Photochemical One-Way Adiabatic Isomerization of Aromatic Olefins

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Contents

I. Overview

Substitution of an anthracene nucleus on an unsaturated linkage leads to a drastic change in the isomerization of the double bond: from the traditionally recognized mutual "two-way" isomerization between the cis and trans isomers to a unique one-way isomerization, solely from cis to trans isomers, through a quantum chain process. Many olefins have been shown to undergo one-way isomerization in an adiabatic way at the triplet state.

This article describes the feature of the one-way adiabatic isomerization of aromatic olefins and imines and structural factors that control the mode of the isomerization. The nature of the quantum chain process in the triplet isomerization is described. Finally, another feature of anthracene-substituted unsaturated compounds, undergoing internal rotation in the excited state, is also described.

II. Introduction

The mechanism and the potential energy surfaces of cis–trans isomerization of olefins have been actively investigated since the extensive works for the sensitized isomerization of stilbenes by Hammond, Saltiel, and co-workers in 1960s.[1–6] As a result it was revealed that stilbene undergoes mutual isomerization between cis and trans isomers in the singlet or triplet manifold on direct irradiation or triplet sensitization, respectively.[1–10] Stilbenes with polar substituents on phenyl rings also resulted in mutual isomerization as revealed by Schulte-Frohlinde and Goerner.[11–14] Because of these works and the calculation by Mulliken for the potential energy surface of the excited and the ground state of ethylene along the rotation of the unsaturated linkage,[15–17] it had long been accepted that the olefins generally would undergo isomerization mutually between their cis and trans isomers.

However, in 1983 Arai, Karatsu, Sakuragi, and Tokumaru reported that substitution of an anthracene nucleus on a C=C double bond led to a novel one-way isomerization, taking place solely from the cis isomer to the trans isomer through a quantum chain process resulting in 100% trans isomer by photoirradiation.[18] This one-way isomerization takes place as an adiabatic process in the triplet manifold on direct irradiation as well as on triplet sensitization.[18–24] Table I briefly compares the behaviors of stilbene and styrylanthracene. The isomerization mode, one-way or two-way, of aromatic olefins in the triplet state is further revealed to be governed by the properties of the substituents on their ethylenic bonds.[25–32] Thus, olefins (ArCH=CHR) having an aromatic group (Ar) with a low triplet energy (E_T) like anthracene (42.0 kcal mol^{-1})[33] undergo the one-way isomerization regardless of the substituents (R) on the other ethylenic carbon.[18–24] Interestingly, 1-styrylpyrene having a pyrene nucleus with a triplet energy slightly higher than anthracene

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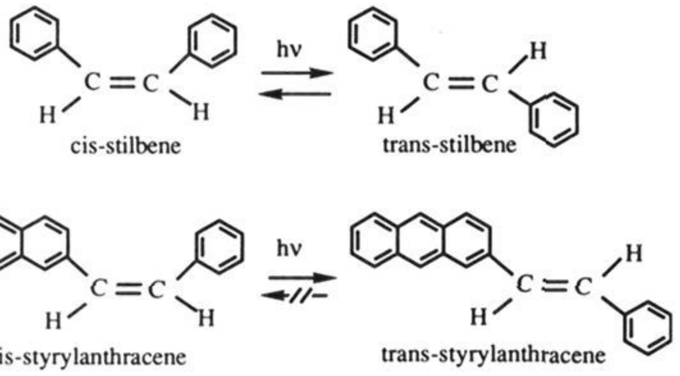
isomerizes by the two-way mode with dual character; the photoisomerization occurs apparently in mutual way; however, cis → trans isomerization takes place through a quantum chain process in the triplet manifold.[25,26]

This article describes on the present status of the features and the potential energy surfaces of one-way *isomerization proceeding as an adiabatic* process at the triplet state by comparing its features to the other modes of the isomerization, particularly, the conventional two-way isomerization, and the factors controlling the mode of isomerization. Moreover, in connection with the behavior of the singlet excited states resulting from direct excitation of some of these olefins, a mention is made to the one-way internal rotation around the single bond connecting an aromatic nucleus to the double bond in contrast to the hitherto accepted nonequilibration of excited rotamers (NEER) concept, that is, no conversion between the rotamers at the excited state.[34-36]

To focus the description to one-way adiabatic process at the excited triplet state, the following types of one-way isomerization are not mentioned: the isomerization via the radical cations of olefins produced by sensitization with electron acceptors like 9,10-dicyanoanthracene,[37] free-radical or atom-catalyzed isomerization,[38] isomerization induced by selective excitation of an isomer among isomers with sensitizers of appropriate triplet energies,[39] or isomerization with proper wavelength of light.



Katsumi Tokumaru was born in Tokyo. He studied at the University of Tokyo to receiving his B.Sc. in 1956 after working with the late Prof. Sanichiro Mizushima on vibrational spectroscopy of internal rotation in the undergraduate research program. Subsequently he did graduate work at the University of Tokyo with Prof. Osamu Simamura on organic free-radical chemistry of organic peroxides and received his degree in 1961. He then worked as a research associate, lecturer, and associate professor at the Department of Chemistry, University of Tokyo. In 1975 he was appointed a full professor of the University of Tsukuba, which was founded in 1973 in a new science city outside of Tokyo. He started his laboratory working on physical organic approach of photochemistry by amalgamating traditional organic methods with methods of physical chemistry. There he served as the department chairmen (1978–1980), Vice President for research development and international relations (1988–1990), and provost of a cluster (1991–present). He has worked for Japanese Photochemical Association, the Chemical Society of Japan (Vice President, 1990–1992). He has also worked as a titular member of IUPAC photochemistry commission (1981–1989) and worked for organization of various international and domestic conferences particularly on photochemistry. He received the 1990 award of the Chemical Society of Japan for his research on photochemistry. He has authored 200 scientific papers on organic free-radical chemistry and photochemistry. His principal research interest is focused on the newly founded isomerization of double bonds and rotation of single bonds in excited unsaturated molecules, behaviors of radical ions of unsaturated compounds, and photoinduced electron transfer of dyes and photoinitiators like organic peroxides.

Table I. Features of the One-Way and Two-Way Isomerization of Aromatic Olefins in the Triplet State

	one-way	two-way
example	2-styrylanthracene	stilbene
at the photostationary state	100% trans	cis + trans
quantum yield of isomerization	$\Phi_{c\to t} \gg 1$	$\Phi_{c\to t}$ = ca. 0.5
	$\Phi_{t\to c} = 0$	$\Phi_{t\to c}$ = ca. 0.5
τ_T	ca. 100 μs	ca. 100 ns
intermediate for deactivation	trans triplet ($^3t^*$)	perpendicular triplet ($^3p^*$)

III. Photoisomerization around the Double Bond

A. One-Way Isomerization of 2-Anthrylethylenes

1. Quantum Yields of Isomerization and T–T Absorption Spectra

Either direct or sensitized irradiation of 2-anthrylethylenes (1) resulted in one-way cis-to-trans isomerization.[18-24,32] Figure 1 illustrates the quantum yield for cis-to-trans isomerization ($\Phi_{c\to t}$) which increases linearly with cis isomer concentration to attain

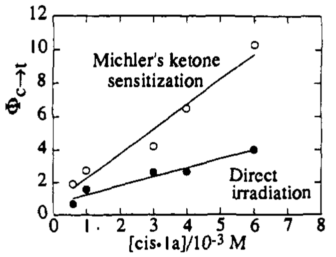
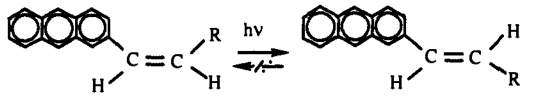


Figure 1. Quantum yields of cis → trans isomerization of **1a** on direct and Michler's ketone sensitization in benzene at room temperature (adapted from refs 19 and 32).

4.0 and 10.3 on direct irradiation and on Michler's ketone sensitization, respectively, at [*cis*-**1a**] = 6 × 10^{-3} M.

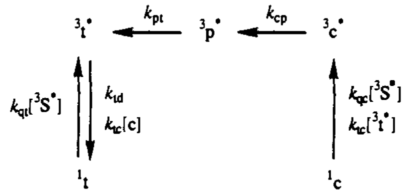


cis-1, a: R=ᵗBu, b: R=Me,
c: R=Ph, d: R=2-naphthyl

trans-1

The triplet potential energy surface of the one-way isomerization was first proposed in 1983[18] as simply descending from the cis triplet ($^3c^*$) to the trans triplet ($^3t^*$), passing through the perpendicular triplet ($^3p^*$) as shown in Figure 2a. In this potential energy surface, the resulting $^3t^*$ undergoes either unimolecular deactivation to the ground-state trans (^1t), or energy transfers to the ground-state cis (^1c) to regenerate $^3c^*$ therefore accomplishing the quantum chain process. Figure 2b shows a typical potential energy surface of the two-way isomerizing olefins like stilbene,[1,2,40–44] in which the deactivation takes place solely from the perpendicular conformation. To explain the specific direction of the one-way isomerization from cis to trans, one could suppose that the energy minimum would be slightly shifted from just perpendicular conformation to trans side (Figure 2c). However, this assumption could not explain the quantum chain process occurring. The energy difference between the triplet surface to the ground-state surface at this conformation is too small to excite ^1c to $^3c^*$. Thus, the above results could be explained by the potential energy surfaces of Figure 2a, which was revised to Figure 4 as described later, and the mechanism described in Scheme I,[18–24,32] where $^3S^*$ is the sensitizer triplet and *k*'s are the rate constants for the corresponding processes.

Scheme I



According to Scheme I, $\Phi_{c\to t}$ is expressed by eq 1 and is linearly increased with the cis isomer concentration as observed in Figure 1, where, Φ_T is the quantum yield of intersystem crossing of the sensitizer, and k_{td} and k_{tc} are the rate constant of unimolecular deactivation from $^3t^*$ and the rate constant of energy transfer from $^3t^*$ to ^1c, respectively.

$$\Phi_{c\to t} = \Phi_T\left(1 + \frac{k_{tc}[\text{cis}]}{k_{td}}\right) \tag{1}$$

Either cis or trans isomer of **1** in benzene at room temperature under degassed conditions affords the same T–T absorption spectra nearly 10 μs after the laser excitation which are illustrated in Figure 3.[19,20,24,32,45–47] The observed spectra are assigned not to $^3p^*$ but to $^3t^*$ on the following grounds. First, to explain the quantum chain process the $^3t^*$ must lie at an energy minimum in the triplet potential energy surface. Second, the observed spectra are shifted to the longer wavelength in the order of R = alkyl (ᵗBu and Me) to phenyl and then to naphthyl, and the intensity at longer wavelength region increases in the same order. If the observed triplets retained perpendicular conformation, **1** would exhibit essentially the same absorption at the longest wavelength due to the biggest chromophore, anthrylmethyl moiety, regardless of the β-substituent R. Third, the observed triplet state has a lifetime of hundreds of microseconds, indicating a large energy difference over the ground state. The perpendicular triplet state ($^3p^*$) is very close in energy to ^1p[44] and, therefore, deactivates to the ground state with shorter lifetime of 10^1 ns as observed for stilbene. Fourth, the results of the calculation of the oscillator strength of the T–T absorptions support the assignment to $^3t^*$ not to $^3p^*$.[20]

2. Potential Energy Surfaces of One-Way Isomerization of 2-Anthrylethylenes

The quantum yields of the isomerization and the T–T absorption spectra indicate that $^3t^*$ is lower in energy than both $^3c^*$ and $^3p^*$ and, therefore, is the most stable conformation in the excited triplet state.[19,20,24,32,45–48]

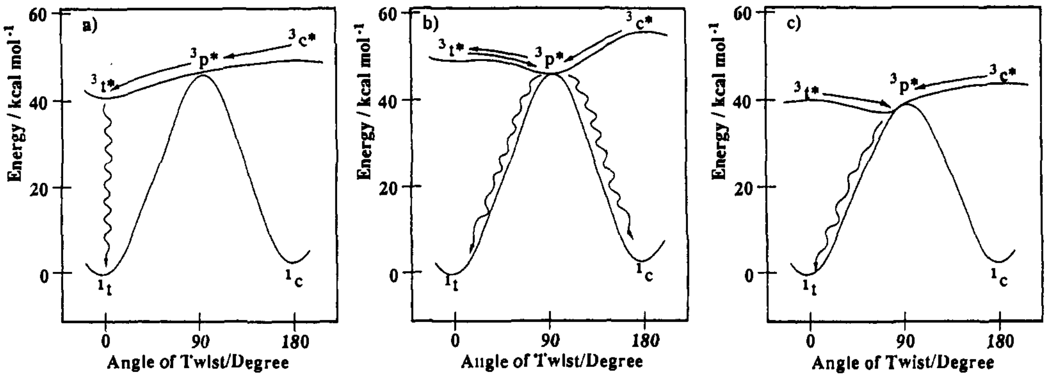


Figure 2. Potential energy surfaces proposed for one-way (a and c) and two-way (b) isomerizing olefins.

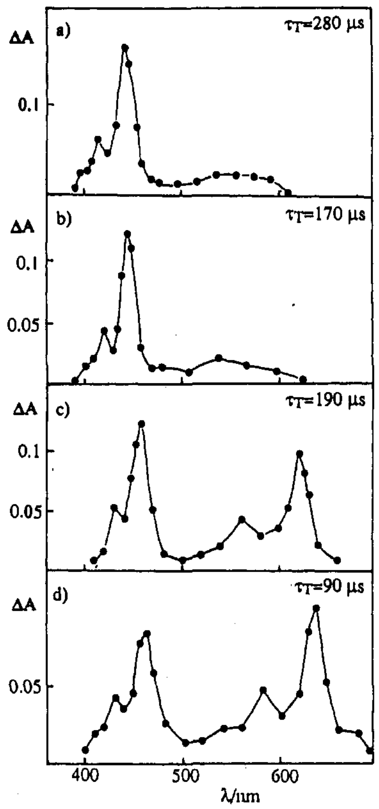
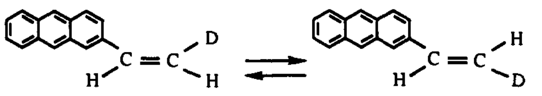


Figure 3. T–T absorption spectra of the anthrylethylenes (1) in benzene at room temperature observed at 10 μs after the laser excitation (adapted from refs 19, 20, and 32).

The $^3c^* \rightarrow {}^3t^*$ conversion proceeds by overcoming an energy barrier as in Figure 4a not as descending from $^3c^*$ to $^3t^*$ as depicted in Figure 2a.

The presence of an activation barrier for $^3c^* \rightarrow {}^3t^*$ isomerization is definitely demonstrated by the temperature effect on the cis–trans isomerization of a deuterated olefin (2-anthryl-CH═CHD, **2**).[49] This olefin has essentially the same electronic energy between its cis and trans isomers, and therefore its potential energy surface must be symmetric between both cis and trans at the ground state.



cis-2 trans-2

The quantum yields of trans → cis isomerization of **2** increased with temperature from 0.02 at 16 °C to 0.1 at 47 °C, indicating that $^3t^* \rightarrow {}^3c^*$ conversion proceeds by overcoming an activation energy of 11.1 kcal mol^{-1} with a frequency factor of 5×10^{11} s^{-1}.[49]

The above indicates that the one-way isomerization of **1a–d** might proceed by the similar across-a-ridge isomerization.[21,24,32] Transient spectroscopy immediately after the laser excitation affords more precise information with which to draw the potential energy surfaces of one-way isomerization in more detail. With **1a**, the absorption (λ_{max} 443 nm) observed immediately after the laser excitation of the cis isomer in benzene at room temperature was changed, shifting the absorption maximum to longer wavelength (λ_{max} 445 nm) at 500 ns after the excitation. The initial absorption was assigned mostly to $^3c^*$ and the later one to $^3t^*$. In the time profile of the transient absorption, the initial decay observed at 440 nm is accompanied by an absorption rise with the same time constant of nearly 500 ns observed at 450 nm. Measurement at varying temperature gave an activation energy of 6 kcal mol^{-1} and frequency factor of 5×10^{10} s^{-1}.[21,24,32]

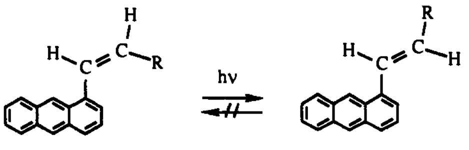
As to **1a**, the activation energy, combined with the energies of $^3c^*$ (E_T = 42.5 kcal mol^{-1}), and $^3t^*$ (42.5 kcal mol^{-1}), determined by their phosphorescence spectra and the energy difference between cis and trans at the ground state (estimated as 5 kcal mol^{-1}), enabled one to draw the potential energy surface for **1a** as shown in Figure 4a.[21,24,32]

In the cis → trans isomerization of **1a**, addition of oxygen strongly suppresses the isomerization due to the quenching of $^3c^*$, giving singlet oxygen which was detected by its characteristic emission at 1.27 μm. Laser excitation of *cis*- and *trans*-**1a** in benzene in the presence of 1.3×10^{-4} M oxygen, afforded singlet oxygen in quantum efficiencies (Φ_Δ) of nearly 0.9 and 0.8 on the basis of $^3c^*$ and $^3t^*$, respectively.[23]

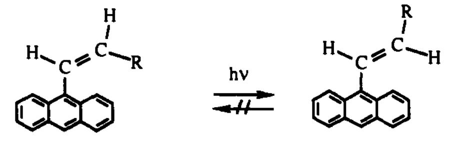
On the other hand, with **1c**, the isomerization of $^3c^* \rightarrow {}^3t^*$ takes place too rapidly to be followed even at the nanosecond time scale. However, on laser excitation, *trans*-**1c** gave nearly the same efficiency of singlet oxygen production as from **1a**, 0.9, while *cis*-**1c** afforded a considerably less amount of singlet oxygen (Φ_Δ = 0.6). A sufficient amount of singlet oxygen would be produced if $^3c^*$ completely changed to $^3t^*$. The above facts together with the failure to observe its $^3c^*$ absorption in the nanosecond time scale suggest that in **1c** $^3c^*$ is located at a very shallow minimum and undergoes twisting more rapidly than it is quenched by oxygen; furthermore, $^3p^*$ may be located at the top or at a very shallow minimum which can be sufficiently passed through rapidly preceding unimolecular deactivation, but can be quenched by oxygen to accelerate the deactivation, therefore giving a reduced amount of singlet oxygen.[23]

These observation together with the phosphorescence data afforded the potential energy surface of **1c** as shown in Figure 4b.

As to the effect of the substitution position of the anthracene nucleus on the photoisomerization, 1- (**3a**) and 9-anthrylethylenes (**4a**) underwent one-way cis → trans isomerization as an adiabatic process similar to 2-anthrylethylenes. The isomerization of $^3c^* \rightarrow {}^3t^*$ in **3a** and **4a** also took place by across-a-ridge isomerization in the time scale of hundreds of nanoseconds.[50]



cis-3, a: R=^{t}Bu, b: R=Ph *trans*-3



cis-4, a: R=^{t}Bu, b: R=Ph *trans*-4

The T–T absorption spectra observed just after the laser excitation gradually shifted to that of trans isomers

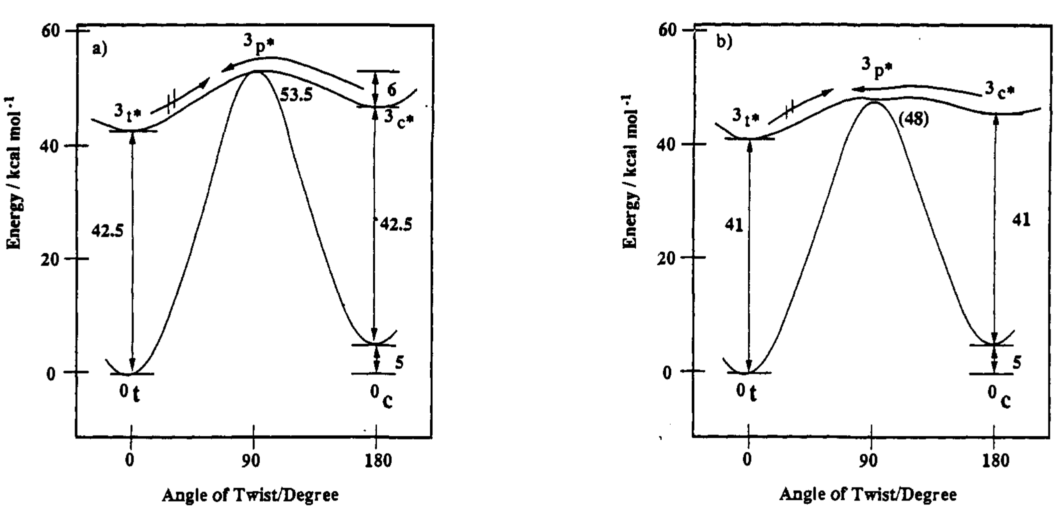


Figure 4. Potential energy surfaces of the isomerization of **1a** (a) and **1c** (b) (adapted from refs 21 and 32).

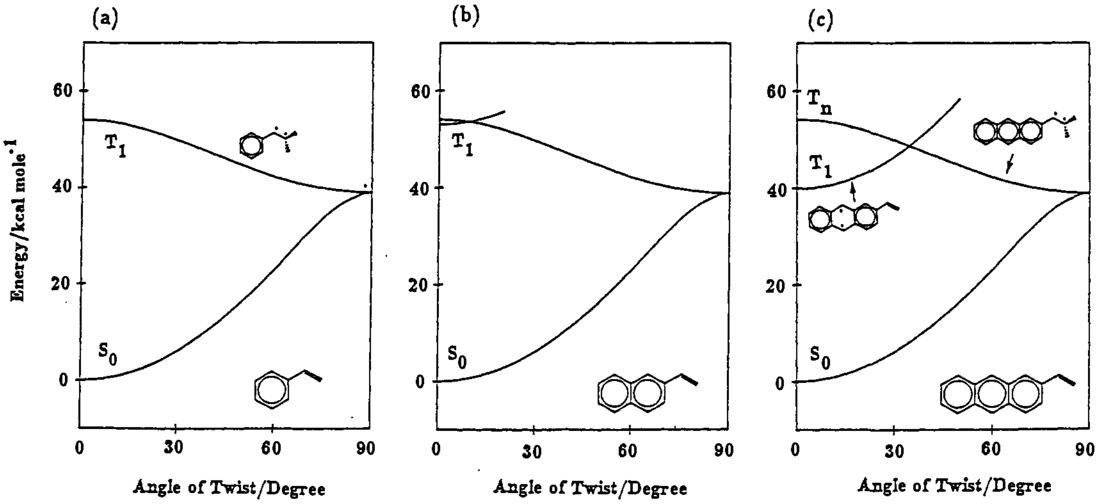


Figure 5. Calculated potential energy surfaces of styrene, 2-vinylnaphthalene, and 2-vinylanthracene (reprinted from ref 51; copyright 1992 Japan Publications Trading Co. (Tokyo)).

in the time scale of 10^2 ns. The barriers for $^3c^* \rightarrow {}^3t^*$ conversion ($E_a(^3c^* \rightarrow {}^3t^*)$) were 4.6 and 3.1 kcal mol^{-1}, for **3a** and **4a**, respectively.[50] Thus, the value of $E_a(^3c^* \rightarrow {}^3t^*)$ decreases in the order of 2-, 1-, and 9-position, probably due to the increase of conjugation between the anthracene nucleus and the double bond which reduces the energy of breaking the double bond.

3. Calculation of the Potential Energy Surface of One-Way $^3c^* \rightarrow {}^3t^*$ Conversion

Figure 5 depicts the calculated potential energy curves of styrene, vinylnaphthalene, and vinylanthracene by MNDO approximation.[51] In the case of styrene (Figure 5a), the lowest triplet state (T_1) corresponds to the "olefin excitation" state in which excitation is mainly localized in the double bond, and its energy decreases with increasing θ and directly correlates to the lowest triplet state at the 90°-twisted structure.

However, in the case of 2-vinylanthracene, at planar geometry, $\theta = 0$, T_1 corresponds to the "ring excitation" state in which excitation is localized in aromatic ring because of the low triplet energy of anthracene nucleus, whereas T_n corresponds to the "olefin excitation" state. With increase of the rotational angle around the double bond the energy of the "ring excitation" state increases while that of the "olefin excitation" T_n state decreases, resulting in crossing of T_1 and T_n curves at $\theta = 35°$ (Figure 5c).

A similar change of the triplet potential energy surfaces was calculated by CS-INDO CI calculations for stilbene, 2-styrylnaphthalene, and 2-styrylanthracene.[52] Calculation by QCFF/PI program indicates that the potential energy surfaces of the photoisomerization of anthrylethylenes also depend on the substitution position of the anthracene ring at 1- and 9-positions and the barrier of the isomerization decreases in this order.[53]

The above calculations indicate that $^3p^*$ of the one-way isomerizing olefins is not necessarily situated as an energy barrier but can be located in a shallow minimum. Thus, the initially resulting $^3c^*$ twists around the double bond to give $^3p^*$, which is not a deep energy minimum; therefore, $^3p^*$ will be alive much lower than 10^{-8} s, precluding the deactivation from $^3p^*$ to the ground state (^1p).

B. Comparison with the Features of the Conventional Two-Way Isomerization

To discuss further the nature of the one-way adiabatic isomerization, some typical features of the conventional two-way isomerization are described below.

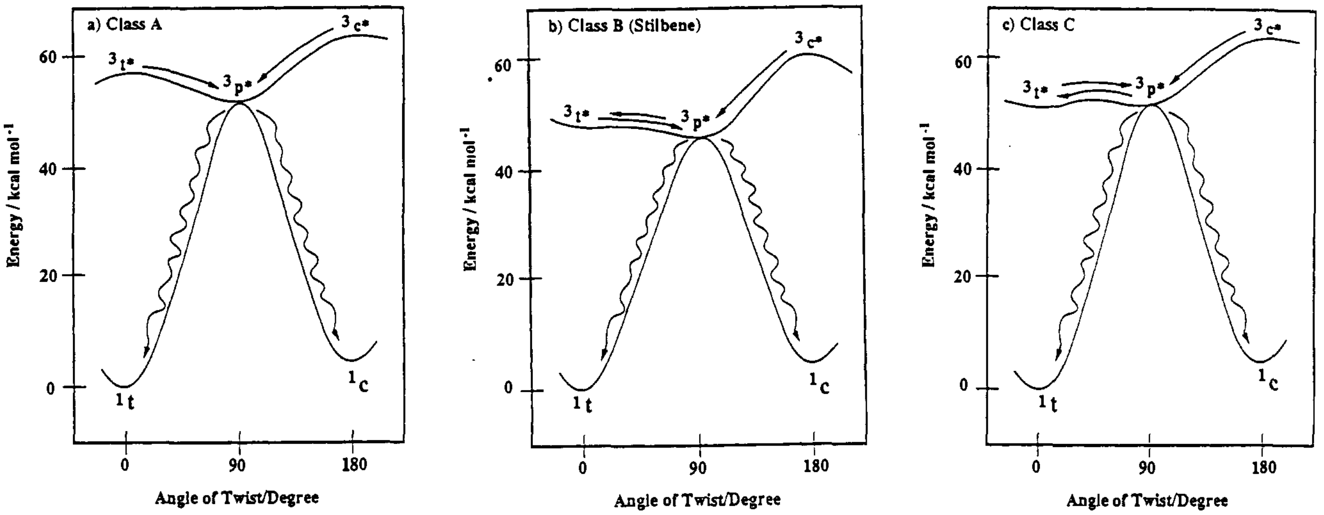


Figure 6. Potential energy surfaces of the photoisomerization of aromatic olefins classified by oxygen and azulene effect on the photostationary state isomer composition (adapted from ref 32).

The potential energy surface of stilbene is shown in Figure 2b.[1,2,40–44] In the ground state, cis lies about 5 kcal mol^{-1} higher than trans due to steric repulsion between the two phenyl groups. In the excited triplet state, $^3c^*$ or $^3t^*$ initially resulting from excitation undergoes twisting around the C═C bond to the more stabilized perpendicular state, $^3p^*$, which subsequently deactivates to the ground state, keeping the same conformation, ^1p, finally giving cis and trans isomers.

On triplet sensitization of stilbene, Saltiel found that addition of azulene increased the ratio of trans to cis isomers at the photostationary state,[1,40] $([t]/[c])_s$, which indicates that $^3p^*$ and $^3t^*$ are both populated as a mixture in a ratio of K_{tp}:1, where K_{tp} is the equilibrium constant between $^3p^*$ and $^3t^*$ ($K_{tp} = [^3p^*]/[^3t^*]$). The apparent quenching rate constant of the stilbene triplet state by azulene (k_q^{Az}), (1–2) × 10^9 M^{-1} s^{-1} in benzene at room temperature, is slower than the diffusion-controlled rate constant and corresponds to $k_{az}/(1 + K_{tp})$, where k_{az} is the rate constant of the energy transfer from $^3t^*$ to Az. These observations enabled to estimate K_{tp} as 8 in benzene.[12]

Furthermore, in the triplet-sensitized irradiation of a naphthylethylene, 2-NpCH═CH^{t}Bu (**5a**), addition of oxygen as well as azulene was shown to increase the $([t]/[c])_s$ values.[54–56] Therefore, $^3t^*$ can be located in an energy minimum and be in equilibrium with $^3p^*$ in triplet state of **5a** and that both oxygen and azulene can quench $^3t^*$ by energy transfer to give trans therefore increasing $([t]/[c])_s$.

On the basis of the different behaviors among the olefins toward azulene and oxygen, the triplet energy surfaces of two-way isomerizing olefins are classified in classes A, B, and C (Figure 6)[32,55] as summarized in Table II, in which included are the rate constants for the quenching of these olefin triplet states by azulene and oxygen measured by laser transient spectroscopy. Usually, cis isomer is less stable than trans isomer in the excited as well as in the ground state as depicted in Figure 6. Therefore, the change of the dynamic behaviors and potential energy surfaces of olefins is mainly determined by the relative stability between $^3t^*$ and $^3p^*$.

In class A, $^3t^*$ is not stable at all and quickly twists along a steep potential curve to $^3p^*$ and neither azulene nor oxygen affected $([t]/[c])_s$ as observed for β-alkylstyrenes (**6**).[57–63] Generally, the rate constants for the sufficiently exothermic energy transfer from $^3t^*$ to oxygen (k_{to}) and azulene (k_{az}) are estimated as (2–3) × 10^9 and (0.8–1) × 10^{10} M^{-1} s^{-1}, respectively, in benzene at room temperature. Accordingly, in the presence of these quenchers in 1 × 10^{-2} M concentration, the pseudo-first-order quenching rate constants are to be (2–3) × 10^7 and 10^8 s^{-1}, respectively. The frequency factor for the twisting around the double bond of the triplet olefins is reasonably assumed as 10^{12} s^{-1}.[21,49,50] Therefore, $^3t^*$ in class A should not have sufficiently long lifetime or sufficient population to be quenched by oxygen or azulene.

Table II. Classification of the Triplet Energy Surfaces of Two-Way Isomerizing Aromatic Olefins (adapted from refs 32 and 55)

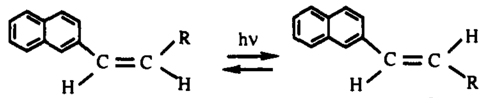
class	example	$k_q^{az\ a}$	$k_q^{ox\ a}$	K_{tp}	$-\Delta G_{tp}{}^b$	ref(s)
A	PhCH═CH$_t$Bu	nq^c	nd^d	>10^2	>3	58,59
B	PhCH═CHPh	(1–2) × 10^9	~8 × 10^9	~8	~1	12
C	2-NpCH═CH^{t}Bu	~7 × 10^9	~3 × 10^9	~1	~0	32,52–54

[a] In dm^3 mol^{-1} s^{-1}. [b] In kcal mol^{-1}. [c] Not quenched. [d] Not determined.

In class B olefins like stilbene[1,2,12,40–44] and 2-styrylnaphthalene (**5b**),[64,65] $^3t^*$ is less stable than $^3p^*$, lies in a shallow energy minimum, and is in equilibrium with $^3p^*$, and therefore, $([t]/[c])_s$ is linearly increased with increase of added azulene, but is not affected at all by oxygen.[36] Oxygen can quench both $^3t^*$ and $^3p^*$ by rate constants k_{to} and k_{po}, where k_{po} (ca. 9 × 10^9 M^{-1} s^{-1}) is nearly three times larger than k_{to} (ca. 3 × 10^9 M^{-1} s^{-1}).[12] The values for k_{po} and k_{to} correspond to $^1/_3$ and $^1/_9$ of the diffusion-controlled quenching rate constant by oxygen in organic solvents considering the spin statistical factor. No observation of the effect of oxygen on $([t]/[c])_s$ supports the above estimated K_{tp} (= 8 in benzene);[12] the population of $^3t^*$ is not sufficient to be quenched by oxygen to affect $([t]/[c])_s$. On the other hand, azulene can change $([t]/[c])_s$, since $^3p^*$ is not quenched by azulene.

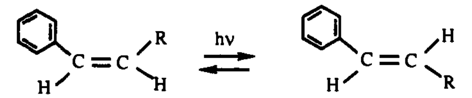
The apparent quenching constant by oxygen ($k_q^{Ox} = (k_{to} + K_{tp}k_{po})/(1 + K_{tp})$) observed by laser photolysis of stilbene, (7.4–9.5) × 10^9 M^{-1} s^{-1},[12] is very close to the value of k_{po}, which supports that oxygen quenches $^3p^*$ efficiently but hardly quenches $^3t^*$ as is observed.

In class C olefins both azulene and oxygen increased $([t]/[c])_s$.[54-56] The observed quenching rate constant by azulene was higher than that of the stilbene triplet, whereas that by oxygen was lower than for stilbene, which means that the population of $^3t^*$ in triplet **5a** is much higher than in stilbene. Therefore, not only azulene but also oxygen can quench $^3t^*$ to increase $([t]/[c])_s$. The T–T absorption spectra observed for **5a** around 420 nm was assigned to $^3t^*$ by comparison with that observed for a model cyclic compound (**7**) with planar geometry.[56] The observed lifetime of the triplet **5a** (120 ns), longer than that of stilbene and shorter than that of anthrylethylenes, supports the idea that the triplet state is composed by a mixture of $^3t^*$ decaying with slower rate constant, k_{td}, and $^3p^*$ decaying with faster rate constant, k_{pd}.



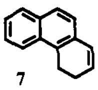
cis-5, a: R=^{t}Bu, b: R=Ph

trans-5



cis-6, a: R=^{t}Bu, b: R=Me

trans-6



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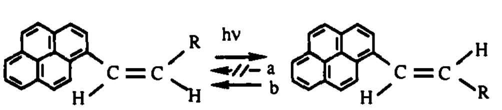
Further lowering of the triplet energy of the aromatic nucleus in class C olefins leads to the one-way isomerizing olefins passing through olefins carrying dual characters of the two-way and one-way isomerization as described below.

C. Photoisomerization of Pyrenylethylenes[25-27]

On benzil-sensitization 1-pyrenylethylenes (**8**) undergo one-way isomerization when R = ^{t}Bu (**8a**); however, when R = Ph (**8b**), it exhibits dual characters of both two-way and one-way isomerization.



cis-8, a: R=^{t}Bu, b: R=Ph

trans-8

8a shows typical behavior of one-way isomerization and its triplet state deactivates solely from $^3t^*$. Thus $\Phi_{c\to t}$ of *cis*-**8a** on benzil-sensitization increased nearly linearly with its concentration in degassed benzene attaining more than 20 at [*cis*-**8a**] = 3.3×10^{-3} M (Figure 7a).[25,26] The stable triplet state is $^3t^*$ (λ_{max} = 445 nm, Figure 8) with a lifetime of 54 μs and is quenched by oxygen with a rate constant of $2.9 \times 10^9\ M^{-1}\ s^{-1}$, a typical value as k_{to}.

On the other hand, in the triplet state of **8b**, $^3t^*$ is the most stable and is in equilibrium with slightly unstable $^3p^*$; the deactivation occurs from both triplet states, since the rate constant of the deactivation is 1000 times faster for $^3p^*$ than for $^3t^*$. The deactivation from $^3p^*$ gives trans and cis isomers as is typical for the two-way mode, and that from $^3t^*$ gives solely the trans isomer, transferring energy to cis isomer to regenerate $^3c^*$ thus leading to quantum chain isomerization of cis to trans isomers as is typical for the one-way mode. The isomerization proceeds in a mechanism depicted in Scheme II.

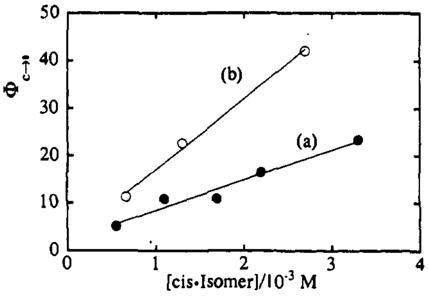


Figure 7. Effect of cis isomer concentration on $\Phi_{c\to t}$ of **8a** (a) and **8b** (b) (adapted from ref 26).

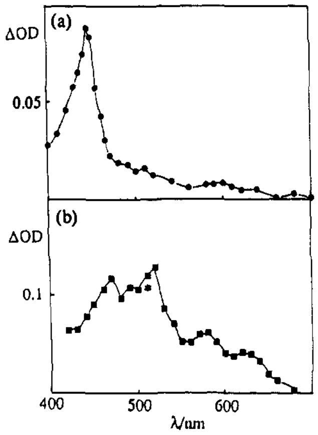


Figure 8. T–T absorption spectra of pyrenylethylenes **8a** (a) and **8b** (b) in benzene at room temperature (adapted from ref 26).

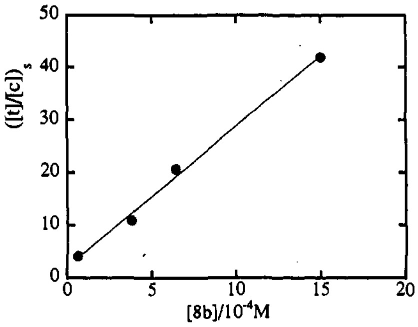
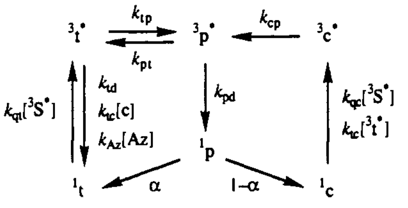


Figure 9. Effect of **8b** concentration on the photostationary state isomer ratio $([t]/[c])_s$ (adapted from refs 25 and 26).

Thus, $([t]/[c])_s$ increases with **8b** concentration to as high as 98/2 at 1.5×10^{-3} M as illustrated in Figure 9[25,26] and, on infinite dilution, still remains at 71/29, much different from 40/60,[1,2,4,6] a typical value for two-way isomerization undergoing deactivation of the triplet state from $^3p^*$. The $\Phi_{c\to t}$ value increased with [*cis*-**8b**] to attain more than 40 at 2.7×10^{-3} M. The triplet state exhibits absorption at 400–650 nm with λ_{max}'s at 470 and 520 nm, decaying with a lifetime of 27 μs at 25 °C, and is quenched by azulene and oxygen with rate constants of 7.3×10^9 and $3.6 \times 10^9\ M^{-1}\ s^{-1}$, respectively, among which the quenching by oxygen gives nearly equimolar amount of singlet oxygen as determined by its emission. Furthermore, the 1-pyrenylmethyl radical, the main chromophore of $^3p^*$ exhibits an absorption at a shorter wavelength region (λ_{max} < 430 nm). The above

Scheme II



facts show that the observed triplet state is mostly comprised from $^3t^*$ along with a small fraction of $^3p^*$ in equilibrium. Actually, the lifetime of the triplet state decreased from 39 to 15 μs with an increase of temperature from 5 to 56 °C due to the increase in population of shorter lived $^3p^*$.

In Scheme II, when $k_{qc} = k_{qt}$ and when $k_{tp} \gg k_{td}$, $k_{tc}[cis\text{-}\mathbf{8b}]$ and $k_{pt} \gg k_{pd}$, i.e., the equilibrium between $^3t^*$ and $^3p^*$ is established ($K_{tp} = k_{tp}/k_{pt}$), $([t]/[c])_s$ and $\Phi_{c\rightarrow t}$ are expressed by eqs 2 and 3, respectively. Here, $[\mathbf{8b}] = [t]_s + [c]_s$ is the total concentration of **8b**, and Φ_T is the quantum yield for *cis*-**8b** triplet formation. These equations explain the concentration dependence of $([t]/[c])_s$ and $\Phi_{c\rightarrow t}$.

$$([t]/[c])_s = \frac{\alpha K_{tp}k_{pd} + k_{td} + k_{tc}[\mathbf{8b}] + k_{az}[Az]}{(1-\alpha)K_{tp}k_{pd}} \tag{2}$$

$$\Phi_{c\rightarrow t} = \Phi_T \frac{\alpha K_{tp}k_{pd} + k_{td} + k_{tc}[cis\text{-}\mathbf{8b}]}{K_{tp}k_{pd} + k_{td}} \tag{3}$$

The lifetime, τ_T, of the **8b** triplets is expressed by eq 4.

$$\tau_T = \frac{1 + K_{tp}}{K_{tp}k_{pd} + k_{td}} \tag{4}$$

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 (2×10^7 s^{-1}) and one-way isomerizing olefins (2×10^4 s^{-1}), respectively. Substitution of these values into eq 4 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 $([t]/[c])_s$ (Figure 9) and $\Phi_{c\rightarrow t}$ (Figure 7) to be ca. 10^{-3}. Therefore, **8b** deactivated from $^3t^*$ and $^3p^*$ in nearly 1 to 1 ratio.

Figure 10a shows that the potential energy surface of **8a** depicted on the basis of the following results. The energies of $^3c^*$ and $^3t^*$ were determined by their phosphorescence as 47 and 44 kcal mol^{-1}, respectively. The energy difference between cis and trans isomers in the ground state was determined by differential scanning calorimetry as 5 kcal mol^{-1}, which is similar to the value of stilbene. In addition the energy difference between $^3p^*$ and $^3t^*$ is estimated as more than 6–7 kcal mol^{-1}, preventing the deactivation from $^3p^*$. Figure 10b indicates the potential energy surface of isomerization of **8b**.

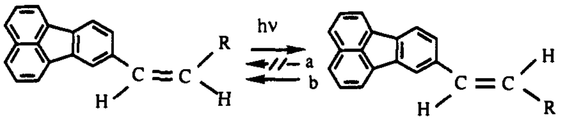
The X-ray analysis of the crystalline *cis*-**8a** revealed that the angle between the pyrenyl ring and the double bond is 90.0°, that is, the totally perpendicular arrangement of the pyrenyl group and the double bond.[66] Therefore, the one-way isomerization of **8a** should take place through some kind of intramolecular excitation transfer from the initially produced excited state of the pyrenyl group to the olefin part in the process of double bond twisting to the perpendicular triplet state ($^3p^*$) finally twisting to the most stable trans triplets ($^3t^*$).

The substitution of polar groups on the *p*-phenyl position of **8b** still keeps the dual character of the isomerization. Thus, triplet-sensitized irradiation of substituted styrylpyrenes, ArCH=CHPy [Py, 1-pyrenyl; Ar, 4-RC_6H_4 (R = CH_3O, CN, and NO_2)] resulted in the mutual isomerization between their cis and trans isomers with increasing $([t]/[c])_s$ with total concentration of their cis and trans isomers. The substituents increased $([t]/[c])_s$ at a certain olefin concentration in the sequence of CH_3O, H, CN, and NO_2, which is due to the increase of relative population of $^3t^*$ to $^3p^*$ in the triplet state in this sequence.[67]

D. Factors Controlling the Mode of Isomerization[19,29,32]

1. Effect of Aromatic Nucleus on the Mode of Isomerization

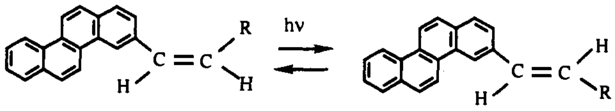
The modes of the isomerization of fluoranthenylethylenes **9**[28–30] are similar to those of pyrenylethylenes (**8**). **9a** (R = ^{t}Bu) isomerizes by the one-way mode; however, **9b** (R = Ph) isomerizes by a dual mechanism of two- and one-way. Chrysenylethylenes (**10**)[31] and a phenanthrylethylene (**11**) undergo two-way photoisomerization.[68–70]



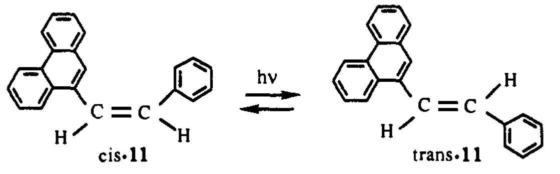
trans-**9**

cis-**9**, a: R=^{t}Bu, b: R=Ph

R=^{t}Bu: one-way R=Ph: dual mechanism



cis-**10**, a: R=^{t}Bu, b: R=Ph trans-**10**



cis-**11** trans-**11**

Table III lists the substituent effects on the mode of the isomerization and the triplet lifetime for two series of olefins, ArCH=CH^{t}Bu and ArCH=CHPh.[12,18–32,56,64,68–74] In the series of ArCH=CH^{t}Bu, aromatic groups with triplet energy higher than chrysene (56 kcal mol^{-1})[33] exhibit two-way mode; however, those with lower than that show one-way mode. The triplet states of olefins undergoing two-way isomerization have a lifetime only in the range of 100 ns; however, those of one-way have a longer lifetime of more than 10 μs.

On the other hand, in the series of ArCH=CHPh, the mode is two-way until the energy of the aromatic nucleus decreases as low as that of anthracene. Substitution of perylene ring with lower triplet energy than anthracene also led to one-way isomerization. However, as described before, the olefins with pyrene and

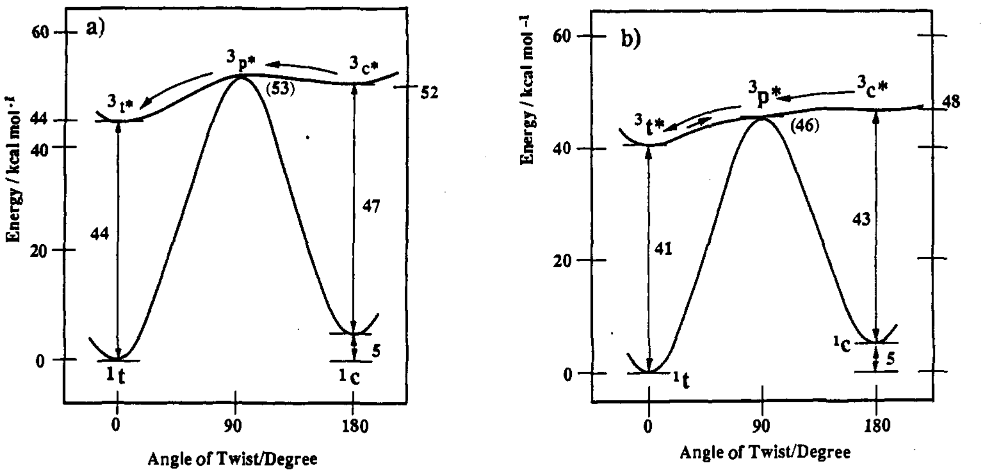


Figure 10. Potential energy surfaces of the isomerization of **8a** (a) and **8b** (b) (adapted from ref 26).

Table III. Modes of the Isomerization and the Triplet Lifetimes of ArCH═CHR

Ar	triplet energy of ArH, kJ mol^{-1}	τ_T, μs (λ_{max}(T–T), nm)		ref(s)
		R = ^{t}Bu	R = Ph	
phenyl	84.3	two-way	two-way 0.063 (<360)	12,58
9-phenanthyl	61.9		two-way 0.43 (460)	68–70
2-naphthyl	60.9	two-way 0.13 (420, 570)	two-way 0.14 (400, 500)	56,64,65
3-chrysenyl	56.6	two-way 0.36 (600)	two-way 0.14 (<400)	31
8-fluoranthenyl	54.2	one-way 25 (440, 580)	two-way (dual) 0.50 (480, 600)	28,29
1-pyrenyl	48.2	one-way 54 (445)	two-way (dual) 27 (470, 520)	25,26
1-anthryl	42	one-way (440, 500)	one-way (570)	50
2-anthryl	42	one-way 280 (450, 540)	one-way 190 (460, 620)	19,20
9-anthryl	42	one-way (410, 435)	one-way (325, ~450)	50,86–88
ferrocenyl	40		inefficient one-way	71,72
3-perylenyl	35		one-way (540, 580)	73,74

fluoranthene nucleus isomerize with dual character of two- and one-way.

In the case of **8b** the free energy change, ΔG_{tp}, from $^3t^*$ to $^3p^*$ is estimated to be 4 kcal mol^{-1} from the K_{tp} value (10^{-3}) at room temperature. The mode of the isomerization approaches one-way with the increase of ΔG_{tp} and finally, at $\Delta G_{tp} \geq 7$ kcal mol^{-1} ($K_{tp} \leq 10^{-5}$), practically one-way isomerization is to be observed; in this situation the deactivation ratio from $^3t^*$ and $^3p^*$ ($k_{td}/k_{pd}K_{tp}$) is estimated to be higher than 100/1.

As mentioned above the isomerization behavior of ArCH═CHR is mainly determined by the triplet energy of the main aromatic group Ar. However, the second substituent R also contributes to determining the mode of isomerization. Thus, the triplet energy surfaces of aromatic olefins can be interpreted as a compromise of these two effects. The key conformations, $^3p^*$ and $^3t^*$, suffer the substituent effects in different manners: (1) the energy of $^3t^*$ decreases with decreasing triplet energy of the main aromatic group Ar, and (2) the energy of $^3p^*$ is not so dependent on the triplet energy of Ar but affected by the property of the second substituent R, to be either alkyl or aryl.

The energy of $^3p^*$ corresponds to that necessary to break the double bond leading to the corresponding 1,2-biradical.[44] In thermal cis–trans isomerization, introduction of a phenyl group instead of an alkyl group reduces the activation energy.[75] Then, when R = Ph in ArCH═CHR, it will also stabilize $^3p^*$ by giving benzyl radical type character to one of the twisted chromophore which tends to favor two-way modes. For typical arylalkenes such as 1-phenylpropene the $^3p^*$ energy is estimated as ca. 53 kcal mol^{-1}.[44,54,56] On introduction of another aryl group in place of R, diarylethylenes such as stilbene **5b** and **9b** have the energy of $^3p^*$ estimated as 45–49 kcal mol^{-1}.[21,26,29,44,54–56,64] These results are therefore quite consistent with the above criteria that the energy of $^3p^*$ is governed by the property of the second substituent R. Thus, the difference of the shape of the triplet energy surface between **1a** and **1c** reflects the effect of phenyl group (Figure 4).

Table IV. Triplet Energies of ArCH═CHR

Ar	triplet energies, kcal mol^{-1}						ref(s)
	R = ^{t}Bu			R = Ph			
	$^3t^*$	$^3p^*$	$^3c^*$	$^3t^*$	$^3p^*$	$^3c^*$	
phenyl	60	53.2		51	46.5	55.5	44
2-naphthyl	~53	·53		~49	~49		54–56,64,65
8-fluoranthenyl	49	≥56	~52	~44	~45.5	~46	29
1-pyrenyl	44	≥51	~46	41	~46	~42	26
2-anthracenyl	42.7	~53	42.5	41.4	≥48	41.5	21

Table IV lists the estimated triplet energies of $^3c^*$ over ^1c and those of $^3p^*$ and $^3t^*$ over ^1t. Roughly speaking, the energy of $^3p^*$ over ^1t is ca. 53 and 46 kcal mol^{-1} for 1-arylalkenes and diarylethylenes, respectively, and is not influenced very much by the size and the triplet energy of the aromatic nucleus. On the other hand, the energy of $^3c^*$ and $^3t^*$ decreases with decreasing the triplet energy of aromatic nucleus; $^3t^*$ becomes more than 6–7 kcal mol^{-1} stabilized than $^3p^*$ when the triplet energy of the aromatic nucleus is lowered to those of fluoranthene **9a** and pyrene **8a**.

When the cis and twisted geometries are similar in energy on the triplet energy surfaces as in **9b**, the probability of the deactivation at the cis side can be neglected since the deactivation from $^3p^*$ will occur with a rate constant of 1000 times faster than those from $^3c^*$ and $^3t^*$.

2. Adiabatic Thermoneutral Isomerization

As described before for **2**, when the cis and trans isomers of an olefin have nearly the same excitation

Table V. Modes of Photoisomerization of Aromatic Olefins in the Triplet State

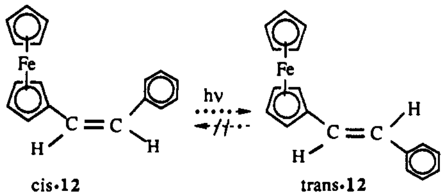
mode	lifetime of the triplet state	quantum yield of isomerization	triplet state situated at potential minimum	triplet undergoing deactivation without quencher	example[a]	ref(s)
two-way	10^1–10^2 ns	$\Phi_{c\to t} + \Phi_{t\to c} \approx 1$	$^3p^*$ ($^3t^*$)	$^3p^*$	PhCH=CHPh	1–6,11–14,31,40–44, 54–59,63–65
two-way with dual character	~10^1 μs	$\Phi_{c\to t} \gg 1$ (increasing with cis concentration) $\Phi_{t\to c} = 0$	$^3p^*$ and $^3t^*$	$^3p^*$ and $^3t^*$	PyCH=CHPh	25–30
one-way	10^1–10^2 μs	$\Phi_{c\to 1} \gg 1$ (increasing with cis concentration) $\Phi_{t\to c} = 0$	$^3t^*$ and $^3c^*$	$^3t^*$	AntCH=CHR	18–24,26,30,50, 74,86,88,91,97
inefficient one-way	very short	$\Phi_{c\to t} \approx 10^{-3}$, $\Phi_{t\to c} = 0$	$^3t^*$ and $^3c^*$	$^3t^*$ and $^3c^*$	FcCH=CHPh	71,72

[a] Py, 1-pyrenyl; Ant, 2-anthryl; R = Me, ^{t}Bu, Ph, and 2-naphthyl; Fc, ferrocenyl.

energies and are nearly the same in energy in the ground state and $^3p^*$ is not situated at an energy minimum, both $^3c^*$ and $^3t^*$ are in an equilibrium and the deactivation may take place from both $^3c^*$ and $^3t^*$. In this case, two-way isomerization takes place for both cis → trans and trans → cis directions as an adiabatic process overcoming an energy barrier. However, the triplet lifetime is nearly the same as the typical one-way isomerizing olefins, because the deactivation takes place only from the planar cis and trans triplet and the quantum chain process for cis → trans and trans → cis isomerization can be expected. This condition was achieved for deuterated vinylanthracenes. In 1 and 8a, however, the higher energies (ca. 5 kcal mol^{-1}) for cis isomers than trans isomers and the possible higher excitation energies of the cis isomers than the trans isomers result in 5–8 kcal mol^{-1} higher energy of the $^3c^*$ than the $^3t^*$. Thus, the equilibrium constant between the cis and trans triplets must be less than 10^{-3}, leading to undetectable deactivation at the cis triplet.

3. An Unsaturated Compound Undergoing No Isomerization

In olefins having the potential energy surface of one-way mode, if the deactivation of $^3c^*$ is accelerated before its twisting, then the isomerization is completely suppressed. Styrylferrocene (12) undergoes no isomerization from trans to cis and isomerizes from cis to trans with extremely low quantum yield with an order of 10^{-3} at room temperature.[71,72] Its potential energy surface must be very similar to 1c, but the presence of ferrocenyl group facilitates the deactivation: a very short lifetime of ferrocene assumed to be 0.6 ns[76] is responsible for the quick deactivation of the triplet state of *cis*-12.



cis-12 trans-12

Another attempt to suppress the isomerization must be the introduction of very low triplet energy to put the energy barrier for rotation from $^3c^*$ to $^3t^*$ higher than 12 kcal mol^{-1} to suppress the isomerization rate.

In summary, Table V compares features of these modes.

4. Relation between the Adiabatic Isomerization and the Mode of Isomerization

The potential energy surface of the isomerization is discussed in terms of adiabatic and diabatic processes. The two-way isomerization of olefins in the triplet manifold without any quencher takes place as a diabatic process by the deactivation at $^3p^*$. However, as mentioned before, the photochemical cis → trans one-way isomerization in the triplet state proceeds by an adiabatic process where the excited state of starting material $^3c^*$ undergoes adiabatic conversion to the excited state of the product $^3t^*$ followed by either unimolecular deactivation to the ground state of the product ^1t or energy transfer to ^1c to generate ^1t and $^3c^*$. The isomerization of 8b also proceeds partly by the way of the adiabatic process: the deactivation from $^3t^*$ occurs as an adiabatic process, but that from $^3p^*$ occurs as a diabatic process. Therefore, two-way photoisomerization usually takes place as a diabatic process, while one-way and two-way isomerization with dual mechanism takes place totally and partly as an adiabatic process, respectively. The one-way isomerization should not necessarily be an adiabatic process.[37–39] Moreover, it occurs with compounds where isomerization of one direction is permitted, but the other direction is prohibited by some structural effects such as intramolecular hydrogen bonding.[77–79] Furthermore, in two-way isomerizing olefins such as stilbene, the isomerization from cis-to-trans isomer can be regarded partly as an adiabatic process in the presence of azulene as a quencher of $^3t^*$;[1,40] azulene quenches $^3t^*$ to give solely trans isomer as an adiabatic process; however, the unimolecular deactivation from $^3p^*$ to give ^1t takes place in a diabatic way.

As to the adiabatic isomerization in the singlet excited state, very precise work of stilbene clearly demonstrated that the direct excitation of cis isomer resulted in the fluorescence emission of both $^1t^*$ and $^1c^*$, suggesting that cis-to-trans isomerization proceeds partly by an adiabatic way even though this contribution is very small ($\Phi_{^1c^*\to{}^1t^*} = 2 \times 10^{-3}$).[80,81] Furthermore, direct excitation of 8b resulted in the adiabatic conversion from $^1c^*$ to $^1t^*$ in high efficiency ($\Phi_{^1c^*\to{}^1t^*} = 0.61$)[82] followed by the fluorescence emission from $^1t^*$.

As the potential energy surface of the isomerization at the triplet state is governed by the triplet excitation energy of the aromatic group, the energy surface at the excited singlet state is also governed by the singlet excitation energy of the aromatic group. Thus, the decrease of the singlet energy of the aromatic nucleus lowers the energy of planar $^1c^*$ and $^1t^*$ more than that of $^1p^*$. Therefore, the change of aromatic group from phenyl to anthryl results in the change of the profile of isomerization on direct irradiation from two-way to one-way. Thus, cis → trans isomerization of stilbene mostly takes place as a diabatic process from $^1p^*$

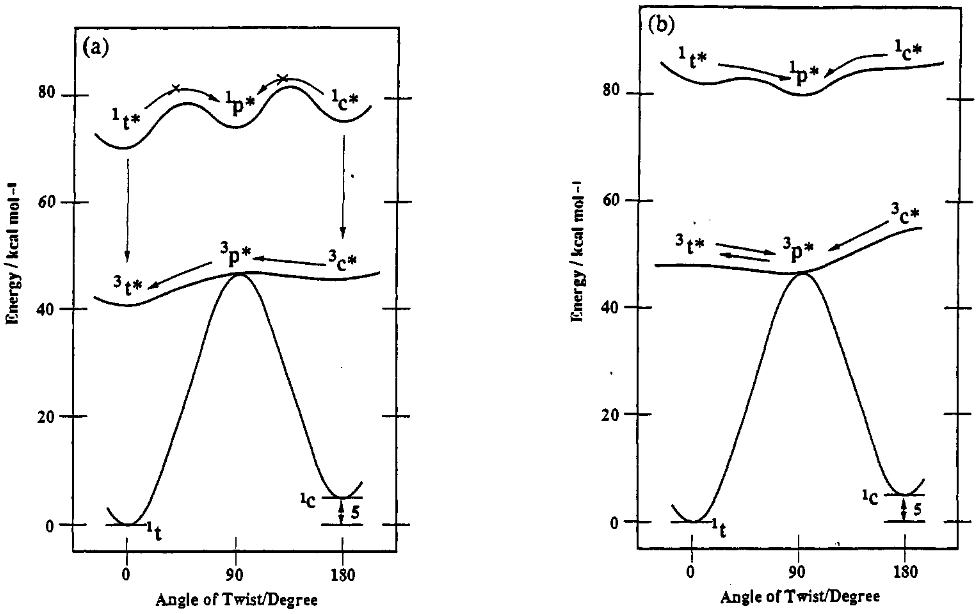


Figure 11. Potential energy surfaces of the isomerization of 2-styrylanthracene (a) and stilbene (b) in the excited singlet and the triplet states.

accompanied by a small contribution of adiabatic deactivation from $^1t^*$, while **1c** does not undergo isomerization in the excited singlet state, probably due to the increase of barrier for isomerization, and does undergo fluorescence emission or intersystem crossing from the initially produced $^1c^*$ to the triplet state, which subsequently undergoes one-way isomerization (Figure 11). The quantum yields of intersystem crossing from $^1c^*$ to $^3c^*$ are determined as 0.59, 0.17, and 0.22 for **1a**, **1c**, and **1d**, respectively.[23]

A compound between these two cases is a pyrenylethylene **8b**. A pyrene group considerably decreases the energy of $^1c^*$ and $^1t^*$ compared to $^1p^*$ to make $^1p^*$ as a barrier of isomerization, which retards the deactivation from $^1p^*$; however, the barrier is not high enough to stop the $^1c^* \rightarrow {}^1t^*$ isomerization. The results for 9-styrylanthracene are briefly mentioned in section F.

E. The Highest Value for the Quantum Yields of Isomerization

Whitten et al.[83] reported that even stilbene and its analogues undergo cis → trans isomerization with high quantum yields on sensitization by porphyrins in the presence of very high concentration of olefins. For example, on palladium octaethylporphyrin sensitization the quantum yield of cis → trans isomerization of stilbene was determined as 1.58 at [*cis*-stilbene] = 1.44 M. In this case the sensitizer triplet state was proposed to work as a chain carrier in the quantum chain processes.

As mentioned before the quantum yields of cis → trans isomerization of **1** and **8** exceed more than 10 at relatively low concentration. In this case the key step is the energy transfer from $^3t^*$ to ^1c. This energy transfer is not exothermic at all, but thermoneutral or slightly endothermic. The reason for the observation of the high efficiency for the quantum chain process owes to a long lifetime of the energy donor in the order of 10^1–10^2 μs. The energy transfer proceeding with rate constants 1 or 2 orders lower than the diffusion-controlled rate constant, 10^7–10^8 M^{-1} s^{-1}, still can efficiently take place in the presence of an appropriate amount of ground-state cis isomer, competing with slow unimolecular decay of $^3t^*$ in the order of 10^4–10^5 s^{-1}, and therefore accomplishing quantum chain process.[19,20,24,32,45–48,84]

Table VI. Estimation of the Quantum Yields of the Isomerization through the Quantum Chain Process at Different Endothermicity of Energy Transfer from $^3t^*$ to ^1c and at Different Concentration at a Fixed Triplet Lifetime at Room Temperature

		$\Phi_{c\rightarrow t}$		
		E_T(cis) − E_t(trans), kcal mol⁻¹		
[cis isomer], M	τ_T, μs	0	3	6
10^{-4}	100	5×10^1	0.7	5×10^{-3}
10^{-3}	100	5×10^2	7	5×10^{-2}
10^{-2}	100	5×10^3	7×10^1	5×10^{-1}
10^{-1}	100	5×10^4	7×10^2	5
1	100	5×10^5	7×10^3	5×10^1

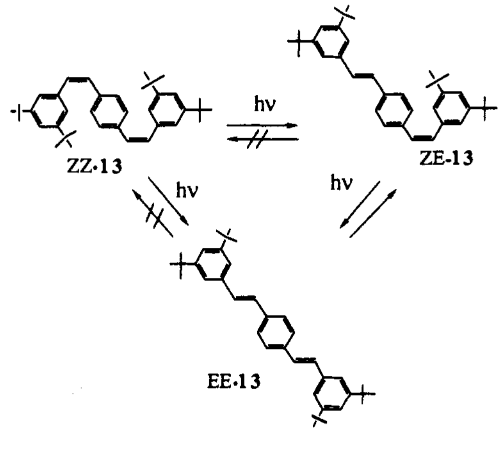
Table VI lists the quantum yields expected for some cases assuming that the energy transfer obeys the Sandros equation.[85] If the triplet energy of cis and trans isomers are nearly the same, the energy transfer from $^3t^*$ to ^1c proceeds at the rate constant of $^1/_2$ of k_{dif} (= 5×10^9 M^{-1} s^{-1}) in hydrocarbons like benzene. The triplet lifetime of one-way isomerizing olefins is ca. 10^{-4} s; thus, on triplet sensitization $\Phi_{c\rightarrow t}$ should be as high as 5×10^2 and 5×10^3 in the presence of 10^{-3} and 10^{-2} M of cis isomer, respectively and even 5×10^5 could be obtained if the compound is soluble up to 1 M concentration.

F. One-Way Isomerization at Both Singlet and Triplet Excited States

Becker et al. reported that **4b** undergoes one-way cis → trans isomerization on diret as well as biacetyl sensitization and proposed that the isomerization takes place as an adiabatic process in both the excited singlet and triplet state.[86] They observed that the fluorescence emission measured on excitation of cis isomer fits not to single but to two exponential decay kinetics, in which one of the observed time constants was the same as that obtained by excitation of trans isomer. This fact indicates that ^{1}c* undergoes isomerization in the excited singlet manifold to ^{1}t* passing through ^{1}p*; therefore, the fluorescence emission of both ^{1}c* and ^{1}t* was observed on excitation of cis isomer. Goerner reported that even on direct irradiation he observed T–T absorption spectra of trans isomer by laser flash photolysis.[87,89] Thus, ^{1}c* may undergo isomerization in the excited singlet state directly, giving ^{1}t* or undergo intersystem crossing to ^{3}c* followed by isomerization to ^{3}t* and both processes take place as the adiabatic process.[86–89]

It should be noted here that in the case of 2- and 1-anthrylethylenes the excited singlet states of cis and trans isomers undergo fluorescence emission or intersystem crossing to the triplet states without accompanying ^{1}c* → ^{1}t* conversion.[18–24,32,90] Therefore, in these olefins the isomerization takes place as an adiabatic process in the triplet manifold.

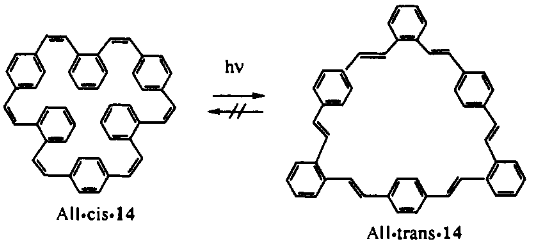
The adiabatic cis–trans isomerization in the excited singlet state was also reported for 4-styrylstilbene **13**.[91] *ZZ* isomer undergoes isomerization to *ZE* and *EE* isomer in the excited singlet state, according to fluorescence spectroscopy. Thus, starting from *ZZ* isomer one can observe the fluorescence decay curve which fits to three components analysis due to the fluorescence of *ZZ*, *ZE*, and *EE* isomers. On biacetyl sensitization **13** undergoes *ZZ* → *ZE* and *ZZ* → *EE* isomerization in the triplet manifold as adiabatic one-way isomerizations. *ZE* isomer also isomerizes to *EE*, where the quantum yields of *ZE* → *EE* isomerization and the photostationary state isomer ratios $[EE]/[ZE]_{pss}$ increased with the diene concentration, the former value exceeding more than unity.[92]



G. One-Way Isomerization and Quantum Chain Process of Polyenes

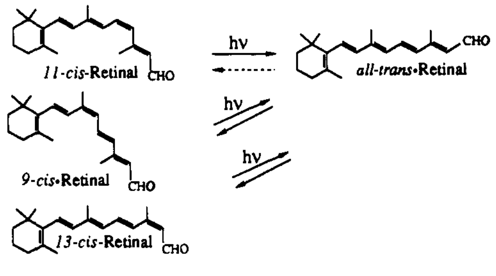
The occurrence of the quantum chain process in the photoisomerization at the triplet state was first reported for conjugated dienes by Hammond et al.[93] almost 20 years ago and subsequently by Hurley and Testa[94] and Saltiel et al.[95] They reported that on triplet sensitization 1,3-pentadiene and 2,4-hexadiene undergo mutual isomerization among the isomers, but the quantum yields of cis → trans isomerization increased with the increase of the diene concentration. Although the quantum yield values are different among the reports, the mechanism involving the energy transfer from diene triplet to diene ground state was proposed. 1,5-Dimethyl-1,3,5-heptatriene was reported to undergo quantum chain photoisomerization.[96]

A cyclic polyene, **14**, undergoes all-cis to all-trans 6-fold isomerizations in the triplet state, while no isomerization from all-trans to all-cis occurs. The T–T absorption spectra observed around 520 nm with a lifetime of 45 μs at room temperature, by exciting either isomer, is assigned to the all-trans triplet, which indicates that the all-cis → all-trans isomerization proceeds by an adiabatic process in the triplet state.[97]



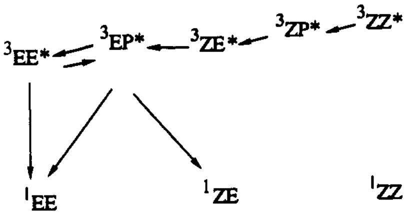
Ramamurthy and Liu reported the effect of the polyene chain length of retinal homologues on the potential energy surfaces of triplet sensitized isomerization.[39] Thus, dienes and trienes undergo unimolecular deactivation from the twisted triplet because the planar trans triplet and the twisted triplet are very close in energy. On the other hand, in tetraenes and higher polyenes the planar structures are stable and rapidly equilibrated in the triplet state; therefore, the deactivation proceeds from planar triplet states. Very interestingly, β-ionol undergoes one-way trans → cis isomerization on sensitization with sensitizers of low triplet energies such as 1-acetylnaphthalene by a diabatic process, while on sensitization with those of higher triplet energies such as acetophenone it undergoes two-way isomerization.[39]

Among the isomers of retinal, 11-cis isomer isomerizes in hexane at the triplet state in an almost one-way fashion to give all-trans isomer through a common excited state, all-trans triplet state, observed by transient Raman spectroscopy.[98–102] On triplet sensitization quantum yield of the 11-cis → all-trans isomerization linearly increases with 11-cis isomer concentration exceeding unity as in typical one-way isomerization.[102] However, the reaction is not completely the real one-way, because at the photostationary state not only all-trans but also 13-cis and 9-cis-retinal was observed in more than 5%.[103,104] Quite recently, even all-trans retinal was reported to undergo adiabatic isomerization to the cis isomers through the quantum chain process in the excited triplet state.[104]

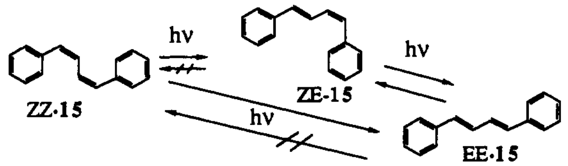


1,4-Diphenylbutadiene (**15**) undergoes *ZZ* → *ZE* and *ZZ* → *EE* one-way photoisomerization in the triplet

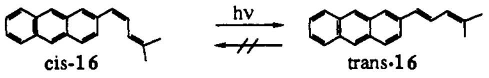
Scheme III



state with a quantum chain process.[105] *ZE* and *EE* isomers undergo mutual isomerization. However, the quantum yields of *ZE* → *EE* isomerization on 9-fluorenone sensitization increased linearly with the total concentration of **15** (quantum chain photoisomerization). On 9-fluorenone sensitization all the isomers exhibited the same T–T absorption spectra (λ_{max} = 390 nm, $\tau_T \approx$ 1.6 μs) at 1 μs after the laser pulse. Furthermore, photostationary mixtures become richer in *EE* with increasing the initial *ZE* concentration. Therefore, it was proposed that unimolecular deactivation occurs from ^{3}EP* and most of the bimolecular deactivation from ^{3}EE*, where EP means the perpendicular geometry at one end of the diene and *E* at the other end (Scheme III).



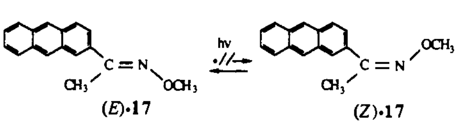
Concerning the photoisomerization of dienes carrying a conjugated group of low triplet energy like anthracene, direct irradiation as well as triplet sensitization of 1-(2-anthryl)-4-methyl-1,3-pentadiene (**16**) leads to one-way cis → trans isomerization through the quantum chain process in the triplet state by an adiabatic conversion of ^{3}c* → ^{3}t*.[106]



H. One-Way Isomerization around the C═N Double Bond

The *E* and *Z* isomers of *N*-methoxy-1-(2-anthryl)-ethanimine (**17**) are stable at room temperature in the dark. (*Z*)-**17** isomerizes to the corresponding *E* isomer on direct (366 nm) as well as benzil-sensitized irradiation (436 nm) in degassed benzene, while the *E* isomer gave no *Z* isomer after prolonged irradiation which resulted in one-way *Z* → *E* isomerization.[107] The quantum yield for *Z* → *E* isomerization of **17** on benzil sensitization is as high as 11 at a concentration of 2.0 × 10^{-3} M. Laser flash photolysis of both (*Z*)- and (*E*)-**17** in benzene in the presence of benzil at room temperature afforded transient absorption assigned to ^3E* with a lifetime of 90 μs. These results indicate that one-way photoisomerization of **17** proceeds through a triplet manifold by an adiabatic conversion of ^3Z* → ^3E* as observed for 2-anthrylethylenes.

Pyrene-substituted imine **18** underwent mutual isomerization between *Z* and *E* isomers in the triplet excited state with the quantum chain process as observed for **8b**. Thus, the triplet potential energy curve of the isomerization around the C═N double bond is also governed by the triplet excitation energy of the aromatic groups. Lowering of their triplet energies results in a change in the isomerization mode from two-way, for the phenylimine **19**[108,109] and naphthylimine **20**,[108,110] to one-way for **17**,[107] passing through the dual mechanism for pyrenylimine **18**.[111]



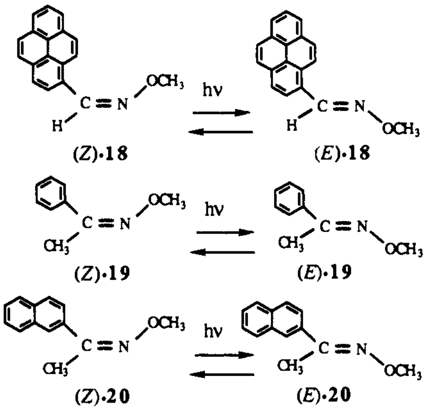


Table VII summarizes the substituent effect on the mode of isomerization of C═N double bond.

IV. One-Way Internal Rotation around the Single Bond in the Excited Singlet State

Excitation of trans isomer of aromatic olefins is accompanied by the internal rotation of the aromatic ring on the unsaturated bond. Some of the one-way isomerizing olefins exhibit the rotational isomerization not only at the long-lived triplet state but also at the short-lived singlet excited state, the latter of which is very much contrasted to many other olefins not undergoing rotational isomerization at the singlet excited state.

Diarylethylenes such as 2-styrylnaphthalene have been the target molecules to study the rotational isomerization around the single bond connecting the aromatic nucleus to the ethylenic carbon.[34-36,112-133] The existence of the conformationally isomeric mixtures around the single bond was revealed by absorption and fluorescence studies.[34,35,112-133] In the excited state, olefins usually undergo isomerization around the double bond to give cis and trans isomers. On photoexcitation of many olefins the double-bond character is decreased at the double bond but is increased at the adjacent singlet bond. Therefore, in the excited state the internal rotation has long been believed not to take place within its lifetime (NEER principle), although in the ground state the internal rotation around the single bond is generally too fast in solution to be followed by spectroscopic methods.

The NEER phenomena were found in many diarylethylenes such as *trans*-**5b**, where the fluorescence spectra depend on the excitation wavelength and the fluorescence decays with two-components of time constants of 3.1 and 23 ns in cyclohexane due to the presence of two rotational isomers.[35] Furthermore,

Table VII. Effect of Aromatic Substituents on the Mode of the Isomerization of ArCR=NOCH$_3$

Ar	R	triplet energy of ArH, kcal mol^{-1}	mode of isomerization τ_T, μs (λ_{max}(T–T), nm)	$\Phi_{Z\rightarrow E}$ ([Z], m)	ref(s)
phenyl	CH$_3$	84.3	two-way	0.35 (3 × 10^{-2})	108,109
2-naphthyl	CH$_3$	60.9	two-way	0.51 (5 × 10^{-2})	108,110
1-pyrenyl	H	48.2	two-way 10 (440)	3.2 (1.3 × 10^{-3})	111
2-anthryl	CH$_3$	42	one-way 90 (450,540)	11 (2.0 × 10^{-3})	107

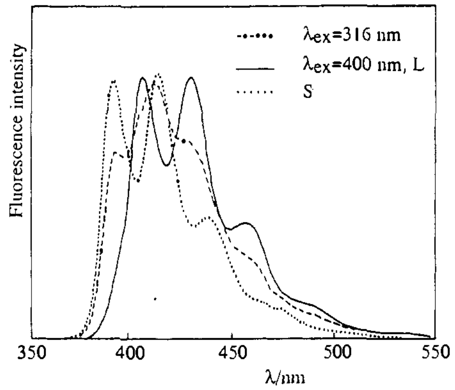
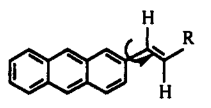


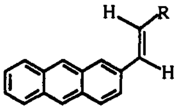
Figure 12. Effect of excitation wavelength on the fluorescence spectrum of 17 (reprinted from ref 133; copyright 1991 American Chemical Society).

trans-3-styrylphenanthrene and *trans*-1,2-di(2-naphthyl)ethylene exhibited similar fluorescence behavior.[68]

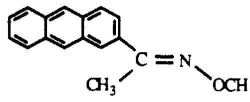
However, it was found that 2-vinylanthracene and its derivatives undergo an efficient internal rotation around the single bond connecting the anthracene ring to the unsaturated bond in the singlet excited state in alkane solution.[125–128] Furthermore, the internal rotation of 2-vinylanthracene[131] and its β-alkyl derivatives[132] takes place almost one-way from one conformer exhibiting the shorter wavelength fluorescence to the other showing the longer wavelength one in benzene or toluene. The rotational isomerization of an anthracene nucleus also takes place around the single bond connecting to a C=N double bond instead of a C=C bond within the lifetime of the excited singlet state of (*E*)-*N*-methoxy-1-(2-anthryl)ethanimine ((*E*)-17).[133]



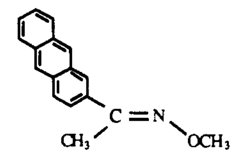
s-trans R=H, Me, t-Bu



s-cis



(*E*)-17 (s-trans)



(*E*)-17 (s-cis)

A. 2-Anthrylimine[133]

The presence of two rotational isomers S and L in (*E*)-17 is shown by the effect of excitation wavelength on the fluorescence spectra (Figure 12), where S and L denote rotational isomers exhibiting absorption and fluorescence spectra at shorter wavelength and that at longer wavelength, respectively.

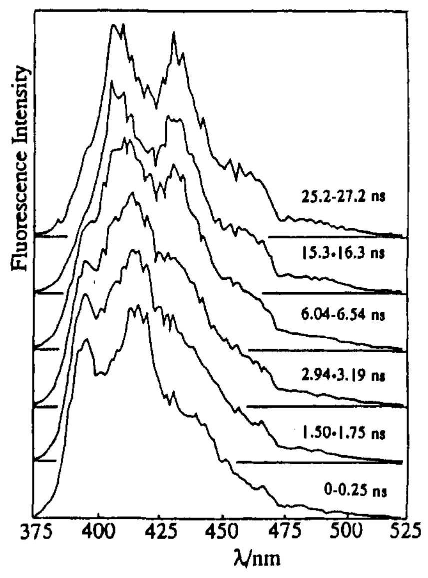
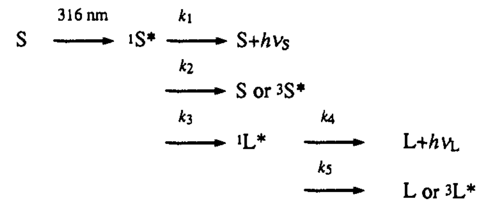


Figure 13. Time-resolved fluorescence spectra of (*E*)-17 in deaerated toluene at 58 °C (adapted from ref 133).

Time-resolved fluorescence spectra of (*E*)-17 observed at 0–250 ps is mostly due to S which shifted to that of L at the nanosecond time scale at 58 °C (Figure 13). The conversion of the rotational isomer of (*E*)-17 takes place in a one-way manner in the excited singlet state from $^1S^*$ to $^1L^*$.

The conversion from $^1S^*$ to $^1L^*$ was retarded with decreasing temperature, and finally at −90 °C in toluene no spectral change was observed due to the lack of $^1S^* \rightarrow {}^1L^*$ conversion. The $^1S^* \rightarrow {}^1L^*$ rotational isomerization proceeds with an activation energy of 4.6 kcal mol^{-1} and a frequency factor of 1.8×10^{11} s^{-1}. Thus, the potential energy surfaces of the single bond rotation of 17 in the ground and excited singlet state are depicted in Figure 14a.



B. 2-Vinylanthracene and Its β-Alkyl Derivatives

The time-resolved fluorescence spectra of 2-vinylanthracene exhibits almost one-way rotation in benzene from a conformer showing shorter wavelength fluorescence (S′) to another with longer wavelength fluorescence (L′).[131,132]

Likewise, on substitution of a methyl and *tert*-butyl group on the terminal carbon of 2-vinylanthracene, *trans*-1a and -1b, exhibit quite similar rotational isomerization in the excited singlet state. Figure 14b depicts the potential energy surface of the internal rotation in the excited singlet state of these compounds.[121,122] The activation energy and the frequency factor for the internal rotation are 3.9, 4.3, and 4.3 kcal mol^{-1} and 1.7, 1.8, and 1.8×10^{11} s^{-1}, for 2-vinylanthracene, 1a, and 1b, respectively.

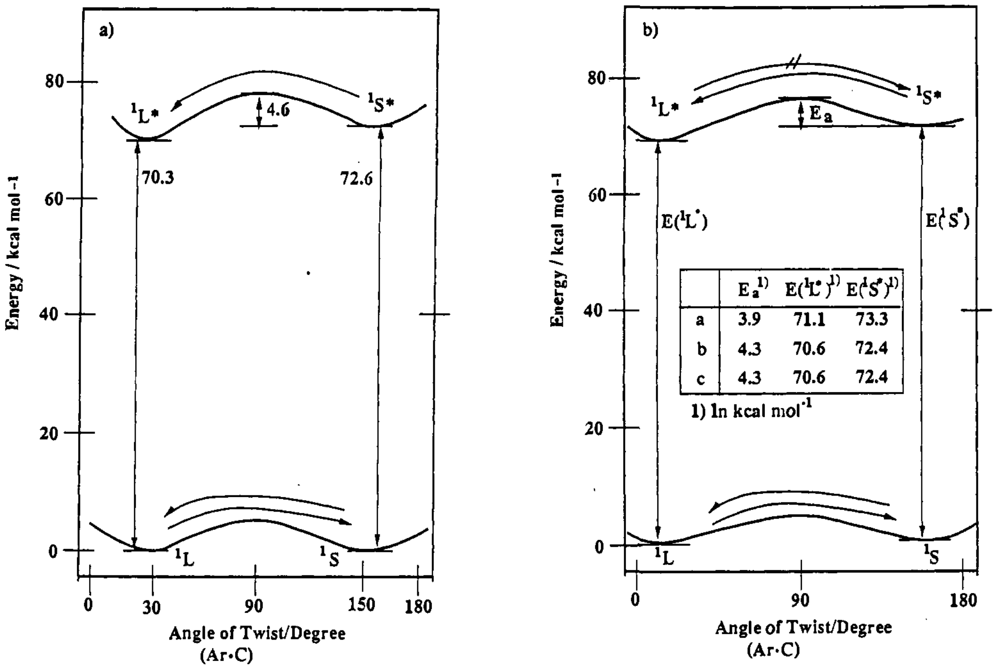


Figure 14. Potential energy surfaces of rotational isomerization of (*E*)-**17** (a) and 2-anthrylethylenes (b): a, 2-vinylanthracene; b, **1a**; c, **1b** (adapted from refs 132 and 133).

Substitution of a phenyl or a naphthyl group on the terminal carbon of 2-vinylanthracene inhibits the single bond rotation in the excited singlet state.[34,117,131] On excitation of *trans*-**1c** and -**1d** with 316-nm laser light, both S and L isomers are excited to show fluorescence of the respective isomers. The spectrum decays with the nanosecond time scale, without exhibiting any fluorescence rise. Furthermore, their decay time constants are not changed at all with temperature, which indicates that the activation barrier for the internal rotation in the excited singlet state might be higher than 7 kcal mol^{-1}.

The lack of the rotational isomerization in **1c** and **1d** can be explained as follows.[34] The introduction of a conjugated group like phenyl or 2-naphthyl on the terminal carbon of 2-vinylanthracene must enhance the conjugation between the anthracene nucleus and the double bond to increase the double-bond character of the single bond between them in the excited singlet state, which accordingly, elevates the barrier for the internal rotation in the singlet excited state.

In the triplet excited state, the T–T absorption of *trans*-**1c** changes in the millisecond time range at −130 °C,[46] which is due to the rotational isomerization in the excited triplet state as supported by the calculation.[52] The occurrence of the rotational isomerization of **1c** in the triplet state is in contrast to the lack of occurrence in the singlet excited state, which is probably due to the longer lifetime of the triplet state than the singlet state.

C. Requirement for One-Way Internal Rotation

The first clear evidence for the rotational isomerization in the excited state was reported for 2-vinylanthracene and its α- or β,β'-dialkyl derivatives.[125–128] Subsequently, the possibility of rotational isomerization in 3,3′-dimethylstilbene[124] and 2-naphthylpentadiene[123] was reported. The internal rotation was proposed to occur in the triplet excited state of **1c**.[46]

On direct irradiation of **1** and **17** the initially produced singlet excited states, $^1c^*$ and $^1t^*$, undergo fluorescence emission and intersystem crossing to the triplet state, but do not undergo isomerization around the double bond in the excited singlet manifold. The lack of the isomerization around the double bond of **17**[107] and **1a** and **1b**[18–24,32] in the excited singlet state can be attributed to the localization of excitation mostly on the anthracene nucleus; as a result, at the singlet excited state, the double bond character is still high at the C═C or C═N bond; however, it is scarcely increased at the single bond between the anthracene nucleus and the double bond.

According to calculation, in the excited triplet state[46,52] the barrier for the internal rotation considerably decreases from 11–13 kcal mol^{-1} for stilbene and styrylnaphthalene to 6 kcal mol^{-1} for **1c**.[52]

The most important factor for the occurrence of the rotational isomerization in the excited state is the localization of the excitation energy in the aromatic part. Then, the next problem, whether the rotational isomerization occurs mutually among the rotational isomers or in a one-way manner, depends not only on the excitation energy but also on the relative stability of the rotational isomers in the ground state. If the singlet excitation energy of a rotamer (S) is 3 kcal mol^{-1} higher than the other (L) and the energies of S and L are the same in the ground state, one can expect that only $^1S^*$ to $^1L^*$ conversion takes place. On the contrary, if the S form is 3 kcal mol^{-1} more stable than the L form in energy in the ground state and the singlet excitation energy of S is 3 kcal mol^{-1} higher than L, $^1S^*$ and $^1L^*$ become the same in energy, and then the interconversion between $^1S^*$ and $^1L^*$ becomes possible.

V. Conclusion

The present status of the one-way isomerization of aromatic olefins proceeding as an adiabatic process at the excited-state surface is reviewed in terms of its mechanism, potential energy surface, and quantum chain process. Attention is paid to revealing the structural factors of molecules governing the mode of the isomerization, in one-way, conventional two-way, and the dual mechanism of both two- and one-way, or retarding even one-way isomerization. In addition, the rotational isomerization between the conformers of the one-way isomerizing olefins at the excited state is described.

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