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Behavior of the Excited Cis Singlet State of a One-Way Isomerizing Olefin. Further Insight into Potential Energy Surfaces of 1-(3,3-Dimethyl-1-butenyl)pyrene

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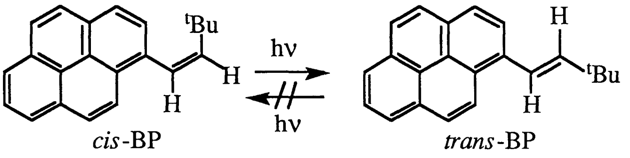
The decay processes of the excited singlet state and potential energy surfaces of 1-(3,3-dimethyl-1-butenyl)pyrene (BP) were investigated. A long-lived fluorescence from the cis isomer and involvement of a quantum chain process for one-way isomerization suggest that the isomerization on direct excitation proceeds in the triplet manifold after intersystem crossing at the cis conformation.

On direct excitation, olefins can undergo photoisomerization in the singlet manifold, triplet manifold, or both depending on the properties of substituents on the ethylenic carbons. In the case of stilbene, cis-trans two-way isomerization occurs mutually between the both isomers in the singlet manifold.[1] However, 2-anthrylethylenes undergo cis-to-trans one-way isomerization in the triplet manifold even on direct irradiation; the initially produced singlet excited state does not undergo isomerization at all, but undergoes efficiently intersystem crossing to the triplet state.[2–4]

We reported previously that 1-(3,3-dimethyl-1-butenyl)-pyrene (BP) undergoes cis-to-trans one-way isomerization on triplet sensitization.[5] In this paper we elucidate the mechanism of its photoisomerization on direct irradiation, which is now revealed to proceed in the triplet state after intersystem crossing of the singlet excited state. In addition, on the basis of fluorescence studies and differential scanning calorimetry we propose the potential energy surfaces of the ground and excited singlet states of BP.



Experimental

Materials. Preparation of *cis*- and *trans*-1-(3,3-dimethyl-1-butenyl)pyrene (BP)[5] and purification of benzil and solvent benzene were done as described previously.[3]

Fluorescence Studies. Fluorescence spectra were measured on a Hitachi F-4000 spectrofluorimeter, and fluorecsence lifetimes were determined using a single photon counting apparatus, Horiba NAES-1100.

Steady Irradiations. Photostationary state isomer ratios and isomerization quantum yields were measured by irradiating degassed benzene solutions of BP with 366-nm light from a 400-W high-pressure mercury lamp through a band pass filter (Corning 7-60, 0-52). The isomer ratio was determined by HPLC (Waters 600 Multisolvent Delivery System) equipped with an LC spectrophotometer (Waters 490 Programmable Multiwavelength Detector) using 1,3-bis(bromomethyl)benzene as an internal standard. 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 detailed laser photolysis set-up was described previously.[3,5] Sample solutions containing BP (1.2×10^{-4} M, M=mol dm^{-3}) were deaerated by three freeze-pump-thaw cycles or by bubbling with argon for 30 min.

Differential Scanning Calorimetry. Energy difference between the ground-state trans (^{0}t) and cis isomer (^{0}c) was obtained by using differential scanning calorimetry (DSC). A Seiko Electric DSC-200/SSC5000 was used at the laboratory of Research Institute for Polymers and Textiles after calibration.[6] Approximately 2 mg of samples were scanned at 2—7.5 °C min^{-1}.

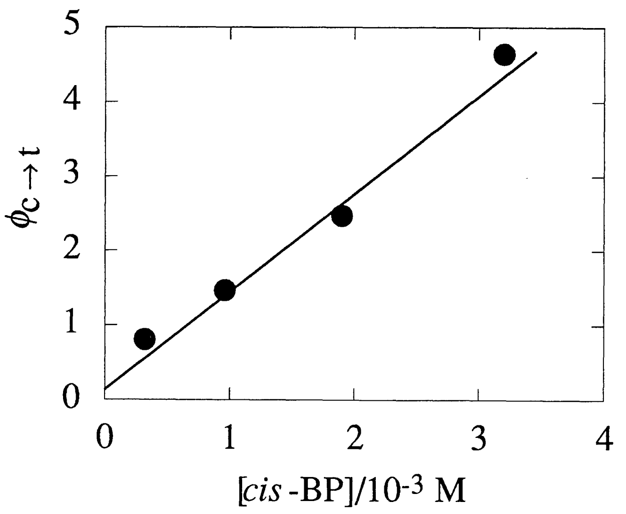


Fig. 1. Plot of quantum yields for cis→trans isomerization of BP ($\phi_{c\to t}$) in benzene as a function of *cis*-BP concentration on direct irradiation.

Results

Photostationary State Isomer Ratios and Isomerization Quantum Yields. Direct irradiation of BP (0.16—1.6$\times$10^{-3} M) with 366-nm light in degassed benzene resulted in 100% of the trans isomer on starting from either cis or trans isomer as observed on triplet sensitized irradiation.[3] The quantum yield for cis→trans isomerization ($\phi_{c\rightarrow t}$) increased almost linearly with increasing cis isomer concentration (0.32—3.2$\times$10^{-3} M), attaining 4.6 at the highest *cis*-BP concentration employed (Fig. 1).

Fluorescence Studies. A freshly prepared sample of *cis*-BP in benzene gave a fluorescence (Fig. 2a) different from that of *trans*-BP (Fig. 2b) at room temperature, while the spectrum was changed gradually to that of *trans*-BP at every scanning (Fig. 3). This is attributed to the photoexcitation of the trans isomer accumulated by photoisomerization of the cis isomer under excitation beam in the spectrometer during the measurement. At 77 K, each isomer showed a fluorescence spectrum (Figs. 2c and 2d) slightly more sharp than that observed at room temperature, without spectral change during the measurement.

The singlet excitation energies were estimated from the 0–0 band of the fluorescence spectrum (378 and 392 nm) to be 76 and 73 kcal mol^{-1} (1 cal=4.184 J) for *cis*- and *trans*-BP, respectively (Fig. 2). The quantum yields (ϕ_f) of fluorescence emission of *trans*- and *cis*-BP (3$\times$10^{-6} M) were determined in benzene as 0.64 and 0.43, respectively, by using pyrene (ϕ_f=0.58)[7] and phenanthrene (ϕ_f=0.11)[7] as standards.

The fluorescence lifetime of *trans*-BP was measured in benzene at room temperature as 65 ns by single photon counting (SPC) technique. It is clear that the excited singlet state of *cis*-BP has a sufficient lifetime to emit its own fluorescence; however, its gradual isomerization to the trans isomer at room temperature during SPC measurements prevented to determine its lifetime directly.

The fluorescence spectra of *cis*- and *trans*-BP were efficiently quenched by oxygen without changing the spectral profile. The Stern–Volmer constants, K_{SV}=$k_q\tau_s$, for fluorescence quenching with oxygen were determined as 1760 and 1170 M^{-1} for *trans*- and *cis*-BP, respectively. By use of the lifetime of singlet excited *trans*-BP (τ_s=65 ns) the quenching rate constant for *trans*-BP was determined as k_q=2.7$\times$10^{10} M^{-1} s^{-1}. If

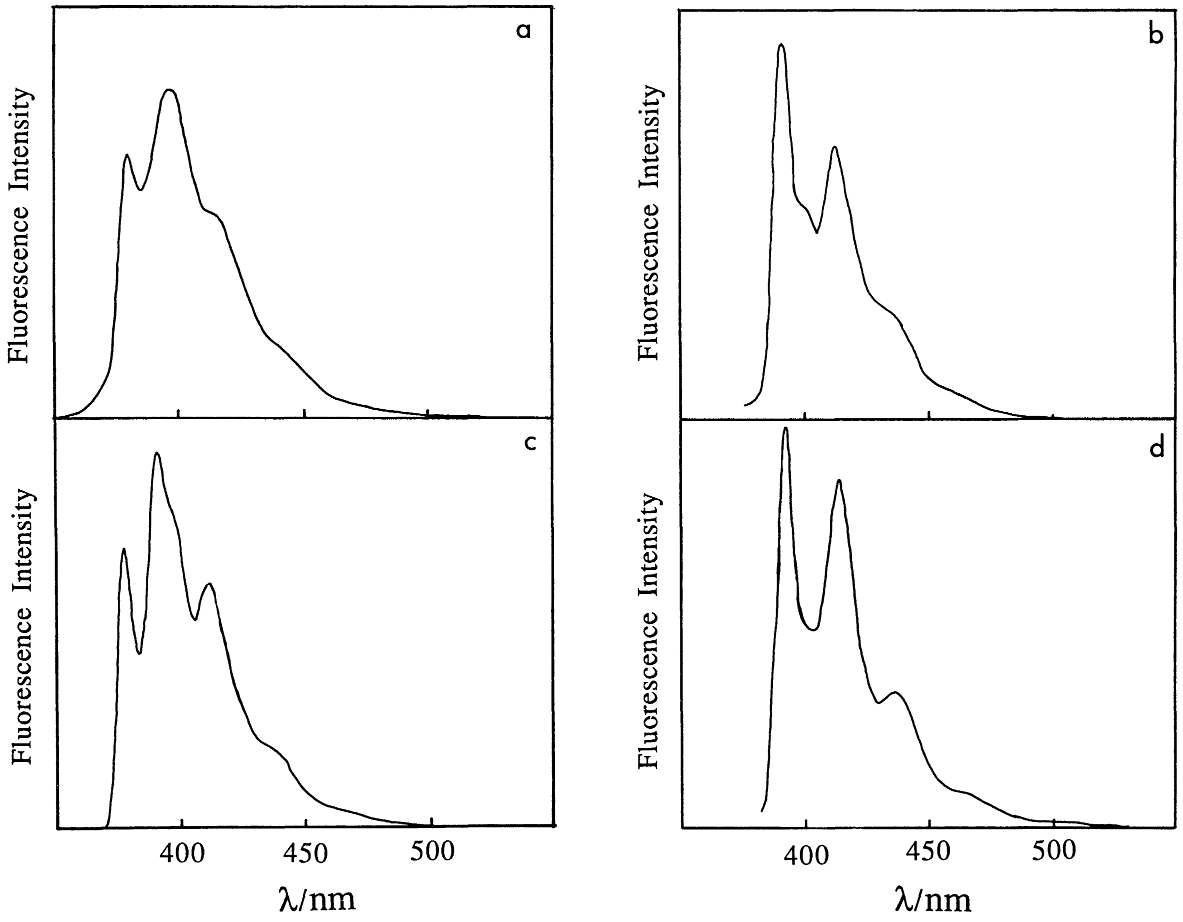


Fig. 2. Fluorescence spectra of *cis*- (a) and *trans*-BP (b) in benzene at room temperature and of *cis*- (c) and *trans*-BP (d) in EPA at 77 K.

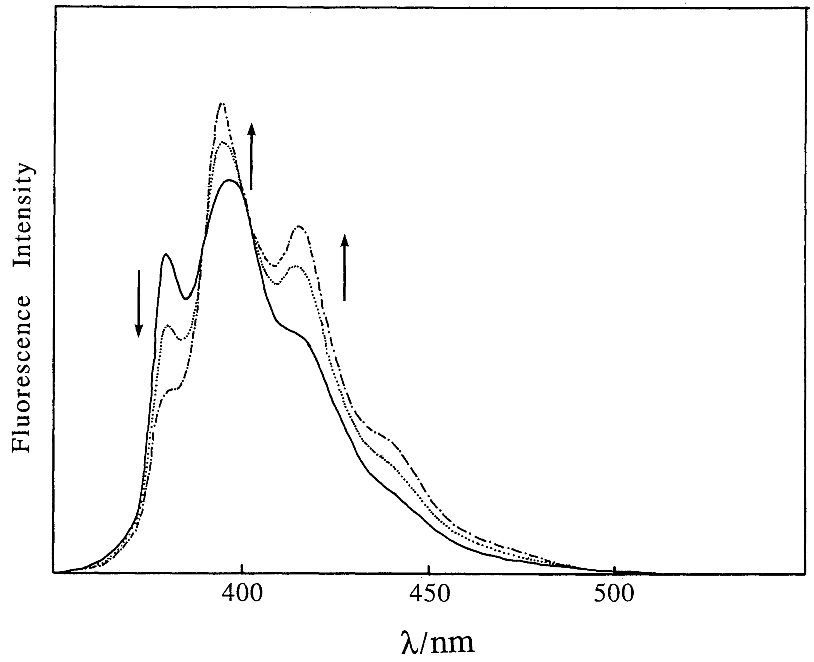


Fig. 3. Fluorescence spectrum change of *cis*-BP in benzene at room temperature.

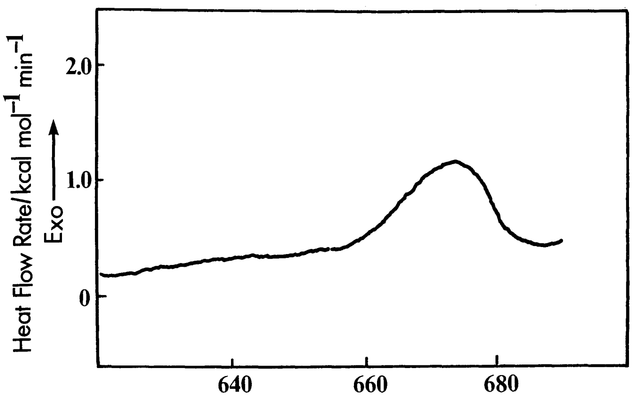


Fig. 4. DSC thermogram obtained for *cis*-BP at a rising rate of temperature of 2.5 °C min^{-1}.

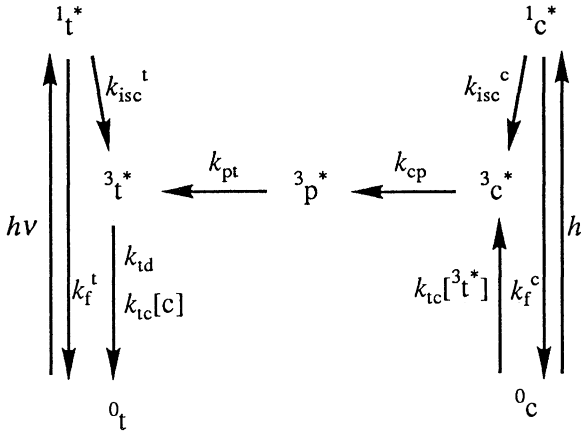
singlet excited *cis*-BP is assumed to be quenched by oxygen with the same rate constant as *trans*-BP, its lifetime is estimated as 43 ns.

Quantum Yields for Intersystem Crossing. Solutions of anthracene and *cis*-BP optically matched at 308 nm (in the absence of benzil) or at 435 nm (in the presence of benzil as a sensitizer) were irradiated with 308-nm or 435-nm laser pulses and the initial T-T absorption intensities (ΔOD_0) were estimated by extrapolating the decay curve to time zero. These ΔOD_0 values combined with the quantum yield for intersystem crossing of anthracene, ϕ_{isc}(An) (=0.75[7]), give ϕ_{isc}(*cis*-BP) of 0.21. This value is almost identical to that of *trans*-BP (0.23).[5]

Energy Difference between Ground-State Cis (^{0}c) and Trans (^{0}t) Isomers. Energy difference between *cis*-BP (^{0}c) and *trans*-BP (^{0}t) in the ground state was obtained from the DSC thermogram (Fig. 4) as 4.9±0.3 kcal mol^{-1} at different rising rates of temperature (2—7.5 °C min^{-1}).

Discussion

Isomerization Mechanism on Direct Excitation. Stilbene isomerizes in a two-way mode in the excited singlet state as well as in the triplet state through a decay at the perpendicular conformation, resulting in a photostationary state mixture of a finite isomer ratio, ([t]/[c])$_s$.[1] In contrast to stilbene, BP undergoes cis-to-trans one-way isomerization with a quantum chain process not only on triplet sensitization but on direct excitation, as evidenced by the photostationary state isomer ratios and isomerization quantum yields. For the one-way isomerization of BP observed on direct irradiation, the following mechanisms can be considered: i) an adiabatic cis-to-trans conversion in the singlet manifold involving a quantum chain process, ii) an isomerization through a decay from the perpendicular conformation on a stilbene-like excited singlet energy surface, and iii) an isomerization on the triplet energy surface after intersystem crossing at the cis conformation. The isomerization mechanism similar to that proposed for the stilbene singlet (mechanism ii) is ruled out since the decay at the perpendicular conformation to the ground state should afford a finite photostationary state isomer



Scheme 1.

ratio instead of 100/0 and also cannot account for the chain process.

cis-BP and *trans*-BP exhibit the fluorescence spectra different from each other. Both spectra were efficiently quenched by oxygen, while the spectral profile of each isomer was essentially unchanged under oxygenated atmosphere. If an adiabatic cis-to-trans conversion in the singlet manifold efficiently took place, the fluorescence spectrum observed for *cis*-BP might consist of those emitted by the cis singlets and the resulting trans singlets, and under oxygenated atmosphere that of *cis*-BP might be more sustained compared to *trans*-BP fluorescence. However, the above results indicate that the *cis*-BP excited singlet is not converted to the *trans*-BP excited singlet, but emits fluorescence or intersystem crosses to the cis triplet. These facts indicate that the *cis*-BP excited singlet is located at an energy minimum, and exclude the possibility of the first mechanism.

Therefore, it is reasonable to propose that the isomerization of *cis*-BP on direct excitation proceeds in the triplet manifold after intersystem crossing of the cis singlet state as depicted in Scheme 1, where k's are the rate constants for the corresponding processes. According to Scheme 1, the quantum yield under direct irradiation is expressed by the following equation, Eq 1,[5,8] where ϕ_{isc}, k_{tc}, and τ_T denote the quantum yield for intersystem crossing of the cis singlet, the rate constant for energy transfer from the resulting trans triplet to the cis isomer, a key step for the quantum chain process, and the lifetime of the trans triplet state, respectively.

$$\phi_{c\to t}=\phi_{isc}(1+k_{tc}\tau_T[cis\text{-BP}]). \qquad (1)$$

The linear dependence of $\phi_{c\to t}$ on [*cis*-BP] in Fig. 1 affords $\phi_{isc}=0.27$ and $\phi_{isc}k_{tc}\tau_T=1.3\times10^3\ M^{-1}$ as the intercept and the slope, respectively. Use of the values reported previously,[5] $\tau_T=1/k_{td}=54\ \mu s$ and $k_{tc}=1.2\times10^8\ M^{-1}\ s^{-1}$, gives $\phi_{isc}=0.25$. The value for ϕ_{isc} is in good agreement with the aforementioned value obtained by laser photolysis (0.21). This result strongly supports that the isomerization takes place at the triplet surface and eliminates a possibility of participation of the singlet state to the isomerization.

The following consideration also supports the mechanism iii. In Fig. 1 the ratio of slope/intercept ($1.3\times10^3\ M^{-1}/0.27=5\times10^3\ M^{-1}$) corresponds to the quenching constant ($k_q\tau$) of the excited state responsible for the quantum chain process. In the singlet state this magnitude of quenching constant could be achieved only when the quenching rate constant is larger than the diffusion-controlled value, because the singlet lifetime of *trans*-BP is 65 ns; thus, k_q should be $7.7\times10^{10}\ M^{-1}\ s^{-1}$. However, energy transfer from $^1t^*$ to *cis*-BP, if it occurs, should take place as an endothermic process with a rate constant much lower than the diffusion controlled, since the singlet excitation energy of *cis*-BP is 3 kcal mol^{-1} higher than that of *trans*-BP. This is contrasted with a reasonable value for k_{tc} in the triplet state.

Potential Energy Surfaces of BP. The energy difference (ΔH) between ^0c and ^0t was obtained as 4.9 kcal mol^{-1} from DSC experiments. This value is very similar to the most reliable value for stilbene (4.6 kcal mol^{-1}).[9] Thus, the energy differences between ^0c and ^0t for diarylethylenes and arylalkylethylenes seem to be similar (ca. 5 kcal mol^{-1}) as we usually assume.

As mentioned above, the cis and trans conformations of the excited singlet state are located at the energy minima with the excitation energies of 76 and 73 kcal mol^{-1}, respectively. The aforementioned failure of isomerization in the excited singlet state indicates the presence of a considerably high energy barrier which prevents the isomerization of $^1c^*$ on the singlet excited energy surface at room temperature. A rough estimation of the cis-to-trans conversion rate (k_{isom}) might be less than 1/100 of the total decay rate ($1/\tau_s=1.5\times10^7\ s^{-1}$). This corresponds to an activation energy higher than at least ca. 7 kcal mol^{-1}, when a range of 10^{11}—$10^{12}\ s^{-1}$ is assumed as the frequency factor, A, in Eq 2.

$$k_{isom}=A\exp(-E_a/RT). \qquad (2)$$

Taking into account the energy barrier for twisting, the top of the energy surface of the singlet excited state must be located at the energy of 88 kcal mol^{-1} higher than ground-state *trans*-BP. There is still no evidence clarifying whether the energy barrier exists at the perpendicular conformation ($^1p^*$) or between $^1c^*$ (or $^1t^*$) and $^1p^*$. However, it is likely that the latter is the case because the energy of $^1p^*$ is usually assumed to be less than 80 kcal mol^{-1} over ^0t.[1]

Previously, we proposed the energy surface of the triplet state of BP undergoing cis-to-trans one-way isomerization by way of an adiabatic process; the

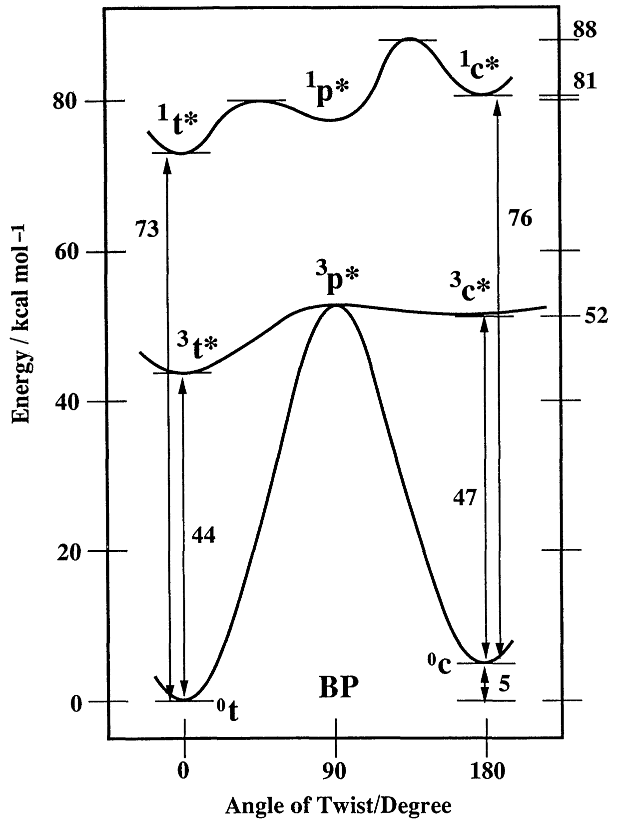


Fig. 5. Potential energy surfaces of cis-trans isomerization of BP.

initially resulting $^{3}c^{*}$ is converted to $^{3}t^{*}$, which either undergoes unimolecular deactivation to trans or transfers energy to cis to give trans and to regenerate $^{3}c^{*}$.

The present experimental results provide us sound basis to depict the potential energy surfaces of BP as shown in Fig. 5.

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