CIS-TRANS PHOTOISOMERIZATION OF 4-(2-(9-ANTHRYL)VINYL)PYRIDINE; AN AZA ANALOGUE OF 1-(9-ANTHRYL)-2-PHENYLETHYLENE

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Abstract — The quantum yields of fluorescence (Φ_f) and *trans* → *cis* photoisomerization ($\Phi_{t \to c}$), trans-4-(2-(9-anthryl)vinyl)pyridine, an aza analogue of 1-(9-anthryl)-2-phenylethylene, were measured in several solvents at room temperature. Φ_f and $\Phi_{t \to c}$ are 0.38 and < 0.01 in hexane and 0.02 and 0.38 in acetonitrile, respectively. As solvent polarity decreases, $\Phi_{t \to c}$ strongly reduced, whereas Φ_f strongly increased. A singlet mechanism of *trans* → *cis* photoisomerization is suggested since $\Phi_{t \to c}$ and Φ_f change in opposite direction.
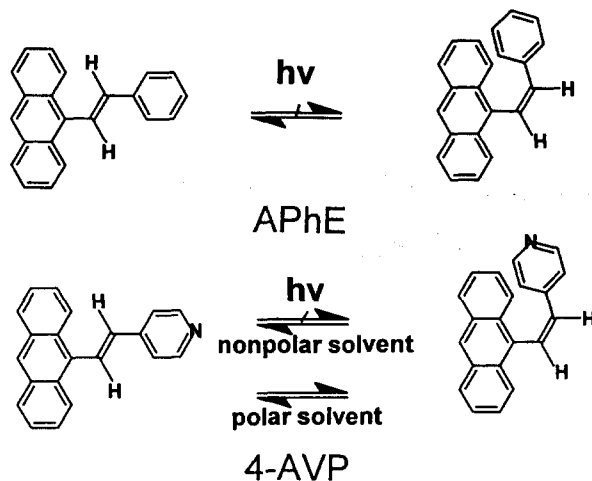
INTRODUCTION

It is well recognized that stilbenes and other similar 1,2-diarylethylenes undergo mutual photochemical isomerization between the *cis* and *trans* isomers through a perpendicularly twisted geometry.[1-9] Recently, several groups have reported examples of one-way photoisomerization from *cis-* to *trans-*isomers or from *trans* - to *cis-*isomers, in contrast to the traditional two-way mode occurring mutually between the two isomers. It is revealed that the modes of isomerization (one-way or two-way) depend on the electronic structure of aromatic substituents on the olefins[10-15] and intramolecular hydrogen bonding.[16,17]

Substitution of aromatic ring with lower excited state energy than anthracene on 1,2-diarylethylenes leads to one-way *cis* → *trans* photoisomerization.[10]

Trans-1-(n-anthryl)-2-phenylethylenes (*trans*-n-APhEs, n=1,2, and 9) exhibit fluorescence and intersystem crossing with substantial quantum yields(Φ_f and Φ_{isc}),[8,10,18-22] but in contrast to other 1,2-diarylethylenes,[1,2] they accomplish very inefficient *trans* → *cis* photoisomerization.[20,21] For 9-APhE, the quantum yield of *trans* → *cis* photoisomerization($\Phi_{t \to c}$) is less than 0.02 in cyclohexane or acetonitrile,[20,21] but the quantum yield of *cis* → *trans* photoisomerization($\Phi_{c \to t}$) of n-APhEs is rather high,[10-12,20,21] the term "one-way" photoisomerization has been used.[10-12]

Introduction of electron accepting or electron donating substituents, such as formyl, phenylsulphonyl, methyl, or methoxy to the *para*-position on the phenyl group of 9-APhE does not lead to a marked increase of $\Phi_{t \to c}$ in nonpolar solvents.[14,20-22] In slightly and strongly polar media, however, *trans* → *cis* photoisomerization is no longer forbidden;$\Phi_{t \to c}$ is strongly increased at the expense of Φ_f and Φ_{isc}.[14] For these 9-APhE derivatives, a triplet route of *trans* → *cis* photoisomerization was excluded.[14]

The photochemistry of aza analogues of 1,2-diarylethylenes have received attention[8,23,24] because the n, π* states introduced by the heteroatom markedly affect the photochemical and photophysical behavior of the compounds by the vibronic perturbation between close-lying π, π* and n, π* states in the lowest excited states.[25,26] The question is now raised whether it is possible to open the pathway

APhE

4-AVP

of *trans* → *cis* photoisomerization by introducing N heteroatom in 9-APhE, as in the effect of substituents. In the present paper, fluorescence and *trans* → *cis* photoisomerization of *trans*-4-(2-(9-anthryl) vinyl)pyridine (t-4-AVP), an aza-derivative of 9-APhE, were investigated.

MATERIALS AND METHODS

Materials. 9-Anthraldehyde, 4-picoline, piperidine, and iodomethane (Aldrich) were used as received. For spectroscopic measurements and photochemical reactions, ethyl ether, ethyl acetate, acetonitrile, ethanol, and methanol of HPLC grade were used and dichloromethane and THF were freshly distilled from P_2O_5 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 silical gel TLC grade 7749 (Aldrich) were used for silica gel column chromatography and thin layer chromatograpy, respectively.

Spectroscopic measurements. ^1H and ^{13}C NMR spectra were obtained on 60 MHz Hitachi R-1200 spectrometer and Bruker AM-200 in chloroform-d or acetone-d_6 or DMSO-d_6 with tetramethylsilane as an internal standard. UV-VIS spectra were recorded on a Hitachi U-321097 spectrophotometer. IR spectra were obtained in KBr pellets on Shimadzu IR-435 spectrometer. FT-IR spectra were recorded on Bomem MB-100 spectrometer. Mass spectra were obtained on Hewlett Packard 5985A GC/MS system by electron impact method.

Fluorescence spectra were recorded on SLM-AMINCO SPF-500C spectrophotofluorometer at room temperature. The absorbance of the solution at the exciting wavelength was less than 0.1 and all the fluorescence spectra were corrected for determination of the fluorescence quantum yields. The fluorescence quantum yields were determined by three independent measurements using quinine sulfate in 0.1 N H_2SO_4(Φ_f =0.55 at 295 K) as standard by following relationship;[27]

$$\Phi_f{}^{sample} = \frac{I_f{}^{sample} \, A_{standard} \, n^2{}_{sample}}{I_f{}^{standard} \, A_{sample} \, n^2{}_{standard}} \, \Phi_f{}^{standard}$$

where Φ_f represents fluorescence quantum yield, I_f is area integrated under corrected fluorescence spectra, A is absorbance at the exciting wavelength, and n is refractive index of solvent.

Photoisomerization quantum yield measurements. The photoisomerization quantum yields were determined by three independent experiments at room temperature under conditions in which the incident light was totally absorbed (3×10^{-4} *M* solution). The solutions of 3 mL in Pyrex test tubes (1.5x10 cm) sealed with septa were deaerated by bubbling with Ar gas for 30 minutes and then irradiated in a merry-go-round apparatus with a Hanovia 450 W medium pressure mercury arc lamp (type 697A36). The irradiation wavelength of 366 nm was isolated using CS 7-37 Corning glass filter and aqueous

$CuSO_4$ solution ($CuSO_4$.5H$_2O$ 5 g/water 100 mL) filter circulated through jacketed quartz photochemical reactor with circulated water bath. Irradiations were carried out to up to 10% conversion to prevent appreciable back reaction. Light intensities were measured by ferrioxalate actinometry.[28] Quantitative analyses for the *trans* → *cis* photoisomerization reaction were carried out by GC or HPLC at flow rate of 3 mL/min using methanol as eluent. GC was carried out with Hewlett-Packard 5890 GC. HPLC was accomplished with Spectra-Physics ODS-1 or Waters μ-Bondapak C_{18} analytical column on a Spectra-Physics SP8810-010 liquid chromatograph eqipped with SP8810 precision isocratic pump.

Synthesis. t-4-AVP were prepared by the reported procedures.[29] 1,4-Dimethylpyridinium iodide : Excess iodomethane (about 0.6 mL, 10 mmol, 2 equiv.) was added dropwise into 10 mL dichloromethane solution of 4-picoline (0.5 mL, 5 mmol). The solution was stirred at room temperature for 1 h and then evaporated dichloromethane and excess iodomethane in vacuo. A pale yellow solid was obtained with about 100% yield. ^1H NMR ($CDCl_3$+acetone-d_6): δ 9.21 (d, H2,6, J=6.42 Hz), 7.98 (d, H3,5, J=6.42 Hz), 4.62 (s, N-Me), 2.70 (s, 4-Me) ppm.

Trans-1-methyl-4-(2-(9-anthryl)vinyl)pyridinium iodide (t-4- MAVP) : A mixture of 9-anthraldehyde (1 g, 4.85 mmol), 1,4 -dimethylpyridinium iodide (1.14 g, 1 equiv.), and piperidine (0.4 g, 1 equiv.) in absolute ethanol (20 mL) was heated at 60°C under N$_2$ atmosphere for 1 h and cooled. Bright orange microcrystals were filtered out and washed with a few milliliters of cooled absolute ethanol. The yield was about 90%. ^1H NMR (DMSO-d_6): δ 9.13-9.10 (d, H2,6), 8.70-8.64 (m, H1′,8′), 8.70-8.64 (d,H7, $^3J_{trans}$=17 Hz), 8.53 (s, H10′), 8.18-8.14 (d, H3,5), 8.08-8.04 (m, H4′,5′),7.60-7.50 (m, H2′,3′ ,6′,7′), 7.18-7.12 (d, H8, $^3J_{trans}$=17 Hz), 4.65 (s,N-Me) ppm. IR (cm^{-1}): 1638s, 1610s, 1185m, 990m, 890 m, 840 m, 820 m, 730 s, 500s. UV-VIS (CH_2Cl_2): λ_{max} 253.2 (ϵ 151,500), 28 5 (19,400), 350 (5,800), 365.0 (7,400), 385.0 (6,500), 480 (4,700) nm.

Trans-4-(2-(9-anthryl)vinyl)pyridine(t-4-AVP) : A mixture of t-4-MAVP (1.9 g, 4.49 mmol) and triphenylphosphine (4.7 g, 4 equiv.) in dimethylformamide (20 mL) was refluxed for 12 h. The resulting mixture was evaporated to dryness under vacuum. The desired product was isolated in 60% yield after column chromatography on silica gel using dichloromethane as eluent. The resulting yellow solid was recrystallized in a hexane/ acetone mixture. ^1H NMR ($CDCl_3$):δ 8.69-8.67 (m, H2,6), 8.44 (s, H10′), 8.24-8.30 (m, H1′ , 8′), 8.11-8.19 (d, H7, $^3J_{trans}$= 16.5 Hz), 8.00-8.07 (m, H4′,5′), 7.53-7.54 (m, H3,5), 7.45-7.52 (m, H2′,3′ ,6′,7′) 6.88-6.95 (d, H8, $^3J_{trans}$ =16.5 Hz) ppm. ^{13}C NMR ($CDCl_3$): δ 150.1, 149.3, 134.5, 131.9, 131.7, 131.6, 131.4, 131.1, 131.0, 129.6, 129.3, 129.1, 128.6, 128.4, 128.1, 127.0, 126.9, 125.8, 125.7, 125.2, 125.0 ppm. Mass (m/e): 113, 126, 140, 203, 281(M$^+$). IR(cm^{-1}): 1590 s, 1410 s, 990 m, 980 m, 890 s, 830 m, 780 m, 730 s. UV-VIS (CH_2Cl_2): λ_{max} 258.4 (ϵ 116,400), 335.2 (12,100), 354 (23,300), 371.2 (35,900), 390.8 (38,100), 460 (sh 1,407) nm.

Cis-4-(2-(9-anthryl)vinyl)pyridine(c-4-AVP) : t-4-AVP (0.1 g, 0.36 mmol) was dissolved in absolute methanol of 300 mL (1.2x10⁻³ *M*) and irradiated at 350 nm for 2 h after the solution was degassed by bubbling with N₂ gas for 30 min. Preparative photochemical reactions were performed at 350 nm with Southern New England Rayonet Photochemical Reactor RPR 100 equipped with RMA-500 Merry-Go-Round Unit and sixteen RPR 3500 Å fluorescent lamps. c-4-AVP was separated by silica gel column chromatography or preparative TLC using ethyl acetate-hexane (1:2,v/v) as eluent. c-4-AVP was carefully handled in the dark room because it is very sensitive to exposure of light. ¹H NMR (CDCl₃): δ 8.51-8.53 (m, H2,6), 8.21 (s, H10′), 8.10-8.13 (d, H7, ³J$_{trans}$=6.2 Hz), 8.00-8.13 (m, H1′ ,4′ ,5′ ,8′ ,),7.38-7.50 (m, H2′ ,3′ ,6′ ,7′), 7.11-7.13 (m, H3,5), 6.93-6.87 (d, H8, ³J$_{trans}$=6.2 Hz) ppm. Mass (m/e): 113, 126, 140, 203, 281 (M⁺). UV-VIS (CH₂Cl₂): λ$_{max}$ 257.6 (ε 34,900), 336.4 (sh, 719), 354.4 (1,337), 370.4 (1,925), 391.2 (1,926), 465 (sh 202) nm.

RESULTS AND DISCUSSION

The absorption spectra of t- and c-4-AVP are structured and appear at similar region, but the absorption of *trans* isomer is less structured and much more intense than *cis* isomer (see Experimental and Figure 1). They exhibit vibrational structure which characterizes the absorption spectrum of the anthracene chromophore. The absorption spectrum did not significantly change with solvents. As in the parent APhE, the structured absorption spectrum of *cis* isomer is distinguishable from the broad one of *trans* isomer.
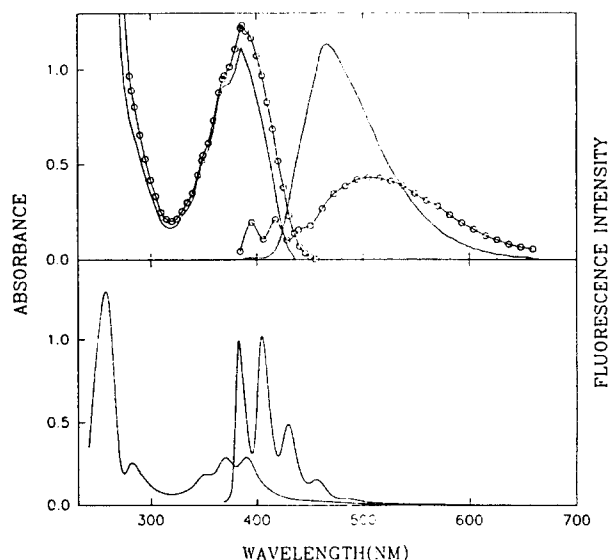
Fluorescence spectra of t- and c-4-AVP at the

Figure 1. UV Absorption (left) and Fluorescence (right) Spectra t-4-AVP(upper) in Hexane (—) and MeOH (-o-) and c-4-AVP (lower) in Dichloromethane (—).

excitation wavelength of 360 nm are shown in Figure 1. The shape of the spectrum is significantly changed with solvents. For t-4-AVP, the broad fluorescence spectrum is observed in nonpolar solvent, in contrast to the absorption spectrum. As solvent polarity increases, anthracene-like structured peaks in shorter wavelength becomes intense with markedly reducing total intensity. This indicates that the anthracene system and the vinylpyridine moiety of t-4-AVP are less conjugated in polar solvent than in nonpolar solvent.

Therefore, t → c photoisomerization in nonpolar solvent is expected to become inefficient in order to avoid the loss of resonance stabilization. Fluorescence spectrum of c-4-AVP (λ$_f$ = 382, 404, 428, 455, 486 nm in CH₂Cl₂) appears similar to that of anthracene but greatly differs from that of t-4-AVP, and broad band observed in t-4-AVP disappears. The fluorescence quantum yield of c-4-AVP is very low (ca.0.09). Therefore, c-4-AVP is suggested to get less conjugation between the anthracene nuclei and the vinylpyridine moiety with more sterically hindered unstable structure than t-4-AVP, and then easily isomerize upon irradiation. Indeed, it is known that the conjugation of the anthracene system with the styryl moiety in the t-APhE isomer as a consequence of their less constrained molecular geometry is borne out in the partial loss of fine structure in absoption spectrum. X-ray structure analyses of crystalline c- and t-APhE reveal that the angles between the plane of the anthracene and the plane of the ethylene double bond are as 79° and 66°, respectively.[20]

The fluorescence maxima (λ$_f$), fluorescence quantum yields (Φ$_f$), and photoisomerization quantum yields (Φ$_{t→c}$) of t-4-AVP in various solvents are summarized in Table 1. The *trans* and *cis* isomers are stable at room temperature in the dark.Φ$_f$ and Φ$_{t→c}$ are strongly affected by solvent polarity in contrast to the parent t-APhE. Φ$_{t→c}$ of t-APhE is virtually zero independently of solvent polarity.[13] Φ$_f$ and Φ$_{t→c}$ of t-4-AVP are 0.38 and < 0.01 in hexane and 0.02 and 0.38 in acetonitrile, respectively. As solvent polarity decreases, Φ$_{t→c}$ strongly reduced, whereas Φ$_f$ strongly increased. Photoisomerization of t-4-AVP is very inefficient in n-hexane as in the case where the parent APhE undergoes the c → t one-way isomerization, but in modeately or strongly polar solvent photoisomerization is no longer inhibited.

The singlet mechanism of *trans* → *cis* photoisomerization is also suggested as reported in the parent t-4-APhE[14,22], since Φ$_{t→c}$ and Φ$_f$ change in opposite direction.

At the photostationary state, dependence of the ratios of c- to t-4-AVP (% *cis*) on solvent polarity are

Table 1. Solvent effect on the fluorescence wavelength maxima and quantum yields and the photoisomerization quantum yields for t-4-AVP[a] and t-APhE[b].

solvent $E_T(30)^c$	t-4-AVP			t-APhE		
	λ_f(nm)	Φ_f	$\Phi_{t\cdot c}$	λ_f(nm)	Φ_f	$\Phi_{t\cdot c}$
hexane 30.9	467	0.38	<0.01			
toluene 33.9	480	0.25	0.04	478	0.45	<0.02
THF 37.4	395,415,480	0.10	0.25			
EtOAc 38.1	395,415,480	0.07	0.33			
CH_2Cl_2 41.1	395,420,480	0.04	0.44	478	0.40	-
CH_3CN 46.0	395,417,495	0.02	0.38	476	0.45	0.003
EtOH 51.9	395,417,505	0.01	0.46	474	0.44	<0.02
MeOH 55.5	393,415,511	0.01	0.30			

[a]At room temperature, excitation wavelength was 360 nm for fluorescence measurements. The argon-saturated solution at room temperature was used for photoisomerization with irradiation wavelength of 366 nm. [b]Taken from ref. 14. [c]Dimroth's empirical solvent polarity parameter.

shown in Figure 2. The similar results are obtained as in the case of $\Phi_{t\cdot c}$. The % cis at the photostationary state is very low (7.1%) in n-hexane, increases upto that of dichloromethane. The values are similar in more polar solvent than in dichloromethane. Upon 366 nm irradiation of t-4-AVP, the % cis reaches upto ca 57% in polar solvent (methanol). In viscous ethanol, some deviation is observed. The efficiency of photoisomerization of t-4-AVP is substantial in all solvents extept in nonpolar solvents. In nonpolar solvent such as n-hexane, 4-AVP isomerizes virtually via one-way mode as in the parent APhE, whereas two-way mode is possible for the photoisomerization in polar solvent.
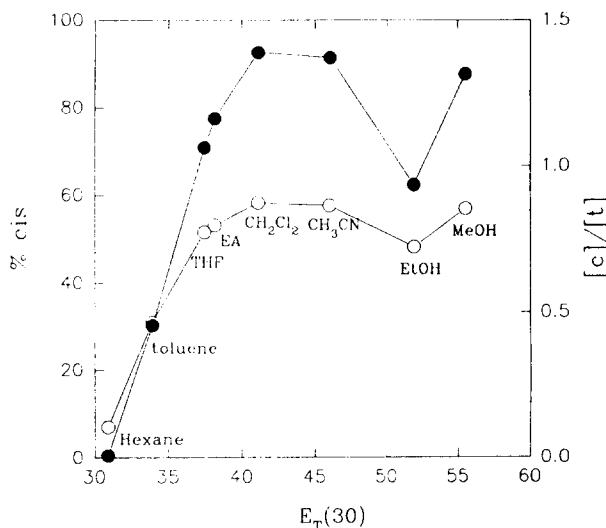

Figure 2. Solvent effect on photoisomerization of t-4-AVP : %cis (-o-) ; [c]/[t] at the photostationary state.

Independently of 366 nm irradiation of t- or c-4 AVP, the same photostationary state which is favoured by the cis isomer is reached. In dichloromethane, the % cis is 58% and 59% when starting from trans isomer and starting from cis isomer respectively, indicating no side product. However, on prolonged irradiation, the compound decomposes.

4-AVP is an isomerizing 1,2-diarylethylene in both one-way and two-way modes even at room temperature, depending on the environment, whereas the parent APhE carries out only one-way isomerization. It is suggested that n, π^* state introduced by N atom in 4-AVP causes a significant change in the potential energy profile of the excited states.

Further mechanistic investigations for the photoisomerization of 4-AVP and comparative studies on someother aza analogues of APhE are now in progress in our laboratory.

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