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One-way cis → trans photoisomerization of azulenylethenes

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Abstract

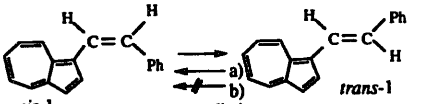
2-Styrylazulene (**2**) and 1,2-di(azulenyl)ethene (**3**) undergo one-way cis → trans isomerization on direct irradiation and on triplet sensitization. The quantum yield of cis → trans isomerization ($\Phi_{c\to t}$) on triplet sensitization increases with the initial cis isomer concentration and exceeds unity ($\Phi_{c\to t}=25$ at [*cis*-**2**] = 1.7×10^{-3} M). The quantum yields of cis → trans isomerization of **2** and **3** are in the region of 10^{-3} on direct irradiation at the higher excited singlet state S_2, but increase with increasing concentration of the cis isomer. These results strongly indicate that, even on direct irradiation of 2-azulenylethenes, one-way cis → trans isomerization takes place as a quantum chain process in the excited triplet state after intersystem crossing. © 1997 Elsevier Science S.A.

Keywords: Fluorescence spectrum; Isomerization; Quantum chain process; T–T absorption

1. Introduction

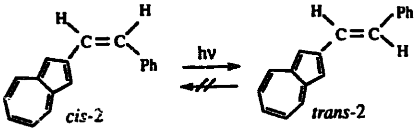
The photochemical cis–trans isomerization of olefins has been extensively investigated [1–8]. Stilbene undergoes two-way isomerization between cis and trans isomers on direct irradiation and triplet sensitization; the former proceeds in the singlet manifold [1–3]. 2-Styrylanthracene isomerizes only from the cis to the trans isomer on direct irradiation and triplet sensitization through a quantum chain process [4–9]. 1-Styrylanthracene also exhibits one-way cis → trans isomerization on direct irradiation and triplet sensitization; on direct irradiation, the quantum yields of cis → trans isomerization are as low as 10^{-2} due to other deactivation processes, such as cyclization to give dihydrophenanthrene-type compounds [10]. 1-Styrylazulene (**1**) and its alkyl derivative undergo two-way isomerization on direct irradiation deactivating from the singlet excited state, but they undergo one-way cis → trans isomerization on triplet sensitization [11]. Thus olefins containing azulene rings seem to exhibit different photochemical behaviour on direct irradiation and on triplet sensitization. Furthermore, the substitution position may contribute to changes in the efficiency and mode of isomerization as observed for 1- and 2-styrylanthracenes [8–10].

In this paper, we report that 2-styrylazulene (**2**) undergoes one-way cis → trans isomerization on direct irradiation and triplet sensitization through a quantum chain process. Furthermore, 1,2-di(azulenyl)ethene (**3**) undergoes a similar one-way isomerization.

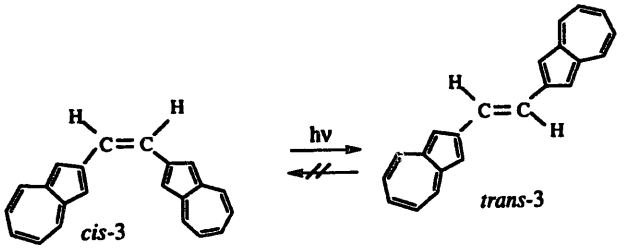


cis-1 *trans*-1

a) on direct irradiation
b) on triplet sensitization



cis-2 *trans*-2



cis-3 *trans*-3

2. Experimental details

2.1. Materials

The procedures for the synthesis of **2** and **3** have been described elsewhere [12].

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The solvent benzene was Luminazol from Dojin Chemical Company. Benzil was recrystallized from ethanol.

2.2. *Photoirradiation procedure and transient spectroscopy*

Absorption and fluorescence spectra were measured on a Jasco Ubest 55 spectrophotometer and a Hitachi F-4000 spectrofluorometer respectively. Fluorescence lifetimes were measured using a single-photon counting apparatus (Horiba NAES-1100).

Laser flash photolyses were performed with 308 nm pulses (XeCl, 10 ns full width at half-maximum (FWHM)) from an excimer laser (Lambda Physik LPX-100) and 425 nm pulses (stilbene 3, 10 ns FWHM) from an excimer laser-pumped dye laser (Lambda Physik FL-3002), with a pulsed xenon arc (Wacom, KXL-151, 150 W) as monitoring light source. The detailed set-up has been described previously [13]. Sample solutions were deaerated by freeze–pump–thaw cycles or by bubbling with argon.

Photoirradiation was performed under a nitrogen atmosphere in benzene with 366 nm light or 436 nm light from a 400 W high-pressure mercury lamp passed through a bandpass filter (Corning 7-60, 0-52) or a glass filter (L-42) and solution filter [14] respectively or with 468 nm light or 656 nm light from a 300 W xenon arc lamp passed through a monochromator or bandpass filter (Melles Griot 03FIR006) respectively. The isomer compositions were determined by high performance liquid chromatography (Waters 600 multisolvent delivery system with a 490 programmable multiwavelength detector).

3. Results and discussion

3.1. *Absorption and fluorescence properties*

Fig. 1 shows the absorption spectra of *cis*- and *trans*-**2** (Fig. 1(a)) and the fluorescence and excitation spectra of *trans*-**2** in benzene solution (Fig. 1(c)). As in the case of 1-styrylazulene [10], the fluorescence from the second excited state (S_2) only was observed from *trans*-**2** (Fig. 1(c)), and no fluorescence was detected from the lowest excited singlet state (S_1). The quantum yield of fluorescence emission is as low as 1.6×10^{-4} in benzene at 24 °C. Both *cis*- and *trans*-**3** exhibit absorption spectra (Fig. 1(b)) at slightly longer wavelengths than the corresponding isomers of **2**, while no fluorescence spectrum was observed from either isomer. The fluorescence lifetime of *trans*-**2** is shorter than the time resolution of the nanosecond fluorescence spectrometer, i.e. less than 100 ps. The energies of the S_1 and S_2 states were estimated from the onset of the absorption spectra to be 40.9 and 66.5 kcal mol^{-1} respectively for *trans*-**2** and 40.8 and 59.5 kcal mol^{-1} respectively for *trans*-**3**. Since the absorption profile in the S_1 region is quite similar for the cis and trans isomers of **2** and **3**, the S_1 energies were estimated to be the same as those of the trans isomers, 40.9 and 40.8 kcal mol^{-1} for *cis*-**2** and *cis*-**3**, while the S_2 energies of *cis*-**2** and *cis*-**3** were estimated from the onset of the absorption spectra to be 66 and 59 kcal mol^{-1} respectively, i.e. similar to those of the corresponding trans isomers.

The anomalous fluorescence observed from the S_2 state of azulene and its derivatives has been discussed in terms of the energy gap between S_2 and S_1. A fluorescence quantum yield of $\Phi_f = 0.058$ from S_2 has been observed for 1,3-dichloroazulene whose energy gap between S_2 and S_1 ($E(S_2\text{–}S_1)$) is as high as 40.9 kcal mol^{-1} [15]. The Φ_f value decreases with decreasing energy gap between S_2 and S_1 and is 0.031 for azulene ($E(S_2\text{–}S_1) = 40.0$ kcal mol^{-1}), 0.0081 for 2-methylazulene ($E(S_2\text{–}S_1) = 36.9$ kcal mol^{-1}), 0.0034 for 2-iodoazulene ($E(S_2\text{–}S_1) = 34.6$ kcal mol^{-1}), approximately 10^{-4} for 2-methoxyazulene ($E(S_2\text{–}S_1) = 30.0$ kcal mol^{-1}) and approximately 10^{-5} for 2-(dimethylamino)azulene ($E(S_2\text{–}S_1) = 20.6$ kcal mol^{-1}). Intersystem crossing does not play an important role in the deactivation processes, since

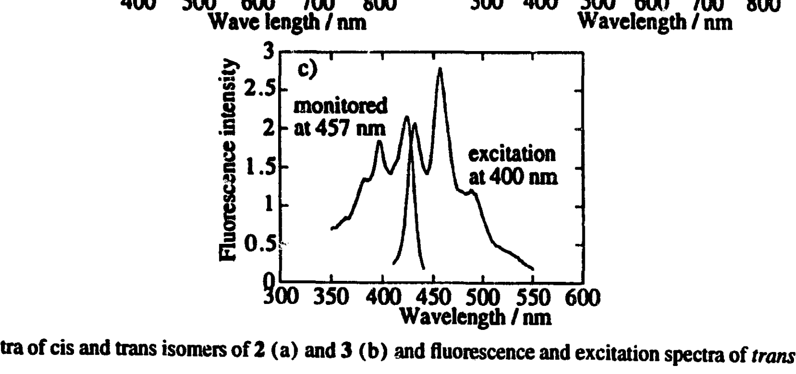

Fig. 1. Absorption spectra of cis and trans isomers of **2** (a) and **3** (b) and fluorescence and excitation spectra of *trans*-**2** (c) in benzene at 24 °C.

2-iodoazulene with a heavy atom exhibits appreciable fluorescence and no acceleration of intersystem crossing [15]. Thus most of the deactivation from S_2 takes place to produce the ground state S_0 or S_1, where S_1 may undergo intersystem crossing to the triplet state T_1.

The energy differences, $E(S_2–S_1)$, for **2** and **3** are estimated from the above values. The value is highest for *trans*-**2** ($E(S_2–S_1) \approx 26$ kcal mol^{-1}) and decreases in the order of *cis*-**2** (approximately 25 kcal mol^{-1}), *trans*-**3** (approximately 19 kcal mol^{-1}) and *cis*-**3** (approximately 18 kcal mol^{-1}). The low Φ_f value observed for *trans*-**2** and the lack of observation of fluorescence from S_2 for *cis*-**2**, *cis*-**3** and *trans*-**3** are in accord with the energy gap dependence described above.

3.2. Quantum yields of cis → trans isomerization

Olefins **2** and **3** undergo one-way cis → trans isomerization on direct excitation and on triplet sensitization. On direct irradiation at the S_1 state with 656 nm light, the quantum yields of cis → trans isomerization are as low as 4×10^{-2} and 1.4×10^{-3} for **2** and **3** respectively at the initial concentrations of [*cis*-**2**] = 1.0×10^{-3} M and [*cis*-**3**] = 1.1×10^{-3} M.

Fig. 2 shows the quantum yields of cis → trans isomerization on direct irradiation ($\Phi^{\mathrm{dir}}_{\mathrm{c \to t}}$) at 366 nm (*cis*-**2**) or 436 nm (*cis*-**3**) and on triplet sensitization ($\Phi^{\mathrm{sen}}_{\mathrm{c \to t}}$) at 468 nm with benzil as sensitizer. Both $\Phi^{\mathrm{dir}}_{\mathrm{c \to t}}$ and $\Phi^{\mathrm{sen}}_{\mathrm{c \to t}}$ increase with increasing concentration of the initial cis isomer. The slope and intercept values for **2** are 19 M^{-1} and 1.1×10^{-3} on direct irradiation and 1.4×10^{4} M^{-1} and 1.1 on benzil sensitization; these values for **3** are 2.8 M^{-1} and 1.7×10^{-4} on direct irradiation and 2.8×10^{3} M^{-1} and 0.86 on benzil sensitization. Since the quantum chain process can only take place on the triplet potential energy surface due to the short lifetime of the excited singlet state, the cis → trans isomerization of **2** and **3** should take place in the triplet manifold even on direct irradiation.

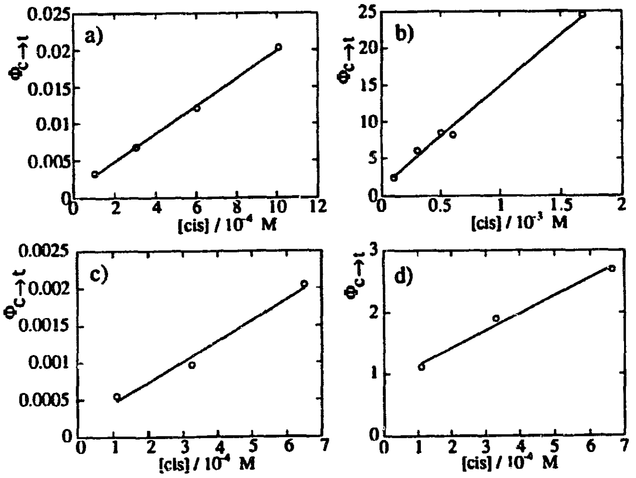

Fig. 2. Effect of the initial cis isomer concentration on the quantum yields of cis → trans isomerization of **2** (a and b) and **3** (c and d) on direct irradiation (a and c) and on benzil sensitization (b and d) in benzene at ambient temperature.

$$
\begin{aligned}
&{}^1c \xrightarrow{h\nu\ (656\mathrm{nm})} {}^1c^* && {}^1c \xrightarrow{h\nu\ (365\ \mathrm{nm})} {}^1c^{**} \\
& && {}^1c^{**} \longrightarrow {}^1c^* \\
&{}^1c^* \xrightarrow{k_d^{\,c}} {}^1c && {}^1S \xrightarrow{h\nu} {}^1S^* \xrightarrow{k_{isc}'} {}^3S^* \\
&{}^1c^* \xrightarrow{k_{isc}} {}^3c^* && {}^3S^* + {}^1c \xrightarrow{k_{sc}} {}^1S + {}^3c^* \\
&{}^3c^* \xrightarrow{k_{c \to t}} {}^3t^* && \\
&{}^3t^* + {}^1c \xrightarrow{k_{tc}} {}^1t + {}^3c^* && \\
&{}^3t^* \xrightarrow{k_d^{\,t}} {}^1t &&
\end{aligned}
$$

Scheme 1.

Thus the mechanism of one-way cis → trans isomerization proceeds via Scheme 1, where the *k* parameters are the rate constants for the corresponding processes and S is the triplet sensitizer. According to Scheme 1, the $\Phi^{\mathrm{dir}}_{\mathrm{c \to t}}$ and $\Phi^{\mathrm{sen}}_{\mathrm{c \to t}}$ values are described by Eq. (1), where Φ_T is the quantum yield of triplet production of azulenylethenes and k_{tc} is the rate constant for energy transfer from the trans triplet ($^3t^*$) to the cis ground state (^1c)

$$\Phi_{c \to t} = \Phi_T \times (1 + k_{tc}\tau_T[\mathrm{cis}]) \qquad (1)$$

From the slope and intercept values of the plots of $\Phi^{\mathrm{dir}}_{\mathrm{c \to t}}$ and $\Phi^{\mathrm{sen}}_{\mathrm{c \to t}}$ vs. [cis], we can calculate the $k_q\tau_T$ values as 1.8×10^{4} and 1.2×10^{4} M^{-1} respectively for **2**. These values agree well with each other. Using their mean, $k_q\tau_T = 1.5 \times 10^{4}$ M^{-1}, and the τ_T value under an argon atmosphere (15 μs, see below), the energy transfer rate constant from $^3t^*$ to ^1c was estimated to be 1.0×10^{9} M^{-1} s^{-1}. This value is slightly lower than the diffusion-controlled rate constant (k_{dif}) in benzene (approximately 1×10^{10} M^{-1} s^{-1}). From Eq. (2) [16] for endothermic energy transfer

$$k_q = k_{\mathrm{dif}} \exp(-\Delta E_a/RT)/[1 + \exp(-\Delta E_a/RT)] \qquad (2)$$

where ΔE_a is the triplet energy difference between the trans and cis isomers, we can estimate that the triplet energy of *trans*-**2** is approximately 1 kcal mol^{-1} lower than that of *cis*-**2**. Similar to this treatment, $k_q\tau_T$ was obtained as (0.3–1.5) $\times 10^{4}$ M^{-1} for **3**. By using the triplet lifetime of **3** (10 μs), the rate constant for energy transfer was calculated to be (0.3–1.5) $\times 10^{9}$ M^{-1}, slightly lower than the diffusion-controlled rate constant, which predicts an energy difference between *cis*- and *trans*-**3** of 1–2 kcal mol^{-1}.

The intercept values obtained on triplet sensitization are close to unity and are in accordance with the quantum yield of intersystem crossing of the sensitizer benzil (0.92) [17]. The quantum yields of intersystem crossing of *cis*-**2** and *cis*-**3** on direct irradiation at S_2 were estimated to be 1.1×10^{-3} and 1.7×10^{-4} respectively from the intercept values obtained on direct irradiation of *cis*-**2** and *cis*-**3**.

3.3. Triplet–triplet (T–T) absorption spectra

Fig. 3 shows the T–T absorption spectra of *cis*- and *trans*-**2** and *cis*- and *trans*-**3** on benzil sensitization under an argon

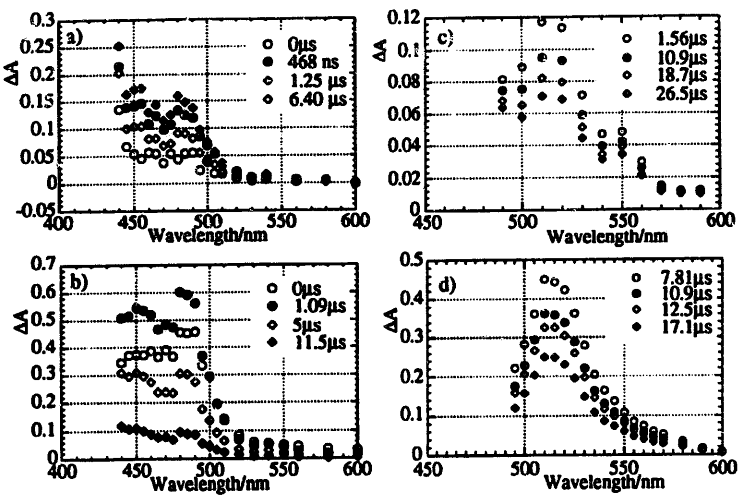

Fig. 3. T–T absorption spectra observed on excitation of *cis*-**2** (a) and *trans*-**2** (b) and *cis*-**3** (c) and *trans*-**3** (d) in the presence of benzil as sensitizer in benzene at 24 °C.

atmosphere with a 425 nm laser pulse. The concentration of **2** used in this experiment was adjusted to 1×10^{-4} M, since *cis*- and *trans*-**2** absorb 425 nm light. Just after the laser pulse, the T–T absorption spectrum of benzil was observed for both isomers (Fig. 3(a) and Fig. 3(b)). Then, energy transfer from the benzil triplet to *cis*- and *trans*-**2** takes place increasing the absorbance and changing slightly the spectral profiles as observed in Fig. 3(a) and Fig. 3(b). Since the triplet energies of the cis and trans isomers of **2** and **3** were reasonably assumed to be equal or slightly lower than the triplet energy of azulene (39.8 kcal $\mathrm{mol^{-1}}$) [18] and are much lower than the energy of the benzil triplet (53.4 kcal $\mathrm{mol^{-1}}$) [17], the energy transfer from the benzil triplet to azulenylethenes should proceed at the diffusion-controlled rate constant (10^{10} $\mathrm{M^{-1}\ s^{-1}}$). Taking into account the concentration of **2** and the rate constant of energy transfer, the energy transfer process is almost complete within 1 μs. Therefore the T–T absorption spectra observed at 5–10 μs after the laser flash in Fig. 3 correspond to the azulenylethene triplets. The lifetimes were determined for both *cis*- and *trans*-**2** to be 15 μs and 30 μs under an argon atmosphere and under degassed conditions respectively. Since the spectra observed on excitation of *cis*- and *trans*-**2** are very similar, except for the increase in the permanent absorption at 440 nm for *cis*-**2** due to the increase in the ground state absorption by cis → trans isomerization, the observed T–T spectra are reasonably assigned to *trans*-**2**. On direct irradiation, **2** gave no detectable T–T absorption spectrum, indicating that intersystem crossing is highly inefficient. Azulenylethene **3** gave similar T–T absorption spectra on benzil sensitization with $\lambda_{max}=510$ nm, and $\tau_T=10$ μs under an argon atmosphere and $\tau_T=54$ μs under degassed conditions (Fig. 3(c) and Fig. 3(d)).

3.4. Mechanism and potential energy surface of cis → trans isomerization

With regard to the mechanism of cis → trans one-way isomerization on S_2 excitation, we may expect isomerization at the higher excited singlet manifold, at the lowest excited singlet manifold or at the triplet manifold. The cis → trans isomerization on S_2 excitation of **2** and **3** takes place as a quantum chain process. Furthermore, excitation at S_1 also brings about one-way cis → trans isomerization with similar quantum yields to S_2 excitation. Thus it seems that on S_2 and S_1 excitation, **2** and **3** undergo one-way cis → trans isomerization after intersystem crossing.

Fig. 4 depicts the potential energy surfaces of one-way photoisomerization of azulenylethenes **2** and **3**. Both compounds should undergo isomerization on similar potential energy surfaces. Thus, on triplet sensitization, cis → trans one-way isomerization should take place on the T_1 potential energy surface. The sensitizer triplet transfers its energy to the cis isomers to give the cis triplet state ($^3c^*$), which undergoes isomerization around the double bond to give the trans triplet ($^3t^*$). The perpendicular triplet state ($^3p^*$) is the transition state for this process. The resulting $^3t^*$ deactivates unimolecularly to the ground state, or ^1t undergoes energy transfer to the cis isomer (^1c) to give $^3c^*$ to accomplish the quantum chain process.

On direct irradiation of **2** with either 656 or 366 nm light, the resulting S_2 or S_1 may undergo internal conversion or intersystem crossing to give $^3t^*$, where the isomerization takes place only in the cis to trans direction. The intercept

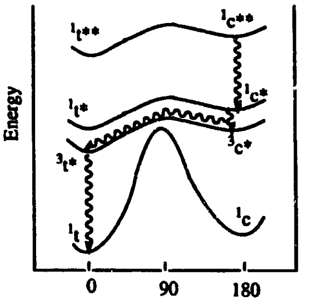

Fig. 4. Potential energy surfaces of one-way photoisomerization of azulenylethenes.

values of the $\Phi^{\mathrm{dir}}_{c\to t}$ vs. [cis] plots give the quantum yields of intersystem crossing as approximately 10^{-3} (*cis*-**2**) and 10^{-4} (*cis*-**3**), which are in accordance with the parent hydrocarbon azulene [15].

Azulenylethenes **2** and **3** absorb most of the visible light and undergo very inefficient cis → trans one-way isomerization. However, on triplet sensitization $\Phi_{c\to t}$ reaches values as high as 25. On direct irradiation in very dilute solution the $\Phi_{c\to t}$ value is as low as 10^{-3}, and on triplet sensitization in the presence of 10^{-2} M of cis isomer $\Phi_{c\to t}$ values as high as 100 can be obtained. Thus we can change the efficiency of cis → trans one-way isomerization of azulenylethenes **2** and **3** by five orders of magnitude from 10^{-3} to 100 by changing the irradiation conditions and the concentration of the initial cis isomer.

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