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Photochemical Cis to Trans One-Way Isomerization of Styrylazulenes on Their Triplet Excited State. Examination of Ethylenes with Non-Benzenoid Substituents of Low Triplet Energies

Takashi Karatsu,* Akihide Kitamura, Tatsuo Arai,† Hirochika Sakuragi,† and Katsumi Tokumaru*,†
College of Arts and Sciences, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263
† Department of Chemistry, The University of Tsukuba, Tsukuba, Ibaraki 305

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1-Styrylazulene and 7-isopropyl-1,4-dimethyl-3-styrylazulene (3-styrylguaiazulene) underwent one-way isomerization from the cis to the trans isomer on triplet sensitization. Their triplet states as intermediates of the isomerization were observed by laser flash photolysis. However, their excitation to either the lowest excited singlet state (S_1) or the second excited singlet state (S_2) by direct irradiation afforded photostationary mixtures comprising 98% of the trans and 2% the cis isomers, which implies the participation of a singlet isomerization path.

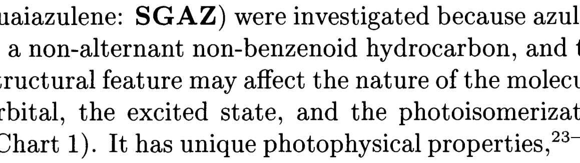
We have reported that anthrylethylenes undergo one-way isomerization from their cis isomers to the trans isomers on the triplet manifold.[1—10] The isomerization proceeds through an adiabatic conversion of the initially produced cis triplet ($^3c^*$) to the trans triplet ($^3t^*$) by passing through a perpendicularly twisted conformation ($^3p^*$). The quantum yields of cis→trans isomerization increase with the cis isomer concentration and far exceed unity. Accordingly, the isomerization takes place in a quantum chain process. An extraordinarily long lifetime of $^3t^*$ on the order of 100 μs enables it to undergo an energy transfer to the cis isomer to regenerate $^3c^*$ in preference to their relatively slow decay, thus accomplishing a quantum chain process. The characteristic feature of the one-way isomerization arises from the potential energy surface where $^3p^*$ is not at a deep energy minimum but at the energy barrier on the way of $^3c^* \rightarrow {}^3t^*$ conversion due to the low triplet energy of the anthryl group. This is in great contrast with many olefins such as stilbene and its derivatives which undergo photoisomerization in a mutual way between cis and trans isomers. In their singlet or triplet excited states, the initial cis or trans excited state (c^* or t^*) twists around the double bond to get to the most stable perpendicular excited state (p^*) situated at an energy minimum, which subsequently deactivates to the ground state giving either cis or trans isomer.[11]

Further examination of arylethylenes with aromatic nuclei with varying triplet excitation energies showed that the mode of isomerization, that is, the conventional mutual two-way or the one-way isomerization, is governed by the triplet energy (E_T) of the aromatic nucleus on the ethylenic carbon.[12—16] 2-Styrylanthracene (anthracene: $E_T = 42$ kcal mol^{-1}, 1 kcal=4.18 kJ)[17] and 3-styrylperylene (perylene: $E_T = 35$ kcal mol^{-1})[17] undergo one-way isomerization[18,19] in contrast to the mutual isomerization of 1-styrylpyrene[13,14] (pyrene: $E_T = 48$ kcal mol^{-1}).[17] For butenylarenes, which have aromatic groups of higher triplet-energy than the corresponding styrylarenes, 1-(3,3-dimethylbutenyl)pyrene[13,14] and 8-(3,3-dimethylbutenyl)fluoranthene[15,16] (fluoranthene: $E_T = 54$ kcal mol^{-1})[17] also undergo one-way isomerization. Now, our interest is to clarify the generality of the one-way isomerization for various olefins substituted with aromatic groups of low triplet energies.[20,21]

In this work, photochemical cis–trans isomerization of 1-styrylazulene (**SAZ**) and 7-isopropyl-1,4-dimethyl-3-styrylazulene (conventionally called as 3-styrylguaiazulene: **SGAZ**) were investigated because azulene is a non-alternant non-benzenoid hydrocarbon, and this structural feature may affect the nature of the molecular orbital, the excited state, and the photoisomerization (Chart 1). It has unique photophysical properties,[23—25] and does not obey Kasha's rule but has anomalous fluorescence ($S_2 \rightarrow S_0$). Moreover, it acts as a typical triplet quencher in photochemical studies and its triplet state shows T–T absorption with $\lambda_{max} = 360$ nm[23,25] decaying with 2—12 μs lifetime depending on experimental conditions and has a very low triplet energy of 39—40 kcal mol^{-1}.[23,24]

Experimental

SAZ. *cis-* and *trans-***SAZ** were synthesized in the manner reported.[26] Azulene was prepared as reported by Hafner[27] from 1-chloro-2,4-dinitrobenzene, dimethylamine (Kodak), and freshly distilled cyclopentadiene in dry pyridine. The crude azulene was purified by sublimation under vacuum after passing alumina column with hexane.



cis-isomer trans-isomer

1-styrylazulene (SAZ); $R_1, R_2, R_3 = H$
7-isopropyl-1,4-dimethyl-3-styrylazulene
(3-styrylguaiazulene, SGAZ);
$R_1, R_2 = CH_3, R_3 = CH(CH_3)_2$

Chart 1.

1-Azulenecarbaldehyde was prepared via formylation of azulene by phosphoryl chloride and dimethylformamide (DMF).[28)]

An ethanolic solution of sodium ethoxide prepared from sodium (1.9 g, 28 mmol) was added under dry nitrogen to an ethanolic solution of 1-azulenecarbaldehyde (2.2 g, 14.1 mmol) and benzyltriphenylphosphonium bromide (6.11 g, 14.1 mmol) prepared from benzyl bromide and triphenylphosphine. The solution was stirred for 4 h, poured into water, washed, and extracted with benzene, and dried over anhydrous sodium sulfate, and the solvent was evaporated. The cis and trans isomers were separated by silica-gel column chromatography with hexane, and crystallized from petroleum ether. The purity of each isomer was measured by HPLC with hexane as >99.9% and >99% (only contained <1% trans isomer) for *trans*- and *cis*-**SAZ**, respectively.

***cis*-SAZ:** Mp 94.0—94.5 °C; ^{1}H NMR ($CDCl_3$) δ=6.65 (d, 1H, J=12 Hz, CH=C), 6.92—7.82 (m, 10H, CH=C and ArH), 8.12—8.43 (m, 3H, ArH); UV (benzene) λ_{max} 315 nm (ε/dm^3 mol^{-1} cm^{-1}:26400), 393 (10400), 620 (300).

***trans*-SAZ:** Mp 162—162.5 °C; ^{1}H NMR ($CDCl_3$) δ= 6.93—7.87 (m, 11H, CH=CH and ArH), 8.10—8.56 (m, 3H, ArH); UV (benzene) λ_{max} 318 nm (ε 26900), 339 (21700), 382 (17500), 400 (20300), 644 (350).

SGAZ. *cis*- and *trans*-**SGAZ** were prepared from 7-isopropyl-1,4-dimethylazulene (guaiazulene, Aldrich) by the same procedures described for **SAZ**.[29)] The purity of each isomer was measured by HPLC with hexane as >99.9% and >98% (only contained <2% trans isomer) for *trans*- and *cis*-**SGAZ**, respectively.

***cis*-SGAZ:** Mp 45.0—45.5 °C; ^{1}H NMR ($CDCl_3$) δ=1.33 (d, 6H, J=7 Hz, C(CH_3)), 2.48 (s, 3H, ArCH_3), 2.99 (s, 3H, ArCH_3), 3.01 (q, 1H, J=7 Hz, CHMe$_2$), 6.48 (d, 1H, J=12 Hz, CH=C), 6.73—7.83 (m, 8H, CH=C and ArH), 7.97—8.01 (m, 2H, ArH); UV (benzene) λ_{max} 287 nm (ε 22100), 325 (21700), 398 (10900), 628 (450).

***trans*-SGAZ:** Mp 84.0—84.5 °C; ^{1}H NMR ($CDCl_3$) δ=1.34 (d, 6H, J=7 Hz, C(CH_3)), 2.62 (s, 3H, ArCH_3), 2.97 (q, 1H, J=7 Hz, CHMe$_2$), 3.04 (s, 3H, ArCH_3), 6.90 (d, 1H, J=12 Hz, CH=C), 6.92—7.60 (m, 8H, CH=C and ArH), 7.91—8.18 (m, 3H, ArH); UV (benzene) λ_{max} 330 nm (ε 25000), 415 (23800), 644 (420).

Laser Flash Photolyses. Laser flash photolyses were done on a system built at the University of Tsukuba. A dye laser (Lambda Physik FL3002, stilbene 3 dye) pumped by an excimer laser (Lambda Physik EMG-101, XeCl, 10 ns fwhm) was used as an excitation light source at 425 nm using a computer-controlled system with a storage scope (Iwatsu TS-8123), as previously reported in detail.[12)]

Absorption and Fluorescence Spectra. Absorption and fluorescence spectra were measured in spectrograde benzene (Dotite) with a Hitachi 220 and U-3000 spectrophotometer and a Hitachi F-4010 spectrofluorimeter, respectively.

Photoisomerization Behavior. A degassed sample containing biacetyl as a triplet sensitizer ([biacetyl]=0.1 mol dm^{-3} in benzene) in a quartz cell (4 ml) was irradiated at ambient temperature in the cell compartment of a Hitachi F-4010 spectrofluorimeter (using a 150 W xenon lamp as a light source). Light irradiation was monochromated at 450±5 or 600±10 nm. The irradiation was also done with a light (366 nm) obtained from a 400 W medium pressure mercury lamp passing through a UVD-36B glass filter. Light intensity was measured by potassium tris(oxalato)ferrate(III) actinometry.[30)] The cis and trans isomers were detected by HPLC (ODS-1251N, 25 cm) with methanol : H_2O=85 : 15.

Results and Discussion

Absorption and Fluorescence Spectra. Figure 1a depicts absorption spectra of *cis*- and *trans*-**SAZ** together with that of azulene. The wavelengths of the absorption maxima of $S_1 \leftarrow S_0$ as well as $S_2 \leftarrow S_0$ absorptions of both isomers are shifted about 70—80 nm from those of azulene, and the spectra are structureless. A weak $S_2 \leftarrow S_0$ absorption band around 340 nm and strong $S_3 \leftarrow S_0$ absorption bands hidden by benzene below 280 nm of azulene[31)] are shifted to 390 and 315 nm and increased in intensity in *cis*- and *trans*-**SAZ**. For $S_1 \leftarrow S_0$ absorption in the visible region, an absorption band around 570 nm of azulene is shifted to 610 and 630 nm of *cis*- and *trans*-**SAZ**, respectively, changing the color (purple to blue-green) from azulene to **SAZ**.

The fluorescence spectra of *trans*-**SAZ** and azulene are depicted in Fig. 1b. The shape of the fluorescence spectra of *trans*-**SAZ** is somehow structureless and broad in contrast with the sharp profile of the fluorescence of azulene. The fluorescence quantum yield for *trans*-**SAZ** ($\Phi_f < 1\times10^{-3}$) was much smaller than that of azulene (Φ_f=0.03), however no fluorescence was detected from *cis*-**SAZ** at ambient temperature.

$T_n \leftarrow T_1$ Absorption Spectra. Figures 2a and 2b depict transient absorption spectra observed after the excitation of cis and trans isomers of **SAZ** (4.4×10^{-5} mol dm^{-3}) with a dye laser (425 nm) in the presence of benzil (5.0×10^{-2} mol dm^{-3}) as a triplet sensitizer in argon-purged benzene at room temperature. At this concentration only 68% of the triplet benzil was quenched by **SAZ**; however, a higher concentration of **SAZ** could not be used since the absorption of ground-state substrates interfered with the observation of the transient absorption at these wavelengths. Both *cis*- and *trans*-**SAZ** gave essentially the same absorption. Thus, immediately after the laser excitation, the $T_n \leftarrow T_1$ absorption band of benzil appeared around 490 nm. Concurrently with its decay a new band assigned to the $T_n \leftarrow T_1$ absorption of **SAZ** was grew 340—430 nm increasing in intensity. Figure 3 shows the decay profile of the triplet benzil at 490 nm and the profile for the rise and decay of $^3t^*$ of **SAZ** at 420 nm. The lifetime of the triplet state of **SAZ** monitored at 420 nm, the absorption maximum, was 4.7 μs based on the first order decay kinetics.

Under similar experimental conditions when 63% triplet benzil was quenched by *cis*- and *trans*-**SGAZ** (3.3×10^{-5} mol dm^{-3}), the $T_n \leftarrow T_1$ absorption appeared as depicted in Figs. 2c and 2d with an absorption maximum at 430 nm, shifted 10 nm to longer wavelengths than **SAZ**, and a lifetime of 4.6 μs.

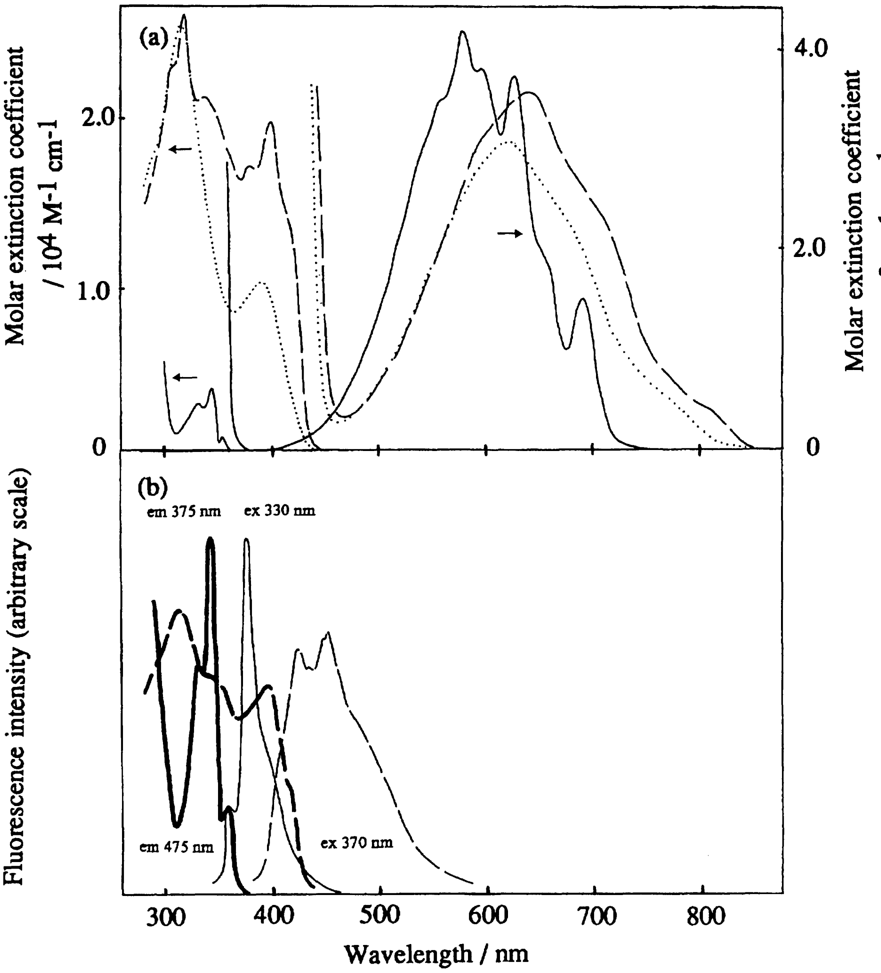


Fig. 1. Absorption (a), and fluorescence and fluorescence excitation (bold line) spectra (b) of azulene (solid line), *trans*- (dashed line) and *cis*-**SAZ** (dotted line), in benzene at ambient temperature. For azulene and *trans*-**SAZ**, fluorescence spectra were measured on excitation at 330 and 370 nm, respectively, and the excitation spectra were monitored at 375 and 475 nm, respectively (1 M=1 mol dm^{-3}).

As mentioned above, both cis and trans isomers of these olefins show similar absorption for their triplet state. However, the $T_n \leftarrow T_1$ absorption spectra obtained by the excitation of the trans isomers of **SAZ** and **SGAZ** are a little sharper than those of the cis-isomers; this seems not to be essential and is caused by the ground state absorptions of the trans isomers, which show absorption tailing to longer wavelengths with larger ε than the cis isomers. The $T_n \leftarrow T_1$ absorption overlaps with the absorption of the ground state of the olefins. Therefore, a larger decrease of the $T_n \leftarrow T_1$ absorption of the trans isomer than the cis isomer results from higher depletion of the ground state trans isomer than the cis isomer. The observed triplets are common from the trans and cis isomers in the time of these observations. The $^3c^*$ initially resulted from excitation of the cis isomers will convert to the common species, which is assigned to $^3t^*$ not to $^3p^*$, since $^3p^*$ would give shorter lifetimes and absorptions at shorter wavelengths than the triplet state of the parent aromatic hydrocarbon, azulene, as seen in other olefins.[3—6]

Triplet Sensitized Isomerization. On irradiation with 450 nm light in argon purged benzene in the presence of biacetyl (0.1 mol dm^{-3}) as a triplet sensitizer, *cis*-**SAZ** completely isomerized to the trans isomer as observed by HPLC and ^{1}H NMR. On the contrary, *trans*-**SAZ** gave no detectable amount of the cis isomer under similar conditions. Thus, *cis*-**SAZ** undergoes cis→trans one-way isomerization in the triplet state.

The quantum yield for cis→trans isomerization, $\Phi_{c\rightarrow t}$, linearly increased with the cis isomer concentration. Figure 4 plots $\Phi_{c\rightarrow t}$ for *cis*-**SAZ** on biacetyl sensitization against [*cis*-**SAZ**] in $(0.50\text{—}5.0)\times10^{-3}$ mol dm^{-3}, where $\Phi_{c\rightarrow t}$ attained 3.8 in the highest concentration used. The slope and the intercept of the plot in Fig. 4 are 606 dm^3 mol^{-1} and 1.1, respectively. Under similar conditions, *cis*-**SGAZ** completely isomerized to the trans isomer, and a linear relation of $\Phi_{c\rightarrow t}$ with the cis isomer concentration gave a slope and an intercept of 539 dm^3 mol^{-1} and 0.71.

The triplet energies of their cis and trans isomers

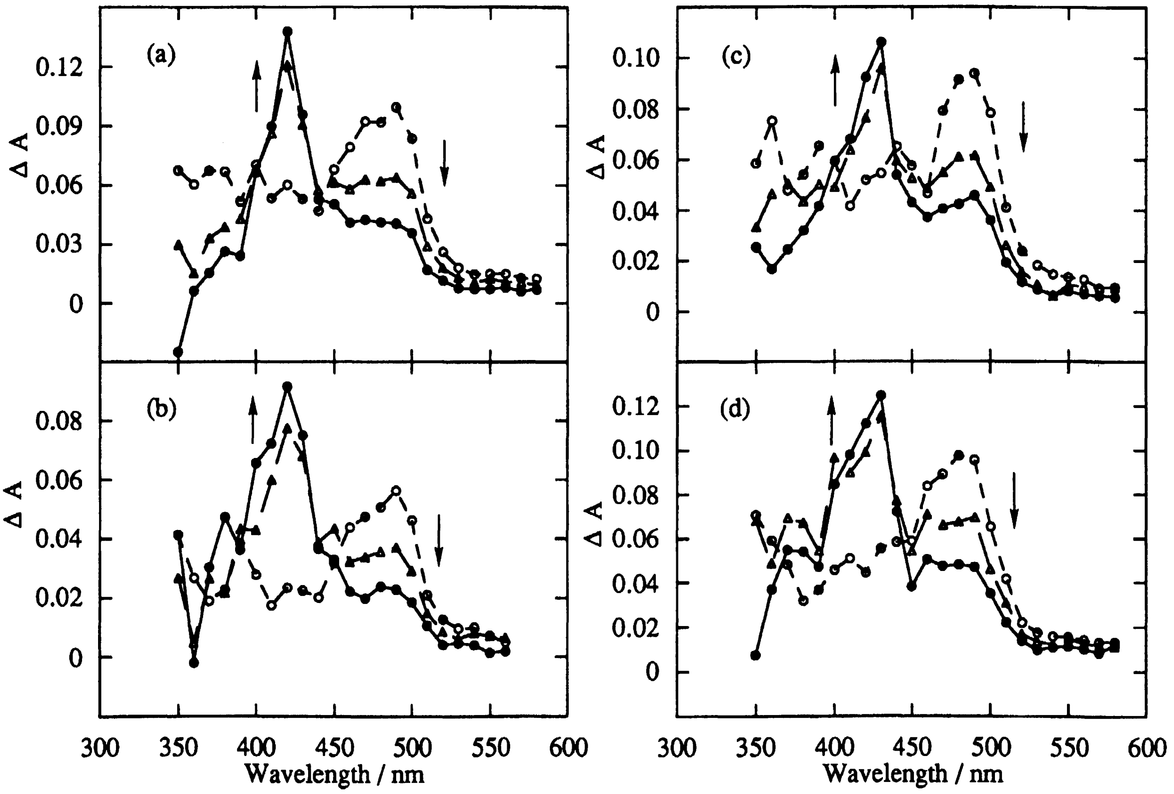


Fig. 2. T–T absorption spectra obtained on excitation of benzil (5×10^{-2} mol dm^{-3}) at 425 nm in the presence of *trans*- (a) and *cis*-**SAZ** (b) (4.4×10^{-5} mol dm^{-3}), *trans*- (c) and *cis*-**SGAZ** (d) (3.3×10^{-5} mol dm^{-3}) in argon-purged benzene. Open circles, triangles, and solid circles show the spectra obtained 160 ns, 1.0 μs and 2.0 μs after the laser pulses.

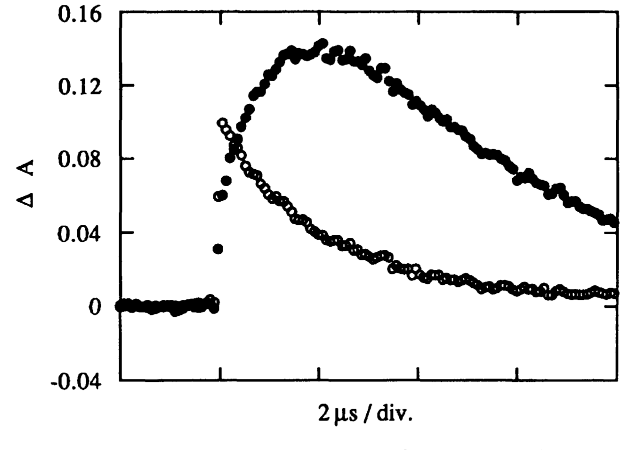


Fig. 3. Decay and rise profiles of the T–T absorption obtained on excitation of benzil at 425 nm in the presence of *trans*-**SAZ** in argon-purged benzene monitored at 490 nm (open circles) and 420 nm (solid circles), respectively.

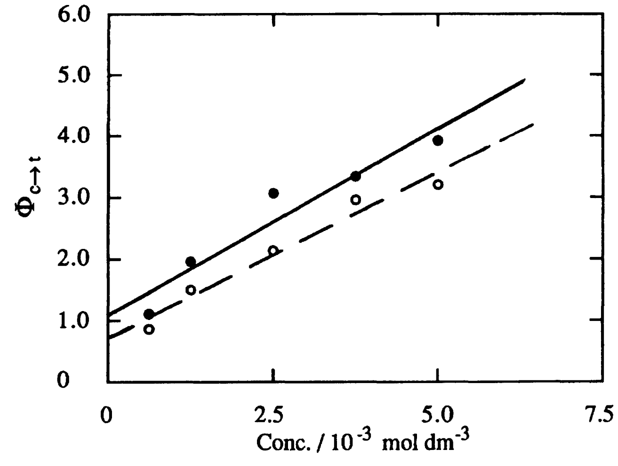


Fig. 4. Isomerization quantum yields ($\Phi_{c\to t}$) on triplet sensitization against the concentration of the cis isomers of **SAZ** (solid circles) and **SGAZ** (open circles).

are estimated as low as or less than that of azulene, 39 kcal mol^{-1}, since the triplet energies of the one-way isomerizing arylethylenes are at most comparable with those of the aryl group on the olefinic unsaturated bond.[1—6] Accordingly, triplet sensitizers such as benzil ($E_T=53$ kcal mol^{-1})[17] and biacetyl ($E_T=56$ kcal mol^{-1})[17] can effectively transfer their triplet energy to both isomers. If the isomerization proceeded through the decay of $^3p^*$ as accepted for isomerization of stilbenes, the photostationary-state isomer ratios $([c]/[t])_{pss}$ would take a non-zero value. However, as described above, **SAZ** and **SGAZ** undergo cis→trans "one-way" isomerization on triplet sensitization.

For the isomerization, the following mechanism, Eqs. 1, 2, 3, 4, and 5 is proposed as previously reported for anthrylethylenes;[1—6]

$$\mathrm{S} \xrightarrow{h\nu} {}^1\mathrm{S}^* \rightarrow {}^3\mathrm{S}^* \tag{1}$$

$$^3\mathrm{S}^* + \mathrm{c} \rightarrow \mathrm{S} + {}^3\mathrm{c}^* \tag{2}$$

$$^3\mathrm{c}^* \rightarrow {}^3\mathrm{p}^* \rightarrow {}^3\mathrm{t}^* \tag{3}$$

$$^3\mathrm{t}^* \rightarrow \mathrm{t} \tag{4}$$

$$^3\mathrm{t}^* + \mathrm{c} \rightarrow \mathrm{t} + {}^3\mathrm{c}^* \tag{5}$$

where S refers to a sensitizer. The cis triplet (^{3}c*) resulting from excitation of the cis isomer (c) (Eq. 2) twists around the ethylenic linkage to attain the trans triplet (^{3}t*) in an adiabatic way (Eq. 3) passing through the perpendicular triplet (^{3}p*) which, like other one-way olefins, is not located at a stable energy minimum.[3,4] As discussed before, the observed transient absorption shows that the most stable triplet is not ^{3}p* but ^{3}t*. The resulting ^{3}t* undergoes either unimolecular deactivation to the ground-state trans isomer (t) (Eq. 4) or energy transfer to c to regenerate ^{3}c* (Eq. 5) therefore accomplishing a quantum chain process.

According to the above scheme, the isomerization quantum yield is expressed by the following equation;

$$\Phi_{\mathrm{c}\rightarrow\mathrm{t}} = \Phi^{\mathrm{s}}_{\mathrm{isc}} \times \frac{k^{\mathrm{s}}_{\mathrm{q}}[\mathrm{c}]}{k^{\mathrm{s}}_{\mathrm{d}} + k^{\mathrm{s}}_{\mathrm{q}}[\mathrm{c}]} \times (1 + k_{\mathrm{q}}\tau_{\mathrm{T}}[\mathrm{c}]) \tag{6}$$

where $\Phi^{\mathrm{s}}_{\mathrm{isc}}$ represents the intersystem crossing quantum yield of a sensitizer, $k^{\mathrm{s}}_{\mathrm{d}}$ and $k^{\mathrm{s}}_{\mathrm{q}}$ represent the rate constants for the decay of the triplet sensitizer and for the quenching of the triplet sensitizer by a cis olefin, respectively, and τ_{T} and k_{q} the lifetime of ^{3}t* and the quenching rate constant of ^{3}t* by c, respectively.

Thus, $\Phi_{\mathrm{c}\rightarrow\mathrm{t}}$ depends on the efficiencies for the formation of sensitizer triplets ($\Phi^{\mathrm{s}}_{\mathrm{isc}}$), for the energy transfer from the sensitizer to the cis isomer $[k^{\mathrm{s}}_{\mathrm{q}}[\mathrm{c}]/(k^{\mathrm{s}}_{\mathrm{d}}+k^{\mathrm{s}}_{\mathrm{q}}[\mathrm{c}])]$, and for the subsequent quantum chain process ($k_{\mathrm{q}}\tau_{\mathrm{T}}[\mathrm{c}]$), i.e., the quantity concerning the efficiency for energy transfer from ^{3}t* to the cis isomer. The efficiency of energy transfer from the triplet excited sensitizer to the olefin is taken to be unity for simplicity because of sufficiently high concentrations of the cis isomers used under our experimental conditions.

The $\Phi_{\mathrm{c}\rightarrow\mathrm{t}}$ value linearly increases with the cis isomer concentration with an intercept of nearly unity as expected from Eq. 6. The intercept of nearly unity reflects that $\Phi^{\mathrm{s}}_{\mathrm{isc}}$ is nearly unity for biacetyl.[32] The slopes of Fig. 4, therefore, correspond to $k_{\mathrm{q}}\tau_{\mathrm{T}}$. Dividing the $k_{\mathrm{q}}\tau_{\mathrm{T}}$ values, 606 and 539 dm^3 mol^{-1}, by the τ_{T} values, 4.7 and 4.6 μs measured under these conditions, gives k_{q} values as 1.3×10^8 and 1.2×10^8 dm^3 mol^{-1} s^{-1} for **SAZ** and **SGAZ**, respectively. These k_{q} values indicate that the energy transfer from ^{3}t* to cis takes place in a nearly isoenergetic way.[33] This shows that the triplet energies for cis and trans isomers are nearly the same for these olefins as in other one-way isomerizing olefins.[1—6] The high efficiency of the quantum chain process is reasonably attributed to the long lifetime of ^{3}t*, which allows the almost isoenergetic energy transfer from ^{3}t* to cis to proceed sufficiently, competing with its deactivation.

Isomerization on Direct Irradiation. Contrary to the triplet sensitization, irradiation of either *cis*- or *trans*-**SAZ** in benzene under argon with 366-nm light populating the S_2 state or 600-nm light populating the S_1 state afforded photostationary mixtures comprising of 98% *trans*- and 2% *cis*-**SAZ** as examined by HPLC. Irradiation of **SGAZ** gave similar results. Thus, direct irradiation of **SAZ** and **SGAZ** led to the mutual isomerization between cis and trans isomers with only 2% of cis isomer at the photostationary state. The quantum yield for cis to trans isomerization on 366 nm light excitation, $\Phi^{\mathrm{direct}}_{\mathrm{c}\rightarrow\mathrm{t}}$, was as small as 0.03 and was not varied with *cis*-**SAZ** concentrations from 10^{-4} to 10^{-3} mol dm^{-3}. The $\Phi^{\mathrm{direct}}_{\mathrm{t}\rightarrow\mathrm{c}}$ was too small to be measured. The $\Phi^{\mathrm{direct}}_{\mathrm{c}\rightarrow\mathrm{t}}$ for **SGAZ** was <0.01.

If the excited singlet states of **SAZ** and **SGAZ** efficiently underwent intersystem crossing to the triplet state, it would undergo isomerization in a quantum chain process with a high quantum yield as observed in styrylanthracene.[1—6] However, this is not the case. Actually, direct laser excitation of **SAZ** and **SGAZ** gave no $\mathrm{T}_n \leftarrow \mathrm{T}_1$ absorption. These behaviors are similar to that of the excited singlet state of azulene, which gives very weak fluorescence and mostly deactivates to the ground states in a non-radiative way.

The above facts together with lack of fluorescence from *cis*-**SAZ** indicate that the isomerization takes place on the excited singlet state though with a very low efficiency. In addition, the much higher population of the trans isomer than the cis one at the photostationary state suggests the participation of the triplet state, however, its contribution is difficult to measure due to the extremely poor efficiency of the triplet formation on direct excitation.

Conclusion

Upon triplet sensitized irradiations, **SAZ** and **SGAZ** which have non-benzenoid azulenyl substituents, undergo one-way isomerization from their cis to trans isomers with a quantum chain process. The isomerization proceeds on the triplet energy surface in an adiabatic way ($^3\mathrm{c}^* \rightarrow {}^3\mathrm{t}^*$). Transient spectroscopy of the triplet states found that styrylazulenes have energy minima at the trans planar geometry, ^{3}t*, but no minimum at the twisted geometry on their triplet potential energy surface. On direct excitation, the isomerization takes place in a mutual way giving photostationary mixtures very rich in trans by participation of the isomerization path through the excited singlet state.

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