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Journal of Photochemistry and Photobiology A: Chemistry 103 (1997) 85–89

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A:CHEMISTRY

Spin-state-dependent two-way and one-way photoisomerization of *N*-methoxy-1-(9-anthryl)-methanimine in the excited state

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Received 7 July 1996; accepted 5 September 1996

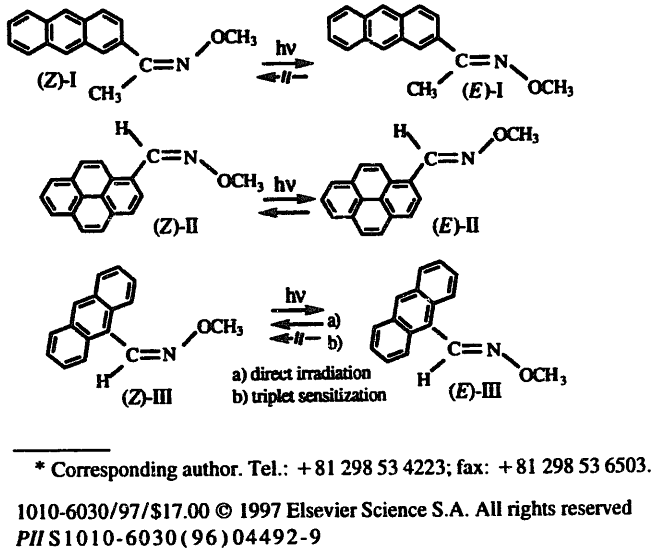
Abstract

On triplet sensitization, *N*-methoxy-1-(9-anthryl)-methanimine undergoes one-way Z → E isomerization; on direct irradiation, it undergoes two-way isomerization between the Z and E isomers. On the basis of the concentration dependence of the quantum yields of Z → E isomerization, and transient and fluorescence spectroscopy, the mechanism of this spin-state-dependent photochemical isomerization is discussed.

Keywords: Fluorescence spectrum; Isomerization: Quantum yield; Triplet–triplet absorption

1. Introduction

We have recently reported that *N*-methoxy-1-(2-anthryl)-ethanimine (I) undergoes one-way Z → E isomerization, proceeding via a quantum chain process, on triplet sensitization, whereas *N*-methoxy-1-(1-pyrenyl)-methanimine undergoes two-way isomerization with a quantum chain process for the Z → E direction [1–5]. Therefore the substituent effect of the aryl group on the isomerization of the C=N double bond appears to be similar to that on the isomerization of the C=C double bond [6–15]. With regard to the effect of the position of substitution, 9-anthrylethenes and 2-anthrylethenes undergo one-way Z → E isomerization in both the excited singlet and triplet states [16–20].



In this paper, it is reported that *N*-methoxy-1-(9-anthryl)-methanimine (III) undergoes one-way Z → E isomerization in the excited triplet state, but two-way isomerization in the excited singlet state. Furthermore, in the excited singlet state, Z → E isomerization proceeds partially as a novel adiabatic process.

2. Experimental details

A mixture of 9-anthracenecarboxyaldehyde and O-methylhydroxyamine hydrochloride was refluxed in ethanol containing sodium acetate for 12 h. Pure *E*- and *Z*-III were separated from the reaction mixture by flash column chromatography over silica gel eluted with hexane–ethyl acetate (95 : 5), and recrystallized from hexane.

Z-III: ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 3.89 (s, 3H, methoxy H), 7.21–7.50 (m, 4H, ArH), 7.94–7.98 (m, 4H, ArH), 8.19 (s, 1H, ArH), 8.42 (s, 1H, H–C=N); melting point (m.p.), 105–105.5 °C. *E*-III: ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 4.15 (s, 3H, methoxy H), 7.47–7.50 (m, 2H, ArH), 7.52–7.50 (m, 2H, ArH), 7.99–8.01 (m, 2H, ArH), 8.45–8.47 (m, 3H, ArH), 9.16 (s, 1H, H–C=N); m.p., 154.5–156.5 °C.

Analysis: calculated for $C_{16}H_{13}NO$: C, 81.68%; H, 5.57%; N, 5.95%; found for *Z*-III: C, 81.41%; H, 5.58%; N, 5.87%.

Irradiation was performed at 366 nm for direct irradiation and at 480 nm for camphorquinone sensitization with a 150 W xenon lamp of a Hitachi F-4000 spectrofluorometer. The photostationary state isomeric ratios and the quantum yields of isomerization were determined in benzene in the presence

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PII S1010-6030(96)04492-9

or absence of camphorquinone. 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). The light intensity was measured using potassium tris(oxalato)-ferrate(III) actinometry.

Laser flash photolysis was performed with a 308 nm Lambda Physik LPX-105 excimer laser (XeCl) as excitation light source and a pulsed xenon arc (Wacom KXL-151, 150 W) as monitoring light source [1].

Time-resolved fluorescence spectra were measured with 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 full width at half-maximum (FWHM)) operated with a continuous wave (CW) Ar^+ laser (Spectra Physics 2060) and a streak scope (Hamamatsu C4334). The jitter of the whole system was approximately 50 ps FWHM.

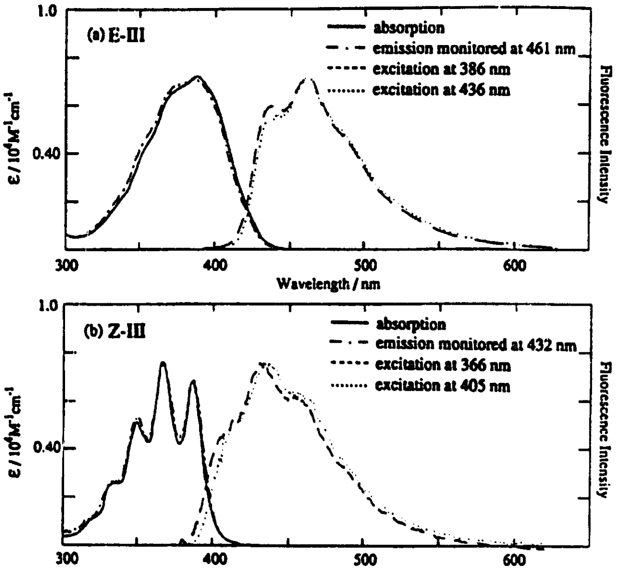


Fig. 1. Absorption, fluorescence and fluorescence excitation spectra of E-III (a) and Z-III (b) in benzene.

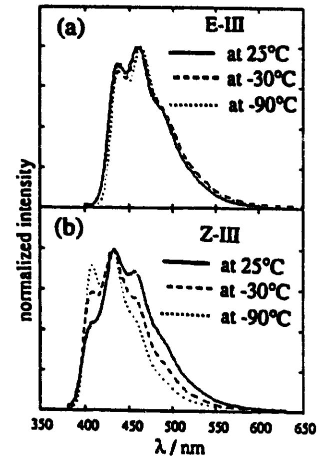


Fig. 2. Effect of temperature on the fluorescence spectra of E-III (a) and Z-III (b) in toluene.

3. Results and discussion

3.1. Absorption and fluorescence properties

Fig. 1 shows the absorption, fluorescence and fluorescence excitation spectra of E- and Z-III in benzene. E- and Z-III exhibit different fluorescence spectra, with their fluorescence excitation spectra well matched to the corresponding ground state absorption spectra. The fluorescence spectrum of E-III is almost the same in the temperature range −90–25 °C, but the spectral profile of Z-III changes with temperature: the intensity decreases in the long-wavelength region with a concomitant increase in the short-wavelength region (Fig. 2). These results indicate that, at room temperature, Z-III undergoes adiabatic $^1Z^* \rightarrow {}^1E^*$ isomerization in the excited singlet state to give the fluorescence of ^{1}E-III* as well as that of ^{1}Z-III*. This is demonstrated more clearly by picosecond fluorescence spectroscopy (Fig. 3). E-III gives the same fluorescence spectrum at all time delays from the excitation laser pulse (2 ps FWHM); however, the fluorescence spectrum of Z-III shifts from the short-wavelength component (accumulated between 0 and 0.417 ns after the laser pulse) to the long-wavelength component (3.13–3.54 ns); the latter is very similar to the spectrum of E-III (Fig. 2). Therefore the spectrum accumulated between 0 and 0.4 ns can mainly be ascribed to Z-III and that at 3.1–3.5 ns to E-III. The fluores-

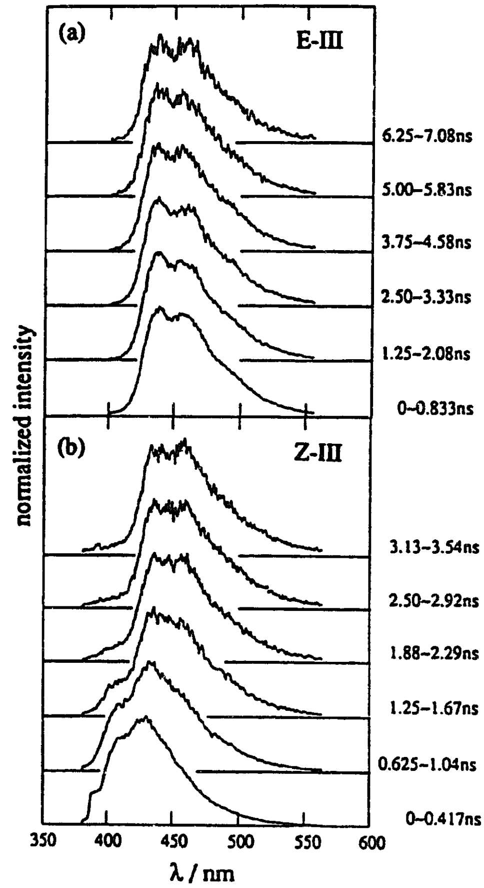


Fig. 3. Picosecond time-resolved fluorescence spectra of E-III (a) and Z-III (b) at room temperature.

cence decay curve of *E*-III observed at 439 nm on excitation at 390 nm fits a single-component analysis to give a fluorescence lifetime of 2.4 ns. The fluorescence decay of Z-III fits a two-component analysis to give 0.40 ns and 2.4 ns; the former corresponds to the decay of ^{1}Z-III* and the latter to ^{1}*E*-III*.

The fluorescence quantum yields of *Z*- and *E*-III on excitation at 366 nm at room temperature were determined to be 0.075 and 0.26, and the quantum yields of intersystem crossing of *Z*- and *E*-III on excitation at 308 nm at room temperature were determined to be 0.14 and 0.12 (using anthracene as a standard).

3.2. *Quantum yields of isomerization and the photostationary state isomeric composition*

On direct irradiation at 366 nm, *E*- and Z-III undergo two-way isomerization to give a photostationary state mixture of [*E*-III]/[Z-III] = 71.5/28.5 (Fig. 4). The quantum yield of Z→E isomerization ($\Phi_{Z\to E}$) increases linearly with the Z isomer concentration from 0.55 at 4.5×10^{-4} M to 0.78 at 1.8×10^{-3} M, whereas the quantum yield of E→Z isomerization ($\Phi_{E\to Z}$) is almost constant, i.e. approximately 0.29 in the concentration range (4.3–17) $\times10^{-4}$ M (Fig. 5).

In contrast, on camphorquinone sensitization, III undergoes one-way Z→E isomerization, with no E→Z isomerization. On camphorquinone sensitization, $\Phi_{Z\to E}$ increases with increasing Z isomer concentration from 1.8 at 3×10^{-4} M to 2.8 at 1.5×10^{-3} M (Fig. 5), indicating that isomerization proceeds as a quantum chain process in the excited state.

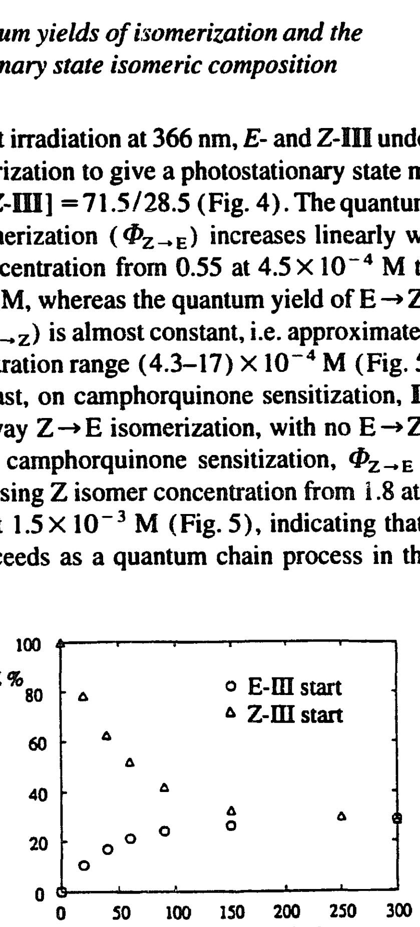


Fig. 4. Time development of the isomeric composition on direct irradiation of *Z*- and *E*-III in benzene at room temperature.

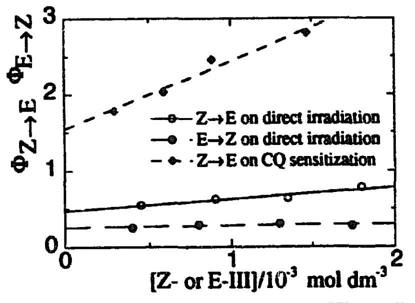


Fig. 5. Quantum yields of Z–E photoisomerization of III on direct irradiation and on camphorquinone sensitization.

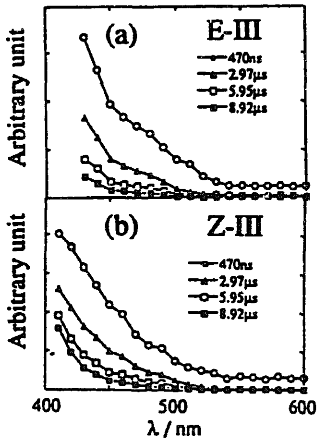


Fig. 6. T–T absorption spectra of *E*-III (a) and Z-III (b) on Michler's ketone sensitization.

3.3. *Triplet–triplet (T–T) absorption spectroscopy*

Fig. 6 shows the T–T absorption spectra of III in benzene observed on Michler's ketone (E_T = 65.6 kcal mol^{-1}) sensitization at 308 nm with an excimer laser. *Z*- and *E*-III give similar T–T absorption spectra with a λ_{max} value shorter than 410 nm, assigned to the E triplet (^{3}E*). Direct excitation of *E*- and *Z*-III at 308 nm also gives similar transient spectra, assigned to ^{3}E*. The triplet lifetimes (τ_T) are 5 µs and 58 µs under an argon atmosphere and degassed conditions respectively.

The T–T absorption spectrum of III is quenched by azulene, giving a fast and slow decay, indicating the energy transfer equilibrium between ^{3}E* and azulene (E_T = 39.8 kcal mol^{-1}) as described in Eqs. (1)–(3)

$$^3\mathrm{E}^* + {}^1\mathrm{Az} \overset{K}{\rightleftharpoons} {}^1\mathrm{E} + {}^3\mathrm{Az}^* \qquad (1)$$

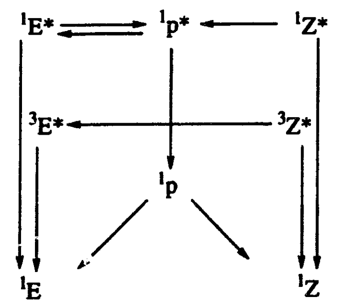
$$K = \frac{[^1\mathrm{E}][^3\mathrm{Az}^*]}{[^1\mathrm{Az}][^3\mathrm{E}^*]} \qquad (2)$$

$$\Delta E_T \approx \Delta G = -RT \ln K \qquad (3)$$

The treatment reported previously [21] gives an equilibrium constant *K* of 0.15 at the initial concentrations of azulene and *E*-III of 4.7×10^{-3} M and 1.4×10^{-3} M respectively. When the free energy change in reaction (1), ΔG, is assumed to be equal to the difference in triplet energy between *E*-III (E_T(*E*-III)) and azulene (E_T(Az)), i.e. $\Delta E_T = E_T(\mathrm{Az}) - E_T(E\text{-III})$, the ΔE_T value is estimated to be approximately 0.8 kcal mol^{-1}. This value enabled us to estimate the energy of ^{3}E* to be 39 kcal mol^{-1} over its ground state.

3.4. *Mechanism of one-way Z→E isomerization of III in the excited triplet state and two-way Z–E isomerization of III in the excited singlet state*

Scheme 1 shows the mechanism of one-way Z→E isomerization in the excited triplet state. In the triplet state, Z→E isomerization takes place as a quantum chain mechanism via



Scheme 1.

energy transfer from $^3E^*$ to ^1Z to regenerate the excited state, as shown in Eq. (4). According to this mechanism, the quantum yield of isomerization on triplet sensitization ($\Phi^{sens}_{Z\to E}$) is described by Eq. (5)

$$^3E^* + {}^1Z \xrightarrow{k_{EZ}} {}^1E + {}^3Z^* \qquad (4)$$

$$\Phi^{sens}_{Z\to E} = \Phi_{isc} \times (1 + k_{EZ}\tau_T[Z]) \qquad (5)$$

The slope of Fig. 5 on camphorquinone sensitization ($\Phi_{isc} \times k_{EZ}\tau_T$) is determined to be 9.0×10^2 mol^{-1} dm^3. We can calculate the k_{EZ} value to be 1.8×10^8 M^{-1} s^{-1} using $\tau_T = 5$ μs determined under an argon atmosphere. This value is slightly slower than the diffusion-controlled rate constant (k_{dif}) in benzene ($k_{dif} \approx 1 \times 10^{10}$ M^{-1} s^{-1}). From Eq. (6) for endergonic energy transfer, where ΔE_a is the triplet energy difference between *Z*- and *E*-**III**, we can estimate that the triplet energy of *E*-**III** is lower than that of *Z*-**III** by approximately 2 kcal mol^{-1} [22].

$$k_{EZ} = k_{dif}\exp(-\Delta E_a/RT)/[1 + \exp(-\Delta E_a/RT)] \qquad (6)$$

On direct irradiation, **III** undergoes two-way isomerization. Two-way isomerization can take place in the singlet potential energy surface either by deactivation at the perpendicular singlet state ($^1p^*$) or by adiabatic mutual isomerization between $^1Z^*$ and $^1E^*$. The fluorescence of both *Z*-**III** and *E*-**III** is observed on excitation of *Z*-**III**, whereas *E*-**III** gives the fluorescence of the E isomer only. Thus fluorescence spectroscopy enables us to estimate the occurrence of $^1Z^* \to {}^1E^*$ adiabatic isomerization, whereas $^1E^*$ does not give $^1Z^*$ directly.

E-**III** is isomerized to *Z*-**III** on direct irradiation by twisting of the double bond to give $^1p^*$, and is deactivated at this conformation to ground state ^1p to give the Z and E isomers. *Z*-**III** is isomerized to *E*-**III** in a two-way process on direct irradiation, with deactivation from $^1p^*$, but partly undergoes an adiabatic $^1Z^* \to {}^1E^*$ process in the excited singlet state followed by deactivation to ground state ^1E. We can estimate the ratio of adiabatic $^1Z^* \to {}^1E^*$ isomerization to diabatic isomerization decaying at $^1p^*$ to be 45 : 55 from the reconstruction of the fluorescence spectrum observed on excitation of *Z*-**III** at room temperature.

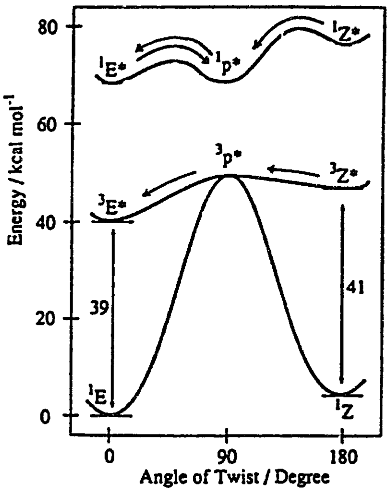


Fig. 7. Potential energy surfaces of one-way and two-way isomerization of **III** in the excited triplet and singlet states respectively.

3.5. Potential energy surfaces of one-way and two-way isomerization in the excited triplet and singlet states respectively

Fig. 7 depicts the potential energy surfaces of one-way and two-way isomerization in the excited triplet and singlet states. One-way Z → E isomerization in the excited triplet state takes place as a quantum chain process as observed for **I** and 2-anthrylethenes. However, the $\Phi_{Z\to E}$ value of **III** is lower than those of **I** and 2-anthrylethenes. For example, $\Phi_{Z\to E}$ is 2.8 at [*Z*-**III**] = 1.47×10^{-4} M, whereas $\Phi_{Z\to E}$ is 23.5 at [*Z*-**I**] = 1.34×10^{-4} M [1]. The energy difference between $^3E^*$ and $^3Z^*$ may be responsible for the different $\Phi_{Z\to E}$ values observed for *Z*-**I** and *Z*-**III**: in **I**, $^3Z^*$ and $^3E^*$ are located at nearly the same energy, but in **III**, $^3Z^*$ is less stable than $^3E^*$ by approximately 2 kcal mol^{-1} as described above.

In the singlet excited state, Z → E isomerization of **III** takes place via both an adiabatic $^1Z^* \to {}^1E^*$ process and a diabatic process with deactivation at $^1p^*$, whereas E → Z isomerization proceeds as a diabatic process with deactivation at $^1p^*$. The above mechanism may occur in the potential energy surface, where $^1p^*$ is located as a very shallow energy minimum and has sufficient time for deactivation to the ground state, and where the barrier for rotation to $^1E^*$ is not very high and further twisting to give $^1E^*$ can take place to yield adiabatic $^1Z^* \to {}^1E^*$ isomerization.

Acknowledgements

The authors thank the Ministry of Education, Science and Culture for a Grant-in-Aid for Specially Promoted Research (No. 03101004).

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