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The Effect of Substitution of 3-Perylenyl Group, an Aromatic Nucleus with a Very Low Triplet Energy, on Photochemical Isomerization of the Unsaturated Bond. Direct Observation of Triplet State Isomerization of a Styrene Derivative

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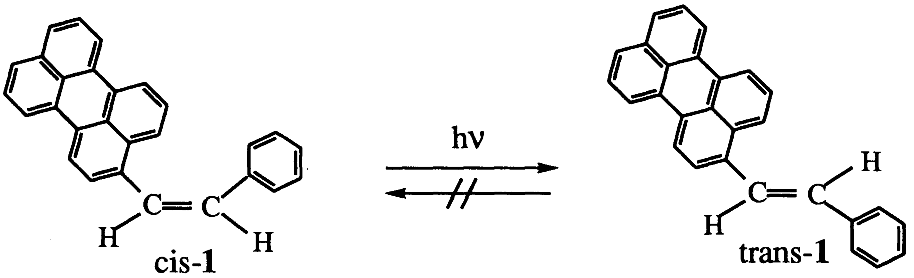
3-Styrylperylene undergoes one-way cis→trans photoisomerization in the triplet state through a quantum chain process. The conversion of cis to trans triplet state was directly observed by laser spectroscopy to proceed with an activation energy of 6.6 kcal mol^{-1}. This finding clearly demonstrates that in the series of styrylarenes, ArCH=CHPh, lowering of the triplet excitation energy of Ar group alters the mode of isomerization from two-way to one-way.

In contrast to the well-accepted photochemical behaviors of olefins such as stilbene undergoing mutual isomerization between cis and trans isomers,$^{1,2)}$ we found that substitution of an anthryl group on an ethylenic bond solely led to cis-to-trans isomerization.$^{3,4)}$ Furthermore, we proposed that lowering of the triplet excitation energy of aromatic nuclei (Ar) on the ethylenic linkage alters the mode of the isomerization from the conventional two-way (mutual) mode to the novel one-way mode as seen in a series of ethylenes of ArCH=CH^{t}Bu.$^{3,5-7)}$ In this series, Ar=phenyl (the triplet energy of ArH, E_T=84.3 kcal mol^{-1}),$^{8)}$ 2-naphthyl (E_T=60.9 kcal mol^{-1}),$^{8)}$ and 3-chrysenyl (E_T=56.6 kcal mol^{-1})$^{8)}$ resulted in two-way isomerization, whereas Ar=8-fluoranthenyl (E_T=54.2 kcal mol^{-1}),$^{8)}$ 1-pyrenyl (E_T=48.2 kcal mol^{-1}),$^{8)}$ and 2-anthryl (E_T=42 kcal mol^{-1})$^{8)}$ led to one-way isomerization. Furthermore, with Ar=2-anthryl, conversion of the cis triplet (^{3}c*) to the trans triplet (^{3}t*) was directly observed by laser photolysis with an activation barrier of 6 kcal mol^{-1}; the ^{3}c*→^{3}t* conversion proceeds with a time constant of ca. 500 ns at room temperature.$^{4)}$ On the other hand, in the series of styrylarenes, ArCH=CHPh, only anthryl group among the above aromatic nuclei was found to induce one-way isomerization,$^{2,3)}$ however, the conversion of ^{3}c* to ^{3}t* took place too rapidly to be observed in nanosecond scale.

To reveal that the triplet excitation energy of aromatic nuclei at the ethylenic carbon effects the mode of the isomerization in the series of ArCH=CHPh and to observe ^{3}c* situated in an energy minimum converting to ^{3}t*, we examined the effect of an aromatic nucleus with a triplet energy lower than that of anthracene in the series of ArCH=CHPh. We now report that substitution of 3-perylenyl group (E_T=35.1 kcal mol^{-1})$^{9)}$ as Ar (3-(2-phenylethenyl)perylene (**1**)) definitely induced one-way isomerization through ^{3}c*→^{3}t* conversion proceeding with an activation barrier of 6.6 kcal mol^{-1} as revealed by transient absorption spectroscopy.

trans-**1**$^{9,10)}$ and cis-**1**$^{10)}$ exhibit different fluorescence spectra. The quantum yields of fluorescence emission (Φ_f) were 0.64 and 0.60, and the fluorescence lifetime were 3.8 and 3.5 ns in benzene for cis- and trans-**1**, respectively.



cis-**1** trans-**1**

On irradiation of cis-**1** in benzene under argon atmosphere with a 366 nm light isolated from a high pressure mercury lamp, cis-**1** was completely converted to trans-**1** where the quantum yield of the isomerization ($\Phi_{c\rightarrow t}$) linearly increased with increasing initial cis-**1** concentration exceeding unity; $\Phi_{c\rightarrow t}$ was as high as 3.1 at initial cis-**1** concentration of 1.15×10^{-3} M.[11] On the contrary, trans-**1** was not changed at all under the similar condition.

The one-way cis→trans isomerization of **1** will proceed by the following scheme[12] likewise to one-way isomerization of other aromatic ethylenes,[3,4] where c and t mean the cis- and trans-**1**, respectively, and the superscripts 1, 3, and * mean the singlet state, the triplet state, and the excited state, respectively. According to this scheme the $\Phi_{c\rightarrow t}$ value is described as Eq. 1, where k_q is the rate constant for energy transfer from $^3t^*$ to ^1c, τ_T (=$1/k_d$) is the lifetime of $^3t^*$, and Φ_{isc} is the quantum yield for intersystem crossing from $^1c^*$ to $^3c^*$.

$$^1c \xrightarrow{h\nu} {}^1c^* \xrightarrow{\Phi_{isc}} {}^3c^* \qquad {}^3c^* \longrightarrow {}^3t^*$$

$$^3t^* + {}^1c \xrightarrow{k_q} {}^1t + {}^3c^* \qquad {}^3t^* \xrightarrow{k_d} {}^1t$$

$$\Phi_{c\rightarrow t} = \Phi_{isc}(1 + k_q\tau_T[\text{cis-}\mathbf{1}]) \quad (1)$$

Excitation of either cis-**1** or trans-**1** in benzene under argon at room temperature with a 308 nm XeCl laser gave the same transient absorption at 800 ns after the pulse. The absorption showed a maximum at 580 nm accompanied by a smaller maximum peak at 540 nm, and decayed with nearly 14 μs lifetime. The same transient absorption was observed on excitation of Michler's ketone as a sensitizer in the presence of either of these isomers with a 360 nm beam from a dye laser pumped by a XeCl laser, which indicates that the observed absorption was due to the triplet state of **1**. Since no isomerization occurs from the trans to the cis, the observed triplet is assigned to $^3t^*$, which is produced either on excitation of trans-**1** or by the conversion of $^3c^*$ resulted from the excitation of cis-**1**.[3,4]

However, lowering of temperature to 193.4-228.8 K enabled one to observe the conversion of $^3c^* \rightarrow {}^3t^*$. On excitation of cis-**1** the absorbance at 510-520 and 550-560 nm were decreased with the concomitant growing of the absorbance at 580 nm in the μs time scale. Figure 1 shows a typical example measured at 205.4 K. The conversion rate constant ($k(^3c^* \rightarrow {}^3t^*)$) was increased from 6.7×10^4 s^{-1} to 1.03×10^6 s^{-1} with increase of temperature from 193.4 K to 228.8 K. The Arrhenius plot gave an activation energy E_a and a frequency factor A for the $^3c^* \rightarrow {}^3t^*$ isomerization as 6.6 kcal mol^{-1} and 2.1×10^{12} s^{-1}, respectively.

The above results clearly support our proposition that the lowering in the triplet excitation energy of aromatic nuclei on the unsaturated bond alters the mode of the isomerization from the traditional two-way to one-

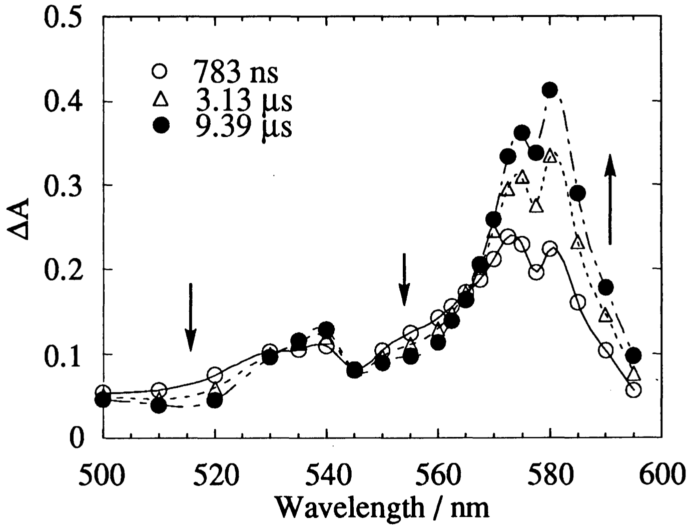
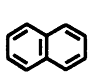
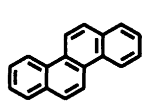
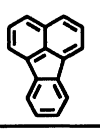
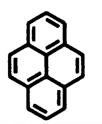
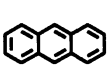
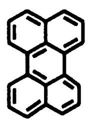


Fig. 1. T-T absorption spectra determined on excitation of cis-1 on 308 nm laser in methylcyclohexane at 205.4 K showing the $^3c^* \rightarrow {}^3t^*$ conversion.

way. Table 1 summarizes the results for the series of styrylarenes. In this series the mode is changed when the triplet excitation energy of aromatic nucleus is reduced less than 48 kcal mol^{-1}, which is nearly 10 kcal mol^{-1} lower than the turning point from the two-way to one-way in the series of ArCH=CH^{t}Bu (57 kcal mol^{-1}) probably due to the effect of the phenyl group to stabilize the $^3p^*$ conformation by delocalization of an unpaired electron.[3)]

To the best of our knowledge this is the first paper to observe directly the $^3c^* \rightarrow {}^3t^*$ isomerization of styrylarenes.

Table 1. The Mode of the Photoisomerization of ArCH=CHPh in the Triplet State

ArH							
E_T(ArH) a)	84.3	60.9	56.6	54.2	48.2	42	35.1
Mode of Isomerization	two-way	two-way	two-way	two-way	two-way	one-way	one-way
λ_{max}(T-T)/nm (τ_T/μs) b)	<360 c) (0.63)	400, 500 d) (0.14)	<400 e) (0.14)	480, 600 f) (0.50)	470, 520 g) (27)	460, 620 h) (190)	540, 580 (100)

a) In kcal mol^{-1}. b) Under degassed condition. c) Ref. 13. d) Ref. 14. e) Ref. 7a. f) Ref. 7b. g) Ref. 6. h) Ref. 4.

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10) A mixture of cis and trans isomers of **1** was prepared from the Wittig reaction of benzyltriphenylphosphonium bromide with 3-perylenecarbaldehyde. The mixture was first recrystallized from hexane to seperate the trans isomer, which was purified by further recrystallization from hexane-benzene (1:1). The remaining matter was further subjected under red light to silica gel flash column chromatography and eluted with hexane-benzene (4:1) to separate the cis and trans isomers. The obtained cis-**1** was purified by recrystallization from hexane-benzene (10:1). cis-**1**: Mp 148-149.5 °C. Found: C, 94.87; H, 5.38%. Calcd for $C_{28}H_{18}$: C, 94.88; H, 5.12%. trans-**1**: Mp 232-233 °C. Found: C, 94.95; H, 5.37%. Calcd for $C_{28}H_{18}$: C, 94.88; H, 5.12%.

11) The plot of $\Phi_{c\rightarrow t}$ vs. [cis-**1**] gave the $k_q\tau_T$ value as $4.6\mathrm{x}10^3$ M^{-1}.

12) If the isomerization took place in the excited singlet state through a quantum chain process, the energy transfer from $^1t^*$ to ^1c to regenerate $^1c^*$ should proceed by the rate constant of $k_q=(k_q\tau_T)/\tau_S$ $=4.6\mathrm{x}10^3\ M^{-1}/3.5\mathrm{x}10^{-9}\ s^{-1}=1.3\mathrm{x}10^{12}\ M^{-1}\ s^{-1}$,11) two orders of magnitude higher than the diffusion controlled rate constant. Thus, the isomerization should take place in the excited triplet state.

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