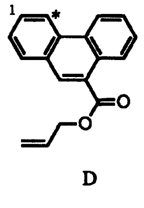
Ester	$\phi_{E\rightarrow Z}$ or $\phi_{Z\rightarrow E}$[b]	ϕ_f[c]	τ_s[d]	k_q	ϕ_q	ϕ_{isc}
E-ABP	0.43	0.13[e]	7.4[e]	6.9×10^7	0.50	0.27
Z-ABP	0.10	0.19	15.3	2.1×10^6	0.06	0.55
9MCP	—	0.25[e]	15.3[e]	—	—	0.55
S1	—	0.20	13.9	8.6×10^6	0.12	0.50
S2	—	0.20	15.7	1.9×10^6	0.03	0.56

a) Measured in 1×10^{-4} mol dm^{-3} in benzene at room temperature. b) Isomerization quantum yields. c) Fluorescence quantum yields for the phenanthrene moiety. d) Fluorescence lifetimes in ns. e) Ref. 1.

When the fluorescence (k_f) and nonradiative deactivation (k_d and k_{isc}) rate constants of the phenanthrenecarboxylate chromophore (^{1}A*) are assumed to be independent of the structure and identical with those of the monochromophoric system, 9MCP, the decrease in the singlet lifetime of bichromophoric systems (^{1}A*–D) can be ascribed to intramolecular quenching, and thus the total quenching rate constant (k_q) for ^{1}A*–D interaction in the excited singlet state can be estimated by using $k_q=1/\tau_s-(k_f+k_d+k_{isc})$, where k_d and k_{isc} are the rate constants for internal conversion and intersystem crossing, respectively. Also, k_f and k_{isc} were estimated from ϕ_f, ϕ_{isc}, and τ_s of the monochromophoric system (9MCP) according to $k_f=\phi_f/\tau_s$ and $k_{isc}=\phi_{isc}/\tau_s$, where ϕ_{isc} was measured to be 0.55 by an emission-absorption technique using anthracene as a reference material (cf. Experimental). The estimated k_q values are in the range of 7×10^7 s^{-1} for *E*-ABP and 2—9×10^6 s^{-1} for *Z*-ABP and S*n*. From these values the quantum yields (ϕ_q) for intramolecular quenching are estimated as listed in Table 1.[13]

The rate constant for intersystem crossing, k_{isc}, was estimated to be 3.6×10^7 s^{-1}, which corresponds to $\phi_{isc}=0.27$ for *E*-ABP. This value is quite reasonable since $\phi_f+\phi_q+\phi_{isc}=0.9$ from the above estimation. Comparison of this ϕ_{isc} value with the isomerization quantum yield of *E*-ABP, $\phi_{E\rightarrow Z}$ (=0.43), indicates that a pathway other than energy transfer from the phenanthrene triplet generated from intersystem crossing of the phenanthrene excited singlet is involved in the isomerization of *E*-ABP. Also, a triplet energy transfer from the phenanthrene triplet to the styrene moiety is assumed not to be efficient since the triplet energy of the latter (60 kcal mol^{-1})[14] is slightly higher than that of the former (58 kcal mol^{-1} determined from the phosphorescence spectrum of 9MCP).

Table 2. Calculated Heats of Formation for Various Conformers of Allyl 9-Phenanthrenecarboxylate

Conformer				
	A	B	C	D
$\Delta\Delta H_f$/kcal mol^{-1}	0.0	0.5	2.1	>5

Therefore, the intramolecular interaction in the excited singlet state produces a triplet state of the styrene moiety probably through exciplex. The singlet excitation energy (E_S) of 9MCP and the energy of an intramolecular exciplex from (*E*)-4-(*p*-methoxyphenyl)-4-hexenyl 9-phenanthrenecarboxylate are estimated to be 78 and 69 kcal mol^{-1}, respectively, from the fluorescence spectra.[1)]

To examine contribution of the triplet state to the isomerization, measurements of T–T absorption were carried out for the bichromophoric esters. Pulsed laser excitation of 9MCP and *Z*-ABP at 337 nm (N_2 laser) in degassed toluene afforded transient absorption spectra having an absorption maximum around 490 nm (Fig. 1), which can be ascribed to the triplets of their phenanthrene moieties;[15)] however, *E*-ABP gave no clear transient absorptions in the same wavelength region.[16)] The triplet lifetimes are estimated as 24 and 4 μs for 9MCP and *Z*-ABP, respectively. These observations are consistent with the effective intramolecular singlet quenching in *E*-ABP, and the shorter triplet lifetime of *Z*-ABP compared with that of 9MCP indicates a slow intramolecular triplet quenching (2.2×10^5 s^{-1}) in *Z*-ABP which might be responsible for its less efficient isomerization to *E*-ABP. It is worth noting that the estimated quantum yields for *Z*-ABP, ϕ_q, $\phi_{Z\rightarrow E}$, and ϕ_{isc}, are, respectively, 0.06<0.10<0.55 in that order (Table 1).

Intramolecular Interactions. Inefficient intramolecular interaction was observed in bichromophores S1 and S2 having no olefinic moiety. For example, irradiation of S2 in benzene afforded only a trace amount of dimeric products, as revealed by a characteristic ^{1}H NMR spectrum due to cyclobutyl hydrogens at δ=4.68.[17)] Also, the fluorescence quantum yield and lifetime of S2 are almost identical with those of 9MCP. These observations indicate that the styryl moiety plays an important role in the interaction. Furthermore, the structural effect on the isomerization and singlet quenching efficiencies (low quantum yields for $Z\rightarrow E$ isomerization and singlet quenching in *Z*-ABP) demonstrated by *E*-ABP and *Z*-ABP indicates a through-space character rather than a through-bond one in this interaction.

Semiempirical molecular orbital calculations were carried out to reveal possible conformations in intramolecular through-space interactions. As a model compound allyl 9-phenanthrenecarboxylate in the excited singlet state was examined by AM1-CI calculations.[18,19)] The heats of formation (ΔH_f) for some conformers were estimated as shown in Table 2. Table 2 shows the difference in $\Delta H_f(\Delta\Delta H_f)$ from that for the most stable conformer A. An unfavorable conformer, D, in which the ester moiety has an *s*-trans configuration between the carbonyl and alkoxyl groups, is more than 5 kcal mol^{-1} higher in energy than conformer A; however, conformer C is only 2 kcal mol^{-1} higher in

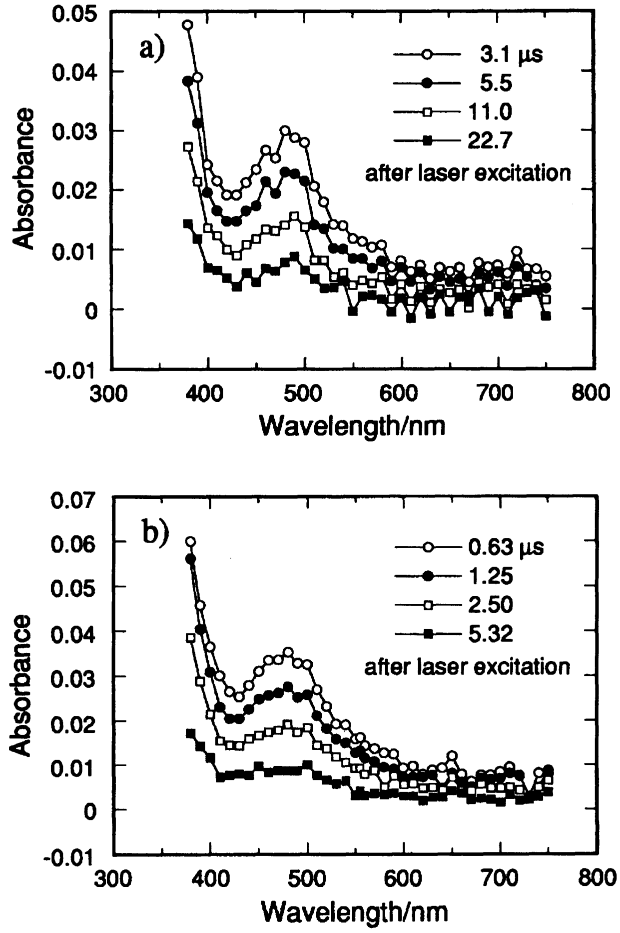


Fig. 1. Transient absorption spectra observed on 337-nm pulsed laser excitation of 9MCP (a) and *Z*-ABP (b) in degassed toluene.

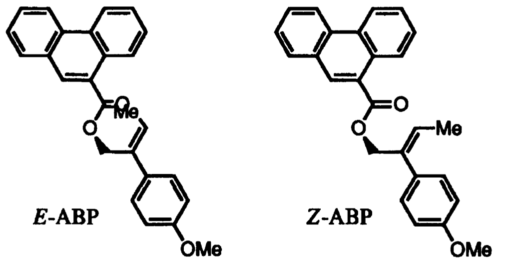


Chart 2.

energy than conformer A, and is assumed to be a candidate for the exciplex conformer interacting in a 2pπ–2pπ fashion between the C=C and C=O double bond. According to the calculations the terminal vinyl carbon and carbonyl oxygen atoms can approach at a distance of 230 pm in conformation C, where the 2pπ–2pπ interorbital interaction integral between the two atoms, $\Delta\beta_{CO}$, is nearly 10 kcal mol^{-1}.

The quenching efficiency might depend on the structure of the styryl moiety among the present bichromophores. The donor parts in bichromophores, *E*-ABP and *Z*-ABP, correspond to (*E*)-3- [(*E*)-EtAN], and (*Z*)-3-(*p*-methoxyphenyl)-2-pentene [(*Z*)-EtAN], respectively. The low quenching efficiency in *Z*-ABP might be attributed to the smaller coefficients in frontier molecular orbitals (FMO's) at the olefinic site due to the nonplanarity of the olefinic moiety.[20] As reported elsewhere,[21] in trisubstituted olefins such as (*Z*)-EtAN the aryl group is highly twisted from the molecular plane, and the calculated coefficients in FMO's at the carbon atom at the 2-position of (*E*)-EtAN are larger than those at the 2-position of (*Z*)-EtAN as is in the singlet quenching rate constants for *E*-ABP and *Z*-ABP (Chart 2).

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