Bull. Chem. Soc. Jpn., ***68***, *1065—1087(1995)*

Accounts

Factors Determining the Adiabatic or the Diabatic Pathway of the Photoisomerization of Unsaturated Bonds

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(Received October 18, 1994)

Ethylenes substituted with aromatic nuclei of low triplet excitation energies undergo cis→trans one-way isomerization in an adiabatic way in the triplet state with a quantum chain process. A new general concept is introduced to cover various types of isomerization in the triplet state: the conventional two-way mutual diabatic isomerization, the newly found one-way isomerization, and inefficient isomerization. This is extended to describe the isomerization in the singlet excited state which occurs in either a diabatic or an adiabatic pathway.

Background. Many unsaturated compounds are known to undergo geometrical isomerization between their cis (Z) and trans (E) isomers upon irradiation.[1—85] The mechanism of the photoisomerization was intensively investigated by Hammmond and his school in USA in the 1960's[1,2] and by Schulte-Fröhlinde and his collaborators in Germany.[18] They utilized newly developed instruments for separation and accurate analysis of materials, particularly for stilbene, PhCH=CHPh, and its derivatives in solution.[16—18] On triplet sensitized irradiation of either cis or trans stilbene (Chart 1), while the resulting triplet state retained either cis or trans configuration, the cis ($^3c^*$) or trans triplet state ($^3t^*$), twisted around the unsaturated bond to get the more stable triplet state with perpendicular conformation. This perpendicular triplet state used be called as the phantom triplet state due to its invisible nature, $^3p^*$; it subsequently underwent diabatic crossing to the ground state of perpendicular conformation, ^1p, and finally afforded either cis (^1c) or trans (^1t) in the ground state with a definite ratio, as illustrated in Fig. 1.[1,3,4] Likewise, on direct irradiation of stilbene, the resulting singlet excited state with cis or trans configuration, the cis or trans singlet excited state, $^1c^*$ or $^1t^*$, converted to the perpendicular singlet state, $^1p^*$; this conversion was followed by deactivation to ^1p, giving ^1c and ^1t.[8—10,12,13]

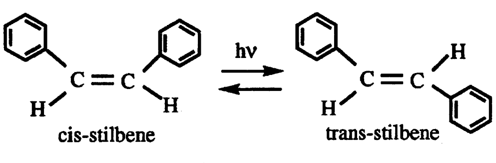


Chart 1.

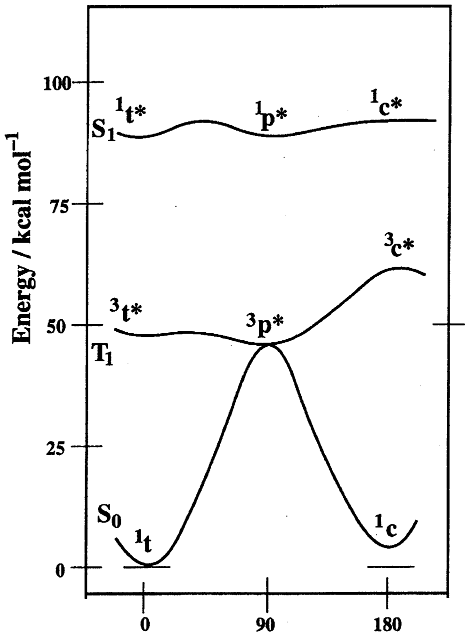


Fig. 1. Potential energy surfaces of photoisomerization of stilbene.

The mechanism of the photoisomerization revealed by precise investigation on stilbene was naturally assumed to cover photoisomerization of every unsaturated compound; it is so cited in standard textbooks for undergraduate course.

Soon after K. T. was appointed at the new university in the newly constructed science city, Tsukuba, in the northeastern suburb of Tokyo, he started to work with T. A. on photoisomerization of 1-arylalkenes with varying types of alkyl groups.[86—89] During the course of the investigation, 3,3-dimethyl-1-(2-naphthyl)-1-butene, 2-NpCH=CH^{t}Bu (Np for naphthyl), was found to exhibit interesting behavior different from stilbene (Chart 2).[87,88] Thus, the triplet state of this compound was found to be composed of a high population of $^3t^*$ equilibrated with $^3p^*$, as revealed by a transient absorption assigned to $^3t^*$ at 400—600 nm; the presence of oxygen resulted in increase of the photostationary ratio of trans to cis isomer, $([t]/[c])_{pss}$, due to quenching of $^3t^*$. In contrast, in stilbene, $^3t^*$ was less stable than $^3p^*$ and addition of oxygen did not affect $([t]/[c])_{pss}$. Oxygen much more effectively quenched the highly populated $^3p^*$ by a spin exchange mechanism, without changing $([t]/[c])_{pss}$, than it quenched less populated $^3t^*$ by an energy transfer mechanism.[87,88]

One-Way Isomerization

The above effect of substitution of a 2-naphthyl group on the unsaturated carbon to stabilize $^3t^*$ was assumed to be due to the triplet energy of a naphthyl group being lower than that of the benzene ring present in styrene and stilbene. Then, to prove this hypothesis, we decided with Takashi Karatsu and Hirochika Sakuragi to introduce a 2-anthryl group on the unsaturated bond in place of a 2-naphthyl group. During the preparation of cis and trans isomers of 1-(2-anthryl)-3,3-dimethyl-1-butene, 2-AntCH=CH^{t}Bu, (Ant for anthryl), the cis isomer isomerized to the trans isomer under room light, whereas the trans isomer was stable (Chart 3). Photochemical studies of this compound led us to the finding that this compound underwent solely cis to trans one-way isomerization, not accompanied at all by reverse trans to cis isomerization, upon direct and triplet sensitized irradiation in solution. Furthermore, another feature was that the quantum yield for the cis to trans isomerization, $\Phi_{c\rightarrow t}$, increased linearly with the cis isomer concentration, far exceeding unity, upon direct and sensitized irradiation.[15,90—92] This result means that $^3c^*$ once produced induced isomerization of many cis molecules by a quantum chain process.

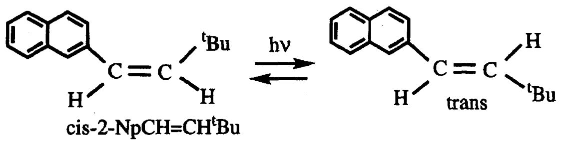


Chart 2.

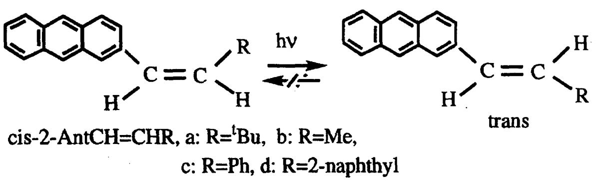


Chart 3.

To understand this novel type of isomerization, we assumed that, in the triplet state of this compound, $^3p^*$ was no longer located at a deep energy minimum as in stilbene, and presented a potential energy surface such as depicted in Fig. 2.[90] Thus, on this potential energy surface, the initially resulting $^3c^*$ twisted around the double bond along the descending slope, passed through $^3p^*$ as rapidly as through other points on the slope preceding the intersystem crossing to ^1p, and finally gave $^3t^*$. The conversion from $^3c^*$ to $^3t^*$ proceeded in an adiabatic way along the potential energy surface of the triplet state. This was contrasted with the isomerization of stilbene and other ethylenes which took place in a diabatic way. The $^3t^*$ underwent either unimolecular deactivation to ^1t or energy transfer to the cis isomer to regenerate $^3c^*$, therefore accomplishing the quantum chain process.[90—93] On excitation of the trans isomer, the resulting $^3t^*$ could not climb up the slope to reach $^3p^*$ and simply deactivates to ^1t. On direct excitation, each of the cis and trans isomers showed a fluorescence spectrum with an intrinsic lifetime. The singlet excited state underwent either fluorescence emission or intersystem crossing to the triplet state of each configuration, among which $^3c^*$ isomerized to $^3t^*$.[90—92,94—97] We named this type of isomerization as one-way isomerization in the first publication in early 1983.[90]

Similarly to 2-AntCH=CH^{t}Bu, 2-anthrylethylene carrying methyl, phenyl, and 2-naphthyl groups at the terminal unsaturated carbon, 2-AntCH=CHMe, 2-AntCH=CHPh, and 2-AntCH=CH-2-Np, underwent one-way isomerization. On laser excitation, both cis and trans isomers of each 2-anthrylethylene afforded

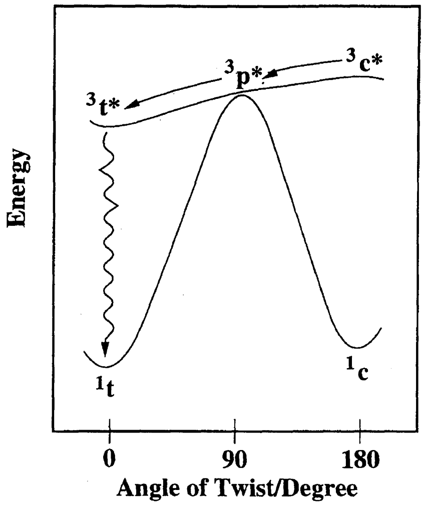


Fig. 2. Potential energy surface of one-way isomerization proposed in 1983.

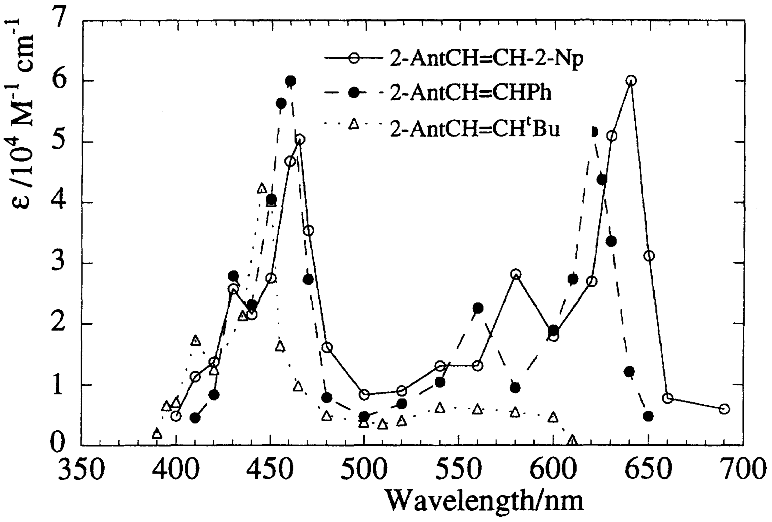


Fig. 3. T–T absorption spectra of 2-anthrylethylenes at room temperature in benzene determined microseconds after the laser pulse.

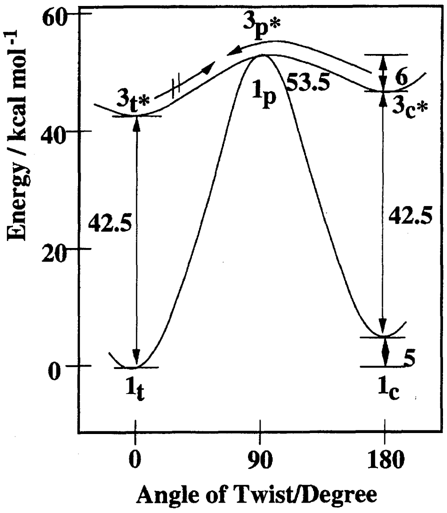


Fig. 4. Potential energy surface of one-way isomerization of 2-AntCH=CH^{t}Bu.

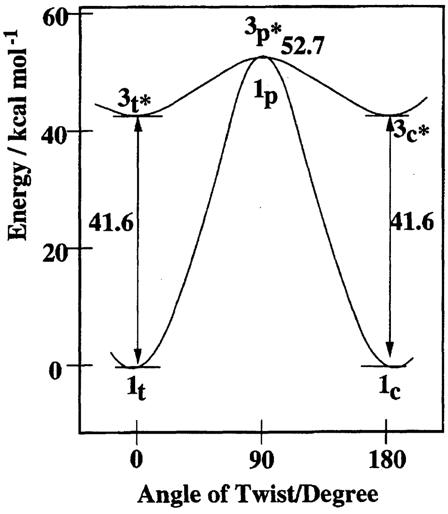


Fig. 5. Potential energy surface of adiabatic photoisomerization of 2-AntCH=CHD.

the same transient absorption in microseconds after the laser pulse, which decayed with a lifetime of hundreds of μs and was assigned to ^{3}t*, not to ^{3}p*. If the triplet states of these ethylenes took the perpendicular conformation, ^{3}p*, they should show nearly the same absorption irrespective of the substituents at long wavelength region, since the largest chromophore should be a 2-anthrylmethyl moiety 2-Ant–C(H)•; in addition, they would decay in lifetimes at most hundreds of nanoseconds like ^{3}p* of stilbene.

However, the triplet state resulting from laser excitation of the 2-anthrylethylenes showed absorption shifting to longer wavelength from alkyl (*t*-butyl and methyl), phenyl and 2-naphthyl and had lifetimes of 100—200 μs, as illustrated in Fig. 3. These results enabled one to assign the observed triplet state definitely to ^{3}t*, since the chromophore of ^{3}t* became larger in the above sequence and ^{3}t* should be alive in much longer lifetime than ^{3}p* due to the larger energy difference over the ground state of the corresponding conformation.

When this isomerization was first presented at the International Conference on Photochemistry in August 1983 in Maryland, U. S. A., many comments were kindly received by Prof. Marye Anne Fox, the chairperson. Some comments tended to assume this isomerization to be an exceptional case due to the presence of a bulky *t*-butyl group, without considering that styrene and 2-naphthylethylene carrying a *t*-butyl group at the other terminal unsaturated carbon isomerized between the cis and trans isomers. The above situation reflected that a concept taken mostly from the works on stilbene influenced the workers at that time.

Subsequently, in the next year (July 1984), when this work was presented at a workshop at the IUPAC Symposium on Photochemistry at Interlaken, Switzerland, several workers paid much attention to the new finding, although some were still suspicious about the signifi-

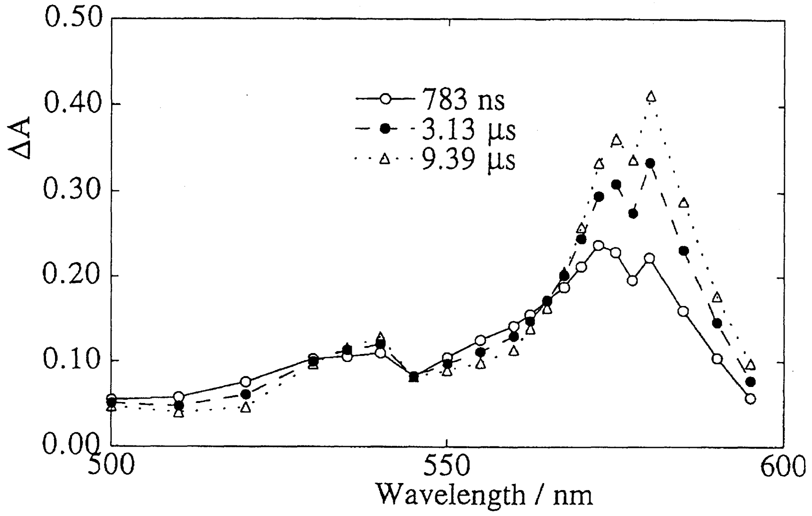


Fig. 6. T–T absorption spectra of 3-PerCH=CHPh in methylcyclohexane at 205.4 K showing $^3c^* \rightarrow {}^3t^*$ conversion.

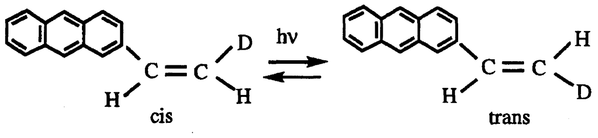


Chart 4.

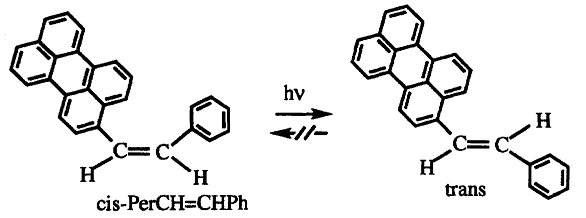


Chart 5.

cance of this fact. Our assignment of the observed long lived triplet state to $^3t^*$ not to $^3p^*$ was soon supported by a semi-empirical calculation of the T–T absorption carried out by Professor Jakob Wirz, Basel, Switzerland, immediately after the Symposium.[98)]

One year later, in July 1985, the new concept was generally recognized through active discussion and many fruitful comments lasting nearly one hour after a plenary lecture by K. T. at the Gordon Conference on Organic Photochemistry chaired by Professor Peter Wagner.

Then the problem was to decide whether $^3c^*$ would be unstable and very short-lived, as depicted in the proposed potential energy surface in Fig. 2 or would be situated at a sufficiently deep energy minimum. In nanoseconds after laser excitation of *cis*-2-AntCH=CH^{t}Bu in benzene at ambient temperature, an absorption with $\lambda_{max}=440$ nm decayed with a rate constant of 2×10^6 s^{-1}; concurrently a new absorption with $\lambda_{max}=445$ nm grew up with the same rate constant and finally decayed with a much longer lifetime.[94)] The former and the latter absorptions were reasonably assigned to $^3c^*$ and $^3t^*$ based on comparison with absorptions of $^3c^*$ and $^3t^*$ observed at 77 K in EPA. The results meant that in 2-AntCH=CH^{t}Bu the initially obtained $^3c^*$ converted to $^3t^*$ in a lifetime of 500 ns at ambient temperature. The Arrhenius treatment revealed that $^3c^*$ converted to $^3t^*$ overcoming an energy barrier of 6.0 kcal mol^{-1} with a frequency factor of 5×10^{10} s^{-1}.

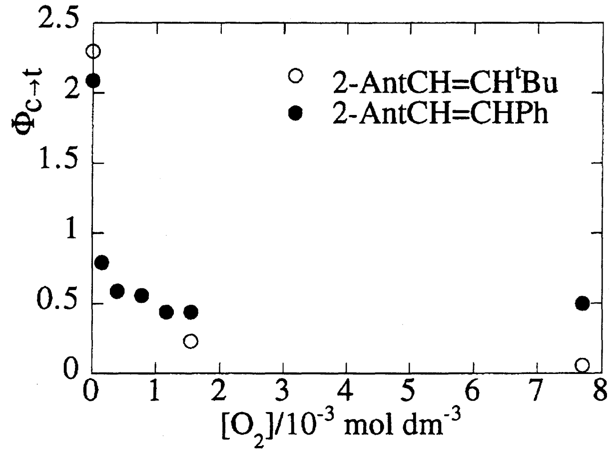


Fig. 7. Effect of oxygen on the quantum yield of cis→trans isomerization of 2-anthrylethylenes.

The observed activation energy for the isomerization and the energies of $^3c^*$ and $^3t^*$ over the ground states determined by their phosphorescence and by rate constants for triplet energy transfer from appropriate triplet sensitizers enabled us to draw a revised potential energy surface, given in Fig. 4.[94)] It was remarkable to be able to draw it based on experimental data.

The presence of an activation barrier in the isomerization was also demonstrated by the following traditional procedure. 2-(2-Deuteriovinyl)anthracene, 2-AntCH=CHD, in which the cis and the trans isomers have essentially the same electronic energy in the ground state and the triplet state, as depicted in Fig. 5, did not isomerize at temperature lower than 10 °C in

On triplet sensitization	**On direct irradiation**	**The net isomerization**
$^1S \xrightarrow{h\nu} {}^1S^*$	$^1c \xrightarrow{h\nu} {}^1c^*$	$^3c^* \longrightarrow {}^3t^*$
$^1S^* \xrightarrow{\Phi_T^S} {}^3S^*$	$^1c^* \xrightarrow{\Phi_{isc}} {}^3c^*$	$^3t^* \xrightarrow{k_{td}} {}^1t$
$^3S^* + {}^1c \longrightarrow {}^1S + {}^3c^*$		$^3t^* + {}^1c \xrightarrow{k_{tc}} {}^1t + {}^3c^*$

Scheme 1. Mechanism for the one-way isomerization in the triplet state.

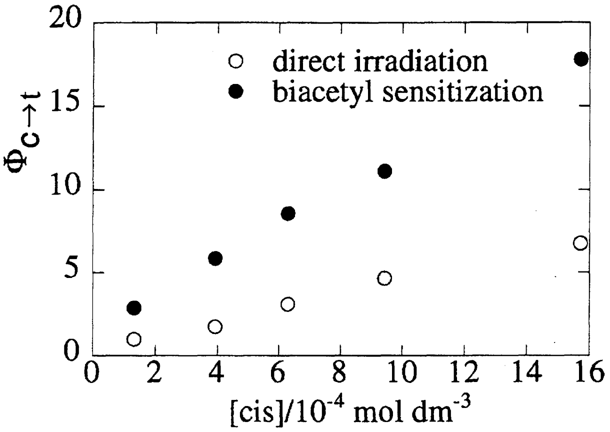


Fig. 8. Effect of cis isomer concentration on the quantum yield of cis→trans isomerization of 2-AntCH=CHPh in benzene.

toluene (Chart 4). But they isomerized above 10 °C and the quantum yield was gradually increased with temperature.[99,100] The Arrhenius treatment showed that the isomerization proceeded with an activation energy of 11.1 kcal mol^{-1} and a frequency factor of 5×10^{11} s^{-1}.

However, on laser excitation of 2-AntCH=CHPh, its cis and trans isomers afforded the same absorption with hundreds μs lifetime due to $^3t^*$ in the nanosecond region after the laser pulse even at 77 K. Both $^3c^*$ and $^3t^*$ were expected to give different absorptions, since $^3c^*$ and $^3t^*$ of a 3-perylenylethylene carrying a phenyl group on the other terminal carbon, 3-Per–CH=CHPh (Per for perylenyl) (Chart 5), showed considerably different absorptions, as depicted in Fig. 6, and $^3c^*$ converted to $^3t^*$ with a rate constant of 1.0×10^6 s^{-1} at 229 K.[101] These results show that the $^3c^*$ of 2-AntCH=CHPh rapidly converted to $^3t^*$, essentially without an activation barrier; in the triplet states of 2-anthrylethylenes, 2-AntCH=CHR, the activation energy for the isomerization much decreased from R=H and ^{t}Bu to R=Ph.

Whether $^3c^*$ was situated at a deep energy minimum or not was further examined based on the effect of oxygen. If $^3c^*$ was at a deep minimum with a sufficiently long lifetime, then, upon irradiation of a cis isomer, addition of oxygen would quench $^3c^*$ by energy transfer. This would result in deactivation of $^3c^*$ to ^1c accompanied by production of the singlet oxygen, thereby, suppressing the isomerization to the trans isomer. On the other hand, if $^3c^*$ was not located at a deep minimum, $^3c^*$ would undergo twisting around the double bond to $^3p^*$ in preference to the quenching by oxygen. The $^3p^*$, if located in a minimum of an appropriate lifetime, would be quenched by oxygen in a spin exchange mechanism with a rate constant (9×10^9 dm^3 mol^{-1} s^{-1}), three times larger than that for quenching of $^3c^*$ or $^3t^*$ by oxygen (3×10^9 dm^3 mol^{-1} s^{-1}) in an energy transfer mechanism.[17,19,96] Then oxygen could accelerate the intersystem crossing from $^3p^*$ to ^1p giving ^1t and ^1c without producing the singlet oxygen. However, if $^3p^*$ was not located in a minimum, $^3p^*$ resulting from $^3c^*$ would further twist to $^3t^*$, which, when located in a deep minimum, would be quenched by oxygen to give ^1t and the singlet oxygen. On excitation of a trans isomer, the produced $^3t^*$, when situated at a deep minimum, would be effectively quenched by oxygen giving the singlet oxygen.

On direct irradiation of *cis*-2-AntCH=CH^{t}Bu in benzene, the presence of oxygen in 8×10^{-3} mol dm^{-3} under 760 Torr of oxygen (1 Torr=133.322 Pa) almost completely suppressed the isomerization, as depicted in Fig. 7, where $\Phi_{c\to t}$ is plotted against the concentration of oxygen.[102] The efficiency for production of the singlet oxygen from the triplet state, Φ_Δ, determined by measuring its characteristic emission at 1.27 μm at 1.3×10^{-4} mol dm^{-3} oxygen, was nearly unity for both the cis (0.9) and the trans (0.8) isomers.[96] Since the isomerization proceeded solely from $^3c^*$ to $^3t^*$, the above results indicate that $^3c^*$ was quenched by oxygen in an energy transfer mechanism before undergoing isomerization to $^3t^*$, and $^3t^*$ was similarly quenched by oxygen. Therefore, not only $^3t^*$ but also $^3c^*$ of 2-AntCH=CH^{t}Bu were shown to be located in a sufficiently deep minimum with a sufficiently long lifetime to be quenched by oxygen. In 2-AntCH=CHPh, addition of oxygen reduced $\Phi_{c\to t}$; however, increase of oxygen concentration was not so effective to reduce $\Phi_{c\to t}$ as in 2-AntCH=CH^{t}Bu which still gave us a problem to be clarified.

Another feature of the one-way photoisomerization, that is, the isomerization proceeding in a quantum chain process, is now described. The mechanism of the one-way isomerization is depicted in Scheme 1, where S denotes the sensitizer and Φ's and k's are the quantum yields and the rate constants for the corresponding processes. According to the above mechanism, the quantum yield for the cis to trans isomerization in the presence of sufficient concentration of the cis isomer ($>1\times10^{-3}$ mol dm^{-3}) on sensitization, $\Phi^{S}_{c\to t}$, and that on direct irradiation, $\Phi^{dir}_{c\to t}$, are written below (Eqs. 1

Table 1. Modes of the Isomerization of ArCH=CHR, the Lifetimes and Absorption Maxima (in Parentheses) of the Triplet States, and Activation Energies (E_a/kcal mol^{-1}) and Frequency Factors (A/s^{-1}) for $^3c^* \rightarrow {}^3t^*$ Isomerization

Ar	Triplet energy of ArH	τ_T/μs (λ_{max}(T–T)/nm)				Refs.
	kcal mol^{-1}	R=^{t}Bu		R=Ph		
Phenyl	84.3	Two-way		Two-way 0.063 (<360)		1,17,86
4-Benzoylphenyl	68.6	Two-way 0.090 (<360)				92b
4-Biphenylyl	65.7	Two-way		Two-way		92b
9-Phenanthryl	61.9			Two-way 0.43 (460)		38—40
2-Naphthyl	60.9	Two-way 0.13 (420, 570)		Two-way 0.14 (400, 500)		21,22,87
3-Chrysenyl	56.6	Two-way 0.36 (600)		Two-way 0.14 (<400)		109
8-Fluoranthenyl	54.2	One-way 25 (440, 580)		Two-way (dual) 0.50 (480, 600)		106—108
1-Pyrenyl	48.2	One-way 54 (445)		Two-way (dual) 27 (470, 520)		104,105
1-Anthryl	42	One-way ≈100 (440, 500)	E_a=4.6 A=5×10^9	One-way ≈100 (570)		110
2-Anthryl	42	One-way 280 (450, 540)	E_a=6.0 A=5×10^{10}	One-way 190 (460, 620)		94,110
9-Anthryl	42	One-way ≈100 (410, 435)	E_a=3.1 A=4×10^8	One-way ≈100 (325, ≈450)		110
Ferrocenyl	40			Inefficient one-way		111
1-Azulenyl	39.8			One-way 4.7 (420)		113
3-Perylenyl	35			One-way ≈100 (540, 580)	E_a=6.6 A=2.1×10^{12}	101

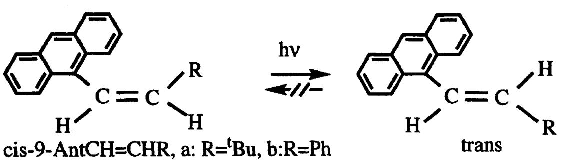
and 2), where Φ_T^S and Φ_{isc} mean the quantum yields for the intersystem crossing of sensitizers used and of the cis isomers, respectively, k_{td} and k_{tc} stand for rate constants for unimolecular deactivation of $^3t^*$ and for energy transfer from $^3t^*$ to ^1c, respectively.

$$\Phi_{c\rightarrow t}^S = \Phi_T^S(1 + k_{tc}[\text{cis}]/k_{td}) \quad (1)$$

$$\Phi_{c\rightarrow t}^{dir} = \Phi_{isc}(1 + k_{tc}[\text{cis}]/k_{td}). \quad (2)$$

The above equations show that $\Phi_{c\rightarrow t}^S$ and $\Phi_{c\rightarrow t}^{dir}$ increase linearly with the concentration of the cis isomers employed; the intercepts correspond to Φ_T^S in the sensitization and Φ_{isc} in the direct irradiation. These values can be compared with those reported or determined by transient absorption; the slopes divided by the intercepts give k_{tc}/k_{td}, which, being multiplied by the observed k_{td}, as the reciprocal of the lifetime of $^3t^*$, affords k_{tc}.

Figure 8 illustrates typical results obtained for 2-AntCH=CHPh, which fit the above equation. The k_{tc} values are ca. 3×10^8 dm^3 mol^{-1} s^{-1}.[97)]



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

trans

Chart 6.

Structural Factors Governing the Mode of the Isomerization

Whereas stilbene, styrene, naphthylethylenes, and many ethylenes isomerized mutually between the cis and trans isomers, 2-anthrylethylenes underwent cis to trans one-way isomerization with a quantum chain process. Was this behavior of 2-anthrylethylenes exceptional or not? If not, what general factors led stilbene and the other compounds to "two-way" mutual isomerization and led 2-anthrylethylenes to one-way isomerization. During the course of establishing a new concept of the one-way isomerization, Becker and his collaborators[14,46—48)] showed another compound undergoing one-way isomerization, that is, 9-AntCH=CHPh and its derivatives (Chart 6). Their works also indicated that anthracene nucleus on the unsaturated carbon led to one-way isomerization. We noticed the role of the triplet excitation energies (E_T) of aromatic nuclei substituted on the unsaturated carbon. Substitution of aromatic nuclei with higher triplet energies like phenyl and naphthyl groups induced two-way isomerization, and an anthryl group with a lower triplet energy resulted in one-way isomerization. To prove this hypothesis, we prepared two series of arylethylenes with aromatic nuclei of varying triplet energies, ArCH=CH^{t}Bu (^{t}Bu might be replaced by Me) and ArCH=CHPh (Chart 7). Table 1[86—92,94—112)] lists the results together with the

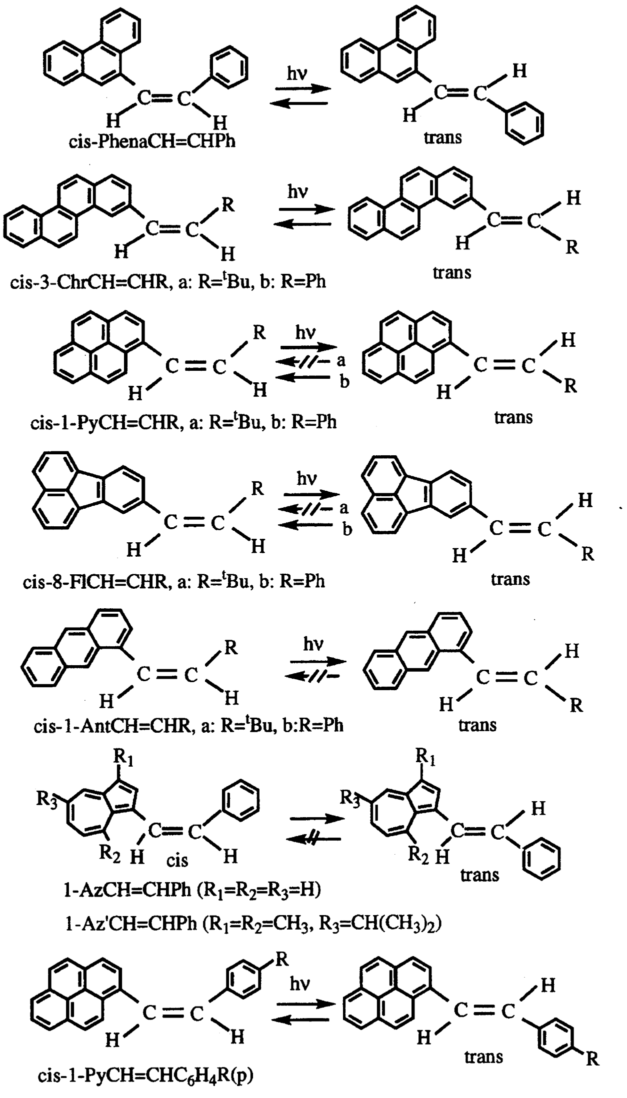


Chart 7.

triplet energies of the aromatic nuclei, lifetimes of the triplet states of the ethylenes, the absorption maxima of the T–T absorption, and the kinetic results for $^3c^*\rightarrow{}^3t^*$ conversion, when available.

In the both series of ethylenes, aromatic nuclei with E_T higher than 56 kcal mol^{-1}, that is, phenyl, 4-benzoylphenyl, 4-biphenylyl, 9-phenanthryl (9-Phena), 2-naphthyl, and 3-chrysenyl (3-Chr) led to typical two-way isomerization. The lifetime of the triplet states were hundreds of nanoseconds or fewer. On the other hand, one-way isomerization was induced in the ArCH=CH^{t}Bu series by those with E_T lower than 54 kcal mol^{-1}, that is, 8-fluoranthenyl (8-Fl), 1-pyrenyl (1-Py), 1, 2, and 9-anthryl. In the ArCH=CHPh series, it was induced by those with E_T much lower than above, that is, lower than 42 kcal mol^{-1}, 1-anthryl, 2-anthryl (including Ph substituted with 4-methoxy, bromo, and nitro), 9-anthryl, 1-azulenyl (1-Az), its isopropyldimethyl derivative (1-Az′), and 3-perylenyl.[104—108,110,113,114] The triplet states of ethylenes undergoing one-way isomerization had lifetimes of 10^1—10^2 μs.

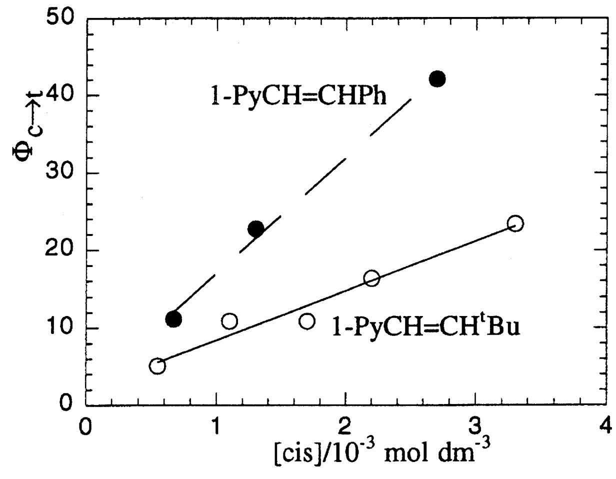
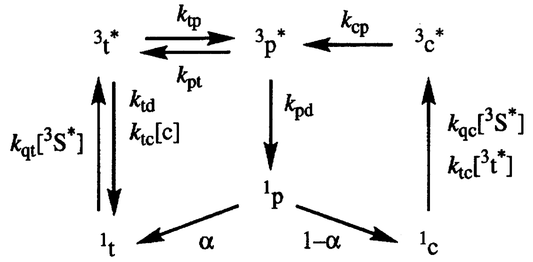


Fig. 9. Effect of cis isomer concentration on the quantum yield of cis→trans isomerization of 1-pyrenylethylenes in benzene.



Scheme 2. Mechanism for the isomerization of dual character in 1-PyCH=CHPh in the triplet state.

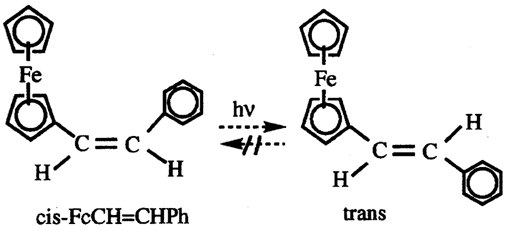


Chart 8.

In the ArCH=CHPh series, aromatic nuclei having E_T lower than 57 and higher than 42 kcal mol^{-1}, that is, 8-Fl (E_T=54 kcal mol^{-1}) and 1-Py (E_T=48 kcal mol^{-1}), led to two-way isomerization. Starting from either isomer they give a photostationary mixture very rich in trans, particularly in high concentration. Furthermore, $\Phi_{c\rightarrow t}$ increased linearly along with the concentration of the cis isomer and attained as large as 40 as depicted in Fig. 9 for 1-PyCH=CHPh.[104] Thus, these ethylenes have a dual character of two-way and one-way isomerizations. Furthermore, the lifetime of the triplet state of 1-PyCH=CHPh was as long as 27 μs,[104] whereas that of 8-FlCH=CHPh remained at 500 ns.[108] Also derivatives of 1-PyCH=CHPh substituted at 4-position, 1-PyCH=CHC$_6$H$_4$R(p) (R=MeO, CN, and NO$_2$)[115,116] behaved likewise to 1-PyCH=CHPh (Chart 7). Therefore, these two types of ethylenes were located on a border of the change from the typical two-way to one-way isomerization.

Two ethylenes in the bottom, FcCH=CHPh (Fc: ferrocenyl) (Chart 8) and 3-PerCH=CHMe, show another type of unique behavior. The examination of these compounds was attempted to find ethylenes which would not undergo any or much isomerization, as described later.

Isomerization of Dual Character

Returning to the behavior of the triplet states of ethylenes of the dual character, their lifetimes are longer than those of the typical two-way isomerization. This result shows that their triplet states are composed by mixtures of shorter-lived $^3p^*$ and longer-lived $^3t^*$ in an equilibrium with an equilibrium constant of K_{tp} $(=[^3p^*]/[^3t^*])$. The absorption spectrum of the triplet state of 1-PyCH=CHPh with λ_{max} of 470 and 520 nm is mostly due to $^3t^*$, since $^3p^*$ would give an absorption at much shorter wavelength. The lifetime of these triplet states, τ_T, is expressed by Eq. 3, where k_{pd} and k_{td} stand for rate constants for deactivation of $^3p^*$ and $^3t^*$, and are assumed to be similar to those for stilbene (2×10^7 s^{-1}) and one-way isomerizing ethylenes (2×10^4 s^{-1}), respectively.

$$\tau_T = (1+K_{tp})/(K_{tp}k_{pd}+k_{td}). \tag{3}$$

Substitution of the assumed values for k_{pd} and k_{td} affords a K_{tp} of the order of 10^{-3} at 25 °C for 1-PyCH=CHPh. Thus, $^3t^*$ is 1000 times more populated than $^3p^*$. However, taking into account the 1000 times larger value for k_{pd} than for k_{td}, deactivation of the triplet states is to take place from two funnels of $^3p^*$ and $^3t^*$ in a nearly 1 to 1 ratio.

Elevation of temperature increases the population of the less populated species, $^3p^*$, therefore reducing τ_T as observed from 39 µs at 5 °C to 15 µs at 56 °C.[104)]

The equilibrium between $^3p^*$ and $^3t^*$ is further confirmed by the quenching effect by azulene and oxygen. Azulene quenches only $^3t^*$ by energy transfer with a rate constant (k_{AZ}) of $(0.8—1)\times10^{10}$ dm^3 mol^{-1} s^{-1} in benzene at ambient temperature for sufficiently exothermic energy transfer, and cannot quench $^3p^*$.[17,21)] Oxygen quenches $^3p^*$ by a spin exchange mechanism with a rate constant (k_{po}) of 9×10^9 dm^3 mol^{-1} s^{-1} and quenches $^3t^*$ by energy transfer with a rate constant (k_{to}) of 3×10^9 dm^3 mol^{-1} s^{-1} for sufficient exothermic energy transfer.[17,21)] Therefore, azulene quenches a mixture of $^3t^*$ and $^3p^*$ with a rate constant of $k_q^{AZ}=k_{AZ}/(1+K_{tp})$, and oxygen quenches with a rate constant of $k_q^{O2}=(k_{to}+K_{tp}k_{op})/(1+K_{tp})$. The higher the population of $^3t^*$, the higher the k_q^{AZ} and the lower the k_q^{O2}. The k_q^{AZ} and k_q^{O2} values for 1-PyCH=CHPh as 7.3×10^9 and 3.6×10^9 dm^3 mol^{-1} s^{-1}, respectively, show, on comparison with the values of stilbene ($k_q^{AZ}=(1—2)\times10^9$, $k_q^{O2}=8\times10^9$ dm^3 mol^{-1} s^{-1}),[17,21)] that the $^3t^*$ is very highly populated in the triplet state of 1-PyCH=CHPh.[104)]

The isomerization of 1-PyCH=CHPh and its derivatives proceeds in a mechanism depicted in Scheme 2.[104)] In this mechanism, on starting from either isomer on triplet sensitization, the resulting $^3p^*$ and $^3t^*$ are in equilibrium. Deactivation from $^3p^*$ leads to two-way isomerization and deactivation of $^3t^*$ results in one-way isomerization. Thus, unimolecular deactivation of $^3t^*$ gives ^1t, and energy transfer from $^3t^*$ to ^1c induces quantum chain isomerization. When the equilibrium between $^3t^*$ and $^3p^*$ is established, $\Phi_{c\to t}$ and $([t]/[c])_s$ are expressed as in Eqs. 4 and 5. The $\Phi_{c\to t}$ fits the observed results, as depicted in Fig. 9.[104)]

$$\Phi_{c\to t} = \Phi_T^S(\alpha K_{tp}k_{pd}+k_{td}+k_{tc}[\text{cis}])/(K_{tp}k_{pd}+k_{td}), \tag{4}$$

$$([t]/[c])_s=\{\alpha K_{tp}k_{pd}+k_{td}+k_{tc}([\text{cis}]+[\text{trans}])\}/(1-\alpha)K_{tp}k_{pd}. \tag{5}$$

The slope corresponds to $\Phi_T^S k_{tc}/(K_{tp}k_{pd}+k_{td})$. By determining K_{tp}, k_{tc} can be estimated. A typical case in 1-PyCH=CHPh shows k_{tc} as 7.1×10^8 dm^3 mol^{-1} s^{-1}.

However, direct determination of the rate constant for the above energy transfer, k_{tc}, by transient spectroscopy, is very difficult, since $^3c^*$ and $^3t^*$ show absorptions which overlap each other.

In the derivatives of 1-PyCH=CHC$_6$H$_4$R(p), $([t]/[c])_s$ tends to increase in the sequence: R=MeO, H, CN, and NO$_2$, due to the decrease of K_{tp} in this sequence from 1.6×10^{-3}, 8.6×10^{-4}, 7.6×10^{-4}, to 4.4×10^{-4}.[115)] Thus, in the equilibrium between $^3p^*$ and $^3t^*$, increase of electron accepting ability of the substituents (R) more effectively increases population of $^3t^*$ than that of $^3p^*$. The ΔG_{tp} increases from 3.8, 4.1, 4.2 to 4.5 kcal mol^{-1} in the above sequence.[115)]

In 1-pyrenylethylenes, substitution of a phenyl group on the terminal carbon leads to isomerization by dual mechanism, whereas that of a *t*-butyl group induces typical one-way isomerization. These results give an insight into the nature of the potential energy surface of the triplet states. Their contrasting behaviors can be understood in terms of potential energy surfaces depicted in Fig. 10 as discussed later.

Inefficient Isomerization

By two approaches we attempted to find ethylenes which did not isomerize at all. One approach was to introduce a substituent such as a ferrocene ring on the unsaturated carbon; this accelerated deactivation.[111)] Another approach was to substitute an aromatic nucleus with a very low triplet excitation energy such as perylene.[101,117)]

In the first approach, an anthryl group of 2-AntCH=CHPh was replaced by a ferrocenyl group (Fc). The triplet state of ferrocene was known to have nearly

Table 2. Effects of Aromatic Substituents on the Mode of the Isomerization of ArCR=NOCH$_3^{\mathrm{a)}}$

Ar	R	Triplet energy of ArH	Mode of isomerization	$\Phi_{Z\rightarrow E}$ ([Z])	Refs.
		kcal mol^{-1}	τ_T/μs (λ_max(T–T)/nm)		
Phenyl	CH$_3$	84.3	Two-way	0.35 (3×10^{-2} M)	43,44
2-Naphthyl	CH$_3$	60.9	Two-way	0.51 (5×10^{-2} M)	43,44
1-Pyrenyl	H	48.2	Two-way 10 (440)	3.2 (1.3×10^{-3} M)	120
2-Anthryl	CH$_3$	42	One-way 90 (450, 540)	22 (1.34×10^{-3} M)	119,120

a) 1 M=1 mol dm^{-3}.

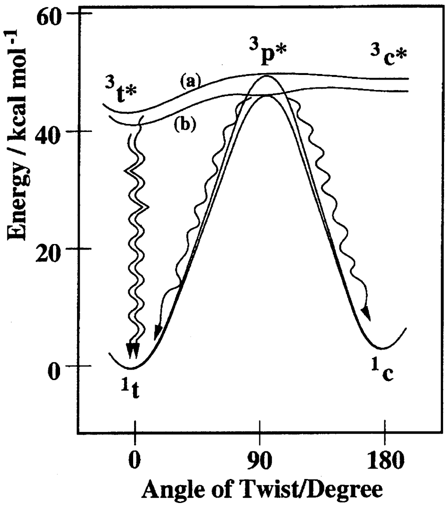


Fig. 10. Potential energy surfaces of isomerization of 1-PyCH=CH^{t}Bu (a) and 1-PyCH=CHPh (b).

the same excitation energy as anthracene but rapidly deactivates within a very short lifetime of less than 1 ns.[118] Therefore, FcCH=CHPh was supposed to have a vey similar potential energy surface to that of 2-AntCH=CHPh, but not to do efficient isomerization even from ^{3}c* to ^{3}t* (Chart 8). Actually, the trans isomer of FcCH=CHPh did not isomerize at all and the cis isomerized to the trans with a very low quantum yield of an order of 10^{-3} at ambient temperature, due to acceleration of deactivation of ^{3}c* by the effect of iron atoms.[111]

The second approach attempted to increase the energy barrier not only from ^{3}t* to ^{3}c* but also from ^{3}c* to ^{3}t* in the series of ArCH=CHAlkyl by introducing an aromatic group of low triplet energy. This was expected to lower the energy of ^{3}t* and ^{3}c* without much affecting the energy of ^{3}p*. The quantum yield of cis→trans isomerization of 3-PerCH=CHMe was determined as low as ca. 10^{-2}.[117]

General Rules for the Effect of Aromatic Groups on the Isomerization of Arylethylenes

One can deduce from the above facts the following general rules for the effect of aryl groups on the isomerization of arylethylenes.

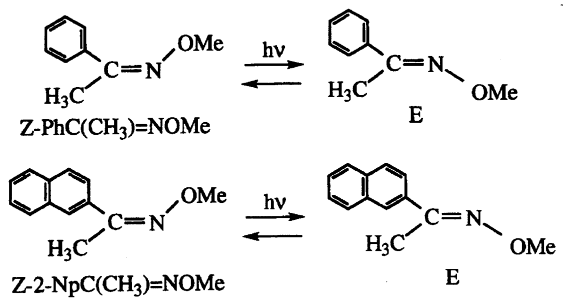


Chart 9.

Rule 1. Aryl groups with high E_T lead to two-way isomerization occurring through deactivation from ^{3}p*, and those with lower E_T result in cis-to-trans one-way isomerization proceeding through deactivation from ^{3}t*.

Rule 2. The ArCH=CHPh series tends to stabilize ^{3}p* more effectively than the ArCH=CHAlkyl series. As a result, change from the two-way mode to the one-way mode occurs with higher E_T of Ar in the ArCH=CHAlkyl series than the ArCH=CHPh series. In the ArCH=CHPh series, aryl groups of moderate E_T values, 8-Fl and 1-Py, lead to isomerization of dual character of two-way and one-way; this occurs through deactivation from two funnels of ^{3}p* and ^{3}t*.

Rule 3. Presence of substituents such as ferrocene, which have lower E_T and undergo rapid deactivation of the triplet state, and of aryl groups with very low E_T such as perylene in 3-PerCH=CHCH$_3$ leads to inefficient isomerization.

The Effect of Triplet Energy of Aromatic Nucleus on the Isomerization of the C=N Unsaturated Bond. The C=N unsaturated compounds have *E* and *Z* isomers. Generally, *E* isomers are stable at ambient temperature in the dark but could isomerize into *Z* isomers on photoirradiation; these, however, facilely revert to the *E* isomers in a thermal process. However, substitution of alkoxyl groups on the nitrogen was found to stabilize the *Z* isomers. The ArC(CH$_3$)=NOMe was reported to photoisomerize between the *E* and *Z* isomers when Ar was Ph and 2-Np (Chart 9).[43,44] We undertook to examine the effect of the triplet energy of Ar groups on the isomerization as we did for arylethylenes. The results are summarized in Table 2.[43,44,119,120]

Table 3. Some Kinetic Values for Cis–Trans Isomerization of Arylethylenes

Compound	k_{tc} a)	$E_T^t(p)$ b)	$E_T^t(Az)$ b)	$E_T^c(p)$ b)	E_T^c b)	ΔH_{tp}	K_{tp}	Refs.
3-ChrCH=CH^{t}Bu	2.7×10^8	55.4		57.2		0.5	0.47	109
3-ChrCH=CHPh		54.9				−0.4	2.0	109
8-FlCH=CH^{t}Bu	2.9×10^7	49			(52)	(>6.5)	(2×10^{-5})	106,107
8-FlCH=CHPh	(6—7)$\times10^8$		44		(46)	1.5	0.1	107
1-PyCH=CH^{t}Bu	1.2×10^8	44		47				104b,105
1-PyCH=CHPh	7.1×10^8		41		(43)	5	2.7×10^{-3}	104
2-AntCH=CH^{t}Bu	3×10^7	42.5	40	42.5				97
2-AntCH=CHPh	3×10^8	41.5	38	41.5				97
2-AntCH=CH-2-Np	3×10^8	41.3	37	41.3				97
1-AntCH=CH^{t}Bu	3.3×10^8	40.7						110b
1-AntCH=CHPh	1.5×10^8	41	38.8					110b
2-AntC(CH$_3$)=NOMe	1.8×10^9		40		(41)			119b
1-AzCH=CHPh	1.3×10^8							113
1-Az′CH=CHPh	1.9×10^8							113

a) In $dm^3\,mol^{-1}\,s^{-1}$. b) Energy of the trans triplet state in $kcal\,mol^{-1}$ determined by phosphorescence measurement ($E_T^t(p)$) and by quenching experiment with azulene ($E_T^t(Az)$). c) Energy of the cis triplet state in $kcal\,mol^{-1}$ determined by phosphorescence measurement ($E_T^c(p)$) and by rate constant of energy transfer (k_{tc}) from $^3t^*$ to ^1c (E_T^c).

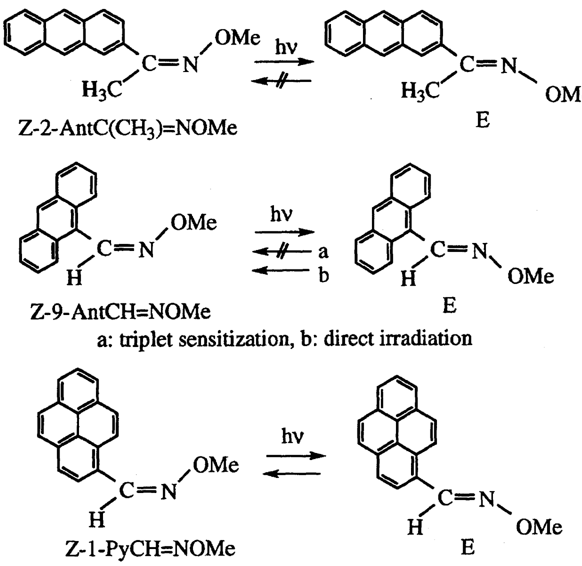


Chart 10.

The effect of Ar group was very similar to that in the arylethylenes, which was supported by calculation.[119c)] Thus, on triplet sensitization, 2-AntC(CH$_3$)=NOMe underwent solely *Z*-to-*E* isomerization. The $^3Z^*$ was converted to $^3E^*$ (λ_{max}: 438 nm) in methylcyclohexane at 16.2 °C with a rate constant of $3.8\times10^6\ s^{-1}$ with an activation energy of 6 $kcal\,mol^{-1}$ and a frequency factor of $1.6\times10^{11}\ s^{-1}$, as determined at −6.8—16.2 °C.[119b)] On benzil sensitization, the $\Phi_{Z\rightarrow E}$ value increased linearly along with the concentration of the *Z* isomer to attain 22 at a 1.34×10^{-3} $mol\,dm^{-3}$ concentration. The behavior of 9-AntCH=NOMe was somehow different from the 2-Ant compound (Chart 10). On camphorquinone sensitization 9-AntCH=NOMe underwent one-way *Z*-to-*E* isomerization, while the quantum yields of cis→trans isomerization remained at 2.8 at a 1.5×10^{-3} $mol\,dm^{-3}$ concentration.[120c)]

Furthermore, the effect of 1-Py group was similar to that in ArCH=CHPh. 1-PyCH=NOMe isomerized mutually between the isomers, however, with $\Phi_{Z\rightarrow E}$ increasing linearly with the *Z* isomer concentration.[120b,120c)] Therefore, like 1-PyCH=CHPh, the triplet state of this compound underwent isomerization in a dual mechanism by way of deactivation from $^3p^*$ for the two-way behavior and that from $^3E^*$ for one-way behavior associated with a quantum chain process.

The *Z*-isomer of 2-AntCH=NPh thermally reverts to the *E*-isomer at ambient temperature. However, at 210 K the *Z*-isomer was thermally stable and underwent one-way *Z*→*E* isomerization in EPA on eosin-Y sensitization. The triplet state decayed with a lifetime of 2 μs.[121)]

On the other hand, N=C and N=N bonds carrying a 2-Ant group at the unsaturated nitrogen atom, 2-AntN=CHPh and 2-AntN=NPh underwent mutual isomerization between the *Z*- and *E*-isomers. The triplet state of the former compound rapidly decayed with a lifetime of less than 200 ns, and the triplet state of the latter compound was not detected in a nanosecond time range.[121)]

Quantum Chain Process

Not only ethylenes undergoing typical one-way isomerization but also those of dual characters of one-way and two-way isomerizations such as 1-PyCH=CHPh undergo quantum chain isomerization by way of energy transfer from the resulting $^3t^*$ to cis.[104,105)]

Table 3 collects k_{tc} values obtained for various unsaturated compounds and the triplet energies (E_T) of $^3t^*$ and $^3c^*$, together with the equilibrium constant of $^3p^*$ with $^3t^*$ and their energy difference in the dual mechanism. The triplet energies are determined by phosphorescence, if emitted, and/or by measurement of the quenching of the triplet state ($^3t^*$) by azulene. Triplet

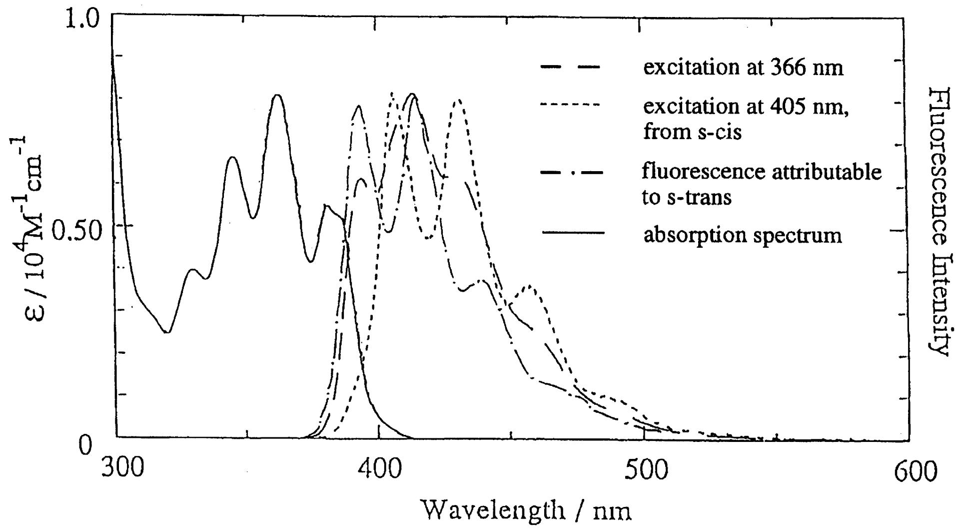


Fig. 11. Absorption and fluorescence spectra of (E)-2-AntC(CH_3)=NOMe.

states of ethylenes with low excitation energies undergo reversible energy transfer to azulene (E_T: 39.5—39.8 kcal mol^{-1}). The analysis of the decay curve of the transient absorption gives the rate constants for the above energy transfer (k_q) from which the difference of the triplet energies between azulene and unsaturated compounds (ΔE) can be estimated by the Sandros equation (Eq. 6).[122)]

$$k_q = k_{\mathrm{dif}}(\exp(-\Delta E/RT)/(1+\exp(-\Delta E/RT))) \qquad (6)$$

However, only a few cis compounds exhibit phosphorescence, and the quenching by azulene can provide the E_T of only the stablest triplet state ($^3t^*$); therefore, the E_T of many cis isomers cannot be estimated by this method.

As Table 3 indicates, the k_{tc} values determined in benzene at ambient temperature are in the range of 10^7—10^8 dm^3 mol^{-1} s^{-1}. This means that the energy transfer from $^3t^*$ to ^1c is slightly endothermic. According to the Sandros equation, the rate constants of 1×10^7, 1×10^8, and 1×10^9 dm^3 mol^{-1} s^{-1} correspond to 4.2, 2.8, and 1.4 kcal mol^{-1} endothermic process. Phosphorescence emitted from both trans and cis isomers shows that in 1-PyCH=CH^{t}Bu E_T for cis is 3 kcal mol^{-1} higher than that for trans,[104,123)] and in 3-ChrCH=CH^{t}Bu E_T for cis is nearly 2 kcal mol^{-1} higher than trans.[109)] These energy differences quantitatively fit the determined k_{tc}.

However, in 2-anthrylethylenes, the phosphorescence of their cis and trans isomers show different spectra but with nearly the same energy for the 0–0 band. If the excitation energies of the cis and trans isomers are the same, they should give a rate constant of $(1/2)k_{\mathrm{diff}}$, 5×10^9 dm^3 mol^{-1} s^{-1}, which is much higher than those observed.

The above discrepancy between the observed and the expected rate constants could be related to the presence of rotamers around the single bond connecting a 2-anthryl group and an unsaturated carbon in unsaturated compounds substituted with a 2-anthryl group.[127—143)] In the ground state at ambient temperature the s-trans rotamers are much more stable than the s-cis. In the triplet state, the resulted s-trans triplet state showing intrinsic absorption is converted to the more stable s-cis triplet state, by overcoming an activation barrier of 7.2 kcal mol^{-1} for *trans*-2-AntCH=CHPh[124)] and 4.6 kcal mol^{-1} for (E)-2-AntCH=NOMe.[126)] The produced s-cis triplet state deactivates to the ground state s-cis rotamer, which is subsequently converted to the more stable s-trans rotamer in the ground state. In *trans*-2-AntCH=CHPh, the triplet excitation energies for the s-trans and the s-cis rotamers are estimated as 41 and 39 kcal mol^{-1}, based on the phosphorescence of the model compounds.[124)] The former is similar to that determined from phosphorescence, 41.5 kcal mol^{-1}, and the latter to that determined from quenching by azulene, 38 kcal mol^{-1}. The phosphorescence certainly arises from the triplet state of the s-trans rotamer as a result of the excitation of the ground state which is almost exclusively populated by the s-trans at 77 K. On the other hand, azulene will quench the s-cis triplet state which is more highly populated in the triplet state at ambient temperature. The above facts suggest that the energy transfer from $^3t^*$ to ^1c in 2-anthryl compounds may take place from the s-cis rotamer of $^3t^*$ to the ground state of the cis isomer, which exists as the s-trans rotamer,

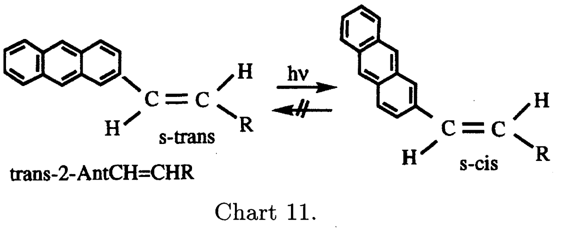


Chart 11.

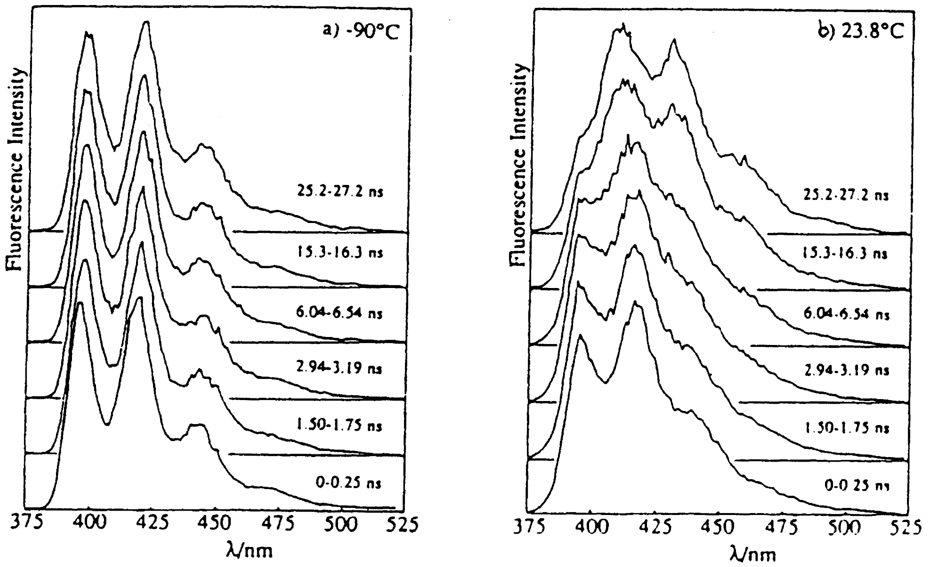


Fig. 12. Time-resolved fluorescence spectra of (*E*)-2-AntC(CH_3)=NOMe in deaerated toluene.

due to high instability of the *s*-cis rotamer by steric hindrance. In this case, the energy transfer must be 2—3 kcal mol^{-1} endothermic, which seemingly agrees with the observation. The initially resulting *s*-trans rotamer of $^3t^*$ will undergo internal rotation to the *s*-cis rotamer more rapidly (ca. 1×10^7 s^{-1} at ambient temperature) than the energy transfer to the cis isomer (estimated as, for example, 3×10^5 s^{-1} in the presence of 1×10^{-3} mol dm^{-3} of the cis isomer).

On the other hand, *trans*-1-PyCH=CH^{t}Bu is to exist mostly as the *s*-trans rotamer, because the *s*-cis is too unstable, due to the steric hindrance in the ground state and also in the triplet state. Accordingly, the *s*-trans rotamer of $^3t^*$ resulting from the $^3c^* \rightarrow {}^3t^*$ isomerization will undergo energy transfer to the *s*-trans rotamer of ^1c without undergoing internal rotation. The triplet excitation energies of these species are those determined from the phosphorescence as 44 and 47 kcal mol^{-1}, respectively.[104,123] Therefore, the excitation energies of the trans and cis isomers, both determined from the phosphorescence, undoubtedly correspond to those of the triplet states participating in the energy transfer, and their energy difference of 3 kcal mol^{-1} well agrees with the observed k_{tc}, 1.2×10^8 dm^3 mol^{-1} s^{-1}

Internal Rotation of Aromatic Nuclei

The trans isomers of unsaturated compounds substituted with a 2-anthryl group, *trans*-2-AntCH=CHR (R: Me, ^{t}Bu, Ph, and 2-Np), 2-vinylanthracene, and (*E*)-2-AntC(CH_3)=NOMe have rotamers, *s*-cis and *s*-trans, around the single bond connecting the anthracene ring and the unsaturated carbon as observed in several diarylethylenes (Chart 11).[124—143] Each rotamer has an intrinsic fluorescence spectrum and lifetime and its own, though very similar, absorption spectrum. Therefore, the apparent fluorescence spectrum depends upon the wavelength for excitation. Figure 11 shows the fluorescence spectrum of 2-AntC(CH_3)=NOMe as a typical example. The *s*-trans shows fluorescence emission with $\lambda_{\max}$ at 394, 415, and 436 nm, and the *s*-cis shows that with $\lambda_{\max}$ at 407, 431, and 457 nm.[125] In the ground state, *s*-trans rotamers are more stable and therefore, more highly populated than the *s*-cis rotamers.[125,126]

On laser excitation of the above compounds other than *trans*-2-AntCH=CHPh and 2-AntCH=CH-2-Np, the initially observed fluorescence is shifted to a different spectrum in nanoseconds lifetime at ambient temperature; however, the spectral change is frozen at 183 K, as shown for (*E*)-2-AntC(CH_3)=NOMe in Fig. 12 (Chart 12).[126] The spectral shifts are due to the internal rotation taking place from the excited singlet state of the *s*-trans rotamer, ^{1}(*s*-trans)* to that of the *s*-cis, ^{1}(*s*-cis)*, competing with deactivation of the ^{1}(*s*-trans)*. For example, in (*E*)-2-AntC(CH_3)=NOMe, in toluene at 23.8 °C, ^{1}(*s*-trans)* decays with a lifetime of

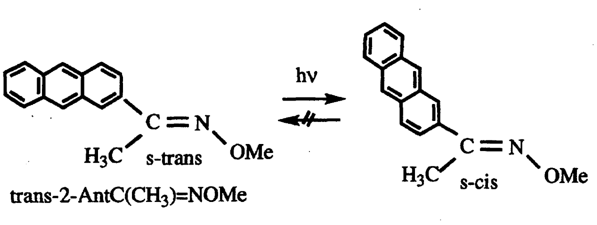


Chart 12.

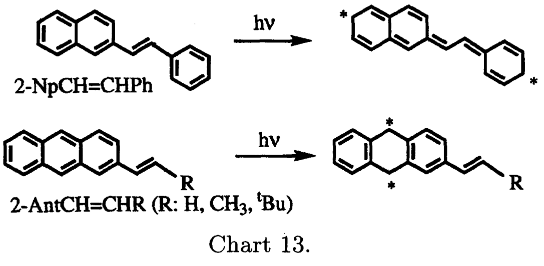


Chart 13.

Table 4. Activation Energies and Frequency Factors for Internal Rotation in the Excited State

Compound	Direction or mode[a)]	E_a / kcal mol^{-1}	A / s^{-1}	Refs.
2-AntCH=CH_2	One-way	3.9	1.8×10^{11}	143
	Two-way	5.3, 6.9		140
2-AntCH=CHMe	One-way	4.3	1.7×10^{11}	143
2-AntCH=CH^{t}Bu	One-way	4.3	1.7×10^{11}	143
2-AntC(CH_3)=CH_2	Two-way	3.7, 4.3		140
2-AntC(CH_3)=$CHCH_3$	Two-way	3.6, 3.9		140
2-AntCH=CHPh	^{3}(*s*-trans)$^*\rightarrow^3$(*s*-cis)*	7.2	2.2×10^{12}	122
2-AntCH=CHC_6H_4(*p*-Br)	^{3}(*s*-trans)$^*\rightarrow^3$(*s*-cis)*	6.9	2.6×10^{12}	114
2-AntCH=CHC_6H_4(*p*-OMe)	^{3}(*s*-trans)$^*\rightarrow^3$(*s*-cis)*	7.4	1.9×10^{12}	114
2-AntC(CH_3)=NOMe	^{1}(*s*-trans)$^*\rightarrow^1$(*s*-cis)*	4.6	1.8×10^{11}	125
2-AntC(CH_3)=NOMe	^{3}(*s*-trans)$^*\rightarrow^3$(*s*-cis)*	4.6	8.9×10^{11}	126

a) In the singlet excited state otherwise noted.

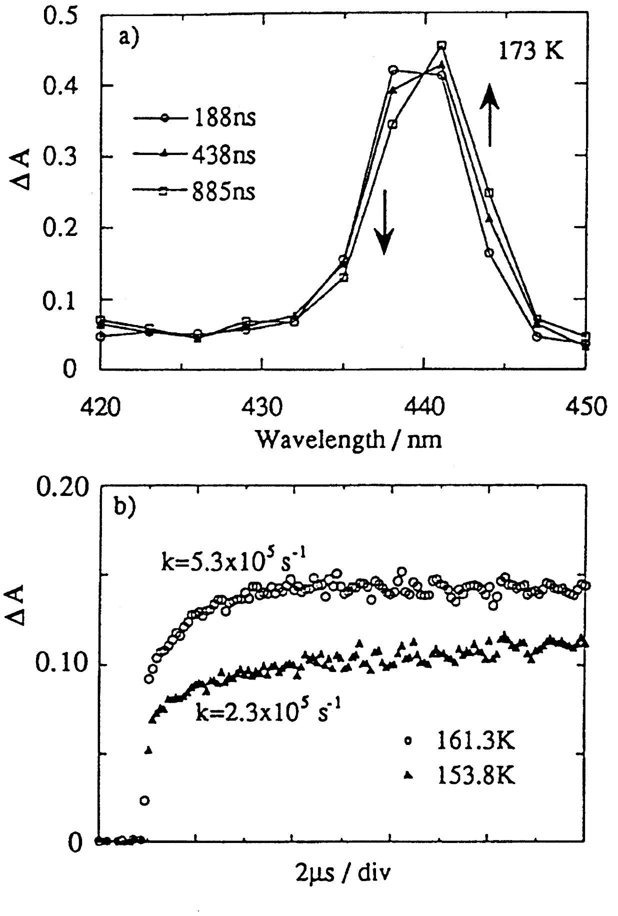


Fig. 13. Time resolved T–T absorption spectra (a) and their grow monitored at 444 nm (b) of (*E*)-2-AntC(CH_3)=NOMe.

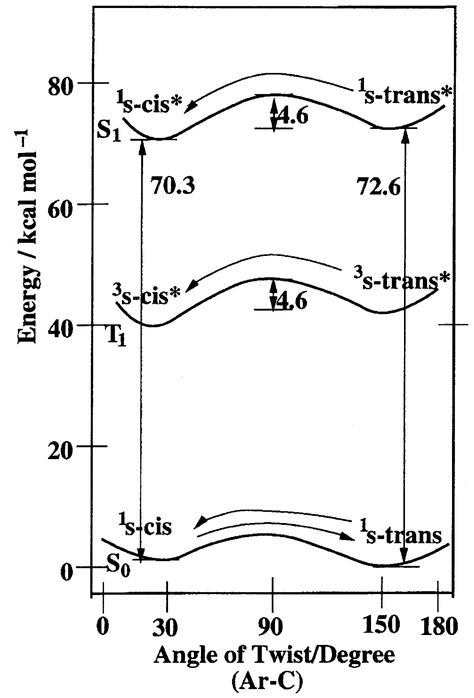


Fig. 14. Potential energy surfaces of one-way internal rotation in the excited states of (*E*)-2-AntC(CH_3)=NOMe.

5.6 ns with a concurrent rise of ^{1}(*s*-cis)*, which subsequently decays with a lifetime of 8.3 ns.

On the other hand, *trans*-2-AntCH=CHPh, *trans*-2-AntCH=CH-2-Np, and other 1,2-diarylethylenes like 2-NpCH=CHPh do not undergo internal rotation in the singlet excited state.[127,129,143b)] The difference in the behavior between those undergoing internal rotation and those not doing is attributed to the difference in the extent of the increase of the double bond character of the single bond concerned upon excitation. In those which do not undergo internal rotation, the single bond connecting an aryl group and an unsaturated carbon increases in the bond order on excitation, due to the increase of the conjugation between the aryl nuclei and the unsaturated bond as schematically drawn above (Chart 13). On the contrary, in those undergoing internal rotation, the increase of the bond order remains small. This accelerates the rotation.

However, in the triplet state, the internal rotation tends to occur more facilely than in the singlet excited state, due to the lifetime of the triplet state being longer than that of the singlet state, since the internal con-

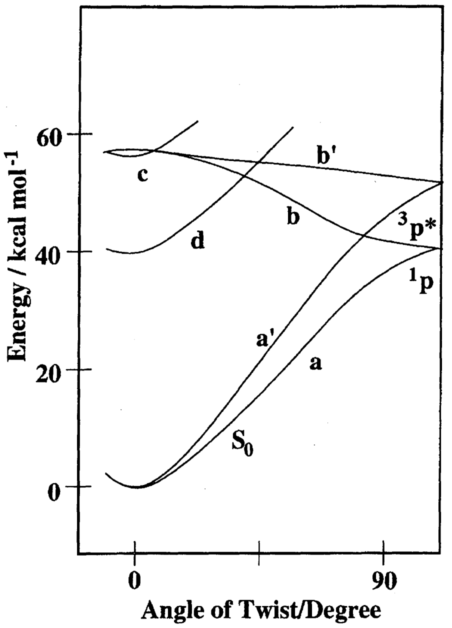


Fig. 15. Calculated potential energy surfaces of styrene, 2-vinylnaphthalene, and 2-vinylanthracene.

version occurs in competition with the deactivation of the excited state. As to *trans*-2-AntC(CH_3)=NOMe, in methylcyclohexane at 173 K, where the ^{1}(*s*-trans)* does not undergo internal rotation, a T–T absorption with λ_{max} at 438 nm decays in a μs lifetime with concurrent rise of T–T absorption with λ_{max} at 442 nm as described in Fig. 13.[126] This is due to the conversion of the initially resulting ^{3}(*s*-trans)* to ^{3}(*s*-cis)* in the triplet state. This conversion proceeds with an activation energy of 4.6 kcal mol^{-1}, an equal amount to that for the conversion of ^{1}(*s*-trans)* to ^{1}(*s*-cis)*, and a frequency factor of 8.9×10^{11} s^{-1}.[126] Figure 14 sketches the potential energy surface of the internal conversion in the ground, the singlet excited, and the triplet states of *trans*-2-AntC(CH_3)=NOMe.

Table 4 summarizes the kinetic data obtained for the internal rotation in the excited state.

The Potential Energy Surface of the Triplet State

The ^{3}p* is generally taken to be very close in energy to ^{1}p in the ground state. The energy of ^{3}p* of ethylenes undergoing two-way isomerization can be determined by photoacoustic spectroscopy and by determination of the energy difference to ^{3}t* from the equilibrium constant with ^{3}t*. The ^{3}p* of 1-arylethylenes, ArCH=CHAlkyl, is generally situated 51—53 kcal mol^{-1} over, and that of 1,2-diarylethylenes, ArCH=CHAr′, is 45—49 kcal mol^{-1} over the ground state of the trans isomer.[15a] Therefore, the ^{3}p* of ArCH=CHAr′ is several kcal mol^{-1} lower in energy than that of ArCH=CHAlkyl over their corresponding ^{1}t due to an additional stabilization of ^{3}p* of ArCH=CHAr′ by conjugation of one of the biradicaloid centers with an Ar′ group.

The lowest triplet states of arylethylenes can generally be depicted by a combination of two functions.[30,31,145,146] One is the "ethylene orbital" or the "olefin-excitation" state in which excitation is mainly localized at the unsaturated bond like π^* orbital of ethylene.[145] Its energy is the highest at trans and cis and decreases with twisting of the unsaturated bond to attain the lowest value at perpendicular conformation. The other is "aromatic orbital" or "ring-excitation" state in which excitation is localized on the aromatic ring.[145] Its energy is the lowest at trans and cis and increases with twisting of the unsaturated bond.

Figure 15 illustrates the potential energy surface calculated by MINDO approximation of ArCH=CH_2 (Ar= Ph, 2-Np, and 2-Ant), in which cis and trans are not distinct.[145] The ground state (S_0) (curve a in Fig. 15), increases in energy with twisting and gets a maximum value at perpendicular conformation. The "olefin-excitation" state (curve b in Fig. 15) decreases in energy from 54 kcal mol^{-1} at $\theta=0°$ (no twisting) to 39 kcal mol^{-1} at $\theta=90°$ (perpendicular twisting) in every compound examined. On the other hand, the "ring-excitation" state increase in energy from 53 kcal mol^{-1} for Ar=2-Np (curve c) and 40 kcal mol^{-1} for Ar=2-Ant (curve d) at $\theta=0°$ to higher values with the twisting. When Ar=Ph, its energy at $\theta=0°$ is too high to be depicted in the figure.

When Ar=Ph, the T_1 state corresponds to the "olefin-excitation" for all values of θ. Even at $\theta=0°$, the "ring-excitation" states is too high to be mixed with the "olefin-excitation" state, and therefore, T_1 at $\theta=0°$ does not have any character of the "ring-excitation". This agree well with the fact that the triplet state of PhCH=CH^{t}Bu is not quenched at all by azulene.[86] If the triplet state were situated at a minimum at ^{3}t*, it would be quenched by azulene.

When Ar=2-Np, the "ring-excitation" state (curve c) is a little lower in energy than the "olefin-excitation" state at $\theta=0°$ and they will be mixed to give the T_1. The energy of the "ring-excitation" state at $\theta=0°$, 53 kcal mol^{-1}, is very close to the energy of ^{3}t* of 2-NpCH=CH^{t}Bu, 55.4 kcal mol^{-1}.[87,88] However, the energy of the "olefin-excitation" state at $\theta=90°$, 39 kcal mol^{-1}, is much lower than the energy of ^{3}p* of these ethylenes, 51—53 kcal mol^{-1}. In 2-NpCH=CH^{t}Bu, K_{tp} is 0.47;[87,88] it means that ^{3}p* is nearly 0.5 kcal mol^{-1} higher in energy than ^{3}t*. Therefore, it is reasonable to revise the energy of the "olefin-excitation" state at $\theta=90°$ and that of the ground state at $\theta=90°$ to ca. 52 kcal mol^{-1}, as depicted as curves b′ and a′ in Fig. 15. Otherwise, the triplet state of 2-NpCH=CH_2 would be highly populated by ^{3}p* and the T–T absorption would mostly originate from ^{3}p*. However, the observed absorption of the triplet state of 2-NpCH=CH_2[144] and 2-NpCH=CH^{t}Bu[87] with λ_{max} at 420 and 570 nm is due to the planar trans triplet state, and the triplet state of 2-NpCH=CH^{t}Bu is ef-

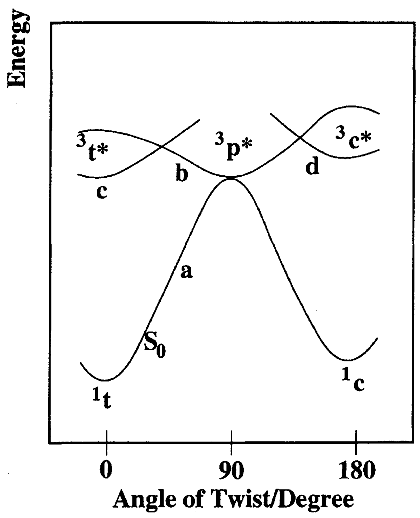


Fig. 16. Potential energy surfaces of photoisomerization in the excited triplet state with two energy barriers.

ficiently quenched by azulene with a rate constant of 7×10^9 $dm^3\,mol^{-1}\,s^{-1}$ reflecting the high population of the planar trans triplet state. Therefore, with twisting the T_1 composed from both the "ring-excitation" and the "olefin-excitation" state at $\theta=0°$ ($^3t^*$) crosses to the "olefin-excitation" state to get $^3p^*$; which is close in energy to, and in equilibrium with, $^3t^*$.

When Ar=2-Ant the "ring-excitation" state (curve d) with an energy as low as 40 $kcal\,mol^{-1}$ at $\theta=0°$ is much lower than the "olefin-excitation" state. With the twisting, the "ring-excitation" state increases in energy and the "olefin-excitation" state decreases in energy leading to crossing of the "ring-excitation" state with the unrevised "olefin-excitation" state at 35°, and with the revised one at larger θ. A case when crossing occurs at θ around 90° corresponds to the potential energy surface depicted in Fig. 5.

The potential energy surface of 2-AntCH=CH_2 should explain the following experimental facts.[99,100] (1) The twisting of the double bond proceeds with an activation energy of 11 $kcal\,mol^{-1}$. (2) The τ_T is essentially unchanged (6—7 μs) at the temperature range of 7—47 °C. (3) The efficiency for production of the singlet oxygen from the triplet state (Φ_Δ), is close to unity (0.7).

If the two states cross at some θ with an energy of 11 $kcal\,mol^{-1}$ higher than the "ring-excitation" at $\theta=0°$, this point would correspond to an activation barrier. This case could explain item (1) in the above facts, but, could not explain items (2) and (3), if $^3p^*$ were located in a sufficiently deep minimum only a few $kcal\,mol^{-1}$ higher than $^3t^*$. Then, $^3p^*$ would be considerably populated in an equilibrium with $^3t^*$, particularly at a temperature higher than the ambient one and $^3p^*$ would deactivate to the ground state with a much higher rate constant than that from $^3t^*$. This would reduce the lifetime of the triplet state and Φ_Δ. This is not the case. Therefore, $^3p^*$ could not be located in such a situation.

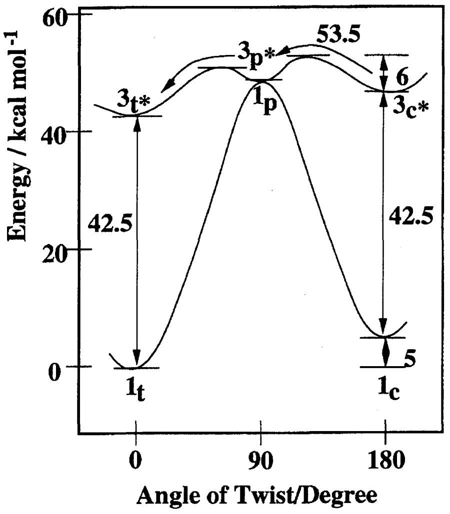


Fig. 17. Possible potential energy surface of photoisomerization of 2-AntCH=CH^tBu.

This point can be more clearly discussed with the potential energy surface of 2-AntCH=CH^tBu, based on the following findings. (1) The $^3c^*\rightarrow{}^3t^*$ conversion proceeds with an activation energy of 6.0 $kcal\,mol^{-1}$ and a frequency factor of 5×10^{10} s^{-1}.[94] (2) The $^3t^*$ never isomerizes to $^3c^*$. (3) The triplet excitation energies of cis and trans are both 42.5 $kcal\,mol^{-1}$.[94] (4) In the ground state cis is assumed to be 5 $kcal\,mol^{-1}$ higher than trans as stilbene.[25] (5) The Φ_Δ is nearly unity from both cis (0.76) and trans (0.88).[96]

If the results calculated by MINDO are qualitatively applied, a potential energy surface such as Fig. 16 can be drawn. Thus, the "ring-excitation" states (curves c and d) and the "olefin-excitation" state (curve b) cross at two positions, that is, at the trans side and the cis side of the perpendicular conformation.

When $^3c^*$ converts to $^3p^*$ across an energy barrier of 6 $kcal\,mol^{-1}$, to accomplish the highly efficient $^3c^*\rightarrow{}^3t^*$ conversion which is observed, the barrier from the $^3p^*$ side to $^3t^*$ should be low enough. Then the resulting $^3p^*$ can efficiently convert to $^3t^*$ before it deactivates from $^3p^*$. If the activation energy from $^3p^*$ to $^3t^*$ is less than 2 $kcal\,mol^{-1}$, $^3p^*$ can convert to $^3t^*$ with a rate constant of 2×10^9 s^{-1}, which is estimated from the observed frequency factor and is 100 times faster than that for the deactivation from $^3p^*$ (2×10^7 s^{-1}). If this activation barrier is increased to 4 $kcal\,mol^{-1}$, conversion of $^3p^*$ to $^3t^*$ would not proceed so fast as above and the rate constant would remain at 6×10^7 s^{-1}, which would be only 3 times larger than that for deactivation from $^3p^*$. It means that only three-fourth of $^3c^*$ could convert to $^3t^*$, a result in contrast with the observed highly efficient $^3c^*\rightarrow{}^3t^*$ conversion. When $^3p^*$ would be located e.g. 4 $kcal\,mol^{-1}$ lower than the energy barrier from $^3c^*$ to $^3p^*$, $^3p^*$ would be only 1 $kcal\,mol^{-1}$ higher than $^3t^*$. This situation would allow $^3t^*$ to convert to $^3p^*$, resulting in the unobserved trans

Table 5. Some Parameters and Kinetic Values of Arylethylenes in the Excited Singlet State and the Quantum Yields of Isomerization on Direct Irradiation

Compound	Es(ArH)[a)]		E_s[a)]	Φ_f	τ_s/ns	Φ_{isc}	$\Phi_{c\to t}$ or $\Phi_{t\to c}$	Refs.
PhCH=CHPh	110	cis	85.7	$\approx 10^{-4}$	$\approx 10^{-3}$		0.34[b)]	12
		trans	88.5	0.04	7×10^{-2}		0.50[b)]	12
8-FlCH=CH^{t}Bu	79.8	cis	70	0.16	28.3		4.7 ([cis]$=6\times 10^{-3}$ M)[c)]	107,108
		trans	69	0.19	19.4			107,108
8-FlCH=CHPh		cis	67	0.40	12.4		0.22 ([cis]$=2.3\times 10^{-3}$ M)[c)]	107,108
		trans	65	0.48	9.7		0.029[b)]	107,108
1-PyCH=CH^{t}Bu	77	cis	76	0.43	43	0.21	4.6 ([cis]$=3.2\times 10^{-3}$ M)[c)]	104,105
		trans	73	0.64	65	0.23		104,105
1-PyCH=CHPh		cis	71	0.60			0.50[b)]	104,105
		trans	71	0.80	5.3			104,105
2-AntCH=CH^{t}Bu	76.3	cis	74.3	0.41	16	0.59	4.0 ([cis]$=6\times 10^{-3}$ M)[c)]	96,97
		trans	72.6	0.50	12	0.46		96,97
2-AntCH=CHPh		cis	71.3	0.59		0.17	6.8 ([cis]$=1.6\times 10^{-3}$ M)[c)]	96,97
		trans	70.2	0.87	9.1 (28.6)	0.11		96,97
2-AntCH=CH2-Np		cis	70.2	0.65		0.22	3.7 ([cis]$=1\times 10^{-3}$ M)[c)]	96,97
		trans	69.7	0.85		0.12		96,97

a) In kcal mol^{-1}. b) Isomerization takes place in the singlet excited state. c) Isomerization takes place in the triplet state after the intersystem crossing.

to cis isomerization.

Therefore, for $^3c^* \to {}^3t^*$ isomerization to proceed efficiently, $^3p^*$ should not be much lower than the activation barrier from $^3c^*$ to $^3p^*$ and should convert to $^3t^*$, if any, across a low energy barrier preceding deactivation from $^3p^*$. To fulfil these requirements, $^3p^*$ should be situated close in energy to the activation barrier. It means that $^3p^*$ should be located either at the barrier or in a shallow minimum around the barrier, as depicted in Fig. 17. Since these two possibilities could not be differentiated by the present spectroscopic methods, the drawing of the potential surface proposed in 1990 is to be accepted for its simplicity. In the series of 2-, 1-, and 9-AntCH=CH^{t}Bu, the lowering of the activation energy from $^3c^* \to {}^3t^*$ conversion in this order[110)] is attributed to the stabilization of $^3p^*$, due to increase of conjugation of the anthryl group with the unsaturated center arising from an increase of electron density at 2-, 1-, and 9-positions of the HOMO and LUMO of anthracene, as calculated by QCFF/PI program.[32,100)]

Replacement of the t-butyl group in 2-AntCH=CH^{t}Bu by a Ph group changes the profile of the potential energy surface, since in 2-AntCH=CHPh no activation energy is observed in $^3c^* \to {}^3t^*$ conversion. As mentioned before,

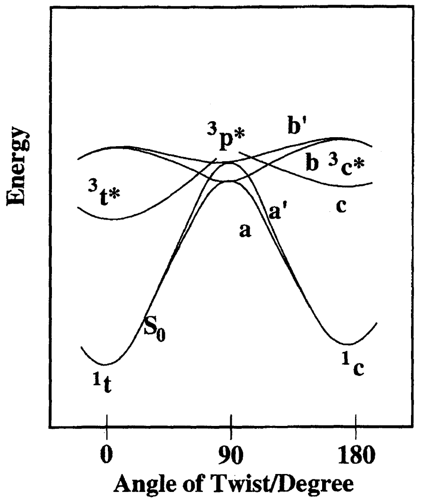


Fig. 18. Potential energy surfaces of photoisomerization of 2- AntCH=CHPh (a, b, c) and 2-AntCH=CH^{t}Bu (a′, b′, c).

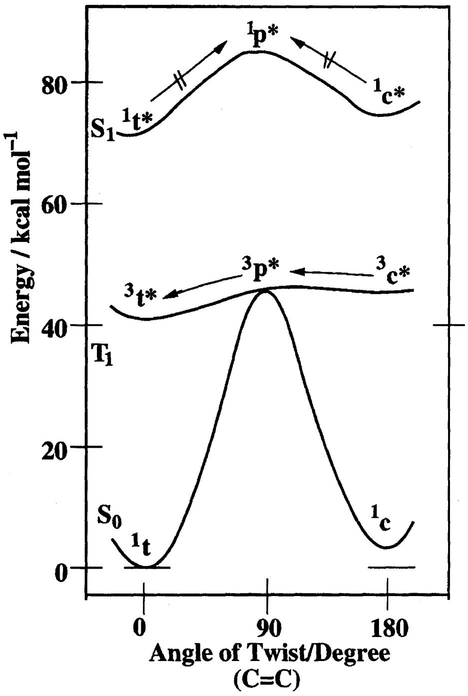


Fig. 19. Potential energy surfaces of photoisomerization of one-way isomerizing olefins.

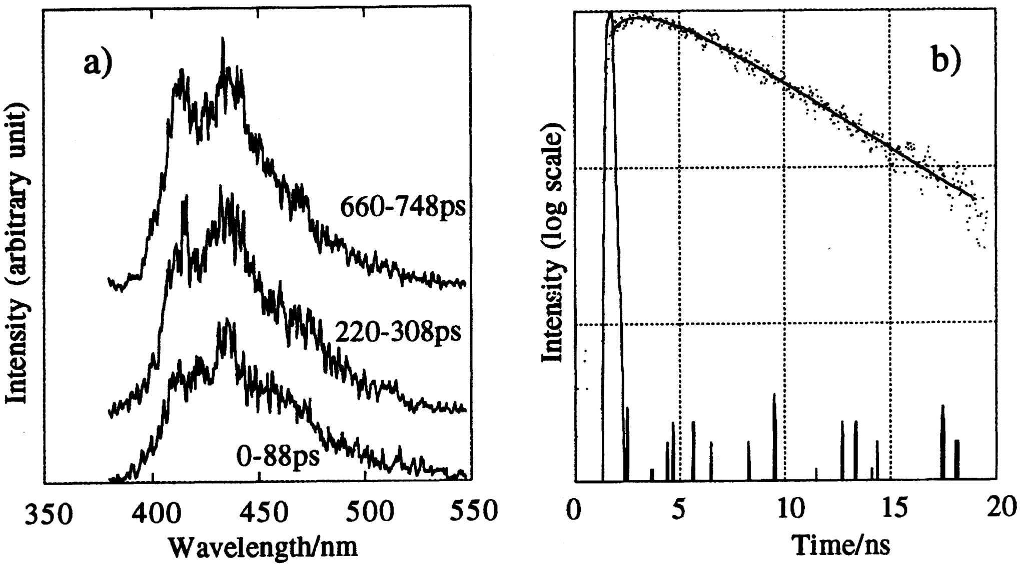


Fig. 20. Time-resolved fluorescence spectra of *cis*-1-PyCH=CHPh at 295 K (a) and the time profile of the decay curve at 288 K in hexane (b).

the height of ^{3}p* in ArCH=CHPh type ethylenes (curve a in Fig. 18) is accepted to be several kcal mol^{-1} lower than that in ArCH=CHAlkyl type ethylenes (curve a′) due to stabilization of ^{3}p* by additional conjugation to the Ph group. Since the E_T of the cis and trans are both 41.5 kcal mol^{-1} and ^{1}c is assumed to be 5 kcal mol^{-1} higher than ^{1}t, the "ring-excitation" state (curve c) starting from ^{3}c* of 46.5 kcal mol^{-1} height over ^{1}t will cross with the "olefin-excitation" state (curve b) to arrive at ^{3}p*, as depicted in Fig. 18.[98] Therefore, ^{3}p* must be near the ridge or in a shallow minimum around the ridge. To accomplish facile ^{3}c*→^{3}t* one-way conversion, the barrier from ^{3}p* to ^{3}t*, if any, should be very low. In the absence of a high barrier from ^{3}c* to ^{3}t*, to avoid the reverse conversion from ^{3}t* to ^{3}p* and further to ^{3}c*, the energy minima for ^{3}p* and ^{3}c*, if any, should be very shallow. Otherwise, ^{3}t* would be thermally equilibrated with ^{3}p* and ^{3}c*, which would deactivate, resulting in the reverse isomerization.

The contrasting behavior between 1-PyCH=CH^{t}Bu undergoing one-way isomerization and 1-PyCH=CHPh undergoing isomerization of dual character of two-way and one-way, can be understood similarly to that of 2-anthrylethylenes.[104,105,123] In 1-PyCH=CH^{t}Bu, ^{3}c* (E_T: 47 kcal mol^{-1} over ^{1}c) as well as ^{3}t* (E_T: 44 kcal mol^{-1} over ^{1}t) are definitely located in minima as depicted in Fig. 10, since each of them emit phosphorescence. Therefore, the "ring-excitation" state will increase in energy with the twisting, starting from either ^{3}c* or ^{3}t*, to cross the "olefin-excitation" state near ^{3}p*. Therefore, ^{3}p* will be slightly higher in energy than ^{3}c* and sufficiently higher than ^{3}t*, which will prevent ^{3}t* from being equilibrated with ^{3}p* to do trans–cis isomerization.

On the other hand, in 1-PyCH=CHPh, the "olefin-excitation" state will be several kcal mol^{-1} lower than that of 1-PyCH=CH^{t}Bu. The ^{3}c* is not located in a sufficiently deep minimum. Therefore, the "ring-excitation" state from ^{3}c* will facilely cross "olefin-excitation" state. The ^{3}p* will be rich enough in the character of the latter state to be placed in a minimum of considerable depth. The energy difference of several kcal mol^{-1} between ^{3}t* and ^{3}p* leads to their equilibration.

Isomerization in the Singlet Excited State

In the singlet excited state of stilbene, the cis shows very weak fluorescence and facilely undergoes isomerization.[12] At ambient temperature, the trans gives very low yield of fluorescence but efficiently undergoes isomerization; however, lowering of temperature increases the efficiency of fluorescence at the expense of isomerization, and at 77 K only fluorescence is emitted but no isomerization takes place.[3] This means that isomerization from the emissive, that is, the lowest excited singlet state proceeds with an activation energy. Excitation of the trans to a higher excited singlet state results in isomerization without an activation barrier.[8] These facts suggest that the trans lowest excited singlet state is rich in the "ring-excitation" state character and the higher excited state is rich in the "olefin-excitation" state. Therefore, with twisting, the "ring-excitation" state will increase in energy from the lowest excited trans and cross with the "olefin-excitation" state and decrease in energy to get the perpendicular singlet state, ^{1}p*, which subsequently deactivates to ^{1}p.

Substitution of larger aromatic nuclei with lower singlet excitation energies (E_S) than benzene ring such as fluoranthene, pyrene, and anthracene rings (E_S=79.8, 77, and 76.3 kcal mol^{-1}, respectively)[112] on the unsaturated bond leads to stabilization of both the trans (^{1}t*) and cis (^{1}c*) singlet excited states. Thus, each cis and trans isomers of these ethylenes exhibits its respective fluorescence spectrum with an intrinsic quantum yield, as summarized in Table 5.

On determining these values for the cis isomers at ambient temperature, we always used fresh and unirradiated samples, since the fluorescence spectra changed to those of trans during repeated measurements at ambient temperature. However, at 77 K, no change of the fluorescence spectra was observed for these cis isomers. Also, in 2-anthrylethylenes, fluorescence spectra and quantum yields varied with wavelength of the irradiating light due to the presence of rotamers.[97,127,135)]

As Table 5 indicates, each cis and trans isomers of these compounds exhibit a rather high yield of fluorescence (Φ_f) and most of them also show a rather high yield of intersystem crossing (Φ_{isc}) except 1-PyCH=CHPh. Generally, Φ_f from cis is lower than that from trans. In 2-AntCH=CHR, Φ_{isc} is higher for R=^{t}Bu than for R=Ph and 2-Np, and particularly, for R=^{t}Bu, $\Phi_f+\Phi_{isc}$ is very close to unity.[96,97)] Direct excitation of these ethylenes other than 1-PyCH=CHPh led to cis to trans one-way isomerization with a quantum chain process. Precise determination of the $\Phi_{c\rightarrow t}$ on direct excitation has revealed that the isomerization proceeds from $^3c^*$ which resulted from the intersystem crossing of the initially produced $^1c^*$. Thus, $^1c^*$ and $^1t^*$ undergo both fluorescence emission and intersystem crossing to $^3c^*$ and $^3t^*$, respectively; $^3c^*$ converts to $^3t^*$, but $^1c^*$ and $^1t^*$ do not undergo isomerization except 1-PyCH=CHPh.[51,147)] Therefore, the rate constants for twisting of the double bond from $^1c^*$ and $^1t^*$ along the singlet excited surface are generally very much lower than those for fluorescence emission and intersystem crossing. It means that the twisting of the double bond from either $^1c^*$ or $^1t^*$ is accompanied by a considerable amount of activation energy, except for 1-PyCH=CHPh, as schematically illustrated in Fig. 19.[51,147)]

The finding of adiabatic one-way isomerization in the triplet energy surface called attention to the possibility for the adiabatic conversion in the singlet excited state. Spalletti, Bartocci, Mazzucato, and Galiazzo found that 1-PyCH=CHPh underwent adiabatic cis to trans isomerization in the singlet state, $^1c^*\rightarrow{}^1t^*$.[51)] Our group found that the behavior of this compound is very much affected by polarity of solvents and substituents.[147)]

For example, on excitation of *cis*-1-PyCH=CHPh in hexane, the decay of $^1c^*$ is accompanied by rise of fluorescence of the trans with nearly the same rate constant of 5.9×10^8 s^{-1} as depicted in Fig. 20.[147)] Determination of rate constants at varying temperature has revealed that $^1c^*\rightarrow{}^1t^*$ conversion proceeds with an activation energy of 6.7 kcal mol^{-1} and a frequency factor of 4.4×10^{13} s^{-1}.[147)] Therefore, $^1c^*$ isomerizes to $^1t^*$ overcoming an energy barrier located around $^1p^*$ similarly to the $^3c^*\rightarrow{}^3t^*$ conversion. The Φ_f for cis (0.72) is slightly lower than that for trans (0.82) as determined at ambient temperature in hexane.

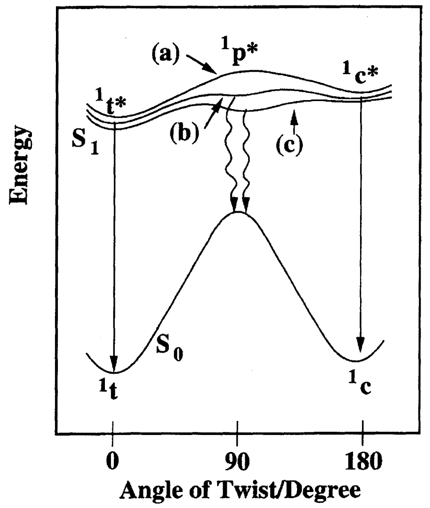


Fig. 21. Effect of solvents and substituents on the potential energy surface of cis-trans isomerization of *cis*-1-PyCH=CHC$_6$H$_4$R(p): (a) non-polar systems, (b) moderately polar systems, (c) polar systems.

In more polar solvents, the activation energy for the $^1c^*\rightarrow{}^1t^*$ conversion is decreased, that is, 5.1, 2.9, and 1.3 kcal mol^{-1} in dibutyl ether, toluene, and 2-methyltetrahydrofuran, respectively.[147)] This corresponds to lowering of the activation energy with increase of polarity of solvents, $E_T(30)$. In acetonitrile, the Φ_f from cis is very much reduced to 0.079 compared to 0.72 in hexane. These facts show that in acetonitrile no more activation barrier exists and $^1p^*$ is situated in an energy minimum, from which the excited state undergoes deactivation to ^1p. The above solvent effect is attributed to the enhancement of zwitter ionic character of $^1p^*$ with the increase of solvent polarity.[148)] The potential energy surface of the isomerization affected by polarity of solvents and polar substituents can be depicted as in Fig. 21.[147)]

It is important that 1-PyCH=CHPh undergoes adiabatic isomerization in the singlet excited state whereas 2-AntCH=CHPh does not, although both of these ethylenes have nearly the same singlet excitation energies and their parent hydrocarbon rings, pyrene and anthracene nuclei, have comparable amounts of the singlet excitation energy. One reason of the above contrasting behavior could be that Φ_{isc} for 1-PyCH=CHPh is very much lower than for 2-AntCH=CHPh. However, if $^1c^*$ of the latter facilely twisted around the double bond, the isomerization could occur in competition with the intersystem crossing. The enhancement of the isomerization mostly results from lowering of the energy for $^1p^*$ as shown by facile isomerization of the $^1c^*$ state of 9-AntCH=NOMe but not of 2-AntCH=NOMe.[119,120)]

Thus, on triplet sensitization, both 2-Ant- and 9-AntCH=NOMe undergo $Z\rightarrow E$ one-way adiabatic isomerization, $^3Z^*\rightarrow{}^3E^*$. On direct irradiation, in the singlet excited state, 2-AntCH=NOMe does not isomerize at all; however, 9-AntCH=NOMe isomerizes mutually between the *E* and *Z* isomers.[119,120] It means that in the potential energy surfaces of the singlet excited state, $^1p^*$ is stabilized in the 9-Ant compound but not so much in the 2-Ant compound. This is attributable to stabilization of the ArC(H)· moiety in $^1p^*$, singlet "biradicaloid", of 9-AntCH=NOMe due to the more conjugative property of 9-Ant group than 2-Ant group, reflecting a much higher electron density of HOMO and LUMO at 9-position than at 2-position. This effect of the substitutional position of an anthracene nucleus is similar to that observed in the triplet isomerization of 2-, 1-, and 9-AntCH=CH^{t}Bu, in which the activation energy for $^3c^*\rightarrow{}^3t^*$ conversion is reduced in this sequence: 6.0, 4.6, and 3.1 kcal mol^{-1} in toluene.[110a]

Also, stabilization of $^1p^*$ of 1-PyCH=CHPh is brought about by the presence of a phenyl group on the terminal carbon, while 1-PyCH=CH^{t}Bu does not isomerize in the singlet excited state. This situation is similar to the triplet states of these 1-pyrenylethylenes.[104,105]

Therefore, for isomerization in the singlet state, stabilization of $^1p^*$ seems an important factor. However, too much stabilization leads to diabatic isomerization. Therefore, for the adiabatic isomerization to take place as in 1-PyCH=CHPh, stabilization of $^1p^*$ is to such an extent as to reduce the energy of the activation barrier from $^1c^*$ to $^1t^*$, but not enough to put $^1p^*$ in a deep energy minimum.

Substitution of polar groups at the 4-position of the phenyl group in 1-PyCH=CHPh and 9-AntCH=CHPh provides an insight into the nature of the excited state. In acetonitrile, *trans*-1-PyCH=CHC$_6$H$_4$NO$_2$(p) does not isomerize and shows very low $\Phi_{\rm isc}$ (0.036).[116] This compound shows fluorescence with a much lower quantum yield ($\Phi_{\rm f}=1\times10^{-3}$) and a larger Stokes shift of 11000 cm^{-1} in acetonitrile than in hexane, in which the Stokes shift remains at 3800 cm^{-1} and $\Phi_{\rm f}$ is 0.04. These facts show that in acetonitrile the initially resulting singlet excited state is relaxed rapidly by solvation and deactivates preceding the isomerization. Actually, in methyltetrahydrofuran at 130 K, the initially observed fluorescence with $\lambda_{\rm max}$ at 530 nm is shifted to that with $\lambda_{\rm max}$ at 590 nm within 540 ps due to dynamic solvation.[149] These observations suggest that $^1t^*$ of 1-PyCH=CHPh can be considerably stabilized with increase of solvent polarity.

9-AntCH=CHPh is practically without trans→cis isomerization in the excited singlet state.[46] However, recently Görner and Sun have found that 9-AntCH=CHC$_6$H$_4$R(p) (R: Me$_2$N, MeO, CN, and NO$_2$) undergo trans→cis isomerization even in non-polar solvents like toluene and the isomerization is accelerated in acetonitrile when R = MeO and CN and suppressed when R = NO$_2$.[50] These observed effects can be attributed to the stabilization of $^1p^*$ by polar substituents and in polar solvents. The effects of polar substituents and polar solvents on the isomerization of arylethylenes still need a lot of study. Saltiel et al. showed that even stilbene could undergo $^1c^*\rightarrow{}^1t^*$ conversion in an efficiency of at most 1%.[12]

Conclusion

In this article, we have shown that several factors, particularly the structure of aryl groups, govern the mode of the isomerization of arylethylenes, in diabatic two-way, adiabatic one-way, and inefficient way, in the triplet and singlet excited states. However, the effect of polar substituents and polar solvents have to be further examined, since most works have been carried out in nonpolar media. Much attention is now paid to the possibility of participation of adiabatic processes in various photochemical reactions.[12,46—48,51,68—72,75—79] Moreover, quantum chain processes with excited states as chain carriers could be employed for amplification of the effect of photons.

This work was carried out by collaboration with the following scientists in this laboratory, to whom thanks are due. Drs. Takashi Karatsu, Hiroaki Misawa, Masahiro Tsuchiya, Yasunao Kuriyama, Hiroaki Okamoto, Hideo Furuuchi, Michael Sundahl, Thomas Ebbesen, M. Sc. Hualing Zeng, Tatsuro Hiresaki, Masami Tsuchiya, Yoshihiko Kikuchi, Takeshi Iwasaki, Yasushi Ogawa, Yasunori Furuya, Yoshihiko Yuda, Ms. Mikiko Noziri, Naoko Nakahigashi, Yaeko Takahashi, Yayoi Watanabe, and Mr. Tomoyuki Asano, Hiroki Kawashima, Masaya Moriyama, Yoshinori Suzuki, Osamu Takahashi, Minoru Isoda, Masaki Obi, and Katsunori Sano. Thanks are also due to Dr. Hirochika Sakuragi for his fruitful discussions during the research.

The authors thank Professor Osamu Kikuchi and his collaborators at the same department for theoretical calculations. The authors also thank Dr. Hiro-o Hamaguchi, previously at the University of Tokyo, now at Kanagawa Academy of Science and Technology, Professor Iwao Yamazaki, Drs. Naoto Tamai, (now at Kansei Gakuin University), and Yoshinobu Nishimura, Hokkaido University, Professor Shigero Oishi, now at Kitasato University, Drs. Katsuhiko Ueno, Yuji Kawanishi, National Institute of Materials and Chemical Research, Tsukuba, Professor R. A. Caldwell, University of Texas at Dallas, and Professor Jakob Wirz, University of Basel, for their kind collaboration.

The authors thank the Ministry of Education, Science and Culture for the Grant-in-Aid for Specially Promoted Research No. 03101004 (K. T. and T. A.) and the University of Tsukuba for President's Special Grant for Education and Research, 1990 (K. T.)

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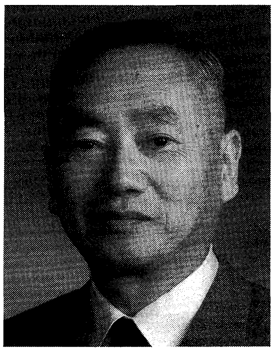

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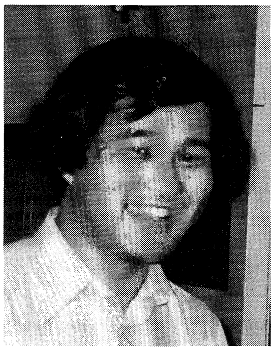

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