

PHOTOCYCLIZATION REACTION OF 1-(9-ANTHRYL)-2-(n-PYRIDYL)ETHENE (n=2, 4) AND 1-(9-ANTHRYL)-2-(2-PYRAZINYL)ETHENE

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Abstract – *trans*-1-(9-Anthryl)-2-(*n*-pyridyl)ethene (*t-n*-APyE, *n*=2 or 4) and *trans*-1-(9-anthryl)-2-pyrazinylene (*t*-APzE) exhibits solvent-dependent fluorescence and efficient *trans*→*cis* photoisomerization. Photochemical reactivities of *t*-2-APyE, *t*-4-APyE, and *t*-APzE have been investigated in nonpolar and polar solvents. In nonpolar solvent, parallel photocyclization reaction occurs very efficiently in competition with the fluorescence and photoisomerization. But, in polar solvent, photocyclization was not observed. It is probably due to the stabilization of charge separated state in polar solvent, which is an intermediate in photoisomerization reaction.

INTRODUCTION

Generally, 1,2-diarylethenes are well-known to undergo *cis* ⇌ *trans* photoisomerization.¹⁻⁵ However, it has been reported in early 1980's that 1,2-diarylethenes containing large aromatic nuclei such as anthryl group carried out one-way photoisomerization.⁶⁻⁸ The photophysical and photochemical behaviors of 1-(*n*-anthryl)-2-phenylethenes (*n*-APE, *n*=1, 2, and 9) have been extensively studied for recent two decades.⁹⁻¹⁴ 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 lowest excited states of the *cis* isomers of 1,2-diarylethenes are generally characterized by a fast *cis* → *trans* photoisomerization rate due to the absence of sizeable barriers in the potential energy curve as a function of the twisting coordinate. The only photoprocess competitive with isomerization in S₁ is dehydrocyclization to polycyclic aromatic hydrocarbons and in some cases, S₁→T₁ intersystem crossing.¹⁻⁵

In the case of 9-APE, photocyclization has also been reported.^{13,15} While the photocyclization of *c*-9-APE is very efficient in nonpolar solvent, photocyclization is very inefficient in polar solvent.

During the study of the photophysical and photoisomerization behavior of some aza derivatives of 9-APE,¹⁶⁻¹⁸ the interesting solvent dependency of fluorescence properties and photoreactivity have been observed. We report here the importance of a side photoreaction, which is thought to be pho-

tocyclization, in the deactivation pathways of the S₁ state in nonpolar solvents.

MATERIALS AND METHODS

Materials For spectroscopic measurements and photochemical reactions, *n*-hexane and acetonitrile of HPLC grade (Merck) were used. Quinine sulfate (Aldrich), standard for fluorescence quantum yield measurement, was purified by recrystallization from water. Kiesel Gel 60 (70-230 mesh, Merck) was used for silica gel column chromatography. All other chemicals are used as received. *trans*-1-(9-Anthryl)-2-(*n*-pyridyl)ethenes (*t-n*-APyE, *n*=2 or 4)¹⁷ and *trans*-1-(9-anthryl)-2-pyrazinylene (*t*-APzE)¹⁸ have been prepared as reported previously.

Spectroscopic measurements The absorption spectra were recorded on a Hitachi U-321097 spectrophotometer. Aminco-Bowman Series 2 luminescence spectrometer was used for steady state fluorescence studies. Excitation wavelength at 360 nm for steady-state fluorescence was employed. Experimental details for measurements of quantum yields of fluorescence and photoisomerization were described previously.¹⁷

Photoirradiation Photolyses were conducted at 350 nm for *t*-2-APyE with Southern New England Rayonet Photochemical Reactor RPR 100 equipped with RMA-500 Merry-Go-Round Unit and sixteen RPR 3500 Å fluorescent lamps.

The HPLC analysis of solution of *t*-2-APyE irradiated at 350 nm shows the formation of two photoproducts. One is photoisomerization product, *c*-2-APyE, and another is photocyclization product.

The irradiated solution was concentrated in vacuo and was chromatographed on silica gel using dichloromethane/*n*-hexane as eluents. Fractions were evaporated and dried under vac-

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Table 1. Absorption and fluorescence spectral data of photocyclization product, *trans*, and *cis* isomers of 2-APyE^{16,17} in acetonitrile in comparison with those of 9-APE.^{9-11,13,15}

compound	λ_a , nm	λ_f , nm	Φ_f	τ_f , ns	k_f , s ⁻¹
9-APE cycl. ^a	315, 331, 347, 364, 384	393, 416, 440, 471	0.06	12	5×10^6
<i>t</i> -9-APE	285, 298, 332, 350, 368, 385	476	0.45	4.3	1×10^8
<i>c</i> -9-APE	332, 350, 368, 388	469	0.05	0.13	3.8×10^8
2-APyE cycl.	357, 376, 395	404, 428, 450, 487, 519	0.05	-	-
<i>t</i> -2-APyE	256, 289, 334, 350, 368, 389	487	0.08	0.9	0.9×10^8
<i>c</i> -2-APyE	286, 334, 352, 370, 389	487	0.02	-	-

^aIn CH₃CN-H₂O

uum. Photocyclization product was characterized by ¹H-NMR, absorption and fluorescence spectral data. ¹H-NMR(CDCl₃) δ 8.83 (1H, anthracene H10), 6.78-7.82 (14H, anthracene and pyridine H), 5.75 (d, J=11 Hz, 1H, central 7-membered ring H), 5.45 (d, J=11 Hz, 1H, central 7-membered ring H).

RESULTS AND DISCUSSION

The photoisomerization of aza-derivatives of 1-(9-anthryl)-2-phenylethene has been a major research subject in our laboratory.¹⁶⁻¹⁹ We reported previously the photophysical properties and photoisomerization behavior of 1-(9-anthryl)-2-(*n*-pyridyl)ethenes^{16,17} and 1-(9-anthryl)-2-pyrazinylethene.¹⁸ The $\Phi_{c \rightarrow t}$ values of *c*-2-APyE, *c*-4-APyE, and *c*-APzE are relatively high in all the solvents tested, whereas the $\Phi_{t \rightarrow c}$ values of the *trans* isomers are very low in nonpolar solvents and increase with increasing solvent polarity. On irradiation of *n*-APyE and APzE in most solvents, photoreaction is simple and only *t* \rightarrow *c* photoisomerization is observed. In *n*-hexane, photoreaction seems to be complicated. In *n*-hexane, the $\Phi_{c \rightarrow t}$ values of *c*-2-APyE, *c*-4-APyE, and *c*-APzE as well as $\Phi_{t \rightarrow c}$ values of the *trans* isomers are very low due to competition with the photocyclization reaction. In order to look deep into these interesting solvent effect on the photoreactivity of some aza derivatives of 9-APE, further investigation was accomplished.

The HPLC analysis of dilute solutions of some aza derivatives of 9-APE (*t*-2-APyE, *t*-4-APyE, and *t*-APzE) in *n*-hexane, irradiated at room temperature, evidenced the formation of two photoproducts: a *trans* isomer and a photocyclization product.

The yield of photocyclization product is markedly dependent on the nature of the solvent. In fact, this yield for all the compounds studied is very high in *n*-hexane, but on going

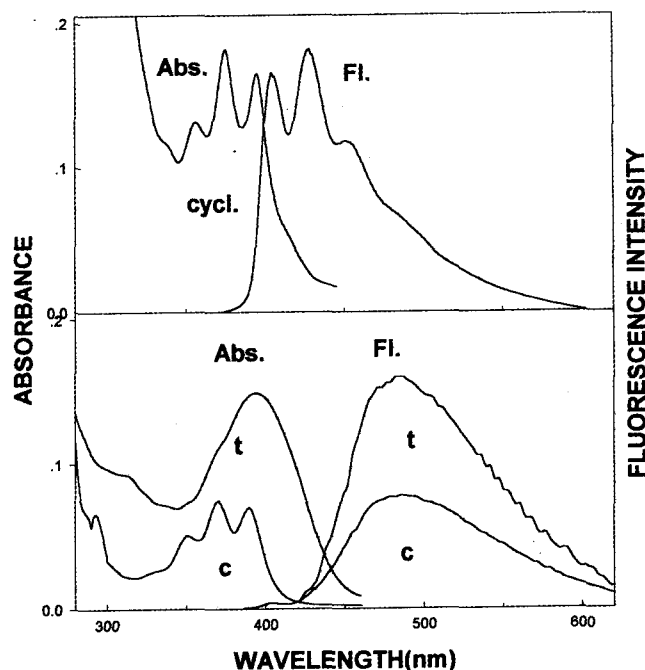


Figure 1. Absorption (left) and fluorescence (right) spectra of photocyclization product (top), *t*- and *c*-2-APyE (bottom) in acetonitrile.

to more polar solvents remarkably reduced and decreased to zero in THF.

Figure 1 shows the absorption and fluorescence spectrum of photocyclization product of *t*-2-APyE in comparison with those of *t*-2-APyE and *c*-2-APyE. The absorption and fluorescence spectra of photocyclization product shows an anthracene-like vibronic structure and a small Stokes shift, an indication of a non-flexible molecule with a preserved anthracene structure, whereas the absorption and fluorescence spectra of *t*-2-APyE and *c*-2-APyE are broad. Table 1 shows the absorption and fluorescence spectral data of photocyclization product, *trans*, and *cis* isomers of 2-APyE^{16,17} in acetonitrile in comparison with those of 9-APE.^{9-11,13,15} The absorption maxima of photocyclization product of 2-APyE in acetonitrile are 357, 376, 395 nm and very similar to those of 9-APE.¹⁵ The fluorescence maxima (404, 428, 450, 487, 519 nm) and quantum yield (0.05) of photocyclization product of 2-APyE in acetonitrile are also very similar to those of 9-APE.¹⁵

Photocyclization and photoisomerization efficiencies of *n*-APyE¹⁷ and APzE¹⁸ in *n*-hexane and acetonitrile are compared with those of 9-APE¹⁵ and are shown in Table 2. In *n*-hexane, 2-APyE, 4-APyE, and APzE as well as 9-APE undergo no *t* \rightarrow *c* photoisomerization and only a photocyclization product is observed. But, in acetonitrile, any side photoreaction for 2-APyE, 4-APyE, and APzE was not observed and only the efficient *t* \rightarrow *c* and *c* \rightarrow *t* photoisomerization occurs. In acetonitrile, 9-APE shows very inefficient *t* \rightarrow *c* photoisomerization and photocyclization is also inefficient, but only efficient *c* \rightarrow *t* photoisomerization occurs.

Table 2. Photocyclization and photoisomerization efficiencies of 9-APE,¹⁵ n-APyE¹⁷ and APzE¹⁸ in n-hexane and acetonitrile.

compound	n-hexane			CH ₃ CN		
	$\Phi_{c \rightarrow cycl}$	$\Phi_{t \rightarrow c}$	$\Phi_{c \rightarrow t}$	$\Phi_{c \rightarrow cycl}$	$\Phi_{t \rightarrow c}$	$\Phi_{c \rightarrow t}$
9-APE	0.27 ^a	<0.01 ^a	0.19 ^a	0.045	0.003	0.41
2-APyE	0.25	~0	0.13 ^b	~0	0.44	0.19
4-APyE	0.23	~0	0.27 ^b	~0	0.37	0.21
APzE	0.20	0.07	0.31 ^b	~0	0.20	0.25

^a in MCH-3MP^b in toluene.

In summary, photocyclization quantum yields for 2-APyE, 4-APyE, and APzE are very high in n-hexane, but on going to more polar solvents remarkably reduced and is practically zero in acetonitrile. On the contrary, t → c photoisomerization quantum yields for 2-APyE, 4-APyE, and APzE are nearly zero or very low in n-hexane, but greatly enhanced in acetonitrile. These are summarized in Figure 2.

On the singlet energy surfaces of 2-APyE, 4-APyE, and APzE, photoisomerization and photocyclization are competitive processes. Photocyclization, which is expected to occur in locally excited state, is observed only in n-hexane. However, t → c photoisomerization, which is thought to occur via intramolecular charge transfer state, is completely inhibited in n-hexane but becomes more efficient in polar solvents.

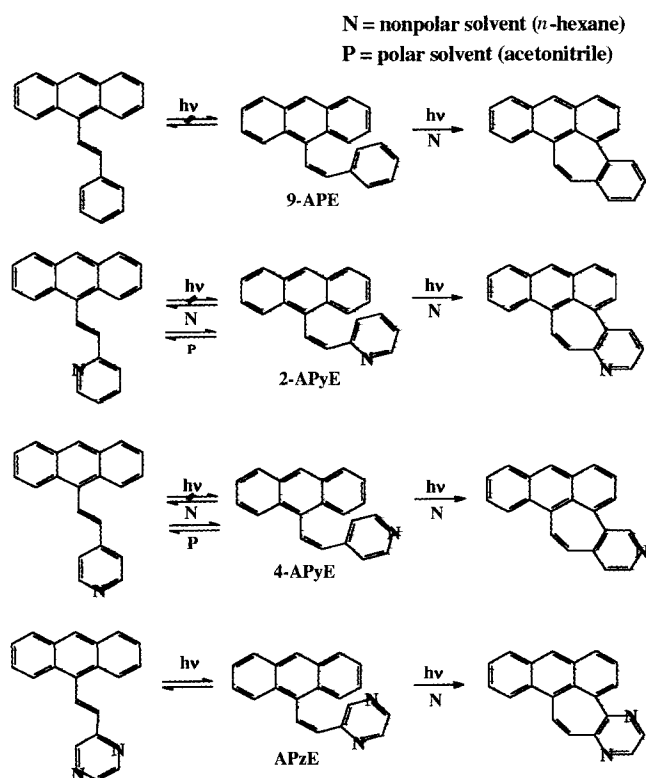


Figure 2. Photocyclization and photoisomerization of 9-APE and some aza derivatives of 9-APE in n-hexane and acetonitrile.

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