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Features of the Quantum Chain Process in the Photochemical One-Way Isomerization of 2-Anthrylethylenes

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Regarding 2-anthrylethylenes which undergo a photochemical cis-to-trans one-way isomerization, their preparative methods are presented. The isomerization of ArCH=CHPh and ArCH=CH(2-naphthyl) (Ar: 2-anthryl) proceeds through a quantum chain process slightly more efficiently than ArCH=CH^{t}Bu. The origin of the high efficiency in the quantum chain process of these ethylenes is discussed.

The photoisomerization of carbon–carbon unsaturated bonds has been extensively investigated, and much precise work has been carried out for stilbene and its derivatives.[1—13] As a results, it has become well accepted that many olefins undergo photoisomerization in a mutual way between the cis and trans isomers. In either a singlet or triple excited state, the initially resulting cis (c*) or trans excited state (t*) twists around the double bond to obtain the most stable perpendicular excited state (p*) situated at an energy minimum; p* subsequently deactivates to the ground state, giving either a cis or trans isomer.

During the course of an investigation on the photoisomerization, we found that the substitution of an aromatic nucleus with a low triplet excitation energy, 42 kcal mol^{-1},[14] (1 kcal≡4.1840 kJ), on the unsaturated bond exerted a dramatic effect so as to change the mode of isomerization from the well-accepted mutual isomerization between two isomers to one-way isomerization occurring solely from the cis to the trans isomers of 2-anthrylethylenes **1a**—**1d**; furthermore, the isomerization proceeded with a very high quantum yield, exceeding unity.[15—19] The quantum yield for a sensitized cis-to-trans isomerization of **1a** was found to increase along with the cis isomer concentration.

We have recently shown the mechanism of the one-way isomerization based on the transient spectroscopy of the triplet state and a photophysical observation of these compounds, particularly for their trans isomers, and quantum-yield measurements, especially for **1a**.[15a,15b,18a] We have found that for **1a** the initially resulting ^{3}c* ($\lambda_{\max}$=440 nm) undergoes twisting around the double bond to get to ^{3}t* ($\lambda_{\max}$=445 nm) with a rate constant of 2.1×10^6 s^{-1} at ambient temperature and an activation energy of 6 kcal mol^{-1}[18a] passing through ^{3}p*, which is not situated at all at an energy minimum, and does not deactivate to the ground state (Fig. 1). The resulting ^{3}t* undergoes an energy transfer to the cis isomer to regenerate ^{3}c* in preference to a unimolecular deactivation to the trans isomer, therefore accomplishing the quantum chain process.

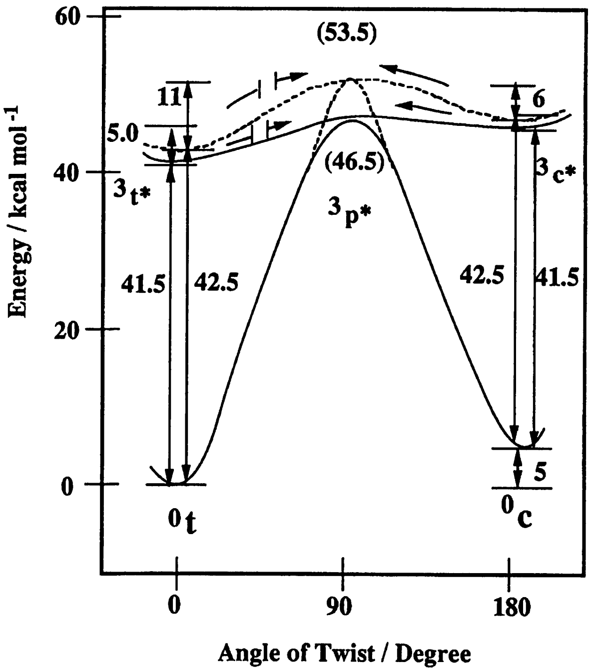
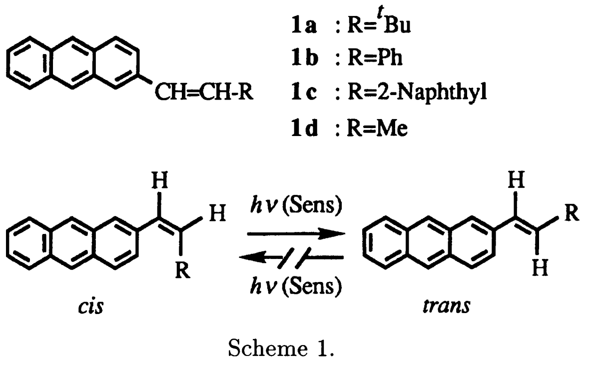


Fig. 1. Estimated triplet potential energy surfaces of **1a** (dashed line) and **1b** (solid line).

This paper intends to present the features of the quantum chain process in the one-way photoisomerization by extending the examination to triplet-sensitized as well as direct irradiation of **1b** and **1c**, together with the characteristics of the fluorescence from their cis isomers, and to describe the preparative procedures of **1a**—**d** (Scheme 1).



Scheme 1.

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Experimental

Materials. It is noted that **1**'s are sensitive to room light to undergo a cis-to-trans isomerization. Therefore, their cis isomers, or their mixtures with trans isomers, were carefully treated under a red lamp or in a dark room.

2-(3,3-Dimethyl-1-butenyl)anthracene (1a). 2-(Bromomethyl)anthracene[20] (5.5 g, 20 mmol) was allowed to react with triphenylphosphine (7.9 g, 29 mmol) in xylene at 100 °C for 24 h to give (2-anthrylmethyl)triphenylphosphonium bromide (**2**) (10.0 g, 93 %).

To a suspension of **2** (10 g, 19 mmol) in dry ether, a hexane solution of buthyllithium (15%, 15 ml) was gradually added with mechanical stirring under dry nitrogen. The stirring was continued for 30 min; then, an ethereal solution of 2,2-dimethylpropanal (70%, 30 ml) was added dropwise. After stirring for 1 h, the reaction mixture was gently refluxed for 30 min. The precipitate was filtered off and the filtrate was washed with water. The ethereal layer was dried over anhydrous sodium sulfate, and evaporation of the solvent gave a mixture of *cis*- and *trans*-**1a**. The cis and trans isomers were separated under a red lamp by silica-gel column chromatography with petroleum ether (bp <69 °C). Both isomers were purified by recrystallization from petroleum ether (cis 1.9 g and trans 1.1 g, 61% in total).

***cis*-1a:** Mp 130.5—132 °C. ^{1}H NMR ($CDCl_3$) δ=1.04 (s, 9H, Me_3C), 5.73 (d, 1H, J=12 Hz, C=CH), 6.58 (d, 1H, J=12 Hz, C=CH), 7.34—7.52 (m, 3H, ArH), 7.80—8.08 (m, 4H, ArH), 8.39 (s, 2H, ArH); UV (cyclohexane) λ_{max} 258.5 nm (ε/M^{-1}cm^{-1} 95100), (M≡mol dm^{-3}) 329 (2100), 344 (3600), 361 (4900), 381 (4000); UV (PhH) λ_{max} 316.5 nm (ε 1700), 331 (3000), 347 (5100), 364 (6900), 384 (5600). Calcd for $C_{20}H_{20}$: C, 92.25; H, 7.74%. Found: C, 92.16; H, 7.93%.

***trans*-1a:** Mp 196—197 °C. ^{1}H NMR ($CDCl_3$) δ=1.15 (s, 9H, Me_3C), 6.43 (d, 1H, J=16 Hz, C=CH), 6.59 (d, 1H, J=16 Hz, C=CH), 7.35—7.71 (m, 3H, ArH), 7.84—8.06 (m, 4H, ArH), 8.37 (s, 2H, ArH); UV (cyclohexane) λ_{max} 262 nm (ε/M^{-1}cm^{-1} 49700), 272 (93500), 282.5 (124000), 312.5 (2000), 330 (3400), 345.5 (5800), 362 (7100), 388.5 (4200); UV (PhH) λ_{max} 315 (ε 2200), 333 (3700), 349 (6400), 366 (7900), 383 (5200), 390 (5000). Calcd for $C_{20}H_{20}$: C, 92.25; H, 7.74%. Found: C, 92.48; H, 7.53%.

2-Styrylanthracene (1b). To a mixture of **2** (4.7 g, 8.8 mmol) and benzaldehyde (3.0 g, 28 mmol) in absolute ethanol (100 ml) was added an ethanolic solution of sodium ethoxide (6 g, 88 mmol) under dry nitrogen with mechanical stirring. The reaction mixture was kept standing for 15 h, and then refluxed for 3 h. After the addition of 100 ml of benzene, the mixture was allowed to cool to room temperature. The precipitated trans isomer was collected by filtration and recrystallized from benzene. The filtrate mainly dissolved the cis isomer, and triphenylphosphine oxide was washed with water after the addition of another 100 ml of benzene and dried over anhydrous sodium sulfate; the solvent was then evaporated. The remaining matter was chromatographed over silica-gel eluted with hexane, and purified by crystallization from hexane to afford the cis isomer with a small amount of the trans isomer (cis 1.3 g and trans 0.8 g, 83% in total).

***cis*-1b:** Mp 144—145 °C. ^{1}H NMR ($CDCl_3$) δ=6.72 (s, 1H, J=12 Hz, C=CH), 6.78 (s, 1H, J=12 Hz, C=CH), 7.2—8.4 (m, 14H, ArH); UV (PhH) λ_{max} 298 nm (ε/M^{-1}cm^{-1} 35900), 351.5 (7500), 369 (9900), 389 (7600). Calcd for $C_{22}H_{16}$: C, 94.24; H, 5.75%. Found: C, 93.89; H, 5.70%.

***trans*-1b:** Mp 244—245 °C. ^{1}H NMR ($CDCl_3$) δ=7.15—8.39 (m, 16H, ArH); UV (PhH) λ_{max} 311 nm (ε/M^{-1}cm^{-1} 58400), 325.5 (62100), 355.5 (11400), 373 (14800), 393 (12200). Calcd for $C_{22}H_{16}$: C, 94.24; H, 5.75%. Found: C, 94.12; H, 5.78%.

2-[2-(2-Naphthyl)ethenyl]anthracene (1c). **1c** was prepared in a similar manner to **1b** by adding an ethanolic solution (20 ml) of sodium ethoxide (1.4 g, 21 mmol) to a mixture of **2** (1.5 g, 2.8 mmol) and 2-naphthalenecarbaldehyde (1.1 g, 7 mmol) in ethanol (15 ml). The cis and trans isomers were separated by column chromatography and crystallized from a mixture of hexane and benzene (cis 0.4 g and trans 0.2 g, 65% in total).

***cis*-1c:** Mp 188—189 °C. ^{1}H NMR ($CDCl_3$) δ=6.87 (s, 2H, CH=CH), 7.17—8.32 (m, 16H, ArH); UV (PhH) λ_{max} 290 nm (ε/M^{-1}cm^{-1} 35300), 318 (32300), 353.5 (10700), 372 (13000), 392 (10000). Calcd for $C_{26}H_{18}$: C, 94.50; H, 5.49%. Found: C, 94.11; H, 5.50%.

***trans*-1c:** Mp 313—315 °C. ^{1}H NMR ($CDCl_3$) δ= 7.1—8.4 (m, 18H, CH=CH and ArH); UV (PhH) λ_{max} 293.5 nm (ε/M^{-1}cm^{-1} 15000), 319 (20400), 334.5 (27200), 358 (6700), 376.5 (8700), 396.5 (8400). Calcd for $C_{26}H_{18}$: C, 94.50; H, 5.49%. Found: C, 94.20; H, 5.49%.

2-(1-Propenyl)anthracene (1d). **1d** was prepared in a similar manner to **1a** by adding an ethereal solution of acetaldehyde (50%, 10 ml) to a Wittig reagent prepared from a hexane solution of butyllithium (15%, 8 ml) and an ethereal suspension of **2** (6.0 g, 11 mmol) under nitrogen. The attempted separation of the cis and trans isomers by silica-gel column chromatography was not satisfactory. Irradiation of the isomeric mixture in benzene in the presence of iodine under nitrogen with a tungsten–halogen lamp afforded the trans isomer.

***trans*-1d:** Mp 180—182 °C. ^{1}H NMR ($CDCl_3$) δ=1.97 (d, 3H, J=6 Hz, CH_3), 6.52 (d-q, 1H, J=14 and 6 Hz, C=CH), 6.70 (d, 1H, J=14 Hz, C=CH), 7.2—8.6 (m, 9H, ArH). Calcd for $C_{17}H_{14}$: C, 93.53; H, 6.46%. Found: C, 93.89; H, 6.38%.

Other Chemicals. Michler's ketone was purified in the following way. After it was dissolved in dilute hydrochloric acid, the solution was filtered. To the filtrate, aqueous ammonia was added. The precipitated ketone was crystallized five times from methanol. Biacetyl was distilled before use. Azulene was sublimed in vacuo before use. Benzene (guaranteed garde) purified by distillation over calcium hydride, or spectrograde benzene was used for various measurements. Spectrograde carbon tetrachloride (Dotite) was used without further purification. The dyes used as sensitizers were purified by precipitation in ethanol–hexane.

Spectroscopy. The absorption spectra of **1**'s were recorded in spectrograde benzene or a cyclohexane solution on a Hitachi 200-20 or a JASCO 660 spectrophotometer. Fluorescence spectra were measured in argon-purged benzene on a Hitachi MPF-4, 850, or F-4000 spectrofluorimeter. A spectral correction was performed in the usual manner with Rhodamine 6G. The fluorescence quantum yields were determined by a comparison of the integrated spectra with that of anthracene as a reference. The fluorescence lifetimes were determined with a Horiba NAES-1100 time-resolved fluorescence spectrophotometer (single-photon counting). The phosphorescence spectra were determined in EPA (ether : isopentane : ethanol=5 : 2 : 2) or 3-methylpentane at 77K with a Hitachi F-4000 spectrofluorimeter with phosphorescence accessories; the spectra were corrected using a standard lamp.

Electrochemical Measurements. The reduction potentials of the dyes employed as sensitizers and the oxidation potentials of the olefins were measured by a cyclic-voltammetry device comprising a potentiostat (Hokuto HA-201) and a function generator (Hokuto HB-104) with the conventional three electrodes (SCE as reference). The voltammograms were measured in acetonitrile with tetraethylammonium perchlorate used as a supporting electrolyte under argon-purged conditions.

Stationary Irradiation. Samples in a Pyrex tube or a 1-cm path-length quartz cuvette were degassed by three freeze-pump-thaw cycles, or purged with argon, placed in front of the light outlet of a lamp-house or in a merry-go-round-type photoreactor (Riko), and immersed in thermostated water (25 °C). Stationary irradiation was performed with a 400-W or a 1-kW high-pressure mercury lamp (Riko or Ushio); the 313-, 366-, and 405-nm lines were isolated through the combination of a Toshiba UV-D33S glass filter and an aqueous potassium chromate solution filter, a Toshiba UV-D36B, and an L-39 glass filter, respectively. Light of 436 nm (half width 10 nm) was obtained from a 100-W Xe lamp (Shimadzu–Bausch and Lomb) through a combination of TB-12 ($\lambda_{\max}=440$ nm, half width 20 nm) and TB-13 ($\lambda_{\max}=449.5$, half width 20 nm) band-pass filters. Dye-sensitized irradiation was performed in an argon-purged benzene–methanol (1 : 1) mixture with 490-nm light isolated through a Shimadzu–Bausch and Lomb monochromator from a 400-W Xe lamp.

The irradiation mixtures were analyzed by GLPC (Shimadzu GC-4CMPF, Silicon OV-17 1-m column) or HPLC (Shimadzu LC-2, Zorbax ODS 15-cm column with acetonitrile or LC-6A, Zorbax ODS 25-cm column with hexane).

The quantum yields for isomerization, $\Phi_{c\rightarrow t}$ were determined by potassium tris(oxalato) ferrate(III) actinometry.[21)]

Laser Flash Photolyses. Laser flash photolyses were performed using a nitrogen laser (National Research Group Inc., 5-ns fwhm, 4 mJ/pulse, or Lambda Physik EMG-101, 8-ns fwhm, 7 mJ/pulse) for excitation at 337 nm, on XeCl excimer laser (Lambda Physik EMG-101, 20-ns fwhm, 150 mJ/pulse) for excitation at 308 nm, and on XeCl excimer laser-pumped dye laser (Lambda Physik FL3002, Stilbene 3) for excitation at 425 nm, and a 150-W xenon lamp as a monitoring light source. The xenon lamp was flashed synchronously with the laser excitation for nanosecond-time-scale experiments. The monitoring light was oriented perpendicularly to the exciting laser beam, passed through a grating monochromator (Union Giken or JASCO CT-25C), and detected with a photomultiplier (Hamamatsu Photonix R446, R212, or R928) and a storage oscilloscope (Iwatsu TS-8123). The trigger pulses were controlled by a digital delay/pulse generator (Stanford Research Systems Inc., DG535). The excitation beam was passed through suitable ND filters (Toshiba), and the monitoring light was passed through a cut-off filter (Corning 3-72, 3-73 or 3-74). The data were analyzed by a personal computer (Sharp MZ-2000 or NEC PC-9801 VX). Sample solutions in benzene were prepared and degassed by five freeze-pump-thaw cycles in a Pyrex tube attached to a 1 cm×1 cm quartz cuvette with a graded seal.

Results

Preparation. The 2-anthrylethylenes **1**'s were prepared by the condensation of appropriate aldehydes with Wittig's reagent of 2-(bromomethyl)anthracene, which was prepared starting from anthraquinone-2-carboxylic acid. The resulting mixture of the cis and trans isomers was carefully chromatographed on silica gel under a red lamp to isolate each isomer.

$$\mathrm{ArCH_2Br} \xrightarrow{\mathrm{Ph_3P}} \mathrm{ArCH_2P^+Ph_3Br^-}$$

$$\xrightarrow{\mathrm{RCHO}} \textit{cis} \text{ and } \textit{trans} \ \mathrm{ArCH{=}CHR}$$

1a – d

Ar : 2-anthryl;

R : ^{t}Bu(a), Ph(b), 2-naphthyl(c), and Me (d)

Photophysics. Table 1 summarizes the photophysical data of **1**, such as fluorescence, phosphorescence, $T_n \leftarrow T_1$ absorption, and the quantum yield for intersystem crossing. Figure 2 depicts their absorption, fluorescence and phosphorescence spectra.

Fluorescence. Both the cis and trans isomers of **1** emit strong fluorescence with quantum yields ranging from 0.4—0.9, though slightly lower for cis than for trans. It is noticeable that these cis and trans isomers exhibit different fluorescence spectra with different lifetimes, although, for **1b** and **1c**, the shape of the fluorescence spectra is somehow structureless and broad, and the difference in spectra between the cis and trans isomers is less clear than **1a**.[15b)]

The fluorescence spectra and fluorescence quantum yields were strongly dependent on the excitation wavelength for the cis and trans isomers of all the **1**'s examined. Particularly, excitation at the longest wavelength edge of the absorption give fluorescence that is different from that at the much shorter wavelength of the absorption. These phenomena are due to the existence of two rotational isomers (rotamers) around the single bond joining the anthryl group and ethylenic carbon; at the longest wavelength only one rotamer is excited.[22—24)]

Phosphorescence. Both the cis and trans isomers gave essentially the same phosphorescence spectra in EPA at 77 K, which are very similar to that of anthracene.[25)] The phosphorescence excitation spectrum of each isomer was found to be well matched to its absorption spectrum. In both the phosphorescence excitation and the absorption spectra, the cis isomer shows a sharp band at 390 nm, though the trans isomer shows two well-defined bands at 380 and 390 nm. However, the cis and trans isomers of **1b** and **1c** exhibit almost identical phosphorescence spectra with each other.

The triplet energy (E_T) of each isomer was determined from the 0,0 band of the phosphorescence spec-

Table 1. Photophysical Data of Anthrylethylenes[a)]

Olefin	E_s [b)]	Φ_f [c)]	Φ_isc [d)]	λ_max(T–T) [e)]	$\varepsilon_\mathrm{T-T}$ [e)]	τ_T [f)]	λ_p [g)]	E_T [h)]
cis-**1a**	74.3	0.41	0.59	440(445)[j)]			672	42.5
trans-**1a**	72.6	0.50	0.46	445	42000	280	668	42.5
cis-**1b**	71.3	0.59	0.17				688	41.5
trans-**1b**	70.2	0.87	0.11 (0.05)[i)]	460	60000 [i)]	190	689	41.5
cis-**1c**	70.2	0.65	0.22				691	41.3
trans-**1c**	69.7	0.85	0.12 (0.03)[i)]	465	50000 [i)]	90	693	41.3
trans-**1d**		0.46	0.46	445		170		

a) The data were determined in benzene except for λ_p and E_T, which were determined in EPA. b) Singlet excitation energies in kcal mol^{-1}. c) Fluorescence quantum yields determined by excitation at 355 nm. Data from Ref. 18b. d) Intersystem crossing quantum yields determined by excitation with 351 nm KrF laser. Data from Ref. 18b. e) Wavelengths and molar extinction coefficients of T–T absorptions in nm and M^{-1} cm^{-1}, respectively. Data from Ref. 15b. f) Triplet lifetimes in μs. Data from Ref. 15b. g) Wavelengths of the 0,0 band of the phosphorescence spectra in nm. h) Triplet excitation energies in kcal mol^{-1}. i) Determined by excitation with 337-nm nitrogen laser. Data from Ref. 24b. j) The absorption maximum at 440 nm observed 160 ns after laser excitation was shifted to 445 nm nearly 10 μs after excitation (see text). Data from Ref. 18a.

trum, as listed in Table 1. The cis and trans isomers of **1**'s examined exhibited essentially the same triplet energies within the experimental error, 42.5, 41.5, and 41.3 kcal mol^{-1} for **1a**, **1b**, and **1c**, respectively.

Quenching of Transient Absorption by Azulene. The feature of the $T_n \leftarrow T_1$ absorption of **1**'s are included in Table 1. The $T_n \leftarrow T_1$ absorptions were quenched with azulene, a typical triplet quencher, in benzene upon 337 nm excitation. The quenching rate constants ($k_\mathrm{q}{}^\mathrm{Az}$) were determined according to

$$k_\mathrm{d}^\mathrm{obs} = k_\mathrm{d} + k_\mathrm{q}{}^\mathrm{Az}[\mathrm{Az}],$$

where $k_\mathrm{d}^\mathrm{obs}$ and k_d are the decay rate constants of **1**'s triplet in the presence and absence of azulene, respectively.

Table 2 lists the rate constants ($k_\mathrm{q}{}^\mathrm{Az}$) for the cis and trans isomers of **1a**, **1b**, and **1c**, as obtained in the azulene concentration range of (0.25—15)×10^{-6} M.

Behavior of the Transient Absorption of the Triplet State under Argon. In order to determine the lifetime of the triplet state of **1**'s under the same condition as the quantum-yield determination, the decay of their transient absorption was examined in 1×10^{-4} M argon-bubbled benzene solution on 9-fluorenone sensitization. Their triplet state decayed with shorter lifetimes (30±5 μs) than in a degassed solution (90—280 μs, depending on the compounds). This indicates that a very small amount of oxygen remaining in the solution quenched the triplet state, and that the observed lifetime of the argon-bubbled solution corresponds to quenching by (7—9)×10^{-6} M of O_2; nearly a 0.5 % amount of oxygen of the air remained in the solution.

Table 2. Quenching Rate Constants ($k_\mathrm{q}{}^\mathrm{Az}$) of $T_n \leftarrow T_1$ Absorption by Azulene Monitored at λ_obs

Compound	$k_\mathrm{q}{}^\mathrm{Az}/10^9\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$	(λ_obs/nm)
Anthracene	5.8 (430)	
trans-**1a**	3.5 (445)	3.5 (450)
cis-**1a**	3.3 (445)	2.9 (450)
trans-**1b**	1.6 (460)	1.4 (620)
cis-**1b**	1.6 (460)	1.5 (620)
trans-**1c**	0.63 (465)	0.69 (640)
cis-**1c**	0.59 (465)	0.57 (640)

Cyclic Voltammetry. The oxidation potentials for *cis*- and *trans*-**1a** were determined in acetonitrile as 1.18 and 1.15 V vs. SCE, respectively, from their peak potentials, due to their irreversible voltammograms.

Triplet Sensitized Isomerization. Upon irradiation with 313-nm light in deaerated benzene in the presence of Michler's ketone (5.0×10^{-2} M) as a triplet sensitizer, *cis*-**1a** completely isomerized to the trans isomer, as observed by GLPC and ^{1}H NMR. The NMR signals of the olefinic hydrogens of *cis*-**1a** (δ=5.73, d, J=12 Hz and 6.58, d, J=12 Hz) were completely transformed to those of the trans isomer (δ=6.43, d, J=16 Hz and 6.59, d, J=16 Hz) upon irradiation in benzene-d_6. On the contrary, the trans isomer did not isomerize at all to the cis isomer under similar conditions. Thus, *cis*-**1a** undergoes a cis→trans one-way isomerization. Although **1a** exhibits a weak absorption at 313 nm, most of the incident light (>99%) is absorbed under the experimental condition by Michler's ketone because of a large difference in the absorbance between the sensitizer and **1a**.

Likewise, *cis*-**1b** (6.3×10^{-4} M), *cis*-**1c** (5.1×10^{-4} M), and a cis and trans (4 : 1) mixture of **1d** (5.0×10^{-4} M) afforded 100% trans isomers upon irradiation with 436-nm light in deaerated benzene in the presence of bi-

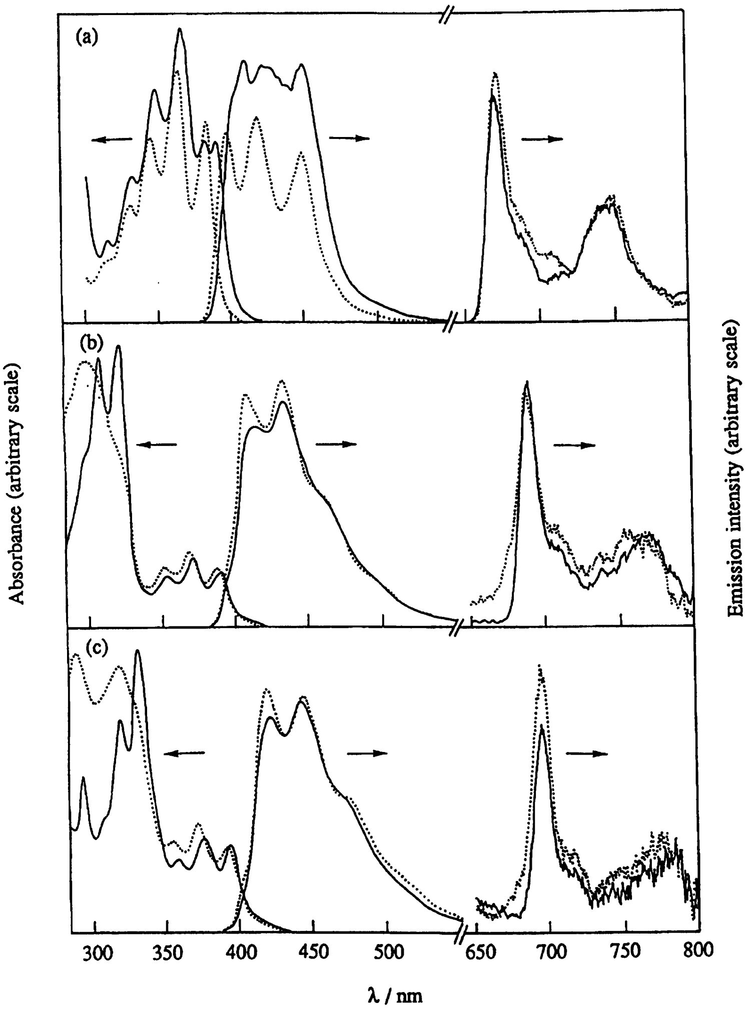

Fig. 2. Electronic absorption spectra, fluorescence and Phosphorescence spectra of cis (dotted line) and trans isomers (solid line) of **1a** (a), **1b** (b), and **1c** (c). The absorption, fluorescence and phosphorescence spectra were measured in benzene at room temperature, in argon purged benzene at room temperature, and in deaerated EPA at 77 K, respectively. The fluorescence spectra were measured by excitation at 364 nm (*cis*-**1a**), 366 nm (*trans*-**1a**), 381 nm (*cis*-**1b**), 384 nm (*trans*-**1b**), 384 nm (*cis*-**1c**), and 382 nm (*trans*-**1c**). The phosphorescence spectra were measured by excitation at 364 nm (*cis*-**1a**), 366 nm (*trans*-**1a**), 370 nm (*cis*-**1b**), 374 nm (*trans*-**1b**), 373 nm (*cis*-**1c**), and 378 nm (*trans*-**1c**).

acetyl (5.0×10^{-2} M) as a triplet sensitizer. The trans isomers of these olefins gave no detectable amount of their cis isomers under similar conditions.

For all of the **1**'s examined, the quantum yield for cis-to-trans isomerization, $\Phi_{c\rightarrow t}$, linearly increased along with increasing the cis isomer concentration. Figure 3a plots $\Phi_{c\rightarrow t}$ for **1a** on Michler's ketone sensitization against [*cis*-**1a**] in $(0.60$—$6.0)\times10^{-3}$ M, where $\Phi_{c\rightarrow t}$ attains 10.3 at the highest concentration employed. Figure 3b indicates that upon biacetyl sensitization $\Phi_{c\rightarrow t}$'s for **1b** and **1c** linearly increased along with increasing the cis concentration in $(0.13$—$1.6)\times10^{-3}$ and $(0.10$—$1.0)\times10^{-3}$ M, respectively, with larger slopes than that for **1a**, attaining 17.4 and 17.8, respectively, at the highest concentrations examined. Much higher concentrations could not be examined because of the limited solubility of **1**'s in benzene. The slopes and intercepts (Int) of the plots in Fig. 3 are listed in Table 3.

Table 3. Kinetic Values of Concentration Effect on the Quantum Yield of One-Way Isomerization

Olefin	Sens[a]	Slope[b] (M^{-1})	Int[b]	$\frac{\text{Slope}}{\text{Int}}$ (M^{-1})
cis-**1a**	—	550	0.72	760
	Michler's ketone	1400	0.88	
cis-**1b**	—	4200	0.43	9800
	Biacetyl	11000	1.6	
cis-**1c**	—	3200	0.38	8400
	Biacetyl	16000	1.4	

a) Triplet sensitizers. b) Values of slopes and intercepts (Int) in Fig. 3.

Isomerization upon Direct Irradiation. Just

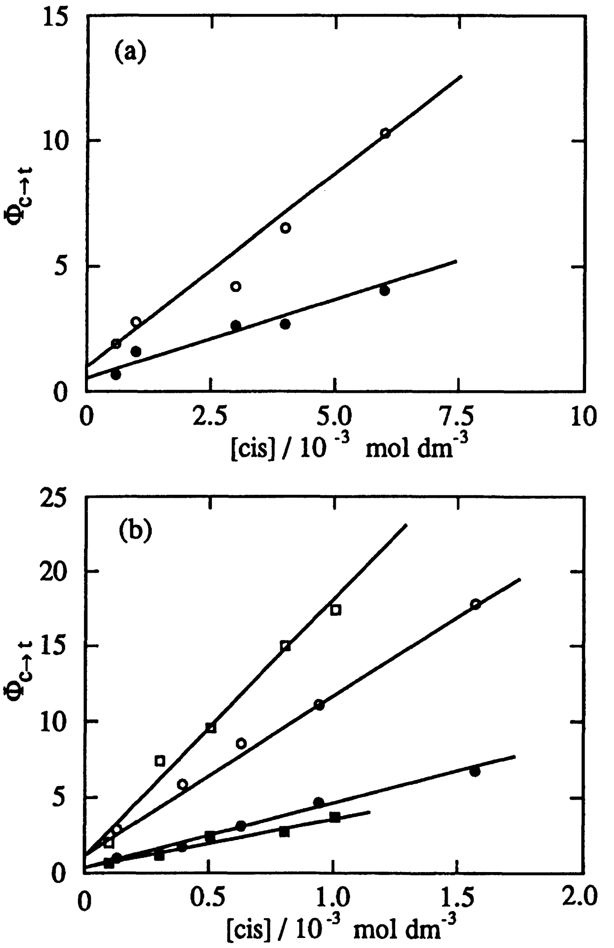

Fig. 3. Effect of cis isomer concentration on cis to trans isomerization quantum yield ($\Phi_{c\to t}$). (a) **1a**, open circles: Michler's ketone sensitization, solid circles: direct irradiation. (b) Circles: **1b**, and squares: **1c**, open marks: biacetyl sensitization, solid marks: direct irradiation.

as in triplet sensitization, direct irradiation of **1**'s in argon-bubbled benzene with 366-nm light resulted in a cis→trans one-way isomerization. As included in Fig. 3, the $\Phi_{c\to t}$'s linearly increased along with increasing the cis isomer concentration, though with smaller slopes than upon triplet sensitization. The slopes and intercepts of these plots ($\Phi_{c\to t}$ vs. [cis]) are also included in Table 3.

Isomerization with Dye Sensitizers. Dyes with varying triplet energies, such as thiazines (thionine and Methylene Blue), xanthenes (fluorescein, Eosin Y, erythrosine, and Rose Bengal) and acridines (proflavine and Acridine Orange), were examined as sensitizers (0.15—4.0×10^{-3} M) for the isomerization of **1a** (1.0×10^{-3} M) in an argon-bubbled mixture of benzene and methanol (1 : 1). Their triplet energies are 33—36, 39—47, 49—51 kcal mol^{-1} for the above-three classes of dyes, respectively.[26] Methanol was used as a co-solvent to dissolve the dyes. The $\Phi_{c\to t}$ values were determined at low conversion (less than 15%) in order to avoid precipitation of the trans isomer at higher conversions. Among the dyes examined, thiazine dyes, that is, Methylene Blue and thionine with lower triplet energies (33 and 36 kcal mol^{-1}, respectively)[26] than the other dyes, failed in sensitization; however, the other dyes with triplet energies higher than 40 kcal mol^{-1} efficiently sensitized the cis→trans one-way isomerization of **1a**. The quantum yields were 3.7, 15, 24, 1.1, 0.56, and 1.9 for Rose Bengal, Eosin Y, erythrosine, fluorescein, Acridine Orange, and proflavine, respectively. For most of the dyes, the quantum yields were much higher than unity, indicating that the isomerization proceeded through a quantum chain process.

Discussion

Potential-Energy Surface of the Triplet State. We previously depicted the triplet potential-energy surface of **1a** based on photophysical and transient kinetic data,[18] as in Fig. 1. As for **1b** or **1c**, it was drawn based on only transient kinetic data; however, the data of the phosphorescence are now utilized. Also, we attempted to compute their potential-energy surfaces by quantum-mechanical calculations.[27]

The results of the phosphorescence indicate that the cis and trans isomers of these ethylenes have nearly the same triplet energies. The triplet energies of the trans isomers can also be estimated from the quenching of their triplet states by azulene. As listed in Table 2, the k_q^{Az} values are in the range of 5×10^8 to 5×10^9 M^{-1} s^{-1}, and are lower than the diffusion-controlled rate constant. This is attributed to the slightly endothermic or thermoneutral nature of the energy transfer from these triplet states (at most 42 kcal mol^{-1} for anthracene)[14] to azulene (39.8 kcal mol^{-1}).[28]

By a comparison of the k_q^{Az} values (listed in Table 2) with those for the triplet states of dibenzo[*b*,*g*]pyrene (E_T = 34.4 kcal mol^{-1}), 5-methyldibenzo[*b*,*h*]pyrene (38.5), dibenzo[*b*,*h*]pyrene (40.2), and anthracene, reported as 9.0×10^7, 2.4×10^9, 2.3×10^9, and 7.4×10^9 M^{-1} s^{-1}, respectively,[29] one can estimate the triplet energies of the trans isomers of **1a**, **1b**, and **1c** as being nearly 40, 38, and 37 kcal mol^{-1}, respectively. However, these values are slightly lower than those determined from phosphorescence measurements, probably due to the difficulty in estimating the triplet energy from the quenching by azulene.

Now, the potential-energy surfaces of **1b** are depicted as in Fig. 1. In **1b** as well as **1c**, the adiabatic ^{3}c*→^{3}t* conversion occurs too rapidly to be detected by spectral changes in the nanosecond range, in contrast to the triplet state of **1a**. This fact suggests that ^{3}p* is comparable in energy with ^{3}c*. The energies for both the cis and trans triplets are estimated to be 41.5 kcal mol^{-1} over their respective ground states for **1b** and 41.3 kcal mol^{-1} for **1c** from the phosphorescence data. The ground-state cis will be ca. 5 kcal mol^{-1} higher in energy than the trans, as reported for stilbene.[5a] Therefore, the triplet energy of $^3c^*$ and the twisted triplets will be 46.5 kcal mol^{-1} over the ground state of the trans, similarly to stilbene.[3b)] Accordingly, these olefins may have a potential-energy surface that is nearly flat from $^3c^*$ to $^3p^*$, and gently descending from $^3p^*$ toward $^3t^*$. The lack of deep energy minimum at $^3c^*$ causes the adiabatic $^3c^* \rightarrow {}^3t^*$ conversion to take place too rapidly to be followed by transient spectroscopy, and to be inefficiently quenched by oxygen.[30)]

As shown in Fig. 1, $^3p^*$ is located nearly 5 kcal mol^{-1} higher than $^3t^*$. Therefore, at room temperature $^3t^*$ could be converted to $^3c^*$ through $^3p^*$ competing with its deactivation to the trans isomer. However, no isomerization takes place from trans to cis. This fact reflects that $^3c^*$ is not located at any deep energy minimum. Once $^3t^*$ gets to $^3c^*$, it returns to $^3t^*$ rapidly, rather than deactivate slowly to cis.

Mechanism for Triplet-Sensitized Isomerization. Upon triplet sensitization, all of the **1**'s employed undergo a cis→trans "one-way" isomerization. Since the triplet energies of their cis and trans isomers are as low as, or less than, that of anthracene, 42 kcal mol^{-1},[14)] triplet sensitizers such as Michler's ketone ($E_T = 62$ kcal mol^{-1})[14)] and biacetyl ($E_T = 56$ kcal mol^{-1})[14)] can effectively transfer their triplet energy to both isomers. This novel-type isomerization proceeded through the following mechanism (Eqs. 1, 2, 3, 4, and 5) as previously proposed:[15a,15b)]

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

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

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

$$^3\mathrm{t}^* \longrightarrow \mathrm{t}, \tag{4}$$

and

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

where S refers to a sensitizer. The cis triplet ($^3c^*$) resulting from excitation of the cis isomer (c) (Eq. 2) twists around the ethylenic linkage to attain the trans triplet ($^3t^*$) state in an adiabatic way (Eq. 3), passing through the perpendicular triplet ($^3p^*$) state, which is not located at a deep energy minimum. The transient absorption spectroscopy showed that the most stable triplet is not $^3p^*$, but $^3t^*$ or $^3c^*$, and that the conversion of $^3c^*$ to $^3t^*$ of **1a** takes place with an activation energy of ca. 6 kcal mol^{-1}.[18)] The resulting $^3t^*$ undergoes either unimolecular deactivation to the ground-state trans isomer (t) (Eq. 4) or an energy transfer to c to regenerate $^3c^*$ (Eq. 5), thus accomplishing the quantum chain process.

An alternative mechanism in which the deactivation would take place at an energy minimum located near to $^3p^*$ in the triplet energy surface, but shifted to the side of trans conformation to give exclusively the trans isomer, is excluded, since the energy to be evolved in the transition from the triplet state to the ground state would be too small to excite the cis isomer to $^3c^*$, leading to a quantum chain process.

A quantum chain process involving regeneration of sensitizer triplets by a back energy transfer from $^3t^*$ to the sensitizer is also ruled out, since the triplet energies of the sensitizers employed are more than 10 kcal mol^{-1} higher than those of **1**'s. Therefore, an energy transfer from $^3t^*$ to the cis isomer is the only possible process to regenerate $^3c^*$, leading to a quantum chain process.

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

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

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

Thus, $\Phi_{\mathrm{c}\rightarrow\mathrm{t}}$ depends on the efficiencies for the formation of sensitizer triplets ($\Phi_{\mathrm{isc}}{}^{\mathrm{s}}$), for an energy transfer from the sensitizer to the cis isomer $[k_{\mathrm{q}}{}^{\mathrm{s}}[\mathrm{c}]/(k_{\mathrm{d}}{}^{\mathrm{s}}+k_{\mathrm{q}}{}^{\mathrm{s}}[\mathrm{c}])]$, and for the subsequent quantum chain process ($k_{\mathrm{q}}\tau_{\mathrm{T}}[\mathrm{c}]$), i.e., the efficiency for an energy transfer from $^3t^*$ to the cis isomer. The efficiency of the 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 under the experimental conditions. The self-quenching of the triplet excited sensitizer is not important in this case. For example, Michler's ketone triplet is quenched by *cis*- and *trans*-**1a** with rate constants of 4×10^9 and 5×10^9 M^{-1} s^{-1}, respectively; however, by Michler's ketone, itself, it proceeds with a much lower rate constant of 8×10^7 M^{-1} s^{-1}.[31)]

The $\Phi_{\mathrm{c}\rightarrow\mathrm{t}}$ value linearly increases along with an increasing cis isomer concentration with an intercept of nearly unity, as expected from Eq. 6, although the intercept of this kind of plots is often accompanied by some experimental error. The slopes of Fig. 3 correspond to $\Phi_{\mathrm{isc}}{}^{\mathrm{s}} k_{\mathrm{q}}\tau_{\mathrm{T}}$, which is assumed to be $k_{\mathrm{q}}\tau_{\mathrm{T}}$, since $\Phi_{\mathrm{isc}}{}^{\mathrm{s}}$ is very close to unity.[14)]

The $k_{\mathrm{q}}\tau_{\mathrm{T}}$ values for **1b** and **1c**, on the order of 10^4 M^{-1}, are much larger than that for **1a**, on the order of 10^3 M^{-1}. Dividing the $k_{\mathrm{q}}\tau_{\mathrm{T}}$ value by the τ_{T} value gives the k_{q} value for each olefin. Determinations of the isomerization quantum yields were carried out under argon bubbling for experimental convenience, where the lifetimes of the triplet state of **1**'s were found to be on the order of 30 µs. The $k_{\mathrm{q}}\tau_{\mathrm{T}}$ values, on the order of 10^4 M^{-1} for **1b** and **1c** with a τ_{T} of 30 µs, give a k_{q} on the order of 3×10^8 M^{-1} s^{-1}. On the other hand, the k_{q} for **1a** is on the order of 3×10^7 M^{-1} s^{-1}.

The triplet energies for the cis and trans isomers are nearly the same as those for these olefins, as indicated by their phosphorescence spectra. Accordingly, process (5) must be nearly thermoneutral, and could be reversible. The above-estimated k_q values seem to be slightly lower than that estimated for a thermoneutral energy transfer, 5×10^9 $M^{-1}\,s^{-1}$, based on Sandros' equation.[32a)] However, the present values seem not to be unreasonable, since the triplet-energy transfer rate constant is not simply governed by the amount of the accompanying free-energy change, as has been recently argued.[32b,32c)] Furthermore, the lower value observed for **1a** than for **1b** and **1c** could be attributed to the presence of a bulky *t*-butyl group located at the cis-side of **1a**, which might exert a steric hindrance in a nearly thermoneutral energy transfer from $^3t^*$.

In spite of the nearly thermoneutral nature of the energy transfer from $^3t^*$ to cis, the energy transfer takes place very effectively, leading to an efficient quantum chain process. It is therefore to be noted that the high efficiency of the quantum chain process is attributed to the long lifetime of $^3t^*$. Thus, the almost isoenergetic energy transfer from $^3t^*$ to cis can proceed sufficiently, competing with the slow deactivation of $^3t^*$. The present results are very different from those reported concerning adiabatic quantum chain processes proceeding through a highly exothermic energy transfer.[33)]

Isomerization upon Direct Irradiation. **1**'s also isomerized in a one-way fashion with quantum yields exceeding unity upon direct irradiation. The cis isomer of stilbene hardly emits fluorescence.[32)] However, the cis isomers of **1**'s exhibited their characteristic fluorescence spectra (Fig. 2), indicating that the $^1c^*$'s are stabilized on the singlet energy surface by the anthryl group, and have lifetimes sufficiently long to emit fluorescence, or to undergo intersystem crossing to the triplet state.

If the singlet state participated in the one-way isomerization upon direct irradiation, and the quantum chain process completely took place on the singlet manifold, the slope in the plot of $\Phi_{c\rightarrow t}$ against the cis-isomer concentration upon direct irradiation, for example, 550 M^{-1} for **1a** (Fig. 3), should be equal to $k_q\tau_s$, where τ_s denotes the lifetime of the trans singlet and k_q means the rate constant for an energy transfer from the trans singlet to the cis isomer. Since τ_s is 10.4 ns,[22)] k_q should be 5.3×10^{10} $M^{-1}\,s^{-1}$. This value is larger than the diffusion-controlled limit in a collisional energy transfer, and is in the region of the rate constants for the trivial and dipole–dipole mechanisms for an energy transfer. None of them occurs, since the singlet excitation energy of *cis*-**1a** is ca. 2 kcal mol^{-1} higher than that of *trans*-**1a**, and the overlap between the fluorescence spectrum of *trans*-**1a** and the absorption spectrum of *cis*-**1a** remains very small. These facts eliminate the above possibility.

Therefore, the isomerization upon direct excitation is reasonably assumed to proceed through the triplet manifold according to the following processes (7—9), followed by processes. 3—5:

$$c \xrightarrow{h\nu} {}^1c^*, \tag{7}$$

$$^1c^* \longrightarrow c + h\nu_f, \tag{8}$$

and

$$^1c^* \longrightarrow {}^3c^*. \tag{9}$$

In this sequence, the quantum yield for cis-to-trans isomerization upon direct irradiation can be expressed by

$$\Phi_{c\rightarrow t} = \Phi_{isc} \times \Phi^T{}_{c\rightarrow t} = \Phi_{isc}(1 + k_q\tau_T[c]), \tag{10}$$

where $\Phi^T_{c\rightarrow t}$ denotes the quantum yield for isomerization in the triplet state $(=1+k_q\tau_T[c])$. The slope in Fig. 3 corresponds to Φ_{isc} $k_q\tau_T$, and the intercept to Φ_{isc}. Although the intercepts in these plots are generally accompanied by some experimental errors, they can be regarded as having the same magnitude as Φ_{isc}, determined by transient spectroscopy. The $k_q\tau_T$ values, obtained as the ratio between the slope and the intercept, are slightly lower than those determined from triplet sensitization, but could be taken to be roughly the same magnitude as the latter by taking account of the inevitable experimental error.

As can be seen in Table 1, the sum of the Φ_{isc} value and Φ_f value is close to unity, except for *cis*-**1b**. Therefore, the **1**'s singlets mostly deactivate by fluorescence radiation and intersystem crossing to the triplet state.

Upon irradiation of **1b** and **1c**, their cis singlet states might deactivate through cyclization to a dihydrophenanthrene derivative, which can be easily oxidized to the corresponding phenanthrene derivative. However, such cyclization products were not detected at all upon irradiation of the trans, and even cis isomers of **1b** and **1c**, in benzene under either degassed, air-saturated, or oxygen-saturated conditions, and even in the presence of iodine under air. No cis isomer was formed under the above-mentioned conditions, although irradiation of *cis*-2-(4-methylstyryl)anthracene under an oxygenated atmosphere was reported to produce cyclization products in very low yield.[27a)] If the isomerization proceeded in a mutual way between the cis and trans isomers, cyclization might take place. The above results are consistent with a mechanism in which the isomerization proceeds in a one-way mode from cis to trans without producing the cis isomer, even upon direct irradiation.

Isomerization with Dye Sensitizers. The finding that various xanthene and acridine dyes with triplet energies higher than 40 kcal mol^{-1} sensitized the one-way isomerization of *cis*-**1a** with a quantum chain process shows that these dyes act as usual triplet sensitizers, but not as electron-accepting sensitizers generating the radical cation of *cis*-**1a**, which might isomerize to the radical cation of *trans*-**1a**, finally giving *trans*-**1a**.[35)] Otherwise, thionine, an ineffective sensitizer, would act as an electron-accepting sensitizer from *cis*−**1a**[$E(^3D^*/D^{-\bullet})=1.40$ V; $E(D/D^{-\bullet})=-0.29$ V vs. SCE in acetonitrile, $E_T=1.69$ eV]; however, no isomerization occured. On the other hand, although the triplet state of Eosin Y [$E(^3D^*/D^{-\bullet})=0.70$ V; $E(D/D^{-\bullet})=$

−1.29 V, E_T=1.99 eV] cannot accept an electron from the olefin, the isomerization proceeds very efficiently with this sensitizer. Furthermore, the oxidation potential of *trans*-**1a** (E_{ox}=1.15 V) is slightly more cathodic than that of *cis*-**1a** (1.18 V), and therefore, a chain reaction through radical cations, $t^{+\bullet}+c \rightarrow t+c^{+\bullet}$, will not efficiently take place.[36]

Conclusion

Preparative methods of anthrylethylenes **1a**—**d** undergoing one-way isomerization are described. The isomerization efficiently proceeds through a quantum chain process; the efficiency is slightly higher for **1b** and **1c** than **1a**. The high efficiency of the quantum chain process is attributed to the long lifetime of ^{3}t*, which enables its nearly thermoneutral energy transfer to cis to take place effectively, competing with its relatively slow decay on the order of 10^4 s^{-1}.

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