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Highly Selective Cis-Trans Photoisomerization of 1-Pyrenylethylenes: Relations between the Modes of Isomerization and Potential Energy Surfaces

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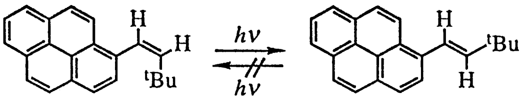
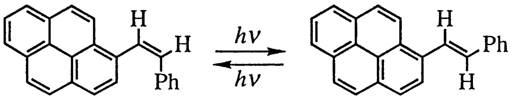
Among 1-pyrenylethylenes with an alkyl (*t*-butyl) or an aryl (phenyl) group on the β ethylenic carbon, 1-(3,3-dimethyl-1-butenyl)pyrene (BP) undergoes cis-to-trans one-way isomerization on benzil sensitization, whereas 1-styrylpyrene (SP) undergoes mutual isomerization between the cis and trans isomers to afford an extremely high photostationary state composition (98%) of the trans isomer. Transient spectroscopy and measurements of the isomerization quantum yields revealed that the trans triplet state is the most stable and populated conformation on the triplet energy surface for both BP and SP; however, a higher degree of stabilization of the trans conformation for BP than for SP compared to the perpendicularly twisted conformation makes BP and SP one-way and two-way isomerizing, respectively.

Since our finding of the photochemical cis-to-trans one-way isomerization of 2-anthrylethylenes,[1,2] we have revealed that the isomerization mode, one-way or two-way, of aromatic olefins in the triplet state is governed by properties of substituents on their ethylenic bonds.[3–6] Thus, olefins (ArCH=CHR) having an aromatic group (Ar) with a low triplet energy (E_T) like anthracene (42.0 kcal mol^{-1})[7] undergo the one-way isomerization regardless of the substituents (R) on the other ethylenic carbon.[1–3] This is contrasting to stilbenes[8,9] and naphthylethylenes[6,10] which undergo the well-known cis-trans two-way isomerization. We recently reported that the mode of isomerization is influenced not only by the aromatic group Ar but also by the other substituent R in ArCH=CHR.[4] For 8-fluoranthenylethylenes (E_T of fluoranthene: 54.2 kcal mol^{-1})[7] a *t*-butyl group in R leads to the one-way isomerization, while a phenyl group brings about the two-way isomerization. In this case the substituent R influences the mode of isomerization. We proposed that 8-fluoranthenylethylenes exhibit boundary behavior of the one-way and two-way isomerizations.[4]

The triplet energy of the Ar group and the nature of the R group (aryl or alkyl) affect the relative location of the trans and twisted triplets on the energy surface. In ArCH=CHR, introduction of an Ar group with a low triplet energy and that of an aryl group as R stabilize the trans triplet and the twisted triplet, respectively, as a decay funnel of the triplet state. The triplet states of anthrylethylenes and stilbenes decay at the trans and twisted triplet, respectively, whereas that of 8-styrylfluoranthene (SF) decays at both geometries showing the two-way isomerization with an extremely high ratio of the trans isomer at the photostationary state.





In a preliminary work we reported that 1-styrylpyrene[11] (SP, E_T of pyrene: 48.2 kcal mol^{-1})[7] also exhibits isomerization behavior similar to SF. Thus, SP seemingly undergoes the two-way isomerization;[12] however, the deactivation of the triplet state occurs not only from the twisted conformation but also from the trans one, therefore giving a very high ratio of the trans isomer at the photostationary state.

This finding led us to investigate the effect of introduction of an alkyl group like a *t*-butyl group instead of a phenyl group on the β-carbon of pyrenylethylene. We describe the results together with the experimental details of SP and discuss the relation between the isomerization behavior and the conformation of the participating triplet states on the basis of measurements of the isomerization quantum yields, transient spectroscopy study, etc.

Experimental

Proton (^{1}H) NMR spectra were recorded on a JEOL JMN-MH-100 spectrometer. Phosphorescence spectra were measured at 77 K in EPA on a Hitachi F-4000 spectrofluorimeter equipped with phosphorescence accessories.

Materials. Benzil and azulene were purified by crystallization and sublimation, respectively. Solvent benzene (Luminazol, Dojin) was used as received.

***cis-* and *trans*-1-(3,3-Dimethyl-1-butenyl)pyrene (BP).** 1-Pyrenecarbaldehyde (10 g, 40 mmol) was converted to 1-pyrenylmethanol with lithiumaluminum hydride (1 g, 26 mmol) in ether (reflux 2 h) (yield 6.1 g, 65%). 1-Pyrenylmethanol (3 g, 1.3 mmol) was reacted with phosphorus tribromide (7 g, 26 mmol) in chloroform to give 1-bromomethylpyrene (2.9 g, 77%); mp 145—146 °C (lit,[13] 145—147 °C). 1-Bromomethylpyrene (2 g, 7 mmol) was refluxed with triphenylphosphine (3.5 g, 13 mmol) in benzene to give the corresponding phosphonium salt (3.1 g, 80%). 2,2-Dimethylpropanal (0.86 g, 9 mmol) was reacted with the Wittig reagent prepared from 1-pyrenylmethyltriphenylphosphonium bromide (3 g, 5.4 mmol) and butyllithium in ether and the mixture was stirred for 13 h. The usual work-up gave a mixture of *cis*- and *trans*-1-(3,3-dimethyl-1-butenyl)pyrene (1.1 g, 72%). The cis and trans isomers were separated under red light by column chromatography on silica gel eluting with hexane and purified by crystallization from hexane.

cis-BP: mp 82.0 °C; ^{1}H NMR ($CDCl_3$, 100 MHz) δ=0.90 (s, 9H, $C(CH_3)_3$), 5.99 (d, 1H, J=12.5 Hz, C=CH), 6.91 (d, 1H, J=12.5 Hz, C=CH), 7.8—8.3 (m, 9H, ArH). Calcd for $C_{22}H_{20}$: C, 92.91; H, 7.09%. Found: C, 93.05; H, 7.10%.

trans-BP: mp 96.8 °C; ^{1}H NMR ($CDCl_3$, 100 MHz) δ=1.28 (s, 9H, $C(CH_3)_3$), 6.48 (d, 1H, J=16.2 Hz, C=CH), 7.36 (d, 1H, J=16.2 Hz, C=CH), 7.88—8.44 (m, 9H, ArH). Calcd for $C_{22}H_{20}$: C, 92.91; H, 7.09%. Found: C, 92.78; H, 7.04%.

***cis*- and *trans*-1-Styrylpyrene (SP).** A mixture of *cis*- and *trans*-1-styrylpyrene[12,14)] was prepared by the Wittig reaction from 1-pyrenecarbaldehyde (2.0 g, 9 mmol) and the ylide prepared from benzyltriphenylphosphonium bromide (3.7 g, 9 mmol) with sodium ethoxide in ethanol according to the preparative procedure of 2-styrylnaphthalene[15)] (yield 1.8 g, 87%). The cis and trans isomers were similarly separated and purified by crystallization from hexane–benzene (90 : 10); *trans*-SP: mp 156 °C (lit,[14b)] 157 °C).

Measurements of Photostationary State Isomer Ratios and Isomerization Quantum Yields. Irradiation was performed with 435-nm light isolated from a 400-W high-pressure mercury lamp through a filter solution of $CuSO_4 \cdot 5H_2O$ (4.4 g dm^{-3}) and $NaNO_2$ (75 g dm^{-3}) in water. The concentrations of each isomer in the reaction mixtures were determined by a high-performance liquid chromatograph (Waters 600 Multisolvent Delivery System) equipped with an LC spectrophotometer (Waters 490 Programmable Multiwavelength Detector) using anthracene or 1,3-bis(bromomethyl)benzene as an internal standard. Benzil was used as a triplet sensitizer. Light intensity was determined by potassium tris(oxalato)ferrate(III) actinometry.

Laser Flash Photolyses. Laser flash photolyses were performed with 308-nm (XeCl, 10-ns fwhm) and 435-nm laser pulses (Stilbene 3, 10-ns fwhm) from an excimer laser (Lambda Physik EMG-101) and an excimer laser-pumped dye laser (Lambda Physik FL-3002), respectively, and with a pulsed xenon arc (Wacom KXL-151, 150 W) as a monitoring light source. The monitoring light coming from a monochromator (JASCO CT-25C) was amplified by a photomultiplier (Hamamatsu Photonics R928) and stored in a storage scope (Iwatsu TS-8123), and the signals were transferred to a personal computer (NEC PC-9801VX21) and accumulated for 3—5 times to be averaged. The system was computer-controlled and the decay curves were analyzed by this computer system. Sample solutions were deaerated by three freeze-pump-thaw cycles or by bubbling argon for 30 min.

Near-infrared emission from singlet oxygen was observed by a germanium p-n junction detector (Hamamatsu Photonics B2144) with a silicon window on excitation of a sample solution by 308-nm excimer laser. The element was reverse-biased (9 V) and placed in series with a load resistor (1kΩ). The response time of this system is less than 3 μs.

Table 1. Photostationary State Isomer Compositions, ([t]/[c])s, of SP in Various Concentrations on Benzil-Sensitized Irradiation in Benzene

[SP]/M	%trans	([t]/[c])s
1.5×10^{-3}	97.7	41.9
6.4×10^{-4}	95.4	20.7
3.8×10^{-4}	91.6	10.9
6.4×10^{-5}	80.2	4.1

Table 2. Photostationary State Isomer Compositions, ([t]/[c])s, of SP in the Presence of Azulene (Az) in Various Concentrations on Benzil-Sensitized Irradiation in Benzene[a)]

[Az]/M	%trans	([t]/[c])s
0	87.3	6.9
4.2×10^{-5}	89.5	8.5
8.4×10^{-5}	92.0	11.5
12.6×10^{-5}	92.3	13.0

a) [SP]=3×10^{-4} M.

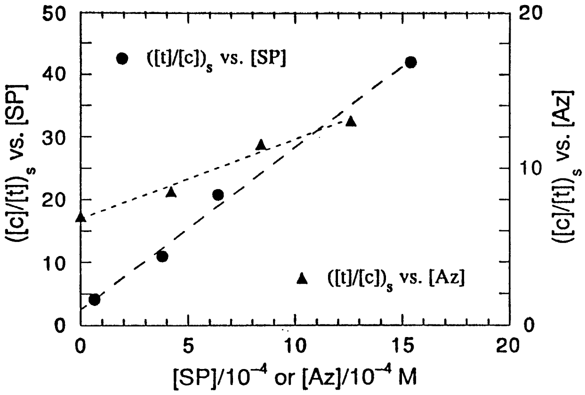


Fig. 1. Plots of the photostationary state isomer ratios, ([t]/[c])s, of SP as a function of the total SP concentration, [SP], or the azulene concentration, [Az].

Results

Photostationary State Isomer Ratios. Benzil (0.2 M, M=mol dm^{-3})-sensitized irradiation of BP (6×10^{-4} M) resulted in 100% trans isomer on starting with either cis or trans isomer in benzene under degassed conditions. On benzil (0.2 M)-sensitized irradiation of SP in benzene, however, the photostationary state isomer composition [([t]/[c])s] increased with increasing SP concentration (6.4×10^{-5}—1.5×10^{-3} M, Table 1 and Fig. 1), exhibiting a value as high as 98/2 at its concentration of 1.5×10^{-3} M on starting with either isomer. On extrapolation to infinite dilution the trans isomer ratio was obtained as 71%. Addition of azulene (Az, 4.2—13×10^{-5} M, [benzil]=0.1 M, and [SP]=3×10^{-4} M), a quencher of planar trans triplets, also increased the ([t]/[c])s value linearly with increasing Az concentration (Table 2 and Fig. 1). Plots of ([t]/[c])s against [SP] and [Az] give the slopes of 2.6×10^4

and 5.1×10^4 M^{-1}, respectively (Fig. 1).

Isomerization Quantum Yields. On benzil (0.05 M)-sensitized irradiation of *cis*-BP in degassed benzene the cis→trans isomerization quantum yield ($\phi_{c\to t}$) increased almost linearly with increasing *cis*-BP concentration (5.5×10^{-4}—3.3×10^{-3} M) attaining more than 20 at [*cis*-BP]=3.3×10^{-3} M (Table 3 and Fig. 2). The $\phi_{c\to t}$ value in benzil (0.1 M)-sensitized isomerization of *cis*-SP also increased with increasing [*cis*-SP] (6.7×10^{-4}—2.7×10^{-3} M) and attained more than 40 at [*cis*-SP]=2.7×10^{-3} M in deaerated benzene (Table 3 and Fig. 2).

Table 3. Quantum Yields for c→t Isomerization of *cis*-BP and *cis*-SP in Various Concentrations on Benzil-Sensitized Irradiation in Benzene

[*cis*-BP]/M	$\phi_{c\to t}$	[*cis*-SP]/M	$\phi_{c\to t}$
5.5×10^{-4}	5.1	6.7×10^{-4}	11.2
1.1×10^{-3}	10.9	1.3×10^{-3}	22.7
1.7×10^{-3}	10.9	2.7×10^{-3}	42.1
2.2×10^{-3}	16.4		
3.3×10^{-3}	23.4		

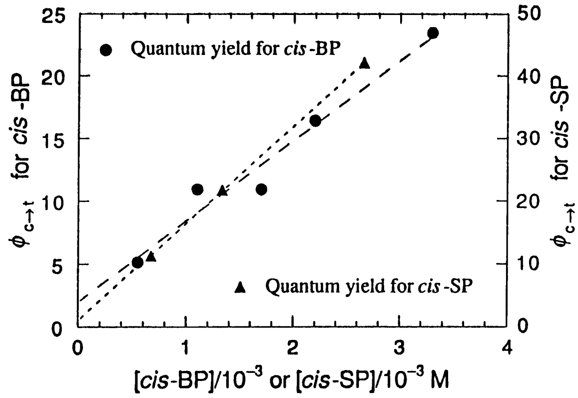


Fig. 2. Plots of the quantum yields for cis→trans isomerization, $\phi_{c\to t}$, of olefins BP and SP as a function of the cis-isomer concentration, [*cis*-BP] or [*cis*-SP].

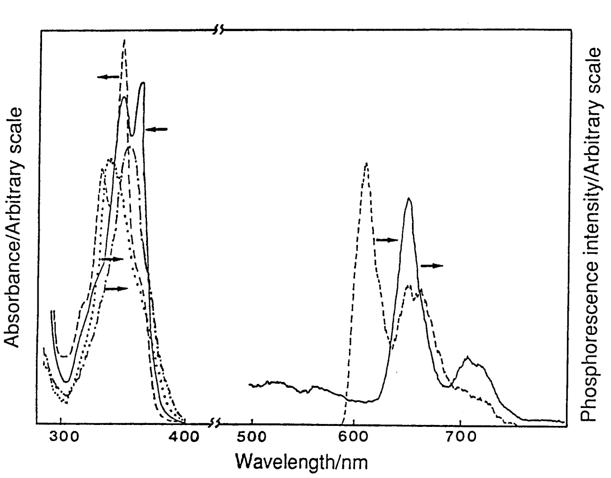


Fig. 3. Absorption spectra in benzene at ambient temperature (a; ----: *cis*, ——: *trans*), phosphorescence (b; ----: *cis*, ——: *trans*), and phosphorescence excitation spectra (c; ······: *cis*, —·—: *trans*) in EPA at 77K of *cis*- and *trans*-BP.

Phosphorescence Spectra. Phosphorescence spectra of *cis*- and *trans*-BP were measured in EPA at 77 K and are shown in Fig. 3 together with their phosphorescence excitation and absorption spectra. For both isomers the excitation spectrum is in good agreement with the corresponding absorption spectrum except fine structures in the absorption spectra due to difference in resolution of the spectrophotometers. The triplet energies for *cis*- and *trans*-BP were estimated to be 47 and 44 kcal mol^{-1}, respectively, from the 0-0 bands, 608 and 647 nm.

Triplet-Triplet Absorption Spectra. The T-T absorption spectra of the olefins were measured at ambient temperature in deaerated benzene solutions by irradiating with 308-nm laser pulses. The spectra of *cis*- and *trans*-BP (3×10^{-4} M) are shown in Fig. 4. *trans*-BP has an absorption band at 400—480 nm (λ_{max} 445 nm). The transient monitored at 445 nm decayed with first-order kinetics to afford a lifetime of 54 μs, and it was quenched effectively by oxygen with a rate constant of 2.9×10^9 M^{-1}s^{-1}. *cis*-BP (3×10^{-4} M) also showed a T-T absorption spectrum very similar to that of *trans*-BP even immediately after laser excitation.

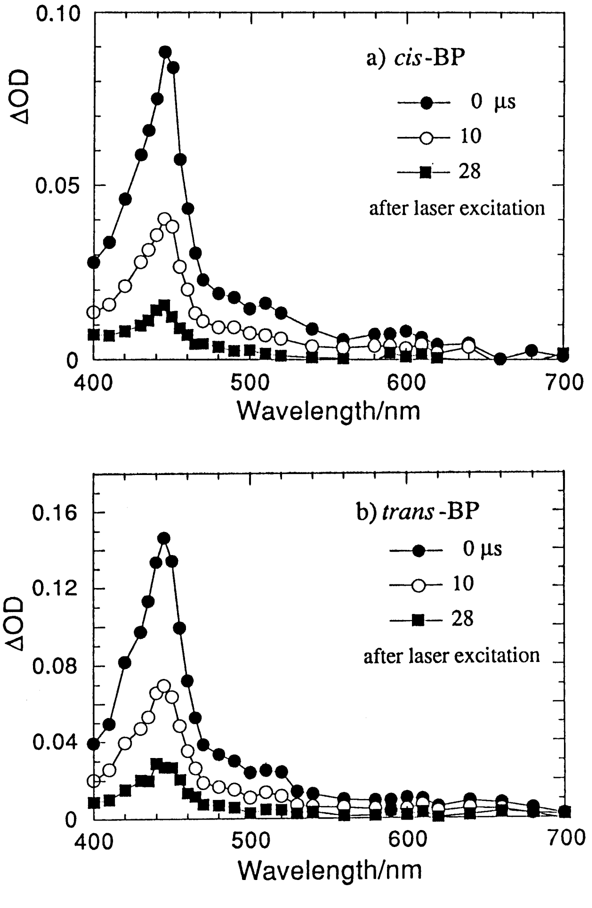


Fig. 4. $T_1\to T_n$ absorption spectra of BP observed on laser excitation of *cis*-BP (a) and *trans*-BP (b).

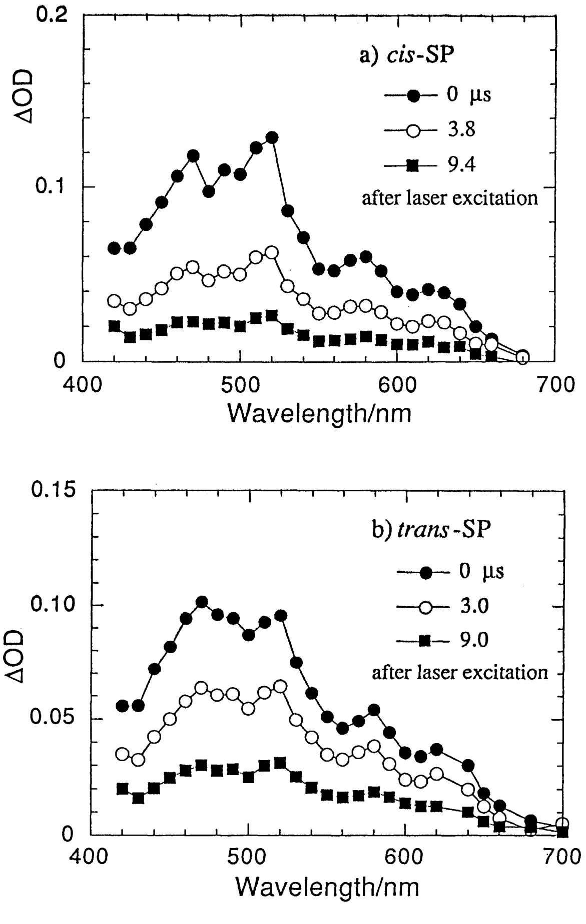


Fig. 5. $T_1 \rightarrow T_n$ absorption spectra of SP observed on laser excitation of *cis*-SP (a) and *trans*-SP (b).

The T-T absorption spectra of *cis*- and *trans*-SP (3×10^{-4} M) exhibit a broad band in the region of 400—650 nm (λ_{max} 470, 520 nm, Fig. 5). Its decay followed first-order kinetics to afford a lifetime of 27 µs as measured at 470 nm. The transients were quenched by oxygen and azulene (Az) with the rate constants of 3.6×10^{9} and 7.3×10^{9} $M^{-1}s^{-1}$, respectively. Erythrosine triplets (E_T: 41.7 kcal mol^{-1}) were quenched by *trans*-SP at a nearly diffusion-controlled rate (k_q= 8.6×10^{9} $M^{-1}s^{-1}$) as determined by the build-up of T-T absorption of the olefin at 480 nm on 510-nm laser excitation in benzene-ethanol (1 : 1).

The lifetime of SP triplets decreased with increasing temperature (5—56 °C) under degassed conditions as depicted in Fig. 6. However, the triplet lifetime of BP was not essentially affected by temperature (Fig. 6).

Laser flash photolyses were performed for benzene solutions of *trans*-SP ($2-10\times10^{-4}$ M) containing azulene ($1-20\times10^{-5}$ M). As shown in Fig. 7, the SP triplets are, after immediate formation, quenched by azulene with a fast exponential decay to establish an energy transfer equilibrium[16,17] between SP and azulene triplets; this equilibrium is subsequently bled with a slow exponential decay.

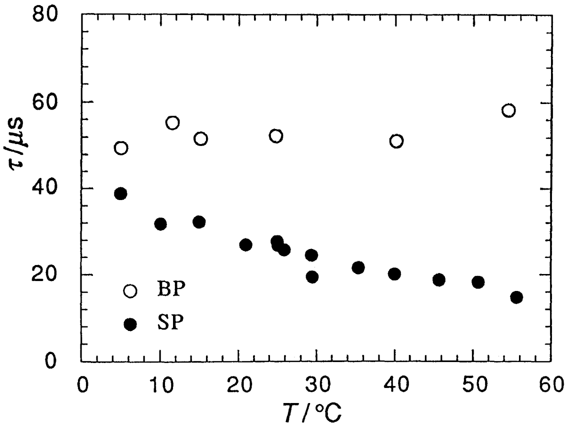


Fig. 6. Plot of the triplet lifetimes of SP and BP as a function of temperature.

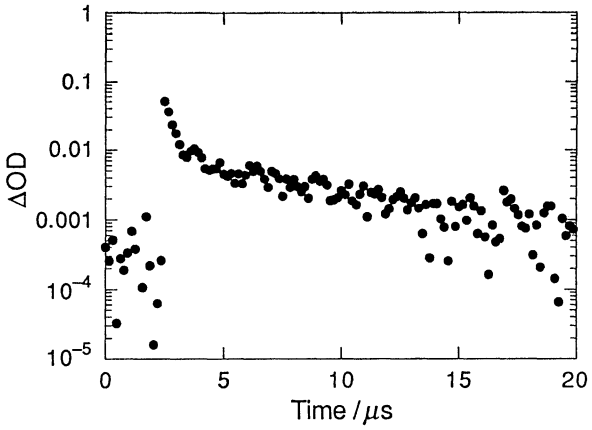


Fig. 7. Semilogarithmic plot for transient absorption monitored at 440 nm after laser excitation of a benzene solution containing SP (6.0×10^{-4} M) and Az (1.0×10^{-3} M).

Table 4. Energy Transfer Equilibrium between SP and Az Triplets[a)]

[SP]/M	[^{3}Az*]/[^{3}SP*]	*K*
2.0×10^{-4}	12.83	5.13
4.0×10^{-4}	18.43	3.68
6.0×10^{-4}	8.52	5.11
1.0×10^{-3}	7.23	7.22

a) [Az]=1.0×10^{-3} M.

For a true equilibrium the free-energy change, ΔG_T, may be assumed to equal the difference in energy between the two triplets, ΔE_T,

$$^3SP^* + Az \rightleftarrows SP + {}^3Az^* \tag{1}$$

$$\Delta E_T = E_T(SP) - E_T(Az) = RT \ln K, \tag{2}$$

where,

$$K = [SP][^3Az^*]/[^3SP^*][Az].$$

On the assumption that a negligible number of triplets are lost through natural decay before the equilibrium is established (i.e., ^{3}SP* lost equals ^{3}Az* generated), a ratio of [^{3}Az*]/[^{3}SP*] can be determined from absorbances immediately after laser excitation and at the time when the equilibrium is established.[16,17] Analysis of the results (Table 4) affords the equilibrium constant, K, of 5.5±1.5, which gives ΔE_T as ca. 1 kcal mol^{-1}. This observation gives the triplet energy, E_T, of $^3t^*$ as 41 kcal mol^{-1} since E_T of azulene is reported to be 39.8 kcal mol^{-1}.[7b]

Absorption Spectrum of 1-Pyrenylmethyl Radicals. Laser flash photolysis (308 nm) of 1-bromomethylpyrene in CCl_4 gave a transient absorption in the wavelength region shorter than 500 nm (λ_{max} 420 nm) as shown in Fig. 8a. The absorption consisted of two decay components [short-lifetime (3 μs) and long-lifetime (more than 50 μs)] in the entire absorption range (Fig. 8b). The lifetime of the fast component decreased with increasing oxygen concentration (k_q= 2.4X10^9 M^{-1} s^{-1}), and in contrast the slow component lifetime did not change significantly with increasing oxygen concentration. Based on these observations the fast component was assigned to 1-bromomethylpyrene triplets and the slow component to 1-pyrenylmethyl radicals.

Quantum Yields for Intersystem Crossing. Benzene solutions of anthracene (An) and *trans*-BP optically matched at 308 nm (A=0.56) were irradiated with 308-nm laser pulses and the initial T-T absorption intensities (ΔOD_{An} and $\Delta OD_{t\text{-BP}}$) monitored at 427.5 and 440 nm, respectively, were estimated by extrapolating the decay curves to time zero (ΔOD_{An}=1.65X10^{-2} and $\Delta OD_{t\text{-BP}}$=4.58X10^{-3}). Then, the ratio of the absorption intensities was measured for anthracene and *trans*-BP in the presence of benzil (0.05 M) by irradiating the sensitizer in the same concentration with laser pulses of the same intensity with changing the concentration of *trans*-BP (5.2X10^{-4}—5.2X10^{-3} M) and anthracene (1.2—6.0X10^{-3} M). In these concentration ranges the ΔOD values were almost constant ($\Delta OD_{Sens,An}$=0.177 and $\Delta OD_{Sens,t\text{-BP}}$=0.162).

The ratio of the intensities, $\Delta OD_{An}/\Delta OD_{t\text{-BP}}$, is described by a product of the ratios of the intersystem crossing quantum yields (ϕ_{isc}) and the molar extinction coefficients (ε) of T-T absorption.

$$\Delta OD_{An}/\Delta OD_{t\text{-BP}} = (\phi_{isc,An}/\phi_{isc,t\text{-BP}})(\varepsilon_{An}/\varepsilon_{t\text{-BP}}). \quad (3)$$

The relative T-T absorption intensity obtained from the plateau values gave the ratio of the extinction coefficients of T-T absorption for anthracene and *trans*-BP.

$$\Delta OD_{Sens,An}/\Delta OD_{Sens,t\text{-BP}} = \varepsilon_{An}/\varepsilon_{t\text{-BP}}. \quad (4)$$

By substituting the above values into Eqs 3 and 4, and by using $\phi_{isc,An}$=0.75,[7] $\phi_{isc,t\text{-BP}}$ was obtained as 0.23.

Quantum Yields of Singlet Oxygen Production. The yield for singlet oxygen resulting from the quenching of trans triplets of BP by oxygen was determined by the following procedure. Optically matched solutions (A=0.73) of *trans*-BP and benzophenone were irradiated with 308-nm laser pulses under aerated condition ($[N_2]/[O_2]$=49) and the decay of singlet oxygen emission at 1.27 μm was followed by a germanium photodiode to determine its initial intensities (Fig. 9). The emission lifetime thus measured was ca. 30 μs, which is in good agreement with the reported singlet oxygen lifetime in benzene.[18] The oxygen concentration of the sample solutions was as low as 2X10^{-4} M in order to avoid the contribution of quenching by oxygen of the substrate in the excited

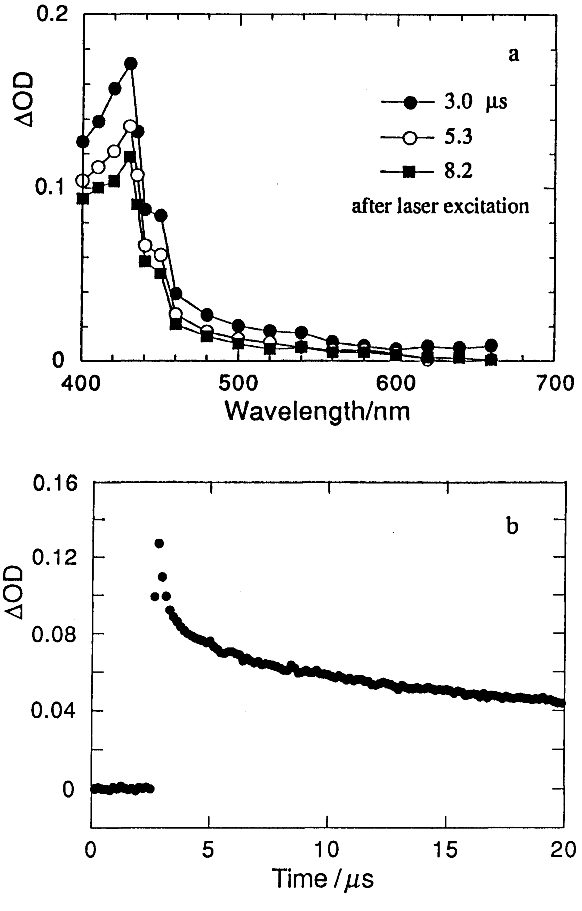


Fig. 8. Absorption spectrum of 1-pyrenylmethyl radicals in carbon tetrachloride (a) and its decay profile monitored at 430 nm (b).

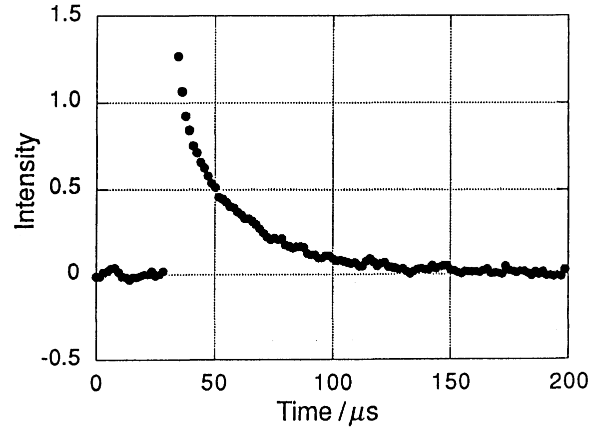
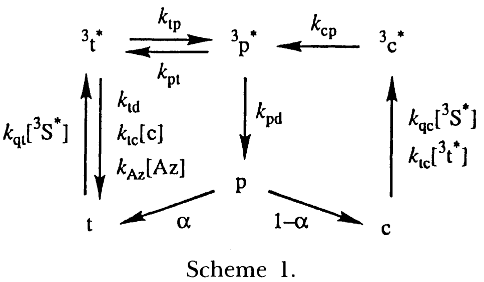


Fig. 9. Decay profile of $O_2(^1\Delta_g)$ emission after laser excitation of an aerated benzene solution containing *trans*-BP (2.2X10^{-5} M).

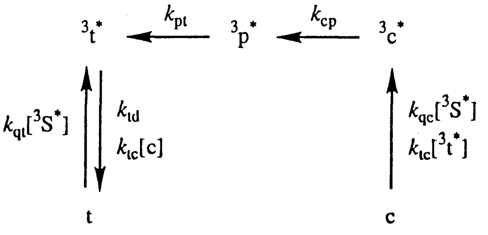
singlet state. Thus, the quantum yields of singlet oxygen on quenching of triplet BP by oxygen was obtained to be 0.91 using the reference yield of singlet oxygen from the quenching of triplet benzophenone (0.29)[18] and the intersystem crossing quantum yield of *trans*-BP obtained above (0.23). Similar measurements were made for SP. The fluorescence quantum yield of *trans*-SP was measured to be higher than 0.9, and therefore, the quantum yield for intersystem crossing is lower than 0.1. Use of this value leads to a value of more than 0.9 as the quantum yields for singlet oxygen formation from SP triplets.

Discussion

Isomerization Mechanism. BP undergoes the cis→trans one-way isomerization on triplet sensitization as observed for 2-anthrylethylenes[1–3] and 8-(3,3-dimethyl-1-butenyl)fluoranthene.[4a] On the other hand, SP gave a photostationary mixture of the cis and trans isomers, clearly indicating that SP undergoes the mutual isomerization between the cis and trans isomers in the excited triplet state. However, the photostationary state isomer ratio, $([\mathrm{t}]/[\mathrm{c}])_\mathrm{s}$, was affected by the total concentration of SP (Fig. 1). Furthermore, the azulene concentration dependence of $([\mathrm{t}]/[\mathrm{c}])_\mathrm{s}$ (Fig. 1) indicates that the trans ($^3\mathrm{t}^*$) and perpendicularly twisted triplets ($^3\mathrm{p}^*$) are in an equilibrium as observed for stilbene[8] and 2-naphthylethylenes.[6,10] That the $([\mathrm{t}]/[\mathrm{c}])_\mathrm{s}$ value extrapolated to infinite dilution (71/29) is shifted far from 50/50 means that the deactivation of the triplet state takes place not only from $^3\mathrm{p}^*$ but also from $^3\mathrm{t}^*$. Although SP and BP are different in the mode of isomerization from each other, both undergo the cis→trans isomerization through a quantum chain process as evidenced by the concentration dependence of the isomerization quantum yield, $\phi_{\mathrm{c}\to\mathrm{t}}$ (Fig. 2).



Scheme 1.



Scheme 2.

On the basis of these results we propose isomerization mechanisms for SP and BP in the triplet state as shown in Scheme 1 and 2, respectively, where $^3\mathrm{S}^*$ is the sensitizer triplet and k's are the rate constants for the corresponding processes. In Scheme 1 the equilibrium between $^3\mathrm{t}^*$ and $^3\mathrm{p}^*$ and the deactivation from $^3\mathrm{p}^*$ are characteristic of the two-way isomerizing olefins, while the decay from $^3\mathrm{t}^*$ and its energy transfer to the cis isomer ($^0\mathrm{c}$) regenerating the cis triplet ($^3\mathrm{c}^*$) are characteristic of the one-way isomerizing olefins. Scheme 2 shows the latter behavior.

According to Scheme 1, $([\mathrm{t}]/[\mathrm{c}])_\mathrm{s}$ and $\phi_{\mathrm{c}\to\mathrm{t}}$ are expressed by Eqs. 5 and 6, respectively. Here, $[\mathrm{SP}]=[\mathrm{t}]_\mathrm{s}+[\mathrm{c}]_\mathrm{s}$ is the total concentration of SP, and ϕ_T is the quantum yield for *cis*-SP triplet formation, and we assume that $k_\mathrm{qc}=k_\mathrm{qt}$.

$$([\mathrm{t}]/[\mathrm{c}])_\mathrm{s}=\frac{\alpha k_\mathrm{pd}(k_\mathrm{tp}+k_\mathrm{td})+k_\mathrm{pt}k_\mathrm{td}+(\alpha k_\mathrm{pd}+k_\mathrm{pt})(k_\mathrm{tc}[\mathrm{c}]_\mathrm{s}+k_\mathrm{az}[\mathrm{Az}])}{(1-\alpha)k_\mathrm{tp}k_\mathrm{pd}-(\alpha k_\mathrm{pd}+k_\mathrm{pt})k_\mathrm{tc}[\mathrm{c}]_\mathrm{s}}$$

$$=\frac{\alpha k_\mathrm{pd}(k_\mathrm{tp}+k_\mathrm{td})+k_\mathrm{pt}k_\mathrm{td}+(\alpha k_\mathrm{pd}+k_\mathrm{pt})(k_\mathrm{tc}[\mathrm{SP}]+k_\mathrm{az}[\mathrm{Az}])}{(1-\alpha)k_\mathrm{tp}k_\mathrm{pd}}, \tag{5}$$

$$\phi_{\mathrm{c}\to\mathrm{t}}=\phi_\mathrm{T}\times\frac{\alpha k_\mathrm{pd}(k_\mathrm{tp}+k_\mathrm{td})+k_\mathrm{pt}k_\mathrm{td}+(\alpha k_\mathrm{pd}+k_\mathrm{pt})k_\mathrm{tc}[\textit{cis}\text{-SP}]}{k_\mathrm{td}k_\mathrm{pt}+k_\mathrm{pd}(k_\mathrm{td}+k_\mathrm{tp}+k_\mathrm{tc}[\textit{cis}\text{-SP}])}. \tag{6}$$

When we assume that $k_\mathrm{tp}\gg k_\mathrm{td}$, $k_\mathrm{tc}[\textit{cis}\text{-SP}]$ and $k_\mathrm{pt}\gg k_\mathrm{pd}$, i.e., the equilibrium between $^3\mathrm{t}^*$ and $^3\mathrm{p}^*$ is established ($K_\mathrm{tp}=k_\mathrm{tp}/k_\mathrm{pt}$), Eqs. 5 and 6 can be reduced to Eqs. 7 and 8, respectively.

$$([\mathrm{t}]/[\mathrm{c}])_\mathrm{s}=\frac{\alpha K_\mathrm{tp}k_\mathrm{pd}+k_\mathrm{tp}+k_\mathrm{tc}[\mathrm{SP}]+k_\mathrm{az}[\mathrm{Az}]}{(1-\alpha)K_\mathrm{tp}k_\mathrm{pd}}, \tag{7}$$

$$\phi_{\mathrm{c}\to\mathrm{t}}=\phi_\mathrm{T}\times\frac{\alpha K_\mathrm{tp}k_\mathrm{pd}+k_\mathrm{td}+k_\mathrm{tc}[\textit{cis}\text{-SP}]}{K_\mathrm{tp}k_\mathrm{pd}+k_\mathrm{td}}. \tag{8}$$

For BP (Scheme 2), $\phi_{\mathrm{c}\to\mathrm{t}}$ is expressed by Eq. 9.[1–5]

$$\phi_{\mathrm{c}\to\mathrm{t}}=\phi_\mathrm{T}\left(1+\frac{k_\mathrm{tc}[\textit{cis}\text{-SP}]}{k_\mathrm{td}}\right). \tag{9}$$

Stable Conformations in the Triplet State. The transient absorption spectra observed for SP (Fig. 5) and BP (Fig. 4) are reasonably assigned to the T-T absorption of their trans isomers on the basis of the following facts; first, the triplet lifetimes (τ_T) of SP (27 μs) and BP (54 μs) are very much longer than that reported for stilbene triplets ($^3\mathrm{p}^*$, 63 ns)[9] and slightly shorter than those for the triplets of 2-anthrylethylenes ($^3\mathrm{t}^*$, 90—280 μs).[1b]

Second, all the spectra are quenched by oxygen with rate constants of ca. $3\times10^9\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$, a reasonable value for energy transfer; this is in excellent agreement with 1/9 of the diffusion rate constant of oxygen in organic solvents predicted by the spin statistical factor.[9,18b] The twisted triplet, $^3\mathrm{p}^*$, might be quenched by oxygen with a higher rate constant of ca. $9\times10^9\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$ due to the spin exchange interaction.[9]

Third, the absorption maximum of the pyrenylmethyl radical, which is the main component of the twisted triplet, was observed in the wavelength region shorter than 430 nm. However, the spectra observed for SP and BP appeared in the longer wavelength regions. Finally, the nearly unit efficiency of the singlet oxygen formation on quenching of the triplet state of SP and BP by oxygen indicates that the stable conformations of the triplet SP and BP have an enough energy to excite oxygen (22.5 kcal mol^{-1}). This clearly means that the stable conformation is located at the planar trans side.

Equilibrium Constant K_{tp} in SP. According to Scheme 1, the lifetime, τ_T, of the SP triplets is expressed by Eq. 10 since the triplet lifetime reflects the relative populations of $^3t^*$ and $^3p^*$.

$$\tau_T = \frac{1+K_{tp}}{K_{tp}k_{pd}+k_{td}}. \qquad (10)$$

The rate constants for deactivation of the twisted and transoid triplets, k_{pd} and k_{td}, can be assumed to be similar to those for stilbene (2X10^7 s^{-1})[9] and 2-styrylanthracene (2X10^4 s^{-1}),[1b] respectively. Substitution of these values into Eq. 10 gives a K_{tp} value of ca. 10^{-3} as an order of magnitude estimation.

Similar values of K_{tp} are obtained by analysis of the concentration dependence of ([t]/[c])s (Fig. 1) and $\phi_{c\rightarrow t}$ (Fig. 2). Since k_{az} is determined to be 1.4X10^9 M^{-1} s^{-1} by laser flash photolysis of *trans*-SP with benzil, Eq. 7 leads to $(1-\alpha)K_{tp}k_{pd}$=3X10^4 s^{-1}, and thus k_{tc}=7.1X10^8 M^{-1} s^{-1}. When we assume that α=1/2 and k_{pd}=2X10^7 s^{-1}, then K_{tp}=2.7X10^{-3} is obtained.

Dependence of $\phi_{c\rightarrow t}$ on [*cis*-SP] (Fig. 2 and Eq. 8) affords a value of 1.5X10^4 M^{-1} for $k_{tc}/(K_{tp}k_{pd}+k_{td})$. By using the above k_{tc} value and assuming that k_{pd}= 2X10^7 s^{-1} and k_{td}=2X10^4 s^{-1}, one obtains 1X10^{-3} for K_{tp}.

Potential Energy Surfaces of SP. The triplet energy of $^3t^*$ was estimated as 41 kcal mol^{-1} from the energy transfer equilibrium between SP and azulene triplets. This value is much lower than the triplet energy of pyrene, and might reflect a destabilization of the ground state with the same geometry as $^3t^*$ due to its steric crowding. The temperature effect on the triplet lifetime provides the energy difference (enthalpy change, ΔH_{tp}) between $^3t^*$ and $^3p^*$. From Eq. 10 K_{tp} is given by Eq. 10′, and thus the free-energy change between $^3t^*$ and $^3p^*$ by Eq. 11.

$$K_{tp} = (\tau_T^{-1} - k_{td})/(k_{pd} - \tau_T^{-1}), \qquad (10')$$

$$\Delta G_{tp} = \Delta H_{tp} - T\Delta S_{tp} = -RT \ln K_{tp}. \qquad (11)$$

By substituting τ_T's determined at varying temperatures and the same k_{td} and k_{pd} values as above into Eq. 10′, K_{tp}'s are calculated to be (0.8—2.4)X10^{-3}. Plot of $R \ln K_{tp}$ against $1/T$ (Fig. 10) affords ΔH_{tp} of ca. 5 kcal mol^{-1} and ΔS_{tp} of ca. 2 cal K^{-1} mol^{-1}.

The energy difference between $^3t^*$ and $^3c^*$ can be estimated to be ca. 2 kcal mol^{-1} from k_{tc} according to the Sandros equation (Eq. 12),[19] where $-\Delta E_{tc}$=$E_T(^3t^*)$ $-E_T(^3c^*)$ and A is assumed to be 10^{10} M^{-1} s^{-1} as the diffusion rate constant in benzene.

$$k_{tc} = A \exp(-\Delta E_{tc}/RT). \qquad (12)$$

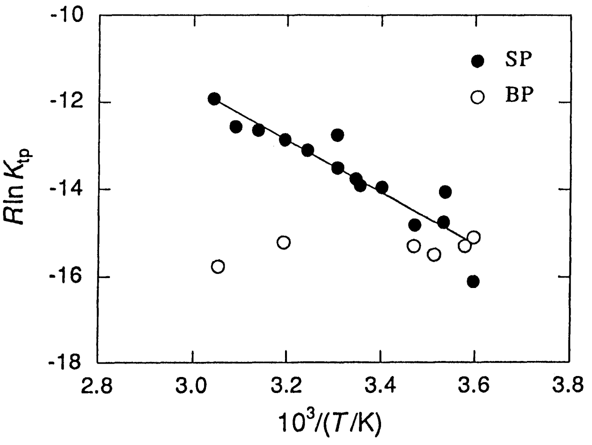


Fig. 10. Temperature dependence of $R \ln K_{tp}$ values calculated from the data in Fig. 6.

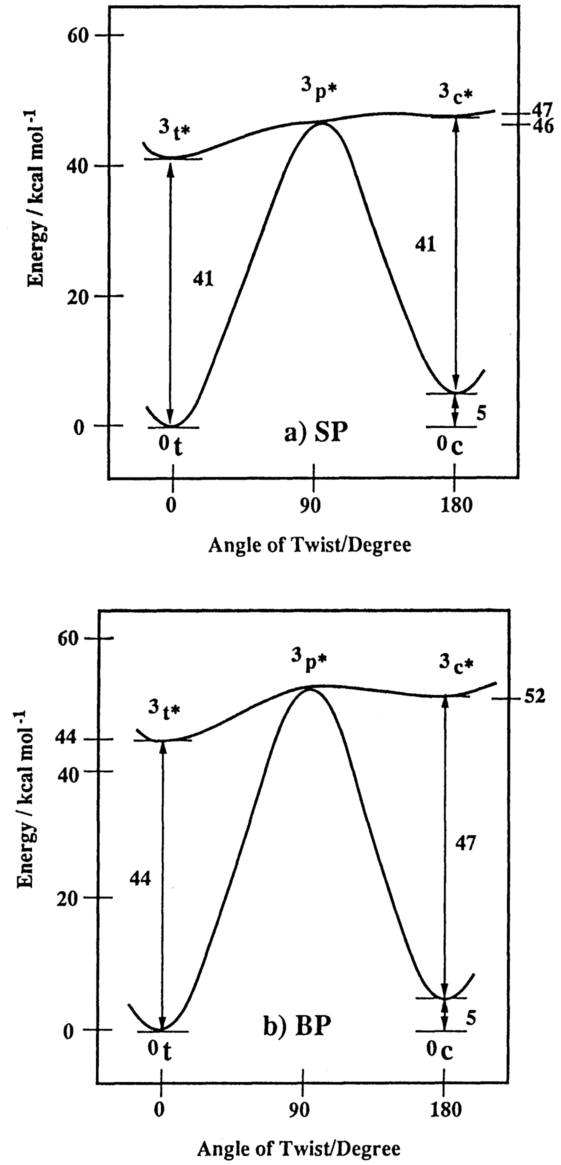


Fig. 11. Triplet energy surfaces of SP (a) and BP (b).

On the basis of these values the triplet energy surface of SP is depicted in Fig. 11a. The energy difference between cis and trans isomers in the ground state is assumed to be the same as that for stilbene, 5 kcal mol^{-1}.[20] On this energy surface the SP triplets populate mainly in ^{3}t* and slightly in ^{3}p*, and thus, the triplets decay from either geometry. ^{3}t* either deactivates slowly to ^{0}t or transfers its energy to ^{0}c to regenerate ^{3}c* accomplishing a quantum chain process, and ^{3}p* deactivates rapidly, because of proximity in energy to the ground state, to give ^{0}c and ^{0}t. In other words, SP has both properties of one-way isomerizing olefins such as 2-anthrylethylenes and a fluoranthenylethylene and of two-way isomerizing olefins such as stilbene, and, to our knowledge, this is the first example of aromatic olefins with two decay funnels.

Potential Energy Surface of BP. The isomerization behavior supports intermediacy of the trans triplet as a stable intermediate of BP photoisomerization. Thus, $\phi_{c\to t}$ increased with increasing cis isomer concentration to attain 20 even at rather low concentrations such as 3×10^{-3} M (Fig. 2). This fact clearly shows that the one-way isomerization proceeds adiabatically through a quantum chain process as reported for 2-anthrylethylenes; the initially resulting ^{3}c* undergoes twisting of the double bond to reach ^{3}t*, which either undergoes unimolecular deactivation to the trans isomer (^{0}t) or energy transfer to the cis isomer in the ground state to give ^{0}t and to regenerate ^{3}c* resulting in the quantum chain process.

According to Eq. 9 the slope of 6.4×10^3 M^{-1} in Fig. 2 is equal to k_{tc}/k_{td}. Use of $\tau_T=1/k_{td}=54$ μs affords k_{tc}, the rate constant of energy transfer from the trans triplet to ground-state cis as 1.2×10^8 M^{-1} s^{-1}. Substitution of this value into the Sandros equation (Eq. 12) gives the energy difference between *cis*- and *trans*-BP of 2.5 kcal mol^{-1}. This value is in good agreement with that determined by phosphorescence measurements (3 kcal mol^{-1}).

When an equilibrium is established between ^{3}t* and ^{3}p*, the temperature affects the triplet lifetime as observed for 1-styrylpyrene and 8-styrylfluoranthene.[4b] However, the temperature exhibited no effects on the triplet lifetime (τ_T) of BP. Since the lifetime measurements usually have some experimental uncertainty, the lower limit of K_{tp} must be 10^{-4}. As mentioned above, the lifetime of the SP triplet is remarkably reduced by an increase of temperature, and ΔH_{tp} is obtained as 5 kcal mol^{-1} ($K_{tp}\approx10^{-3}$ at room temperature).

If the ΔS_{tp} value for BP is assumed to be the same as that for SP, ΔH_{tp} is estimated as 6—7 kcal mol^{-1}. Therefore, ^{3}t* of BP is more than 6—7 kcal mol^{-1} stabilized in energy than that of ^{3}p*. This value is slightly higher than the stabilization of ^{3}t* compared to ^{3}p* in SP. The energy difference between cis and trans isomers in the ground state is again assumed to be the same as that for stilbene, 5 kcal mol^{-1}.[20] Therefore, the triplet energy surface of BP is drawn as in Fig. 11b.

Comparison of BP and SP Isomerization. The data are summarized in Table 5. The isomerization mode is totally different between SP and BP since BP undergoes the one-way isomerization but SP does the two-way isomerization. Moreover, the triplet lifetime of SP depends on the temperature whereas that of BP does not. However, the cis-to-trans isomerization quantum yields increase with increasing cis isomer concentration in both olefins. Their triplets have similar lifetimes and are quenched by oxygen with similar rate constants. The behavior of the present olefins arises from the properties of their trans triplet being the most stable conformation. In the triplet potential energy surfaces in Fig. 11, the cis and twisted geometries are similar in energy and the trans geometry is the most stable in both cases.

BP undergoes the cis→trans one-way isomerization with a remarkable quantum chain process along a triplet potential energy surface similar to those of the typical one-way isomerizing olefins such as anthrylethylenes. As mentioned above, the enthalpy difference between the trans triplet (^{3}t*) and the twisted

Table 5. Comparison of Aromatic Olefins in the Mode of Isomerization and Features of the Triplet State

	Stilbene[a)]	SP	BP	2-Styrylanthracene[b)]
Mode	Two-way	Two-way	One-way	One-way
Decay funnel	^{3}p*	^{3}p*,^{3}t*	^{3}t*	^{3}t*
%Trans at pss[c)]	42	98[d)]	100	100
τ_T	63 ns	27 μs	54 μs	190 μs
$\phi_{c\to t}$	0.42	22[e)]	23[f)]	19[g)]
K_{tp}	5—25	10^{-3}	$<10^{-5}$	0
$E_T(^3t^*)$/kcal mol^{-1}	49	41	44	42.5
$k_q(O_2)$/M^{-1} s^{-1}	8×10^9	3.6×10^9	2.9×10^9	3.5—4.5×10^9
k_{az}/M^{-1} s^{-1}	1.5×10^9		7.3×10^9	1.6×10^9
k_{tc}/M^{-1} s^{-1}		7×10^8	1.2×10^8	5.8×10^7
ΔE_{tc}/kcal mol^{-1}		2	2.5	3

a) Ref. 8. b) Refs. 1, 3, and 5. c) At the photostationary state. d) At 1.5×10^{-3} M. e) At 1.3×10^{-3} M. f) At 3.3×10^{-3} M. g) At 1.6×10^{-3} M.

triplet ($^3p^*$) is greater than 6—7 kcal mol^{-1} and seems to be too large to suffer temperature effects on the equilibrium between them.

As shown in the potential energy surfaces the trans geometry is the most stable conformation for both of BP and SP in the triplet state as well as in the ground state. However, the mode of the isomerization is different between them. In the triplet manifold, β-alkylstyrenes exist exclusively as a twisted conformation, whereas, when an aryl group is substituted in the β-position of styrene instead of an alkyl group, stilbene and styrylnaphthalene take both of the trans and twisted conformations because of stabilization of the former geometry by the aryl substitution.

Introduction of an aromatic nucleus with a lower triplet energy such as fluoranthene (E_T: 54.2 kcal mol^{-1})[7] leads to a more stable trans triplet than the twisted one as in 8-styrylfluoranthene ([$^3t^*$]/[$^3p^*$]=10); however, its unimolecular deactivation proceeds exclusively through the twisted triplet because the trans triplet is three orders of magnitude lower in the deactivation rate than the twisted triplet ($k_{pd}=2\times10^7$ s^{-1} and $k_{td}=2\times10^4$ s^{-1}).

As a result of further lowering in the triplet energy of the aromatic substituent, SP shows an equilibrium much shifted to the trans triplet with a K_{tp} value of ca. 10^{-3}, which is just the reciprocal of the ratio of the deactivation rate constants of the two geometries; thus, both deactivation processes appear to be equally contributing. The enthalpy difference between the two geometries is 5 kcal mol^{-1}. If the entropy difference between the trans and twisted triplets is similar among the olefins, the enthalpy difference plays the main role. Thus, the more stabilized $^3t^*$ compared to $^3p^*$ in enthalpy, the more important the deactivation from the trans triplet, finally leading to the one-way isomerization in which the deactivation occurs solely from $^3t^*$. This situation will arise when $^3t^*$ is about 6—7 kcal mol^{-1} more stabilized than $^3p^*$ as in 2-styrylanthracene.

Introduction of a naphthyl, a fluoranthenyl, or a pyrenyl group in a β-alkylstyrene, β-*t*-butylstyrene, instead of the phenyl group leads to a similar result mentioned above; however, the 6—7 kcal mol^{-1} energy difference between $^3t^*$ and $^3p^*$ is achieved in the fluoranthenyl and pyrenyl (BP) derivatives since the energies of $^3p^*$ in this series is 7—10 kcal mol^{-1} higher than those in the above styryl series.

When the cis and twisted geometries are similar in energy on the triplet energy surfaces as in SP, the probability of deactivation at the cis side can be neglected since the deactivation from $^3p^*$ will occur at a rate 10^3 times faster than those from $^3c^*$ and $^3t^*$. This kind of the energy surface arises from the energy difference in ground-state isomers.

If the cis and trans isomers of an olefin have nearly the same excitation energies and are nearly the same in energy in the ground state, and $^3p^*$ is not situated at an energy minimum, both $^3c^*$ and $^3t^*$ result in an equilibrium and the deactivation may take place from both geometries. In the present olefins, however, the higher energies (ca. 5 kcal mol^{-1}) for cis isomers than trans isomers and the higher excitation energies of the cis isomers compared to the trans isomers result in 5—8 kcal mol^{-1} higher energy of the cis triplet than the trans triplet. Thus, the equilibrium constant between the cis and trans triplets must be less than 10^{-3} leading to undetectable deactivation at the cis triplet.

Conclusion

1-Pyrenylethylenes exhibited border behavior distinguishing the one-way and two-way isomerization. The BP triplet behaves in a very similar way to other typical one-way isomerizing olefins, while the SP triplet behaves in a highly different way from the typical two-way isomerizing olefins. Although the isomerization can be simply described as one-way or two-way based on the apparent direction of the isomerization, the behavior of participating triplet states must be classified by delicate features of the triplet energy surface which is very much dependent on the properties of substituents. Especially, for the two-way isomerization, there are many possible potential energy surfaces which can make a bridge from the typical two-way to one-way isomerization. Thus, SP exhibits the two-way isomerization; however, the most stable and populated triplet state is the trans triplet, and the deactivation occurs not only from $^3t^*$ but also from $^3p^*$ since their energy difference is smaller than that for BP.

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