

Photochemical isomerization around the C=N double bonds of *N*-methoxy-1-(1-pyrenyl)methanimine in the excited state

Tatsuo Arai *, Yasunori Furuya, Katsumi Tokumaru

Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan

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Abstract

N-Methoxy-1-(1-pyrenyl)methanimine (**VII**) undergoes mutual isomerization between the *Z* and *E* isomers around the C=N double bond on triplet sensitization. The quantum yields of *Z* → *E* isomerization increase linearly with the initial *Z* isomer concentration exceeding unity. Furthermore, a considerably long-lived triplet state assigned to the *E* triplet is observed on laser photolysis. On the basis of these experimental findings, the mechanism of isomerization of **VII**, proceeding by a dual two-way and one-way mode, is discussed.

Keywords: Isomerization; Isomer ratio; Quantum yield; Triplet–triplet absorption

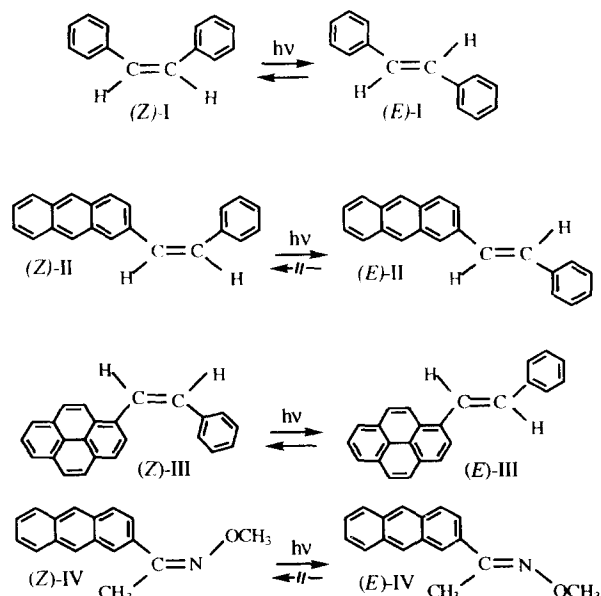
1. Introduction

Recently, the effects of aryl groups on photochemical *Z*–*E* isomerization have been studied extensively [1–10]. We have reported that the substitution of aromatic nuclei with low triplet energies, such as anthracene, on the ethylenic bond strongly affects the dynamic behaviour of arylethenes in the excited state [8–10]. Stilbene (**I**) undergoes mutual isomerization between the *Z* and *E* isomers in the excited triplet state [1–3], while 2-styrylanthracene (**II**) undergoes one-way *Z* → *E* isomerization with a quantum chain process [8–12]. Furthermore, 1-styrylpyrene (**III**) exhibits dual character of both one-way and two-way isomerization [10,13]: **III** undergoes mutual isomerization between the *Z* and *E* isomers, but the quantum yield of *Z* → *E* isomerization increases with increasing *Z* isomer concentration exceeding unity.

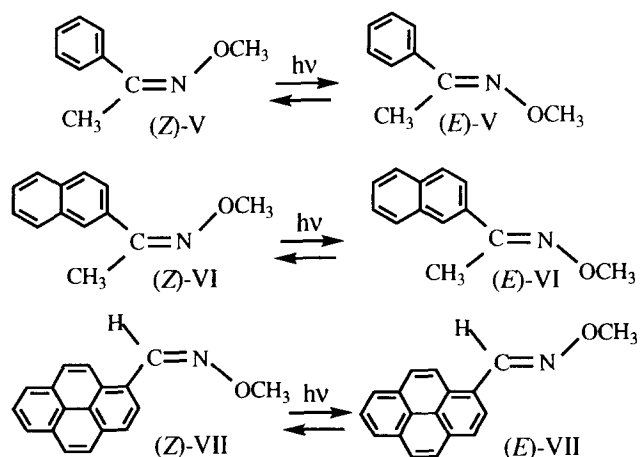
The mechanism of *Z*–*E* isomerization of C=N and N=N double bonds is often discussed from the viewpoint of inversion and rotation around the double bonds [14,15]. As regards the photochemical isomerization of the C=N double bond, we have found that substitution of an anthracene nucleus on the C=N double bond leads to one-way *Z* → *E* isomerization of **IV** [16], as in the ethylenic bond, although the phenyl- and naphthyl-substituted C=N compounds **V** and **VI** undergo two-way isomerization on triplet sensitization. Therefore it is worthwhile to examine the effect of aryl groups

on the photochemical behaviour of the C=N double bond, and compare the results with those obtained for the C=C double bond.

We studied the effect of substitution of a 1-pyrenyl group on –CH=NOMe (**VII**). **VII** undergoes mutual isomerization between the two isomers, but the isomerization for the *Z* → *E* direction proceeds via a quantum chain process. Furthermore, the possible mechanism of isomerization around the C=N double bond of ArCH=NOMe was discussed from the viewpoint of the inversion and rotation mechanisms.



* Corresponding author.



2. Experimental details

A mixture of 1-pyrenecarboxyaldehyde and O-methylhydroxylamine hydrochloride was refluxed in ethanol containing sodium acetate for 12 h. Pure *E*- and *Z*-VII were separated by flash column chromatography over silica gel (eluted with hexane–ethyl acetate (95 : 5)) and recrystallized from hexane.

Z-VII: $^1\text{H-NMR}$ $\delta = 4.1$ (s, 3H), 7.9–8.6 (m, 9H), 9.0 (m, 1H); m.p., 63–65 °C. **E-VII:** $^1\text{H-NMR}$ $\delta = 4.0$ (s, 3H), 7.9–8.5 (m, 9H), 8.3 (m, 1H); m.p., 122–124 °C. Analysis: calculated for $\text{C}_{18}\text{H}_{13}\text{NO}$: C, 83.37%; H, 5.05%; N, 5.40%; found **Z-VII**: C, 83.48%; H, 5.04%; N, 5.37%; found **E-VII**: C, 83.16%; H, 4.97%; N, 5.36%.

Irradiation was performed with 436 nm light isolated from a 400 W high pressure mercury lamp through a solution filter ($4.4 \text{ g dm}^{-3} \text{ CuSO}_4 \cdot 5\text{H}_2\text{O} + 2.7 \text{ M NH}_3 + 75 \text{ g dm}^{-3} \text{ NaNO}_2$ in water). The light intensity was measured using potassium tris(oxalato)ferrate(III) actinometry. The photostationary state isomer ratios and quantum yields of isomerization were determined in benzene in the presence of benzil as a triplet sensitizer. The conversion was analysed by high performance liquid chromatography (HPLC, Waters 600 multisolvent delivery system and 490 programmable multiwavelength detector with a 740 data module).

Laser flash photolysis was performed with a 308 nm excimer laser (Lambda Physik LPX-105; XeCl) or a 425 nm pulsed laser (Lambda Physik FL-3002 dye laser; stilbene 3; pumped by the above excimer laser), with a pulsed xenon arc (Wacom KXL-151, 150 W) as monitoring light source [16].

Time-resolved fluorescence spectra were measured by a system consisting of a titanium sapphire laser (Spectra-Physics 3900 equipped with a frequency doubler (SP390) and a pulse selector (SP3980); approximately 2 ps FWHM) operated with a CW Ar^+ laser (Spectra Physics 2060) and a streak scope (Hamamatsu C4334). The jitter of the whole system was approximately 50 ps FWHM.

3. Results and discussion

3.1. Absorption and fluorescence properties

Z-VII exhibits an absorption spectrum at a shorter wavelength than **E-VII** (Fig. 1(a)). **E-VII** shows a fluorescence spectrum with a 0–0 band at 397 nm ($72.1 \text{ kcal mol}^{-1}$) at room temperature and at -90°C (Fig. 1(b)). **Z-VII** exhibits a fluorescence spectrum similar to that of **E-VII** at room temperature; the fluorescence excitation spectrum of **Z-VII** almost matches the absorption spectrum of **E-VII**. Therefore, at room temperature, **Z-VII** efficiently isomerizes to **E-VII**, which subsequently absorbs light to give fluorescence. However, at -90°C , **Z-VII** gives a fluorescence spectrum which is red shifted by approximately 10 nm relative to the fluorescence spectrum of **E-VII** (Fig. 1(b)); the fluorescence excitation spectrum of **Z-VII** agrees well with the absorption spectrum of **Z-VII**. Furthermore, using picosecond fluorescence spectroscopy in a flow cell system, **E-VII** and **Z-VII** give different fluorescence spectra with λ_{max} at 398 nm and 392 nm respectively on irradiation at 370 nm. Since these

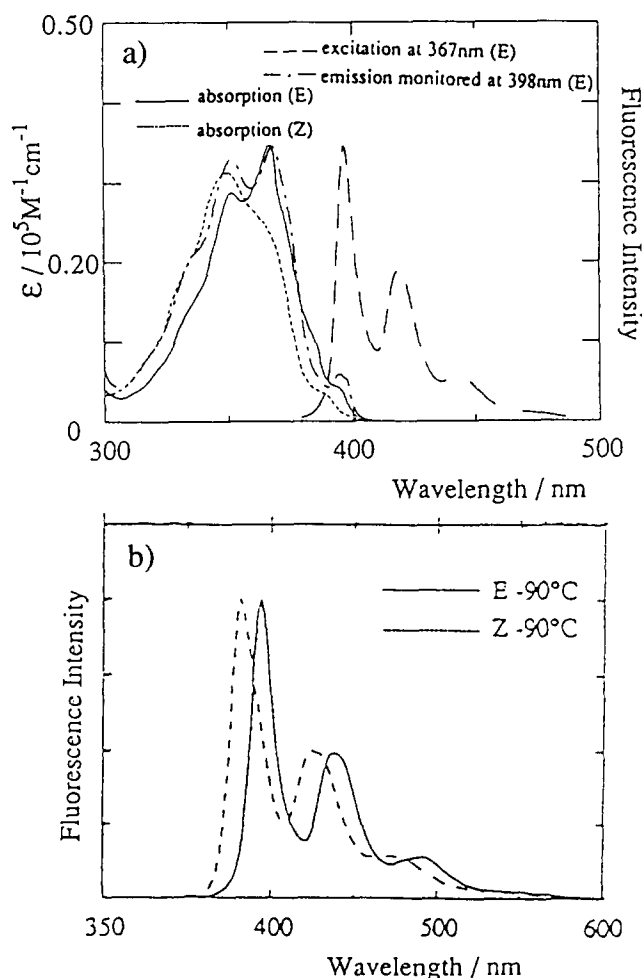


Fig. 1. Absorption, fluorescence and fluorescence excitation spectra of *Z*- and *E*-VII at room temperature in benzene (a) and at -90°C in toluene (b).

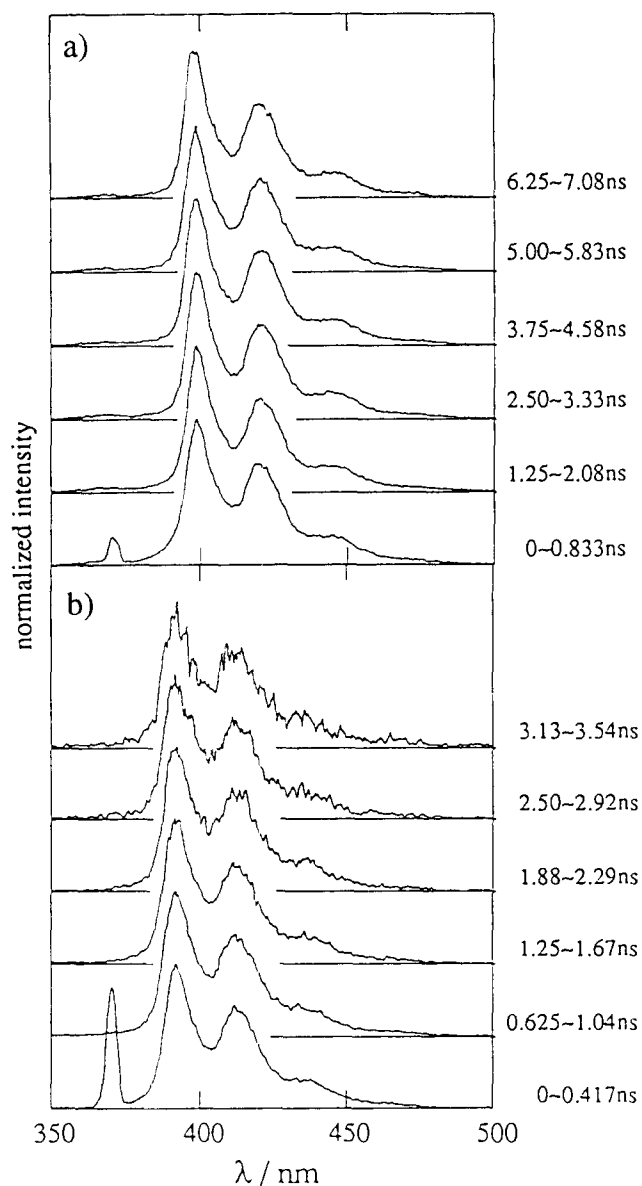


Fig. 2. Picosecond time-resolved fluorescence spectra of *E*-VII (a) and *Z*-VII (b) at room temperature observed on excitation at 370 nm in toluene.

spectra decay without a change in the spectral profiles, they are assigned to *E*- and *Z*-VII singlet excited states respectively (Fig. 2). The singlet lifetimes of *E*- and *Z*-VII were determined to be 9 ns and 0.8 ns respectively.

3.2. Photostationary state isomer ratios and quantum yields of triplet-sensitized isomerization

On benzil-sensitized ($\Phi_{isc} = 0.92$) irradiation at 436 nm in degassed benzene, VII isomerizes mutually between *Z* and *E* isomers. Fig. 3 shows the effect of the concentration of VII on the photostationary state isomer ratio ($([E]/[Z])_{pss}$), indicating that the *E* isomer content increases linearly with the total concentration of VII to attain $[E]/[Z] = 16$ at $[VII] = 7.8 \times 10^{-4}$ M, where the *E* isomer content is as high as 94%. The intercept and slope were obtained as 2.13 and

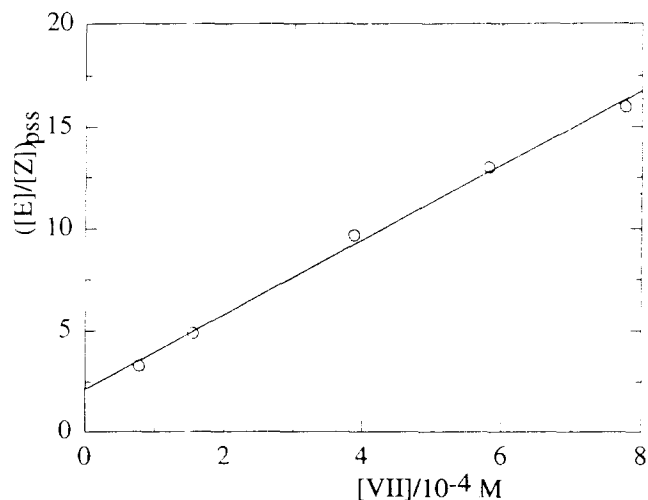


Fig. 3. Effect of the concentration of VII on the photostationary state isomer ratio in benzene on 436 nm irradiation.

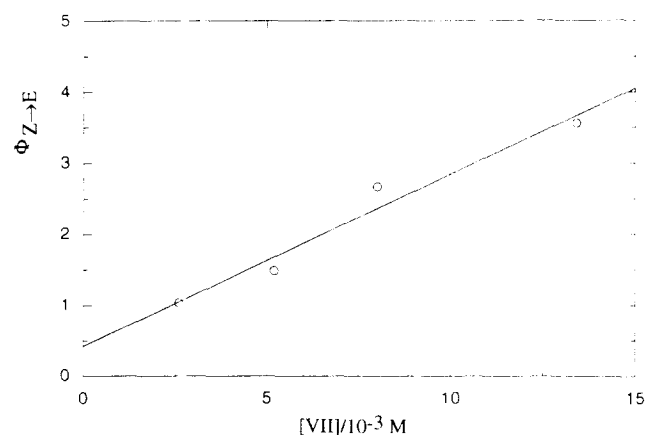


Fig. 4. Effect of the *Z* isomer concentration on the quantum yield of *Z* → *E* isomerization in benzene on 436 nm irradiation.

$1.82 \times 10^4 \text{ M}^{-1}$ respectively. The above concentration effect on $([E]/[Z])_{pss}$ indicates that deactivation will take place not only from the perpendicular triplet state (${}^3p^*$), but also from the planar *E* triplet (${}^3E^*$) as described later.

As shown in Fig. 4, the quantum yield of *Z* → *E* isomerization ($\Phi_{Z \rightarrow E}$) of VII on benzil sensitization increases linearly with the initial *Z*-VII concentration, exceeding unity, indicating that *Z* → *E* isomerization takes place by a quantum chain process. The values of the intercept and slope were determined to be 0.42 and 240 respectively.

3.3. Laser photolysis

Laser flash photolysis of *E*-VII (1.1×10^{-4} M) and *Z*-VII (1.2×10^{-4} M) in benzene in the presence of benzil (0.06 M) affords practically the same triplet-triplet (T-T) absorption with a lifetime of 10 μs under degassed conditions at room temperature (Fig. 5). The T-T absorption of VII is quenched by oxygen and azulene with rate constants of $4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $6.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ respectively. Oxygen generally quenches ${}^3E^*$ and ${}^3p^*$ by energy transfer and

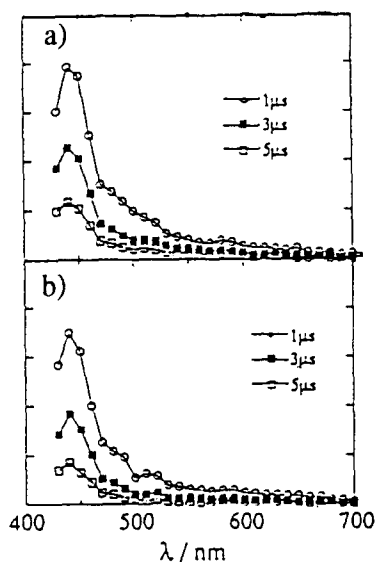


Fig. 5. T-T absorption spectra of *E*-VII (a) and *Z*-VII (b) observed on benzil sensitization in benzene (425 nm irradiation).

acceleration of intersystem crossing with rate constants of one-ninth and three-ninths of the diffusion-controlled rate constant (approximately $3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ respectively) [3,17]. The observed value is very close to the former and indicates that oxygen quenches the T-T absorption of VII by an energy transfer mechanism. Furthermore, the observed quenching rate constant of the T-T absorption of VII by azulene is relatively close to the diffusion-controlled rate constant (approximately $1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) [18]. These results indicate that the observed T-T absorption spectrum can be assigned to $^3E^*$ and not to $^3p^*$.

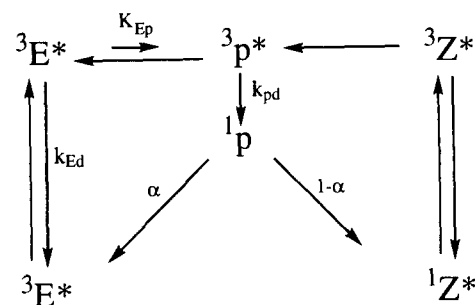
3.4. Mechanism of *Z*-*E* isomerization in the triplet state

Scheme 1 shows the mechanism of *Z*-*E* isomerization of VII. The triplet state is equilibrated between $^3p^*$ and $^3E^*$ ($K_{Ep} = [^3p^*]/[^3E^*]$) and deactivates from these two conformers; the population of the latter is predominant as discussed later. The deactivation from $^3p^*$ (rate constant, k_{pd}) gives a mixture of the *E* and *Z* isomers; the fraction α giving the *E* isomer is assumed to be 0.5 [8–10]. The deactivation from $^3E^*$ gives exclusively the *E* isomer. $^3E^*$ unimolecularly deactivates to the ground state (rate constant, k_{Ed}) or transfers its energy to 1Z to regenerate the triplet state (rate constant, k_{EZ}) to accomplish a quantum chain process. According to Scheme 1, the quantum yields of *Z* → *E* isomerization and the photostationary state isomer composition are expressed by Eqs. (1) and (2). Furthermore, the triplet lifetime ($\tau_T = 10 \mu\text{s}$) is described by Eq. (3).

$$\phi_{Z \rightarrow E}^{\text{sens}} = \phi_{\text{isc}} \times \frac{k_{Ed} + \alpha k_{pd} K_{Ep} + k_{EZ}[Z]}{k_{Ed} + k_{pd} K_{Ep}} \quad (1)$$

$$\left(\frac{E}{Z}\right)_{\text{pss}} = \frac{k_{Ed} + \alpha k_{pd} K_{Ep} + k_{EZ}[Z]}{(1 - \alpha) k_{pd} K_{Ep}} \quad (2)$$

$$\tau_T = \frac{1 + K_{Ep}}{k_{Ed} + k_{pd} K_{Ep}} \quad (3)$$



Scheme 1.

The K_{Ep} value is estimated from the intercept of Fig. 3 ($(k_{Ed} + \alpha k_{pd} K_{Ep}) / (1 - \alpha) k_{pd} K_{Ep} = 2.13$) and Eq. (2) to be 2×10^{-3} and from the triplet lifetime τ_T and Eq. (3) to be 4×10^{-3} ; the mean ($(3 \pm 1) \times 10^{-3}$) gives the Gibbs energy difference between $^3p^*$ and $^3E^*$ to be approximately 3.5 kcal mol $^{-1}$, where the latter is more stable than the former. The low value of K_{Ep} (approximately 3×10^{-3}) and the deviation of the intercept value of Fig. 3 (2.13) from the usual value of unity indicate that deactivation also takes place from the planar *E* triplet ($^3E^*$). We can calculate the ratio of the deactivation from $^3p^*$ ($k_{pd} K_{Ep} / (k_{Ed} + k_{pd} K_{Ep})$) and $^3E^*$ ($k_{Ed} / (k_{Ed} + k_{pd} K_{Ep})$) to be approximately three using $K_{Ep} = 3 \times 10^{-3}$, $k_{pd} = 2 \times 10^7 \text{ s}^{-1}$ and $k_{Ed} = 2 \times 10^{-4} \text{ s}^{-1}$. Thus the deactivation of triplet VII takes place not only from $^3p^*$, but also from $^3E^*$, to show the dual character of one-way and two-way isomerization.

The k_{EZ} value is determined from the slope of Fig. 3 and Eq. (2) to be $1.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ using $k_{Ed} = 2 \times 10^4 \text{ s}^{-1}$, $k_{pd} = 2 \times 10^7 \text{ s}^{-1}$ and $K_{Ep} = 3 \times 10^{-3}$. This value is slightly lower than the diffusion-controlled rate constant (k_{dif}) in benzene (approximately $1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$). From the Sandros equation (Eq. (4)) [18] for endoergic energy transfer

$$k_{EZ} = k_{\text{dif}} \exp(-\Delta E_a/RT) / [1 + \exp(-\Delta E_a/RT)] \quad (4)$$

where ΔE_a is the triplet energy difference between *E*- and *Z*-VII, we can estimate that the triplet energy for *E*-VII is approximately 1 kcal mol $^{-1}$ lower than for *Z*-VII.

Similarly, the energy of $^3E^*$ ($E_T(^3E^*)$) can be estimated as approximately 40 kcal mol $^{-1}$ by modifying Eq. (4) (k_{EZ} is replaced by k_{az} and *Z* corresponds to azulene) and using the observed quenching rate constant by azulene ($k_{az} = 6.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$).

The lifetime of the *E* triplet (10 μs) is similar to that of arylethene carrying a pyrenyl group (III) (27 μs) [13]. Furthermore, the photoisomerization behaviour of VII, i.e. mutual isomerization with a quantum chain process for the *Z* → *E* direction, is similar to that of III.

Therefore the above results clearly indicate that, in the isomerization of the Ar-C=N double bond, the excitation energy of the Ar group governs the potential energy curve of the isomerization. Thus lowering the triplet excitation energy of the aryl group results in a change in the isomerization

Table 1
Photochemical $Z \rightarrow E$ isomerization of ArC(R)=NOCH_3

Ar	R	E_T of ArH	Mode of isomerization τ_T (μs) (λ_{max} (T-T) (nm))	$\Phi_{Z \rightarrow E}$ ([Z])	$\Phi_{E \rightarrow Z}$ ([E])
Phenyl	CH_3	84.3	Two-way ^a	0.40 ^a (0.2 M)	0.40 ^a (0.2 M)
2-Naphthyl	CH_3	60.9	Two-way ^b	0.51 ^b (0.05 M)	0.37 ^b (0.05 M)
1-Pyrenyl	H	48.2	Two-way 10 (440)	3.2 (1.3×10^{-3} M)	
2-Anthryl	CH_3	42	One-way ^c 90 (450, 540)	22 ^c (1.34×10^{-3} M)	

^a From Ref. [19].

^b From Ref. [20].

^c From Ref. [16].

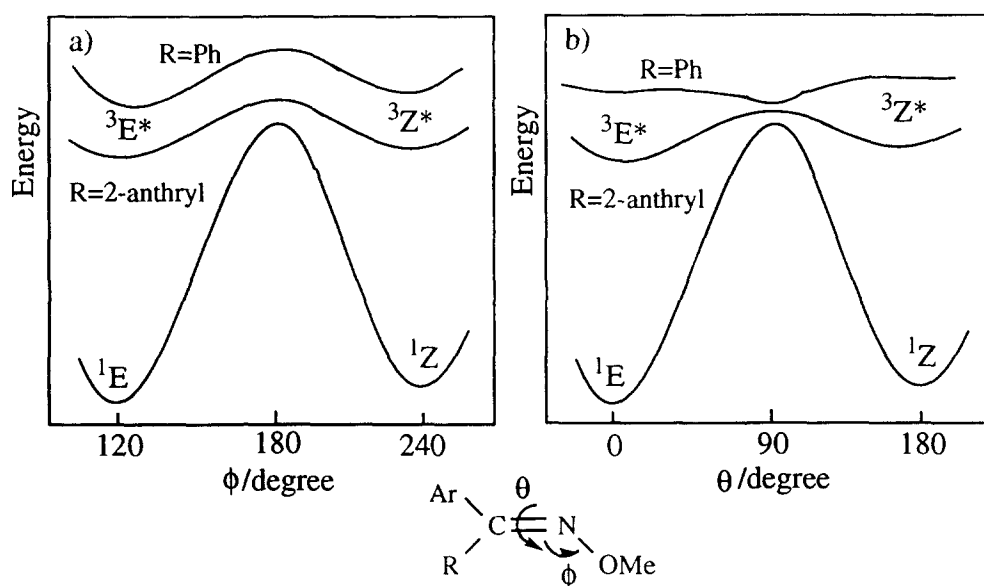


Fig. 6. Possible potential energy surfaces of $Z \rightarrow E$ photoisomerization of N -methoxy-1-(1-aryl)ethanimine (ArC(R)=NOMe) in the triplet state: (a) inversion mechanism; (b) rotation mechanism.

mode from typical two-way for **V** and **VI** to typical one-way for **IV**; a dual one-way and two-way mechanism is observed for **VII**. Table 1 summarizes the isomerization modes and quantum yields of isomerization depending on the substituent on the $\text{C}=\text{N}$ double bond [16,19–21]. The quantum yields of $Z \rightarrow E$ and $E \rightarrow Z$ isomerization of **V** were reported to be almost the same at 0.4 on benzophenone sensitization [19]. However, the $Z \rightarrow E$ isomerization of **IV** and **VII** takes place as a quantum chain process.

With regard to the mechanism of isomerization around the $\text{C}=\text{N}$ double bond, two candidates (inversion and rotation mechanisms) are possible and these mechanisms have been discussed on the basis of theoretical calculations [15]. The potential energy surfaces are depicted in Fig. 6. In the inversion mechanism (Fig. 6(a)), the angle ϕ of $\text{C}=\text{N}-\text{OMe}$ must move from approximately 120° (E) to approximately 240°

(Z) with the transition state at $\phi = 180^\circ$. Qualitatively, in this mechanism, the conformation at $\phi = 180^\circ$ must always be located as an energy barrier because of the change in hybridization from stable sp^2 to sp . Thus, irrespective of the substituent on the $\text{C}=\text{N}$ bond, the planar ${}^3E^*$ and ${}^3Z^*$ must be more stable than the transition state ($\phi = 180^\circ$), and therefore deactivation from the conformation $\phi = 180^\circ$ may not take place. In this case, we can expect a quantum chain process and long triplet lifetime for any substituent comparable with the one-way isomerizing anthrylimine **IV**.

However, in the rotational mechanism around the $\text{C}=\text{N}$ double bond (Fig. 6(b)), the substituent can affect the isomerization mode around this double bond in a similar manner to that observed for the $\text{C}=\text{C}$ double bond, as shown by the present results. Therefore the experimental findings on the effect of substituents on the mode of isomerization and triplet

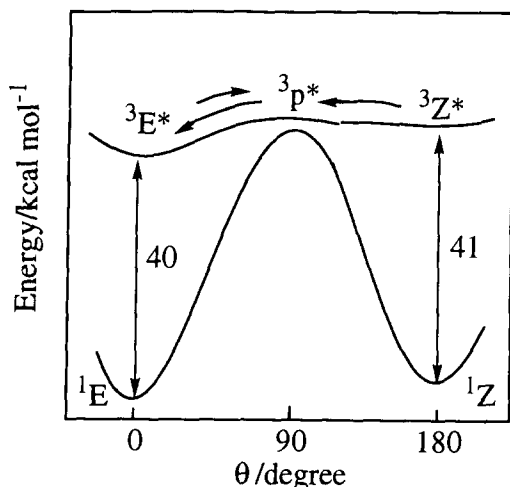


Fig. 7. Potential energy surfaces of isomerization of VII.

lifetime strongly support the rotational mechanism for isomerization of the C=N double bond in the excited triplet state.

Fig. 7 depicts the potential energy surfaces of *Z*–*E* isomerization of VII based on the experimental findings described above.

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