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Photoisomerization behavior of 1-(9-anthryl)-2-(2-pyrazinyl)ethene, a diaza analogue of 1-(9-anthryl)-2-phenylethene

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Abstract

The fluorescence properties and photoisomerization behavior for *trans* and *cis* isomers of 1-(9-anthryl)-2-(2-pyrazinyl)ethene (APzE), a diaza analogue of 1-(9-anthryl)-2-phenylethene (9-APE), were studied. The fluorescence maximum (λ_f), quantum yield (Φ_f), and lifetime (τ_f) of *t*-APzE were solvent-dependent reflecting the intramolecular charge transfer character in the lowest excited singlet state. However, in polar protic solvent, some discrepancy was observed probably due to protonation on the nitrogen atoms. The photoisomerization of *t*-APzE was observed even in very nonpolar solvent, in contrast that the parent *t*-9-APE did not photoisomerize in any solvent and photoisomerization of monoaza analogues *t*-1-(9-anthryl)-2-(*n*-pyridyl)ethenes (*n*-APyE) was very inefficient in nonpolar solvent. The quantum yield of the *trans* → *cis* photoisomerization ($\Phi_{t\to c}$) of *t*-APzE was also solvent-dependent. Not only the inverse dependence for Φ_f and $\Phi_{t\to c}$ of *t*-APzE on the temperature and the solvent polarity but also biacetyl-sensitized photoisomerization experiment indicate that the photoisomerization of *t*-APzE occurs, at least in part, via the excited singlet state. In air-saturated solution, another side photoproduct was observed in all solvent examined and identified as anthraquinone, a photo-oxidation product. For *c*-APzE, the τ_f is too short to measure and Φ_f is relatively low. Quantum yields of fluorescence and *cis* → *trans* photoisomerization of *c*-APzE in various solvent and temperature indicate singlet mechanism for the *cis* → *trans* photoisomerization of *c*-APzE in polar solvent but mixed singlet/triplet mechanism in nonpolar solvent. On irradiation of *c*-APzE, the photo-oxidation product was not generated at all in any solvent. In *n*-hexane, photocyclization competing with photoisomerization was observed both for *t*- and *c*-APzE. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Photoisomerization; Fluorescence; Solvent effect; Temperature effect; 1-(9-Anthryl)-2-(2-pyrazinyl)ethene; Diaza derivative of 1-(9-anthryl)-2-phenylethene

1. Introduction

The photochemical and photophysical behaviors of 1-(*n*-anthryl)-2-phenylethene (*n*-APE, $n = 1$, 2, and 9) have been extensively studied [1–15]. They exhibit efficient *cis* → *trans* photoisomerization but do not undergo *trans* → *cis* photoisomerization. Large energy barriers against twisting for *trans* isomers were attributed to localization of excitation energy in anthracene moiety. The dominant photoisomerization pathway of *c*-2-APE has been reported recently to be singlet adiabatic photoisomerization ($^1c^* \rightarrow {}^1t^* \rightarrow {}^1t$) [3,12], contrary to triplet adiabatic photoisomerization ($^1c^* \rightarrow {}^3c^* \rightarrow {}^3t^* \rightarrow {}^1t$) proposed by Arai and Tokumaru [1,2]. One-way *cis* → *trans* isomerization of *c*-9-APE [13,16] has been reported to occur mainly via triplet adiabatic pathway in nonpolar solvent and singlet diabatic/adiabatic mixed pathway ($^1c^* \rightarrow {}^1p^* \rightarrow {}^1p \rightarrow {}^1t$ or $^1c^* \rightarrow {}^1t^* \rightarrow {}^1t$) in polar solvent. Because *t*-*n*-APE is photochemically nonreactive, main decay pathway of its lowest excited singlet state is fluorescence and intersystem crossing but internal conversion is not negligible for *t*-9-APE [11]. However, in some 9-APE derivatives bearing electron-donating or electron-withdrawing substituent, the diabatic *trans* → *cis* photoisomerization ($^1t^* \rightarrow {}^1p^* \rightarrow {}^1p \rightarrow {}^1c$) has been observed conceivably in the singlet manifold by way of intramolecular charge transfer processes, which is more efficient in polar solvent [17–20,16].

The photochemistry of aza-derivatives of two-way photoisomerizing diarylethenes such as aza-stilbenes [21,22], aza-1-naphthyl-2-phenylethenes [23–25] and aza-1-phenanthryl-2-phenylethenes [21,26], has been extensively investigated. The introduction of nitrogen atom to diarylethenes produces low-lying n,π^* states and the vibronic perturbation of the lowest π,π^* state by a close-lying n,π^*

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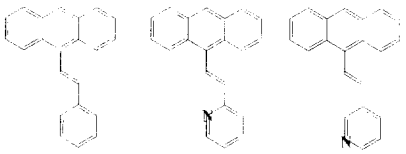
state can lead to an efficient $S_1 \rightarrow S_0$ internal conversion, thus affecting photophysical and photochemical behavior. When several nitrogen atoms are introduced into diarylethenes, n,π^* state may become the lowest excited state and this can lead to an efficient $S_1 \rightarrow T_1$ intersystem crossing.

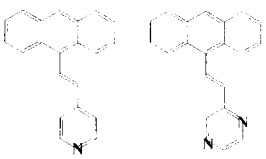
In our previous paper [27], the photophysical properties and photoisomerization behavior of 1-(9-anthryl)-2-(*n*-pyridyl)ethenes (*n*-APyE, $n = 2$, 3, or 4), mono-aza analogues of 9-APE, have been reported together with the influence of nitrogen position, temperature, and solvent polarity on those. It was inferred that introduction of nitrogen atom, especially in *para* position of phenyl ring of 9-APE, induces the lowering of the energy barrier against twisting of central double bond on the excited singlet energy surface in polar solvent probably through the intramolecular charge transfer and makes *trans* → *cis* photoisomerization feasible, although not in nonpolar solvent. A singlet mechanism for *trans* → *cis* photoisomerization has been proposed.

The present paper describes the fluorescence properties and photoisomerization behavior of 1-(9-anthryl)-2-(2-pyrazinyl)ethene (APzE), a diaza analogue of 9-APE in various solvents and temperatures in comparison with those of 9-APE (a parent hydrocarbon) and *n*-APyE ($n = 2$–4, mono-aza analogues of 9-APE).

The parent hydrocarbon 9-APE does not accomplish the *trans* → *cis* isomerization but only *cis* → *trans* isomerization, i.e., one-way photoisomerization is observed both in nonpolar and polar solvent. The photoisomerization of *n*-APyE ($n = 2$, 3, or 4) is changed from one-way mode to two-way mode on going from nonpolar to polar solvent. In contrast, APzE exhibits two-way photoisomerization even in nonpolar solvents. Intramolecular charge transfer between pyrazinylethene and anthracene moieties overcomes the restriction against rotation in the excited singlet state and the n,π^* state introduced by two nitrogen in APzE affects extensively the excited state property.



t-9-APE **t-2-APyE** **t-3-APyE**



t-4-APyE **t-APzE**

2. Experimental details

2.1. Chemicals

For spectroscopic measurements and photochemical reactions, *n*-hexane, ethyl acetate, acetonitrile, and methanol of HPLC grade (Merck) and methylcyclohexane and ethanol of spectrophotometric grade (Aldrich) were used. Dichloromethane, toluene, and tetrahydrofuran were freshly distilled from P_2O_5, CaH_2, and Na, respectively. Quinine sulfate (Aldrich), standard for fluorescence quantum yield measurement, was purified by recrystallization from water. Kiesel Gel 60 (70–230 mesh, Merck) and RP-18 F_{254s} TLC plate (Merck) were used for silica gel column chromatography and thin layer chromatography, respectively. All other chemicals are used as received.

2.2. Synthesis

t-APzE was synthesized by the Wittig reaction between 9-anthrylmethyltriphenylphosphonium bromide and 2-pyrazinecarboxaldehyde. 2-Pyrazinecarboxaldehyde was prepared by careful reduction of tetrahydrofuran solution of 2-pyrazinecarboxylic acid methyl ester using $LiAlH_4$ at −78°C [28]. 9-Anthrylmethyltriphenylphosphonium bromide was prepared by bromination of 9-methylanthracene in carbon tetrachloride using *n*-bromosuccinimide, followed by the reaction of triphenylphosphine in toluene. In dimethylsulfoxide (60 ml) solution of 9-anthrylmethyltriphenylphosphonium bromide (4 g, 7.3 mmol), sodium methoxide (0.4 g, 7.4 mmol), and 2-pyrazinecarboxaldehyde (1.0 g, 9.2 mmol) was added and stirred at 100°C for 1 h. The resulting mixture was poured into distilled water, extracted three times with ethyl ether, rinsed several times with water, and dried with anhydrous magnesium sulfate. The resulting solution was concentrated in vacuo and was chromatographed on silica gel using hexane/ethyl acetate = 1/2 as an eluent in order to remove the unreacted starting materials and side products. The resulting yellow solid (0.98 g, 48% yield) involving *t*-APzE and *c*-APzE which exhibited very similar retention times was further separated on RP-18 F_{254s} TLC plate (Merck) using methanol as a developing solvent in the dark room because *cis* isomer is very sensitive to light and revert rapidly to *trans* isomer by the daylight. *t*- and *c*-APzE are characterized by NMR, IR, UV, and mass spectral data.

t-APzE yellow solid. IR: 3046, 1635, 1515, 1396, 1145, 1015, 983, 875, 724 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.08(1H, d, $J = 16$ Hz, H8), 7.52–7.48 (4H, m, H2′, 3′, 6′, 7′), 8.02–8.06 (2H, m, H4′, 5′), 8.23–8.38 (2H, m, H1′, 8′), 8.46 (1H, s, H10′), 8.52 (1H, d, $J = 3$ Hz, H3), 8.68 (1H, d, $J = 3$ Hz, H4), 8.69 (1H, d, $J = 16$ Hz, H7), 8.7 (1H, s, H6) ppm. EI-MS: m/e 282[M]$^+$, 203.

c-APzE yellow solid. IR: 3044, 1620, 1515, 1467, 1396, 1145, 1012, 854, 733 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.32 (1H, d, $J = 12$ Hz, H8), 7.40–7.50 (4H, m, H2′, 3′, 6′, 7′), 7.59 (1H, d, $J = 1.6$ Hz, H6), 7.63 (1H, d, $J = 12$ Hz, H7), 8.00–8.05 (2H, dd, $J = 8.0$, 0.7 Hz, H4′, 5′), 8.08 (1H, d, $J = 3.2$ Hz, H3), 8.12–8.16 (2H, dd, $J = 8.0$, 0.7 Hz, H1′, 8′), 8.40 (1H, dd, $J = 3.2$, 1.6 Hz, H4), 8.46 (1H, s, H10′) ppm. EI-MS: m/e 282[M]$^+$, 203.

2.3. Spectroscopic and photochemical measurements

^{1}H NMR spectra were obtained on 300 MHz Bruker DRX 300 spectrometer in chloroform-d_1. Mass spectra were measured on Hewlett-Packard 5890 series II gas chromatograph-5972 series mass selective detector. IR spectra were recorded in KBr pellets on Midac Prospect-IR spectrometer. The absorption spectra were recorded on a Hitachi U-321097 spectrophotometer. Aminco-Bowman Series 2 luminescence spectrometer was used for steady sate fluorescence measurements. SLM-AMINCO 48000S phase resolved spectrometer was used for the measurement of fluorescence lifetimes. Excitation wavelength at 360 nm for steady-state fluorescence measurement, excitation wavelength at 385 nm and emission wavelength at 470 nm for fluorescence lifetime measurement, and irradiation wavelength of 366 nm for photoisomerization were employed in argon-saturated solution. Concentration of *t*-APzE and *c*-APzE for the determination of quantum yield of fluorescence were controlled to be ca. 1×10^{-5} M or below, where the absorbances of the solutions at the excitation wavelength (360 nm) were usually at the value of 0.07–0.08, to avoid inner filter effects. Concentration of *t*-APzE and *c*-APzE for the measurements of quantum yield of photoisomerization was ca. 6×10^{-4} M in which all incident light was absorbed.

3. Results and discussion

3.1. Absorption and fluorescence study

The absorption spectra of *t*-APzE and *c*-APzE at room temperature (Fig. 1) appear at similar region, but *c*-APzE shows weaker, more structured, and blue-shifted absorption than *t*-APzE as in parent 9-APE [6,9,10] and *n*-APyE ($n=2$–4) [27]. The absorption maxima(λ_a^{max}) of *t*-APzE are 368 ($\varepsilon=7800$), 387 (10,700), and 401 (10,000) nm in acetonitrile. The absorption spectrum of *t*-APzE is more structured than those of *t*-9-APE [6,9,10] and *t*-*n*-APyE [27], which exhibits only single maximum at around 386 nm with shoulder bands. λ_a^{max} of *c*-APzE in acetonitrile are 335 ($\varepsilon=3400$), 352 (5200), 370 (7500), and 390 (7400) nm, which are similar to λ_a^{max} of *c*-9-APE [6,9] and *c*-*n*-APyE [27]. The absorption spectra of *t*-APzE and *c*-APzE are insensitive to the solvents of various polarity.

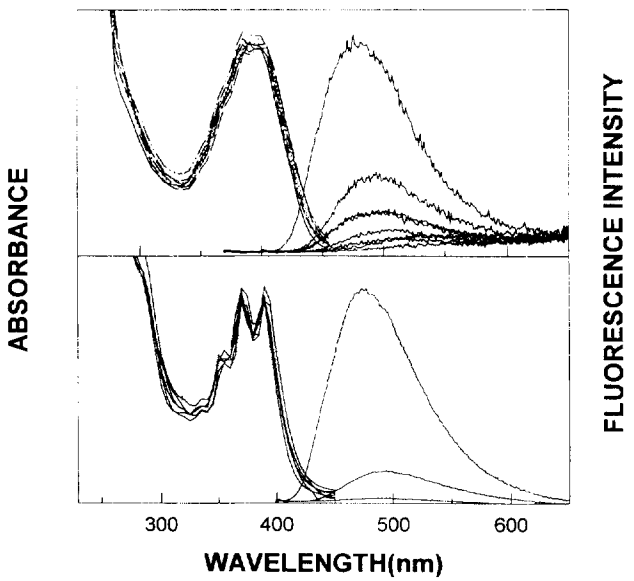


Fig. 1. Absorption (left) and fluorescence (right) spectra of *t*-APzE (upper) and *c*-APzE (lower) in various solvents at room temperature. Absorption spectra are similar in all solvents examined. Fluorescence intensity is reduced with increasing the solvent polarity.

Fluorescence spectra of *t*-APzE and *c*-APzE at room temperature (Fig. 1) show very similar structureless shape but fluorescence maximum (λ_f) of *t*-APzE is slightly longer than that of *c*-APzE.

Fluorescence properties of the parent *t*-9-APE [6,9,10,17,19,20] are independent of the solvent polarity but those of *t*-*n*-APyE ($n=2$ and 4) [27], mono-aza analogues, are strongly dependent on the solvent. Φ_f of *t*-APzE (0.37) is lower than those of parent *t*-9-APE (0.48 in cyclohexane) [20] and *t*-*n*-APyE (0.43–0.49, $n=2$–4) [27] in *n*-hexane. Moreover, τ_f (3.3 ns) of *t*-APzE is slightly shorter than those of parent *t*-9-APE (3.6 ns in cyclohexane) [20] and *t*-*n*-APyE (3.5–3.7 ns, $n=2$–4) [27] in *n*-hexane, due to low-lying n,π^* state leading to efficient radiationless deactivation. As shown in Table 1, as the solvent polarity is increased, Φ_f and τ_f of *t*-APzE is markedly decreased and λ_f is pronouncedly red-shifted. This remarkable solvent dependence of fluorescence reflects a polar charge transfer character of the excited singlet state. The value of k_f (Table 1) obtained from Φ_f and τ_f of *t*-APzE is similar to those of parent *t*-9-APE and *t*-*n*-APyE [27], indicating that the fluorescent state of these compounds is of the similar nature. Fluorescence of *t*-APzE becomes structured and blue-shifted on going from room temperature to 77 K (Fig. 2) and fluorescence maxima at 77 K (Table 2) are almost independent of solvent polarity similar to those of 9-APE [17] and *t*-*n*-APyE [27]. For *t*-APzE, λ_f at room temperature is 479 nm in *n*-hexane, but fluorescence at 77 K shows two maxima of 446 and 474 nm in methylcyclohexane. Similarly to Φ_f of *t*-9-APE [17] and *t*-*n*-APyE ($n=2$–4) [26] at 77 K, Φ_f of *t*-APzE at 77 K is even smaller than unity indicating the efficient intersystem crossing. In determination of Φ_f at 77 K, considerable error may be included because it is assumed that absorbance ratio of sample (APzE) and reference (9,10-diphenylanthracene) is not changed on going from room temperature to 77 K.

It has been reported that Φ_f of *c*-9-APE [13,17] and *c*-*n*-APyE ($n=2$–4) [27] in polar solvent are smaller than those in nonpolar solvent. As shown in Table 3, Φ_f of *c*-APzE is also decreased with increasing the solvent polarity and λ_f is almost independent of the solvent polarity. Lower Φ_f of *c*-APzE than that of *t*-APzE indicates the barrierless twisting around ethenic bond in *cis* isomer. *Trans* and *cis* isomers of APzE have lower Φ_f than parent 9-APE and *n*-APyE, indicating efficient nonradiative decay such as internal conver-

Table 1
Fluorescence maxima (λ_f), lifetime (τ_f), quantum yield (Φ_f), and photoisomerization quantum yield ($\Phi_{t\to c}$ or $\Phi_{c\to t}$) of *t*-APzE and *c*-APzE at room temperature in various solvents[a]

Solvent	*t*-APzE					*c*-APzE		
	λ_f (nm)	τ_f (ns)	Φ_f	$k_f\times10^{-9}$ (s^{-1})	$\Phi_{t\to c}$	λ_f (nm)	Φ_f	$\Phi_{c\to t}$
Hexane[b]	472	3.3	0.37	0.11	0.07	470	0.24	0.31
Toluene	485	1.8	0.16	0.09	0.14	490	0.06	0.24
THF	485	0.7	0.08	0.11	0.17	488	0.011	0.26
EtOAc	485	0.6	0.07	0.12	0.18	485	0.009	0.23
CH_2Cl_2	491	0.5	0.05	0.10	0.19	492	0.003	0.24
CH_3CN	494	–	0.03	–	0.20	482	0.002	0.25
EtOH	530	–	0.02	–	0.13	490	0.007	0.23
MeOH	536	–	0.01	–	0.09	538	0.002	0.26

[a]Excitation wavelength at 360 nm for fluorescence measurements and irradiation wavelength of 366 nm for photoisomerization.
[b]Photocyclization reaction competes with photoisomerization and fluorescence.

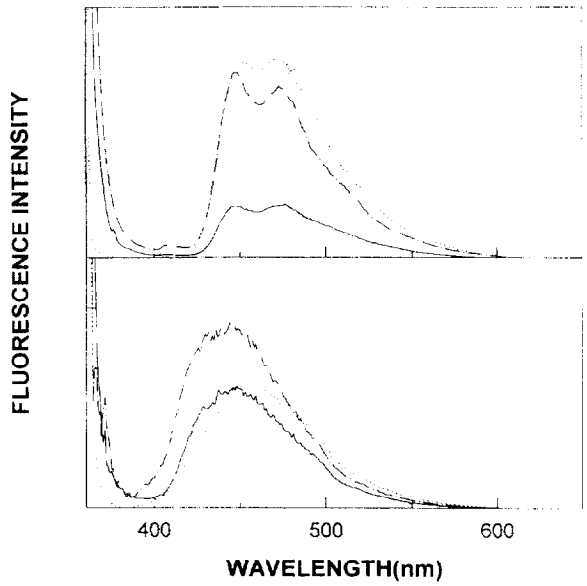


Fig. 2. Fluorescence spectra of *t*-APzE (upper) and *c*-APzE (lower) at 77 K in MCH (solid line), MCH (dot-dashed line), and ethanol (dotted line).

Table 2
Fluorescence maxima (λ_f) and quantum yield (Φ_f) of *t*-APzE and *c*-APzE at 77 K in various solvents[a]

Solvent	*t*-APzE		*c*-APzE	
	λ_f (nm)	Φ_f	λ_f (nm)	Φ_f
Methylcyclohexane	446, 474	0.21	449	0.29
2-Methyltetrahydrofuran	448, 474	0.48	449	0.40
Ethanol	448, 470	0.52	457	0.20

[a]Excitation wavelength at 360 nm.

sion and intersystem crossing induced by two nitrogen atoms. τ_f of *c*-APzE is too short to measure with our instrument. Fluorescence spectra of *c*-APzE at 77 K are still broad but blue-shifted compared with those at room temperature (Fig. 2 and Table 2).

Table 3
Photoreaction of *t*-APzE and *c*-APzE in the absence and presence of biacetyl in toluene and acetonitrile at 450 nm irradiation[a]

[Biacetyl], M	[*c*-APzE] produced in photoreaction of *t*-APzE, M		[*t*-APzE] produced in photoreaction of *c*-APzE, M	
	Toluene	Acetonitrile	Toluene	Acetonitrile
0	3.1×10^{-7}	3.1×10^{-4}	4.6×10^{-5}	3.6×10^{-5}
0.19	4.5×10^{-5}	2.4×10^{-5}	8.9×10^{-5}	3.9×10^{-5}

[a]Absorbance of *t*-APzE (4.7×10^{-4} M) and biacetyl (0.19 M) at 450 nm is 0.16 and 0.90 in acetonitrile, and 0.33 and 2.12 in toluene, respectively. In biacetyl photosensitization reaction, direct absorption by *t*-APzE cannot be neglected. Absorbance of *c*-APzE at 450 nm is 0.02 in acetonitrile and 0.01 in toluene. In biacetyl photosensitization reaction, direct absorption by *c*-APzE can be neglected. Moreover, 450 nm Hanovia low pressure mercury lamp which showed broad band emission and was not monochromatic was used as light source. Therefore, we did not try to estimate biacetyl sensitized photoisomerization quantum yield.

3.2. Photoisomerization of t-APzE

The quantum yield of *trans*→*cis* photoisomerization ($\Phi_{t\to c}$) of *t*-APzE upon 366 nm irradiation is dependent on solvent polarity (Table 1). In *n*-hexane, *t*-APzE undergoes inefficient but measurable *trans*→*cis* photoisomerization while parent *t*-9-APE [6,7,10,17] and *t*-*n*-APyE ($n=2$–4) [27] exhibit practically no photoisomerization. However, as the solvent polarity increases, $\Phi_{t\to c}$ for *t*-APzE increases similar to those of *t*-2-APyE and *t*-4-APyE, while still virtually zero for *t*-9-APE and *t*-3-APyE. Φ_f strongly decreases but $\Phi_{t\to c}$ moderately increases with increasing the solvent polarity while both $\Phi_{t\to c}$ and Φ_f in *t*-2-APyE and *t*-4-APyE show strong solvent dependence. $\Phi_{t\to c}$ of *t*-APzE is lower than those of *t*-2-APyE [27] is probably due to more efficient nonreactive radiationless deactivation induced by the lower-lying n,π^* state in *t*-APzE than in *t*-*n*-APyE. Therefore, $\Phi_{t\to c}$ of *t*-APzE is enhanced only moderately even at low temperature. $\Phi_{t\to c}$ and Φ_f of *t*-APzE show, at least partly, inverse relationship in varying the solvent polarity (Table 1). The

excited state involved in *trans* → *cis* photoisomerization is presumed to be a singlet excited state with the polar intramolecular charge transfer character as in some *t*-9-APE derivatives [17–20] containing electron-donating and electron-withdrawing substituents and some *t*-9-anthrylethene derivatives [29] containing electron-withdrawing substituent such as ester or nitrile and *t*-*n*-APyE ($n=2$ or 4) [27]. However, the contribution of the triplet state to photoisomerization cannot be completely excluded. *t*-APzE exhibits less efficient photoisomerization in polar protic solvent such as methanol. The reason can be explained that the hydrogen-bonding or protonation on the nitrogen atom of *t*-APzE in protic solvent results in decrease of the photoisomerization efficiency.

For *t*-*n*-APyE, introduction of a nitrogen atom into phenyl moiety of 9-APE contributes to induce some change on the excited singlet energy surface such that the activation barrier against twisting and/or the energy of the excited perpendicular state is lowered through intramolecular charge transfer process and thereby enhancement of $\Phi_{t\rightarrow c}$ with Φ_f decreasing and τ_f being shortened. However, for *t*-APzE, introduction of two nitrogen atoms into phenyl moiety of 9-APE induces not only lowering the activation barrier against twisting on the excited singlet energy surface but also more efficient radiationless deactivations. In spite of Φ_f decreasing and τ_f being shortened, $\Phi_{t\rightarrow c}$ of *t*-APzE in polar solvent is only moderately increased and smaller than that of *t*-*n*-APyE ($n=2$ or 4) because the photoisomerization in the singlet manifold competes with efficient radiationless deactivation.

Azulene quenching experiments on photoisomerization of *t*-APzE in toluene and acetonitrile was carried out and $\Phi_{t\rightarrow c}$ is practically unchanged in the azulene concentration range between 1×10^{-3} and 8×10^{-3} M. As shown in Table 3, production of *c*-APzE was greatly reduced in biacetyl-sensitized photoisomerization of *t*-APzE both in toluene and acetonitrile at irradiation of 450 nm. These results support the singlet mechanism for photoisomerization of *t*-APzE as suggested above. Absorbance of *t*-APzE (4.7×10^{-4} M) and biacetyl (0.19 M) at 450 nm is 0.16 and 0.90 in acetonitrile, and 0.33 and 2.12 in toluene, respectively. In biacetyl photosensitization reaction, because direct absorption by *t*-APzE at 450 nm is not negligible (13% in toluene and 15% in acetonitrile where [*t*-APzE] $=4.7\times10^{-4}$ M, [biacetyl] = 0.19 M), *trans* → *cis* photoisomerization could not be completely inhibited. Moreover, 450 nm Hanovia low pressure mercury lamp which showed broad band emission and was not monochromatic was used as light source. Therefore, we did not attempt to estimate biacetyl-sensitized photoisomerization quantum yield.

Irradiation of *t*-APzE in air-saturated solution gives *c*-APzE and a side photoproduct X in all solvent examined. Exceptionally, in *n*-hexane, the photoreaction is complicated by the production of another side photoproduct Y expected as a cyclization product. A side photoproduct X has been isolated by silica gel column chromatography and characterized as a anthraquinone by spectral analysis. Absorption spectrum in acetonitrile exhibits maxima at 252, 262 (shoulder), 272 (shoulder), and 323 nm with very weak broad band around 400 nm. EI-mass spectrum shows a molecular ion peak at *m*/*e* 208. ^{1}H NMR spectrum in $CDCl_3$ is very simple and shows only two multiplets (1:1) at 7.8 and 8.3 ppm. The amount of this photo-oxidation product is practically independent of the solvent polarity. In the biacetyl sensitized experiment in acetonitrile, the formation of anthraquinone is markedly increased. Therefore, this photo-oxidation reaction should proceed on the triplet manifold. Anthraquinone is not detected on irradiation of *c*-APzE as well as *t*- and *c*-APyE. The prolonged irradiation of *t*-APzE leads to severe decomposition to give tar-like material. *t*-APzE is very unstable and susceptible to photo-oxidation relative to *t*-9-APE and *t*-*n*-APyE.

3.3. Temperature dependence on fluorescence and photoisomerization of t-APzE

Φ_f of *t*-9-APE, even if no photoisomerization was observed, was reported to increase with decreasing temperature both in nonpolar and polar solvents [10]. As shown in our previous report [27], while Φ_f of *t*-*n*-APyE ($n=2$, 4) are independent of temperature and $\Phi_{t\rightarrow c}$ is practically zero in nonpolar solvent, Φ_f is increased but $\Phi_{t\rightarrow c}$ is complementarily decreased with decreasing temperature in polar solvents. For *t*-APzE, $\Phi_{t\rightarrow c}$ is decreased and Φ_f is increased with decreasing temperature both in non-polar and polar solvent. The temperature dependence on Φ_f and $\Phi_{t\rightarrow c}$ of *t*-APzE in *n*-hexane, toluene, and methanol between 50 and −20°C is represented in Table 4. Φ_f was measured in *n*-hexane and methanol, but $\Phi_{t\rightarrow c}$ was studied in toluene and methanol, because in *n*-hexane the determination of $\Phi_{t\rightarrow c}$ was complicated by the formation of a side photoproduct Y (probably photocyclization product). Plots of log Φ_f and log $\Phi_{t\rightarrow c}$ vs. T^{-1} for *t*-APzE in *n*-hexane, toluene, and methanol between 50 and −20°C are shown in Fig. 3. Assuming that the *trans* → *cis* photoisomerization occurs in the singlet manifold and is the only activated process in the excited singlet state, from plots of $\ln(\Phi_{t\rightarrow c}^{-1}-1)$ vs. T^{-1}, activation energy for photoisomerization of 2.1 kcal/mol both in toluene and methanol was obtained. The intramolecular charge transfer interaction in the lowest excited singlet state is inferred to lead low torsional barrier even in toluene probably due to the presence of low-lying n,π^* state. Inverse solvent and temperature dependence on Φ_f and $\Phi_{t\rightarrow c}$ of *t*-APzE reveal that *trans* → *cis* photoisomerization proceeds via the excited singlet state.

3.4. Photoisomerization of c-APzE

The quantum yield of *cis* → *trans* photoisomerization ($\Phi_{c\rightarrow t}$) of *c*-APzE upon 366 nm irradiation at room temperature is practically independent of solvent polarity (Table 1), similar to $\Phi_{c\rightarrow t}$ of *c*-*n*-APyE ($n=2$,4) [27]. This is in contrast that $\Phi_{t\rightarrow c}$ of *t*-APzE is relatively inefficient in nonpolar

Table 4
Temperature effect of fluorescence quantum yield (Φ_f) and photoisomerization quantum yield ($\Phi_{t\to c}$ or $\Phi_{c\to t}$) of *t*-APzE and *c*-APzE in hexane or toluene as a nonpolar solvent and in methanol as a polar solvent[a]

Temperature (K)	*t*-APzE				*c*-APzE			
	n-Hexane	Toluene	Methanol		Toluene		Methanol	
	Φ_f	$\Phi_{t\to c}$	Φ_f	$\Phi_{t\to c}$	Φ_f	$\Phi_{c\to t}$	Φ_f	$\Phi_{c\to t}$
323	0.33	0.22	0.008	0.15	0.05	0.22	0.001	–
313	0.34	0.20	0.009	0.13	0.05	0.21	0.001	0.28
303	0.35	0.18	0.009	0.11	0.05	0.23	0.002	–
293	0.36	0.17	0.009	0.11	0.06	0.26	0.002	0.27
283	0.37	0.14	0.009	0.09	0.06	0.24	0.002	0.26
273	0.39	0.13	0.010	0.09	0.05	0.22	0.002	0.21
263	0.39	0.12	0.010	0.07	0.05	0.20	0.002	0.23
253	0.39	0.10	0.012	0.07	0.04	0.20	0.002	0.22

[a] Φ_f of *t*-APzE was measured in *n*-hexane and methanol, but $\Phi_{t\to c}$ was studied in toluene and methanol, because in *n*-hexane the determination of $\Phi_{t\to c}$ was complicated by the competing photocyclization.

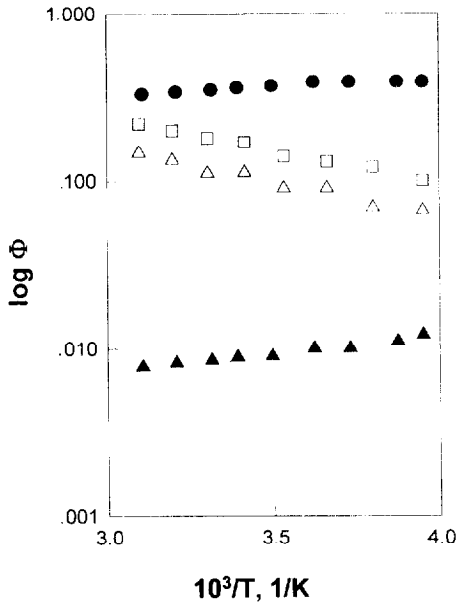


Fig. 3. Plots of log Φ_f (filled symbol) and log $\Phi_{t\to c}$ (open symbol) vs. T^{-1} for *t*-APzE in *n*-hexane (circle), toluene (square), and methanol (triangle) between 50 and −20°C.

solvent and increases with the solvent polarity. Contrary to the other solvents, in *n*-hexane the HPLC analysis of photoreaction mixture of *c*-APzE on 366 nm irradiation shows the formation of *t*-APzE and a side photoproduct Y as in *c*-9-APE [13] and *c*-*n*-APyE ($n=2, 4$) [27]. The HPLC retention of this side photoproduct Y is very close to that of *c*-APzE. Therefore, $\Phi_{c\to t}$ of *c*-APzE in *n*-hexane is difficult to determine. However, except in *n*-hexane, photoreaction seems to proceed cleanly to give only *t*-APzE. We did not try to isolate and characterize this photoproduct Y, but tentatively assigned this one as a photocyclization product. In parent *c*-9-APE, only side photoproduct other than photoisomerization to *t*-9-APE in nonpolar solvent was assigned to be a photocyclization product and in polar solvents the formation of Y became very inefficient competing with more efficient photoisomerization [13]. It is proposed in *n*-hexane that photocyclization proceeds via the singlet manifold while photoisomerization occurs mainly by a triplet mechanism with contribution of some degree of singlet mechanism, due to substantial barrier to twisting in singlet manifold. As the solvent polarity is increased, torsional energy barrier on the singlet energy surface is decreased by the contribution of intramolecular charge transfer. Therefore, even in toluene photoisomerization occurs mostly in the singlet manifold while photocyclization product is not produced at all. Similar mechanism has been suggested for the photoreaction of *c*-APE [13].

As shown in Table 3, the production of *trans* isomer upon irradiation of *c*-APzE at 450 nm is very inefficient in acetonitrile both in the presence and absence of biacetyl. But the production of *trans* isomer in toluene is increased twice but still inefficient in biacetyl-sensitized photoisomerization of *c*-APzE on irradiation of 450 nm. Absorbance of *c*-APzE at 450 nm is 0.02 in acetonitrile and 0.01 in toluene. In biacetyl photosensitization reaction, direct absorption by *c*-APzE at 450 nm is negligible (0.6% in toluene and 1.8% in acetonitrile where $[c\text{-APzE}]=4.7\times10^{-4}$ M, [biacetyl] = 0.19 M). These results imply the singlet mechanism for photoisomerization in polar solvents and some contribution of triplet pathway, i.e., the singlet/triplet mixed mechanism, in nonpolar solvents as suggested above.

3.5. Temperature dependence on fluorescence and photoisomerization of *c*-APzE

The temperature dependence of Φ_f and $\Phi_{c\to t}$ in toluene and methanol between 50 and −20°C is represented in Table 4 for *c*-APzE. Plots of log Φ_f and log $\Phi_{c\to t}$ vs. T^{-1} for *c*-APzE in toluene, and methanol between 50 and −20°C are shown in Fig. 4. We did not use *n*-hexane as a solvent to avoid the complication by competitive photocylization reaction mentioned above. In methanol, $\Phi_{c\to t}$ of *c*-APzE is slightly increased and Φ_f is slightly decreased with increasing temperature, especially above room temperature. Such an

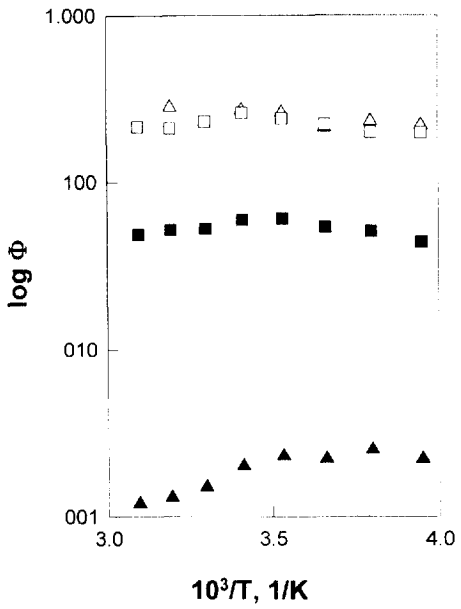


Fig. 4. Plots of log Φ_f (filled symbol) and log $\Phi_{c\to t}$ (open symbol) vs. T^{-1} for *c*-APzE in toluene (square) and methanol (triangle) between 50 and −20°C.

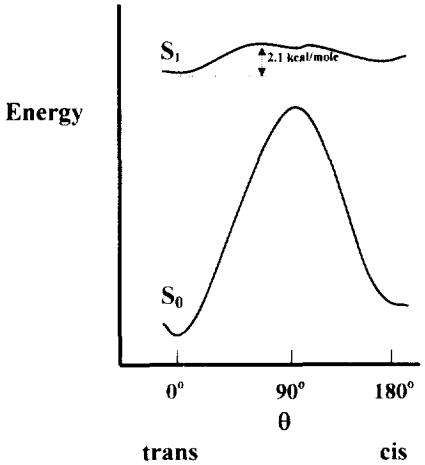


Fig. 5. Schematic representation of potential energy surfaces for the ground and lowest excited singlet states of APzE as a function of the torsional angle (θ) about the ethenic bond.

inverse but small temperature dependence of $\Phi_{c\to t}$ and Φ_f of *c*-APzE implies very low activation barrier for *cis* → *trans* photoisomerization, as found for 9-APE [13]. Photoisomerization proceeds via an excited singlet state in polar solvent as suggested above. In toluene, while Φ_f remains constant, $\Phi_{c\to t}$ of *c*-APzE is slightly increased from 253 K to 293 K but slightly decreased above 293 K. Decomposition reaction such as polymerization seems to compete with photoisomerization above 293 K. This is in agreement for singlet/triplet mixed mechanism for photoisomerization in nonpolar solvent as suggested above.

Schematic representation of potential energy surfaces for the ground and lowest excited singlet states of APzE as a function of the torsional angle (θ) about the ethenic bond is shown in Fig. 5. For the parent hydrocarbon, 9-APE [11,12], the lowest excited singlet state has anthracenic nature but not ethenic. As a consequence, the activation barrier against twisting of ethenic bond is so high (17.8 kcal/mol [11]) that *trans* → *cis* photoisomerization of 9-APE is inhibited and only *cis* → *trans* isomerization, i.e., one-way photoisomerization, is observed both in nonpolar and polar solvent. In APzE, the low-lying n,π^* state changes the excited singlet state surface toward low activation barrier (ca. 2.1 kcal/mol) for *trans* → *cis* photoisomerization. Intramolecular charge transfer between pyrazinylethene and anthracene moieties overcomes the restriction against rotation in the excited singlet state and a shallow minimum at ca. 90° is expected as shown in Fig. 5. As a result, two-way photoisomerization is observed in APzE.

4. Nomenclature

APzE	1-(9-Anthryl)-2-(2-pyrazinyl)ethene
9-APE	1-(9-Anthryl)-2-phenylethene
n-APyE	1-(9-Anthryl)-2-(*n*-pyridyl)ethene

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