Short Communication

A new "one-way"-photoisomerizing aromatic olefin: the effect of a fluoranthenyl group on the triplet energy surface

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On direct and triplet-sensitized irradiation the cis isomer of 8-(3,3-dimethyl-1-butenyl)fluoranthene (*cis*-I) isomerized to its trans isomer (*trans*-I) with a yield of 100%; however, *trans*-I did not isomerize to *cis*-I under similar conditions. The concentration dependence of the isomerization quantum yield and transient spectrum measurements indicate that the cis → trans isomerization on direct irradiation also proceeds adiabatically on the triplet manifold. This type of "one-way" isomerization can be ascribed to reaction on the triplet energy surface, on which the trans geometry is more stabilized than the twisted geometry by the introduction of a large aromatic moiety and thus the former is the sole decay funnel to the ground state.

1. Introduction

It has long been accepted that olefins generally undergo mutual photoisomerization between their cis and trans isomers, and there have been intensive investigations on stilbenes [1 - 7], naphthylethylenes [8, 9] and styrenes [10, 11]. However, we recently found that olefins bearing a 2-anthryl group on the ethylenic linkage undergo cis → trans "one-way" isomerization and proposed a novel mechanism for this isomerization [12, 13]. Thus, the cis triplet ($^3c^*$) generated by energy transfer undergoes twisting adiabatically to give the trans triplet ($^3t^*$) which either deactivates to the trans isomer or undergoes energy transfer to the cis isomer to regenerate $^3c^*$. In this mechanism the deactivation of the triplet state occurs exclusively from $^3t^*$. This is in strong contrast with the mechanism accepted for stilbenes and other compounds [1 - 9], in which the deactivation of the triplet state takes place from the twisted geometry ($^3p^*$), thus giving a mixture of cis and trans isomers.
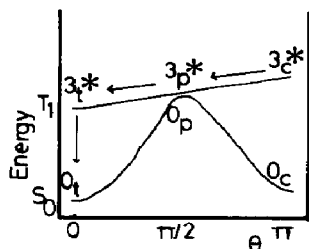

Fig. 1. Triplet energy surface of one-way-photoisomerizing olefins.

For the occurrence of one-way isomerization we proposed a triplet energy surface which decreases in energy monotonically with the angle of twist around the ethylenic bond from the cis to the trans geometry (Fig. 1) [12, 13]. This type of triplet energy surface might be created by the introduction of an aromatic moiety with a low triplet energy which stabilizes $^3t^*$ to a greater extent than $^3p^*$. To investigate this further, we prepared another aromatic olefin, 8-(3,3-dimethyl-1-butenyl)fluoranthene (I) and examined its photochemical behaviour on direct and sensitized irradiation.

2. Results and discussion

On irradiation sensitized with ketones (in benzene) and dyes (in 50vol.%methanol—50vol.%benzene) such as biacetyl, Michler's ketone, acridine orange and proflavine, cis-I isomerized efficiently to trans-I with a yield of 100%.

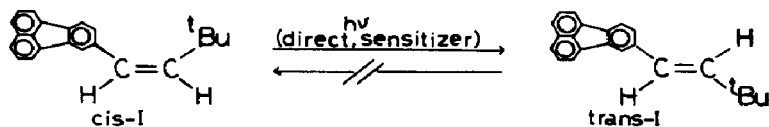

Table 1 summarizes the effects of various sensitizers examined. Of the sensitizers employed, those with triplet energies higher than 205 kJ mol^{-1} sensitized the cis → trans isomerizatrion; the calculated free energy changes $\Delta G°$ for electron transfer [21] from the sensitizer triplets to cis-I are not correlated with the efficiencies. On the contrary, none of the sensitizers employed sensitized trans → cis isomerization. The quantum yield for cis → trans isomerization increased linearly with increasing [cis-I] and exceeded unity at a concentration as low as 1×10^{-3} M for sensitization by Michler's ketone. These results can be reasonably taken to imply that the present isomerization takes place through the same mechanism as that proposed for the photoisomerization of anthrylethylenes; introduction of a fluoranthenyl group, whose triplet energy is nearly 225 kJ mol^{-1} [17], significantly affects the triplet energy surface, as observed for the anthrylethylenes (Fig. 1).

Direct irradiation of cis-I in benzene also led to its 100% isomerization to trans-I; however, trans-I did not isomerize to cis-I under similar conditions. The quantum yield increased linearly with increasing [cis-I], as shown in

TABLE 1

Quantum yields for triplet-sensitized isomerization of cis-I [a]

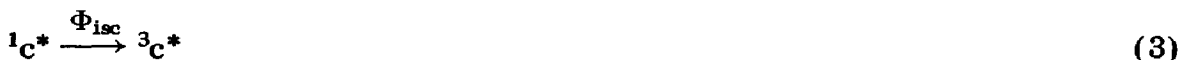| Sensitizer	E_T (kJ mol^{-1})	Φ_{isc}^S [b]	$\Phi_{c \to t}$	$\Phi_{c \to t}/\Phi_{isc}$
Thionine	165 [c]	0.55 [g]	0.0	0.0
Rose bengal	185 [d]	0.76 [h]	0.0	0.0
Eosin Y	190 [e]	0.44 [i]	0.0	0.0
Fluorescein	195 [e]	0.05 [g]	0.0	0.0
Acridine orange	205 [e]	0.30 [i]	0.81	2.7
Proflavine	215 [e]	0.45 [i]	0.57	1.3
Biacetyl	230 [f]	1 [f]	4.9	4.9
Michler's ketone	260 [f]	1 [f]	2.3	2.3

[a] $[cis\text{-}I] = 1 \times 10^{-3}$ M.
[b] Quantum yield for intersystem crossing of sensitizer.
[c] From ref. 14.
[d] From ref. 15.
[e] From ref. 16.
[f] From ref. 17.
[g] From ref. 18.
[h] From ref. 19.
[i] From ref. 20.
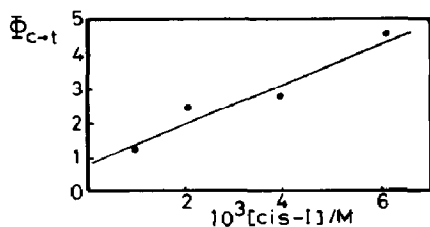
Fig. 2. Effect of cis-I concentration on its isomerization quantum yield on direct irradiation.
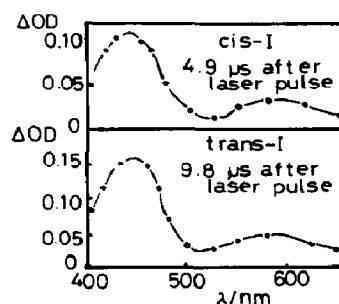
Fig. 3. T–T absorption spectra of cis-I and trans-I in benzene.

Fig. 2, indicating that the isomerization proceeds through a quantum chain process. The intercept (0.83) in Fig. 2 corresponds to a quantum yield which has no contribution from the quantum chain process.

cis-I exhibited a fluorescence spectrum different from that of trans-I in both shape and lifetime. The fluorescence quantum yield Φ_f was determined as 0.16 for cis-I and 0.19 for trans-I in benzene at ambient temperature. If the internal conversion from the excited singlet of cis-I can be reasonably neglected, i.e. $\Phi_{isc} + \Phi_f = 1$, then $\Phi_{isc} = 1 - \Phi_f = 0.84$. This value is in good agreement with the intercept in Fig. 2 mentioned above. Therefore, it can be assumed that on direct irradiation the isomerization takes place from the triplet state (Scheme 1).

The triplet mechanism is supported by measurements of transient absorption spectra of cis- and trans-I. Figure 3 shows the transient spectra

observed on nitrogen laser excitation of the olefin (4×10^{-4} M) in benzene. Both isomers exhibit the same spectra, having two bands at 400 - 480 and

$$^0C \xrightarrow{\ h\nu\ } {}^1C^* \tag{1}$$

$$^1C^* \xrightarrow{\ \Phi_f\ } {}^0C + h\nu_f \tag{2}$$

$$^1C^* \xrightarrow{\ \Phi_{isc}\ } {}^3C^* \tag{3}$$

$$^0S \xrightarrow{\ h\nu'\ } {}^1S^* \tag{1'}$$

$$^1S^* \xrightarrow{\ \Phi_{isc}^S\ } {}^3S^* \tag{2'}$$

$$^3S^* + {}^0C \longrightarrow {}^0S + {}^3C^* \tag{3'}$$

$$^3C^* \longrightarrow {}^3P^* \longrightarrow {}^3t^* \tag{4}$$

$$^3t^* \xrightarrow{\ k_d\ } {}^0t \tag{5}$$

$$^3t^* + {}^0C \xrightarrow{\ k_q\ } {}^0t + {}^3C^* \tag{6}$$

Scheme 1.

550 - 650 nm with the same lifetime ($\tau_T = 25$ μs) as measured at the peak wavelengths. Under similar conditions fluoranthene exhibited its T–T absorption at 400 - 440 nm ($\tau_T = 30$ μs). The spectra of the olefin were effectively quenched by azulene ($E_T = 165$ kJ mol^{-1} [22]); the quenching rate constant was determined as 3.6×10^9 M^{-1} s^{-1} on excitation of cis-I. From these results the observed transient spectra can be reasonably assigned to the trans triplet.

The results of stationary irradiation and flash photolysis indicate that the triplet mechanism describes the cis → trans one-way isomerization on direct irradiation (Scheme 1). According to this mechanism, the quantum yield is expressed by

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

where k_q is a rate constant for the energy transfer from $^3t^*$ to cis-I. Dividing the slope (600 M^{-1}) by the intercept (0.83) in Fig. 2 gives $k_q\tau_T$ as 720 M^{-1}.

This magnitude of quenching rate can only be achieved in the singlet state when the quenching rate constant is larger than the diffusion-controlled value. However, the trivial and dipole–dipole mechanisms for energy transfer are not likely to be in operation, because the singlet energy of cis-I is higher than that of trans-I and there is only a small overlap between the fluorescence spectrum of trans-I and the absorption spectrum of cis-I. A mechanism involving a ground state complex can be also ruled out since there was no evidence for the formation of such a complex in either the absorption and fluorescence spectra or the transient absorption spectra for various concentrations of trans-I.

k_q is calculated to be $2.9 \times 10^7 \, M^{-1} \, s^{-1}$ by using the τ_T (25 µs) obtained above. The following equation is established for endothermic energy transfer [23]:

$$k_q = A \exp\left(-\frac{\Delta E_a}{RT}\right)$$

where

$$-\Delta E_a = \Delta E_T = E_T(trans\text{-I}) - E_T(cis\text{-I})$$

On substituting $k_q = 2.9 \times 10^7 \, M^{-1} \, s^{-1}$ into this equation and assuming $k_q = 5 \times 10^9 \, M^{-1} \, s^{-1}$ at $\Delta E_T = 0$, the energy transfer from $^3t^*$ to cis-I is estimated to be endothermic by 13 kJ mol^{-1}.

The above results clearly indicate that the triplet energy surfaces are not essentially the same for all types of aromatic olefin (for example, compare those proposed for stilbenes [1 - 7]) but that they are highly dependent on the structure of the aryl groups on the ethylenic linkage; the energy of $^3t^*$ seems especially to be mainly governed by the triplet energy of the aryl group [12, 13, 24]. For this reason, olefins bearing an aryl group with a low triplet energy, such as anthryl and fluoranthenyl, undergo one-way isomerization through the quantum chain process, and the trans triplet, which is lower in energy than the twisted triplet, is the key intermediate of isomerization.

3. Experimental details

3.1. Materials

A mixture of cis- and trans-I was synthesized by the condensation of dimethylpropanal with the ylide prepared from (8-fluoranthenyl)methyltriphenylphosphonium bromide and butyllithium in ether. The cis and trans isomers were separated by silica gel column chromatography by eluting with hexane and were crystallized from benzene. Sensitizers were purified by crystallization or distillation. Benzene was distilled over calcium hydride; methanol was distilled after being dried by Zeolite A-3.

3.2. Quantum yields

Quantum yields for cis → trans isomerization were determined using potassium tris(oxalato)ferrate(III) actinometry [25]. Irradiation was performed at 435 nm for biacetyl sensitization, at 313 nm for Michler's ketone sensitization and at 366 nm for direct irradiation. All of these lines were isolated from a 400 W high pressure mercury lamp with appropriate filters. Under dye-sensitized conditions irradiation was performed with 490 ± 10 nm light isolated from a 500 W xenon lamp through a Shimadzu–Bausch and Lomb monochromator. The samples were deaerated by bubbling with argon.

3.3. Fluorescence spectra

Fluorescence spectra were recorded on a Hitachi MPF-4 spectro-fluorometer at room temperature and fluorescence quantum yields were calculated by comparing corrected fluorescence spectra of the olefins with the spectrum of fluoranthene as a standard [26].

3.4. Laser flash photolyses

Laser flash photolyses were performed using a nitrogen laser (5 ns; 4 mJ per pulse) for excitation at 337.1 nm and a 150 W xenon lamp as the monitoring light source. A photomultiplier (Hamamatsu Photonix R446 or R212) and a storage oscilloscope (Iwatsu TS-8123) were used for the detection. The samples were degassed by 3 - 5 freeze–thaw cycles.

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