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Photoisomerizable DNA Ligands. Photoisomerization of Anthrylvinylpyridinium Derivatives

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Two potential DNA intercalators capable of cis→trans isomerization, 9-[2-(N-methylpyridinium-4-yl)vinyl]anthracene (**1**) and 9,10-bis [2-(N-methylpyridinium-4-yl)vinyl] anthracene (**2**), have been prepared, characterized and their spectral and photoisomerization behavior have been studied. Both ligands exhibit low fluorescence quantum yields in aqueous solution and substantial enhancement of emission in the presence of DNA. Two-way isomerization was observed for **1**, while trans→cis process appeared to be inefficient for ligand **2**. An intramolecular charge transfer excited state was suggested to explain the differences in spectral behavior and photoisomerization of ligands.

Key words: anthrylvinylpyridinium ligands, DNA, fluorescence, intercalator, photoisomerization

There is a considerable current interest in the photophysics and photochemistry of supramolecular systems containing electronically coupled photoactive parts for energy- and electron transfer processes [1,2]. The semirigid structure of a DNA duplex makes it an attractive organized medium for the creating such photochemical reaction systems. Recently, we have shown, that 1,4-bis[2-(1-methylpyridinium-4-yl)vinyl]benzene (pMPVB) organized on the DNA can undergo photoisomerization [3,4]. Moreover, DNA affected this process due to the preferences in binding affinity towards particular isomers [4]. The ability of the DNA duplex to behave as an efficient organized medium for cis-trans isomerization has been further explored on a supramolecular system consisting of pMPVB and $Ru(phen)_3^{2+}$ both assembled on the DNA. The ligand underwent one way cis→trans isomerization induced by the electron transfer from the photoexcited Ru complex [5]. These results prompted us to design new dyes containing an extended aromatic rings system that could impose steric hindrance on the isomerization. With regards to this goal, ligands possessing the anthracene moiety appear to be appealing, since beside expected steric effects, anthracene exhibits intriguing photochemical behavior and plays an important role in

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the energy transfer processes [6]. When the anthryl group substitutes one of phenyl rings in stilbene, neither one of the two isomers can be coplanar with the central ethylene bond, hindrance being relieved by twisting about the quasi-single bonds [7,8]. Thus, incorporation of an anthracene unit as a central part of distilbazolium dye should result in distortion of its planar geometry and may affect DNA binding properties of the ligand as well as the photoisomerization process. Upon intercalation, ligand should be interlocked in DNA matrix, due to the twisting of vinylpyridinium arms and the DNA complex is expected to be kinetically stable, similarly as threading intercalators [9].

In this paper we describe the synthesis, spectral properties and photoisomerization of two anthrylstilbazolium ligands.

EXPERIMENTAL

Materials: Preparation of 9-[2-(N-methylpyridinium-4-yl)vinyl]anthracene iodide (1): A mixture of 3.76 g (16 mmol) of N-methyl-4-picolinium iodide and 3.10 g (16 mmol) of 9-anthraldehyde in 50 ml of ethanol was heated under reflux for 22 h with piperidine (few drops) as a catalyst. After being cooled to room temperature, the precipitate was collected by filtration, washed with hot diethyl ether, and dried under reduced pressure. The crude crystalline product was dissolved in ethanol, worked up with charcoal, and recrystallized from ethanol. Yield 26%; m.p. 257°C. Found: C, 61.74; H, 3.99; N 3.28; I, 28.85%. Calcd. for $C_{22}H_{18}NI$: C, 62.37; H, 4.25; N, 3.31; I, 30.00%. ^{1}H NMR (250 MHz, DMSO-d_6): δ_H 4.34 (3H, s, N^+Me), 7.34 (1H, d, J = 16.8 Hz, H-vinylic), 7.61 (4H, dd, anthryl H-2,3,6,7), 8.18 (2H, d, anthryl H-4,5), 8.38 (2H, d, anthryl H-1,8), 8.52 (2H, d, J = 6.4 Hz, pyridyl H-3,5), 8.72 (1H, s, anthryl H-10), 8.96 (1H, d, J = 16.2 Hz, H-vinylic), 9.00 (2H, d, J = 6.5 Hz, pyridyl H-2,6).

Preparation of 9,10-bis [2-(pyridine-4-yl)vinyl]anthracene (2a): A mixture of 1.68 g (5 mmol) of 9,10-dibromoanthracene, 1.33 g (12.5 mmol) of 4-vinylpyridine, 0.06 g (0.26 mmol) of palladium diacetate, 0.06 g (2 mmol) of tri-o-tolylphosphine, and 10 ml of dry triethylamine was heated at 100–110°C for 72 h under argon in a capped Pyrex tube. The cooled reaction mixture was diluted with water and chloroform (all solids dissolved), the organic phase was separated, and the aqueous layer was extracted with $CHCl_3$ (2×100 ml). Combined organic extracts were washed with water (100 ml) and dried over anhydrous $MgSO_4$. Evaporation of the solvent and crystallization from chlorobenzene gave 0.33 g of product (17%); m.p. 298–300°C. ^{1}H NMR (250 MHz, $CDCl_3$): δ_H 6.90 (2H, d, J = 16.5 Hz, H-vinylic), 7.53 (8H, m, anthryl + pyridyl H), 8.17 (2H, d, J = 16.5 Hz, H-vinylic), 8.32 (4H, m, anthracene H), 8.69 (4H, d, J = 4.6 Hz, pyridyl H-2, H-2′).

Preparation of 9,10-bis[2-(N-methylpyridinium-4-yl)vinyl]anthracene ditriflate (2): Dicationic ligand was prepared by the reaction of methyl trifluoromethanesulfonate (triflate) with **2a** in $CHCl_3$. The precipitate was filtered and recrystallized from methanol/hexane mixture. Yield 62%; m.p. >300°C. Found: C, 53.59; H, 3.69; N, 3.88%. Calcd. for $C_{32}H_{26}N_2F_6S_2O_6$: C, 53.92; H, 3.67; N, 3.93%. ^{1}H NMR (250 MHz, DMSO-d_6): δ_H 4.34 (6H, s, N^+Me), 7.30 (2H, d, J = 16.5 Hz, H-vinylic), 7.65 (4H, dd, anthryl H-2,3,6,7), 8.41 (4H, dd, anthryl H-1,4,5,8), 8.51 (4H, d, J = 6.5 Hz, pyridyl H-3,3′,5,5′), 8.94 (2H, d, J = 16.5 Hz, H-vinylic), 8.99 (4H, d, J = 6.4 Hz, pyridyl H-2,2′,6,6′).

Calf thymus DNA (CT-DNA) was purchased from Sigma and was used without further purification. All the experiments were conducted in HEPES buffer (10 mM 2-[4-(2-hydroxyethyl)-1-piperazinyl]ethanesulfonic acid, pH 7.2). Sodium chloride was added to obtain the desired salt concentration. A Milli-Q filtered water (Millipore Co.) was used throughout.

Measurements: ^{1}H NMR spectra were recorded on Bruker AC250P, or Varian Mercury 300 spectrometers operating at 250 and 300 MHz , respectively, using tetramethylsilane (TMS) as an internal standard. Absorption spectra were recorded with Specord M40 (Jena), or Hitachi U-3300 spectrophotometers equipped with a SPR 10 temperature controller. Steady state fluorescence measurements were carried out

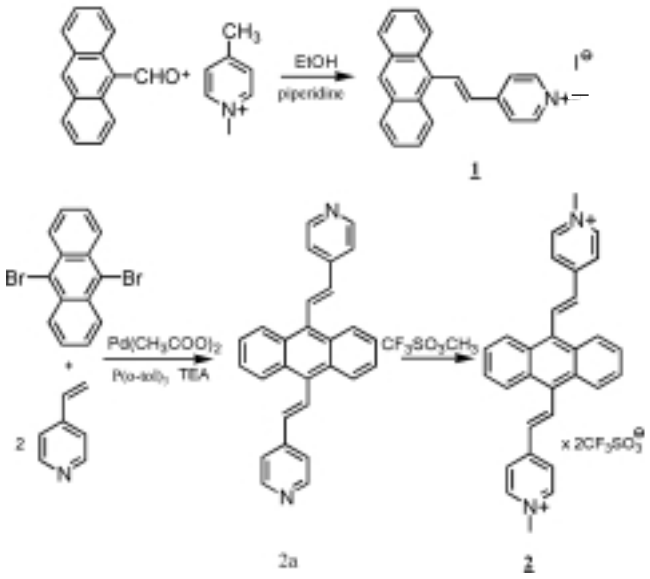
using Shimadzu RF5000, or Hitachi F4500 spectrofluorimeters with excitation and emission band widths of 5 nm. Cell compartments were thermostated at 25°C. All measurements were carried out using 10 mm quartz cell, and the spectra were corrected at 280–600 nm range using Rhodamine B as a photon counter (a microprocessor operated correction mode).

Photoisomerization experiments. An aqueous dye solution (30 μM) was irradiated in the thermostated (25°C) cell compartment of spectrofluorimeter equipped with a 150 W Xe lamp at a selected wavelength. Nitrogen was purged through solution during irradiation and absorption spectra were recorded at desired time intervals. Alternatively, the progression of photoisomerization was controlled with a LaChrom HPLC system (Merck/Hitachi) that enabled the separation of cis and trans isomers of both dyes as described previously [3].

RESULTS AND DISCUSSION

Synthesis: Monosubstituted anthryl derivative **1** as a trans isomer was obtained by the conventional aldol condensation (Scheme 1), and although synthesis of this compound and its non-methylated analog have been reported before [10], the corresponding cis isomer was isolated and characterized for first time. To our knowledge, there are no literature reports on second ligand, 9,10-bis[2-(N-methylpyridinium-4-yl)vinyl]anthracene (**2**). Two-step synthesis route is outlined in Scheme 1. A Heck-type reaction [11] of dibromoanthracene with 4-vinylpyridine catalyzed by palladium diacetate in the presence of tris(o-tolyl)phosphine afforded the free base **2a** that was subsequently quaternized with methyl trifluoromethane sulfonate in good yield. Less efficient quaternization agents (MeI and dimethylsulfate) gave a mixture of mono- and dimethylated products.

Scheme 1



Both ligands gave satisfactory elemental analysis and were characterized by ^{1}H NMR and IR spectroscopies. They are fairly soluble in methanol and DMSO, whereas solubility in water is modest. Dyes are stable as solids and their stock solutions in DMSO (1 mM) do not decompose for several weeks when protected from light.

Spectral properties: The freshly prepared solutions of anthrylvinylpyridinium dyes **1** and **2** contained more than 95% of trans isomer as indicated from HPLC analysis and ^{1}H NMR (the coupling constant of vinyl protons was 16.5 Hz, characteristic for derivatives of trans-stilbene). Upon exposure to visible light, a mixture of isomers was obtained that could be separated by HPLC giving for both ligands only two isomers, E and Z for **1**, and E,E and E,Z for **2** (abbreviated hereafter simply as trans and cis, respectively). The electronic absorption spectra of particular isomers are shown in Figure 1 and their spectral characteristics are collected in Table 1. All dyes exhibit strong absorption band at *ca*. 255 nm (λ^1_{max}) classified as $S_0 \rightarrow S_3$ transition of anthryl moiety [12] and a broad long wavelength band in the visible region (λ^2_{max}) corresponding to a charge transfer (CT) transition from anthracene unit to the pyridinium ring [13]. Isosbestic points (λ_{iso}) were detected at 378 and 402 nm for **1** and **2**, respectively. Attachment of second vinylpyridinium arm (ligand **2**) resulted in a bathochromic shift and hyperchromicity of the visible band (Fig. 1, Tab. 1) that indicate enhanced conjugation of π-electronic system. Similar features were reported for 1,4-distilbazolium dye [3]. Twisted conformation of cis isomer disturbs in efficient π-electron conjugation that results in a blue shift and hypochromicity of this band that is typically observed for many diarylethenes [14]. Interestingly, in case of *cis* **1**, beside a broad band at 430 nm, a new absorption band emerged in the 340–390 nm range (Fig. 1) that possesses vibronic structure, characteristic for anthracene chromophore. Such spectral changes support the weakening of conjugation between anthryl chromo-

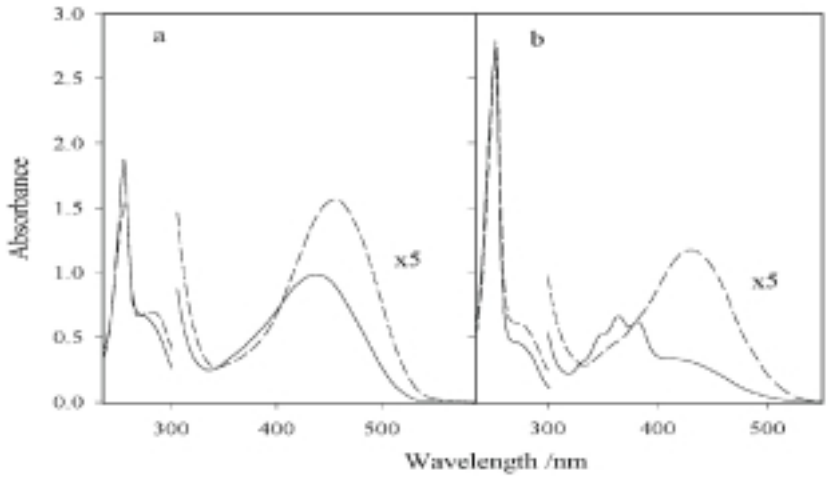


Figure 1. Absorption spectra of cis (solid line) and trans (broken line) isomers of ligand **2** (a) and **1** (b). Conditions: [ligand] = 20 μM, [NaCl] = 50 mM, HEPES buffer (10 mM, pH 7.2).

phore and vinylpyridinium system and were reported also for other anthrylethylene derivatives [13,15–17]. On the contrary, the spectrum of *cis* **2** shows no signs of anthryl chromophore, and only broad CT absorption band is observed.

Table 1. Spectral properties of the isomers of anthrylvinylpyridinium ligands.

ligand	λ^1_{max}/nm [$\varepsilon\times10^4$/M^{-1} cm^{-1}]	λ^2_{max}/nm [$\varepsilon\times10^4$/M^{-1} cm^{-1}]	λ_{iso}/nm [$\varepsilon\times10^4$/M^{-1} cm^{-1}]
trans **1**	253 (14)	432 (1.17)	378 (0.59)
cis **1**	253 (13.5)	366 (0.66)	378 (0.59)
trans **2**	256 (7.7)	457 (1.57)	402 (0.72)
cis **2**	256 (9.2)	437 (0.99)	402 (0.72)

The differences in spectral behavior of *cis* **1** and *cis* **2** can be explained in terms of the structural features of both ligands. Figure 2 shows optimized structures of all isomers and in Table 2 are given their optimized equilibrium geometries. Computations were carried out by PM3 method (CAChe, Fujitsu). There are no significant differences in the geometries of particular conformations between ligands **1** and **2**. The trans geometries are generally in good agreement with the published structures of metal complexes containing trans 9-anthrylvinylpyridine ligand, obtained by X-ray diffraction [18,19]. The computed values of dihedral angles between anthracene-ethylene and pyridine-ethylene for trans conformations are 29.4 and 2.17° for **1** (37.6 and 0.5° for **2**), while their experimental values are 39.5 and 0°, respectively [18]. Thus, in trans conformations the pyridinium ring is almost coplanar with the ethylenic bond, contrary to anthracene moiety that is twisted markedly. Isomerization of one vinylpyridinium arm in ligand **2** appeared to have no effect on the structure of the second arm, which retains its trans conformation with unchanged geometry (Fig. 2, Tab. 2). Since anthracene remains conjugated with this vinylpyridinium arm, the spectral properties of cis **2** should resemble those of *trans* **1** (*cis* **2** and *trans* **1** possess

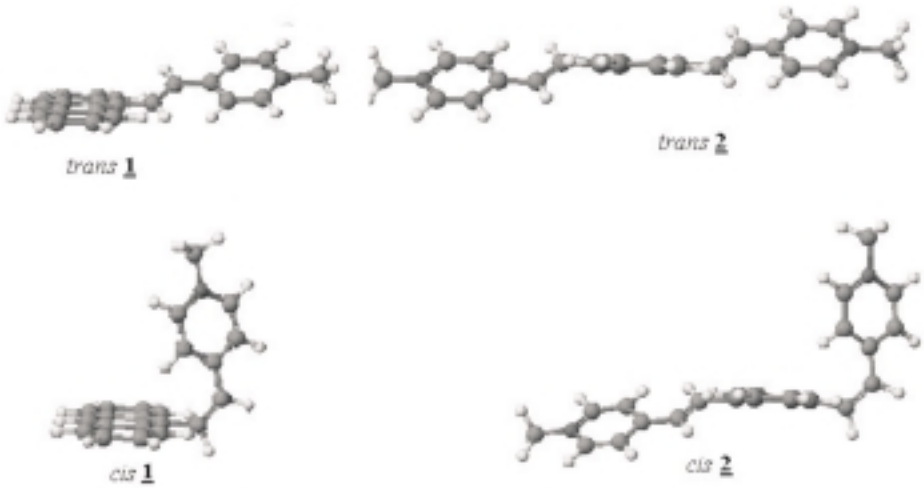
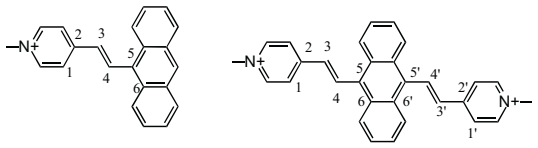


Figure 2. CAChe-generated optimized structures of cis and trans isomers of ligands **1** and **2**.

similar chromophore) that agrees with experimental data (Fig. 1). The observed changes in dihedral angles and in the lengths of double bonds confirm the weakening of π-electron conjugation in cis conformation. Trans configurations are thermodynamically more stable as expected (ΔE = 2.4 and 4.2 kcal/mole for **1** and **2**, respectively).

Table 2. Geometries of the anthrylvinylpyridinium derivatives in trans and cis conformations optimized by the semiempirical PM3 calculations (CAChe).



	R[1] [Å]			υ[2] [°]			E[3] [kcal mol^{-1}]
	2–3 (2′–3′)	3–4 (3′–4′)	4–5 (4′–5′)	1–2–3–4 (1′–2′–3′–4′)	2–3–4–5 (2′–3′–4′–5′)	3–4–5–6 (3′–4′–5′–6′)	
trans **1**	1.43	1.36	1.44	2.2	176.8	29.4	256.2
cis **1**	1.45	1.34	1.47	31.0	1.6	86.3	258.6
trans **2**	1.45	1.35	1.46	0.5	177.0	37.6	484.1
	(1.45)	(1.35)	(1.46)	(–0.41)	(–177.0)	(–37.5)	
cis **2**	1.45	1.34	1.47	34.7	1.9	89.9	488.3
	(1.45)	(1.35)	(1.46)	(–1.07)	(–174.7)	(–34.5)	

[1]interatomic distance; [2]dihedral angle; [3]optimized potential energy.

The solutions of dyes in DMSO and MeOH showed minor bathochromic shift of bands when compared to aqueous solutions. Neither new absorption bands nor significant deviation from linearity of calibration graphs were observed, which suggested that these anthryl derivatives exist in aqueous solution and in organic solvents as monomers and do not undergo aggregation (such a process is common in case of fused aromatic heterocyclic drugs [20,21]).

The fluorescence spectra of the ligands are shown in Fig. 3. Both dyes exhibit a broad weak emission band at *ca*. 600 nm (cis and trans isomers showed similar emission), however, ligand **1** exhibits a much lower fluorescence quantum yield. The large Stokes shifts (165 and 155 nm for **1** and **2**, respectively) indicate substantial difference between ground and excited state geometries [22]. In the presence of CT DNA an enhancement of emission was observed for both ligands (Fig. 3). The enhancement factor depended on the ligand/DNA ratio and approaches a value about 10 at high DNA concentration. The position and shape of emission band were not affected by the presence of DNA. The enhancement of fluorescence may be explained by the protection of the dye from the rotational deactivation (isomerization) or by the effect of lower polarity of DNA microenvironment. The quantum yield of fluorescence was re-

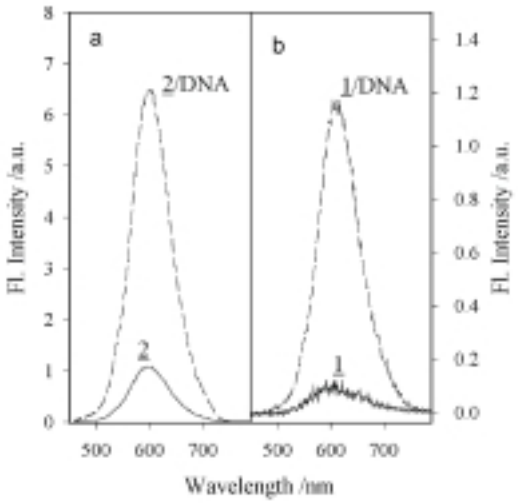


Figure 3. Fluorescence emission spectra of aqueous solution of ligands **1** and **2** in the absence (solid line) and the presence of DNA (broken line). Conditions: [ligand] = 10 μM, [DNA] = 140 μM, [NaCl] = 50 mM, HEPES buffer (10 mM, pH 7.2), λ_{ex} = 470 nm.

ported to be very sensitive to the polarity of solvent for 9-anthrylvinylpyridines [13,17] and for 9-anthrylstyryl derivatives possessing electron donating or accepting groups [15,23]. The excited state with intramolecular charge separation has been proposed as explanation of large Stokes shift and very low quantum yield of fluorescence for these compounds [17,23]. Thus, both dyes can be regarded as examples of such excited state charge transfer systems since vinylpyridinium moiety possesses electron accepting property [17]. It should be noted that bisvinylpyridinium derivative **2** shows remarkable higher fluorescence efficiency and a bit smaller Stokes shift that suggests lower charge transfer properties of its excited state compared to ligand **1**. That sounds reasonable when one considers the effect of the second vinylpyridinium arm which decreases the electron donating properties of the anthracene unit.

Photoisomerization: Upon irradiation with monochromatic light, the absorption spectra of aqueous solutions of *trans* **1** and *trans* **2** change gradually, showing hypochromicity and a blue shift of long wave absorption bands as shown in Figure 4. Clear isosbestic points suggest only a two-component equilibrium in good agreement with HPLC analysis where two isomers were detected. There is a distinct difference in photoisomerization when one compares spectral changes of both ligands (Fig. 4). Contrary to ligand **2**, which shows only modest changes in the absorption spectrum with time of irradiation, the monosubstituted derivative **1** exhibits a significant hypochromicity. Moreover, the spectrum of final isomeric mixture of **1** at the photostationary state (pss) resembles that of cis isomer alone (Fig. 1b and Fig 4a) and indicates a very high degree of conversion of trans isomer. Reverse changes in ab-

sorption spectrum were observed upon irradiation the isomeric mixture at shorter wavelength (λ = 365 nm). On the other hand, rather modest changes in absorbance for ligand **2** (Fig. 4b) suggest an inefficient isomerization and low content of cis isomer at a pss, although isomerization was also reversible when the sample was irradiated at 380 nm.

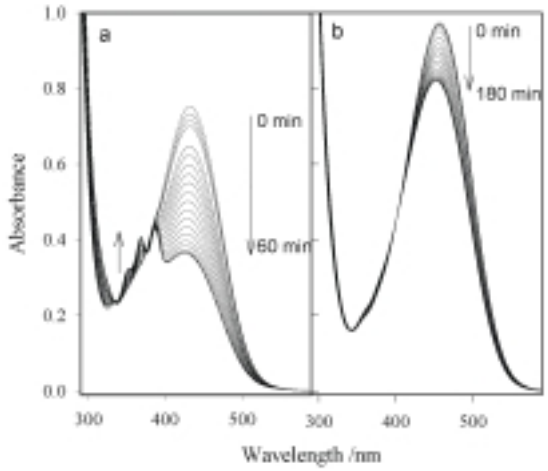


Figure 4. Photoisomerization effect on the absorption spectra of *trans* **1** (a) irradiated at 450 nm and *trans* **2** (b) irradiated at 480 nm. Total irradiation time was 60 and 180 min for **1** and **2**, respectively. Conditions: [ligand] = 6.3 μM, [NaCl] = 50 mM, HEPES buffer (10 mM, pH 7.2).

Determination of quantum yields of isomerization was carried out by the method of Gauglitz [24] using the following equation:

$$\phi_{TC} = \left\{ \left[\left(A_1^{\neq} \frac{A_2 - A_{pss}}{A_2 - A_1} - A_2^{\neq} \frac{A_1 - A_{pss}}{A_2 - A_1} \right) \ln\left(\frac{A_1 - A_{pss}}{A_2 - A_{pss}} \right) \right] + (A_1^{\neq} - A_2^{\neq}) \right\} / Q$$

where A_1, A_2, and A_{pss} are absorbances at time t_1, t_2, and at *pss*, respectively, $A^{\neq} = A/(1 - 10^{-A})$, $Q = I_0 \Delta t(\varepsilon_T + \varepsilon_C \phi_{CT}/\phi_{TC})/v$ with ε being molar absorptivities of respective isomers, v – the volume of the irradiated sample, $\phi_{TC}/\phi_{CT} = ([cis]/[trans]) \times (\varepsilon_C/\varepsilon_T)$, and I_0 – the light flux intensity at the wavelength of irradiation (Es s^{-1}) determined by potassium ferrioxalate actinometry [25].

The results of calculations are collected in Table 3. The values of *pss* for respective ligands vary with the wavelength of irradiation, whereas quantum yields of isomerization are wavelength independent in accordance with the fundamental relationship *pss* = ([*cis*]/[*trans*]) = $(\varepsilon_T/\varepsilon_C) \times (\phi_{TC}/\phi_{CT})$. Thus, isomerization at shorter wavelengths, where cis isomer has higher molar absorptivity compared to that of trans, gives lower values of the photostationary states. The quantum yields of cis→trans isomerization are comparable for both ligands (0.32 and 0.27 for **1** and **2**,

respectively) contrary to ϕ_{TC} which is lower for **2** by a factor of ~2.5 compared to that for ligand **1**. Very low ϕ_{TC} for ligand **2** suggests one-way type isomerization, whereas photoreaction of ligand **1** can be regarded as two-way process. However, the conventional two-way mechanism that has been reported for stilbenes and azastilbenes should be rather excluded for ligand **1** since it cannot explain the observed differences in the isomerization of both ligands. Such a mechanism operates for planar compounds, which undergo photoisomerization *via* a perpendicular state in which the central double bond is twisted by 90° [14]. Then, the excited perpendicular state, which is at a minimum on the excited singlet potential energy surface, undergoes internal conversion to the ground perpendicular state from which both trans and cis ground state isomers are produced. It should be noted that trans isomers of stilbenes and azastilbenes have planar structure and excitation energy is mainly localized on the ethylenic bond, while larger aryl groups like anthracene preclude planar ground state conformations due to steric repulsion (Fig. 2). Moreover, lowest excited states become more localized on the anthracene group that may change completely the photoisomerization pathways. Taking into account the spectral properties and differences in photoisomerization quantum yields of vinylpyridinium ligands, an isomerization mechanism, that involves charge separation character of excited singlet state, seems to be more plausible. Similar explanation of the isomerization behavior has been proposed for anthrylstyrenes containing electron-donating and -accepting substituents [21]. There have been shown that certain polar groups in the para position of styryl ring facilitate trans→cis photoisomerization [15,16,23,26–30]. As postulated by Goerner [23], the locally excited singlet state (^{1}t*) subsequently relaxes to a charge transfer singlet state (A*) that twists to a perpendicular state (^{1}p*). Next, ^{1}p* undergoes internal conversion to the trans and cis ground state isomers. The ^{1}t* state is responsible for the emission, but does not undergo isomerization. The fluorescence deactivation pathway competes with the relaxation into the charge transfer state (A*), which deactivates by isomerization. Consequently, the charge transfer nature of excited state implies an inverse relationship between the fluorescence and the isomerization quantum yields with solvent polarity [15,23,29]. On the other hand, the parent compound 9-styrylanthracene does not undergo trans→cis isomerization irrespective to solvent polarity [15,26]. One-way cis→trans isomerization of this ligand has been explained by mechanism that assumes the excited singlet state without charge transfer character and different shape of excited state potential energy surface with no minimum for perpendicular conformation that results in an adiabatic isomerization [26]. Excitation of the cis isomer generates the excited trans isomer directly by twisting the central ethylenic bond by 180° in the excited cis conformation (no energy barrier across the excited perpendicular state) [27].

Although isomerization studies for ligands **1** and **2** were carried out in aqueous solution exclusively, the enhancement of the fluorescence intensity observed in the presence of DNA (microenvironment with lower polarity [31]) supports plausibility of charge transfer character of excited singlet state for these ligands. This character is more pronounced for ligand **1**, which exhibits clear two-way isomerization and very

low fluorescence quantum yield in aqueous solution. On the other hand, the very low value of ϕ_{TC} for ligand **2** suggests substantially lower charge transfer properties of its excited state, that resembles behavior of unsubstituted 9-styrylanthracene. The replacement of a phenyl ring in 9-styrylanthracene by pyridinium group must enhance the polarity of the excited state of ligand **1** and thereby quantum yield of trans→cis isomerization. The ϕ_{TC} of ligand **2** is not enhanced, thus efficiently in accordance with the expected lower polar character of the excited state, since second vinylpyridinium arm in 10-position of anthracene lowers the electron donating properties of anthracene moiety, thus diminishes the charge transfer character of excited singlet state of ligand **2**.

Table 3. Photoisomerization data of anthrylvinylpyridinium derivatives: pss (photostationary state composition), ϕ_{TC}, ϕ_{CT} (quantum yield of trans→cis and cis→trans photoisomerization).

Compound	λ_{irr} [nm]	$\varepsilon_{cis}\times10^4$ [M^{-1} cm^{-1}]	$\varepsilon_{trans}\times10^4$ [M^{-1} cm^{-1}]	pss[1)]	ϕ_{TC}/ϕ_{CT}	ϕ_{TC}	ϕ_{CT}
1	450	0.24	1.03	2.47	0.57	0.18	0.32
	365	0.66	0.38	0.37	0.62	0.21	0.32
2	480	0.58	1.30	0.63	0.28	0.075	0.27
	380	0.51	0.43	0.22	0.26	0.07	0.27

[1)] *pss* = [*cis*]/[*trans*].

Isomerization equilibria are expected to change dramatically in the presence of DNA, therefore, anthrylvinylpyridinium ligands could be applied as a polarity probe for DNA microenvironment. Further investigations, including DNA binding studies, are in progress.

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