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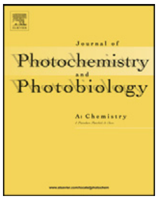

Photochemistry and DNA-affinity of some stilbene and distyrylbenzene analogues containing pyridinium and imidazolium iodides

C.G. Fortuna [a], U. Mazzucato [b], G. Musumarra [a], D. Pannacci [b], A. Spalletti [b,*]

[a] Dipartimento di Scienze Chimiche, Università di Catania, 95125 Catania, Italy
[b] Dipartimento di Chimica, Università di Perugia, 06123 Perugia, Italy

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ABSTRACT

The relaxation properties of the excited states of some trans-1,2-diarylethene analogues (where one aryl group is a methylpyridinium or dimethylimidazolinium group and the other one is a π-excessive furyl or pyrrolyl group) and two all-trans-distyrylbenzene analogues (where the central ring is a methylpyridinium group and the side rings are furyl or methylpyrrolyl groups) have been investigated in buffered (pH 7) aqueous solutions. The compounds of the diarylethene series generally undergo efficient trans → cis photoisomerization while the yield of the radiative deactivation is very small at room temperature. The corresponding distyrylbenzenes display small yields of radiative/reactive pathways and mainly deactivate by internal conversion. The solvent effect on the spectral behaviour indicates the occurring of intramolecular charge transfer ("push–pull" compounds) which can induce interesting non-linear optical properties.

Some experiments on the interactions with DNA, which might affect the cell metabolism, showed a modest binding affinity for the compounds with one ethenic bond and two aromatic rings. The complexation constant increases substantially in compounds with two ethenic bonds (three aromatic rings) and in the halogen-substituted compounds. The formation of ligand–DNA complexes affects only slightly the competition of the radiative/reactive relaxation from the lowest excited singlet state.

1. Introduction

As well known for stilbene-like molecules, trans isomers of styrylpyridinium salts are generally very sensitive to UV irradiation rapidly isomerizing to a cis/trans (Z/E) equilibrium mixture. 1,2-Diarylethenes where one aryl group is a π-excessive pentatomic group acting as a donor (D) and the other one is a π-deficient pyridinium group acting as an acceptor (A), separated by an ethene bridge (E), have been described to behave as push–pull (D–E–A) systems displaying interesting intramolecular charge transfer (ICT) properties, useful for applications in optoelectronics [1]. They can also form complexes with DNA [2], possibly affecting the cell metabolism, thus being of interest for potential antitumor activity [2–4].

In principle, the peculiar properties of the quaternized azastilbenes and azadistyrylbenzenes are expected to affect the photobehaviour of the corresponding neutral molecules. Previous studies (often carried out in surfactant assemblies for microenvironment characterization [5]) were mainly concerned with the 4-styryl-substituted pyridinium cations [6]. The radiative relaxation of these molecules is generally very scarce (with yields <1%), slightly increasing in a polar solvent and reaching high values, close to 1, in rigid matrices at low temperatures only. The photoreactivity (trans-cis isomerization, dimerization, association) strongly depends on the experimental conditions (substituents at the phenyl group, nature of the anion, solvent and temperature) [6]. Conductivity measurements on some iodides have indicated that the compounds are fully dissociated in polar solvents at low concentration [7]. In these conditions the photoisomerization quantum yields of 1-methyl-4-styrylpyridinium iodide is $\sim$50% (little affected by substituents and nature of the anion), a maximum value expected for the diabatic mechanism. In fact, similarly to the neutral molecules, the cations are assumed to isomerize by this common mechanism implying a twisting around the ethenic bond towards an energy minimum at the perpendicular configuration (perp, at about 90°), followed by a $S_1 \rightarrow S_0$ internal conversion (IC) or $T_1 \rightarrow S_0$ intersystem crossing (ISC) and relaxation to the ground-state cis and trans isomers in roughly a 1:1 branching ratio. The photoreaction can be thus schematized: $^{1,3}\text{trans}^* \rightarrow {}^{1,3}\text{perp}^* \rightarrow {}^{1}\text{perp} \rightarrow \alpha\,{}^{1}\text{cis} + (1-\alpha)\,{}^{1}\text{trans}$, where the partitioning factor α is assumed to be $\sim$0.5 in most cases [8] (it has to be noted that the recent literature prefers to describe the radiationless processes at the perp region as conical intersections [9]). In dilute solutions the trans isomers of the cations were

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[*] Corresponding author. Tel.: +39 075 5855575; fax: +39 075 5855598.
E-mail address: faby@unipg.it (A. Spalletti).

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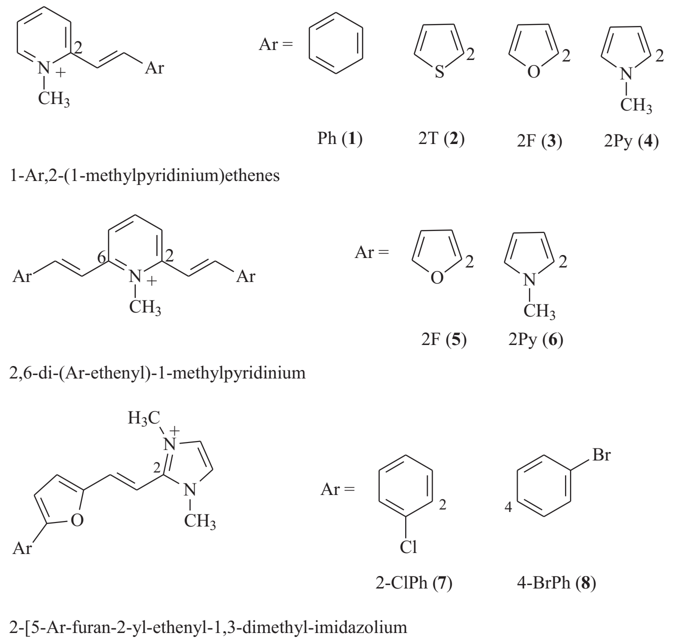


Scheme 1. Trans cations of the iodide salts investigated (cations **2** and **4** were studied in a previous work [10] and here reported for comparison).

found to generally isomerize in the singlet manifold, unless the substituent induces a significant triplet population [6].

In a previous paper we investigated some trans-1-heteroaryl-2-(1-methylpyridinium-2-yl)ethene iodides where the heteroaryl group was a thienyl, Br-thienyl or pyrrolyl group [10]. In the present work we extend the photophysical and photochemical investigation to some 1,2-diarylethenes where one aryl group is a pyridinium or imidazolinium iodide and the other one is a phenyl, a furan-2-yl or a 5-Ar-furan-2-yl (with Ar = *o*-Cl- or *p*-Br-phenyl) group. The behaviour of two distyrylbenzene analogues with a central 2,6-substituted pyridinium group and side furan-2-yl and pyrrol-2-yl groups was also studied. Aim of this work was to study the competitive relaxation processes of the lowest excited states of these compounds, examining also the occurring of ICT processes. For some of them, the reactive trans/cis process was found to prevail whereas internal conversion is the dominant deactivation for others and the radiative pathway is generally very scarce.

It was also interesting to measure their binding affinity towards DNA. When these salts bearing one or more isomerizable double bonds are associated to DNA, their photobehaviour (isomerization quantum yield and photostationary state, pss, composition) may change significantly because of the different binding affinity of DNA towards the trans or cis geometrical isomer [2]. The results obtained on the interaction between DNA and the six salts here investigated showed a modest binding affinity for the pyridinium derivatives with one ethenic bond and two aromatic rings. The complexation constant increased substantially in compounds with two ethenic bonds (three aromatic rings) and in the halogen-substituted compounds. The changes in the competition of the radiative/reactive relaxation from the lowest excited singlet state induced by the formation of ligand–DNA complexes were also investigated.

2. Experimental

The trans isomers investigated (compounds **3** and **5**–**8** in Scheme 1) have been synthesized at the Catania laboratory. The synthesis, spectroscopic characterization as well as preliminary *in vitro* antitumor tests have been reported elsewhere [3,4,11]. The styryl compound (**1**) was prepared at the Perugia laboratory by quaternization of *E*-2-styrylpyridine, synthesized for previous works by standard procedures [12]. The compounds **2** and **4**, reported in a previous paper [10], are included in Scheme 1 for comparison. The cis isomers were obtained by UV irradiation and separated by semi-preparative HPLC using a Phenomenex Jupiter C18, 250 × 21.2 mm, 10 μm, column. The photophysical and photochemical behaviour was studied in buffered (ETN) water at pH 7.0. Some measurements were also carried out in acetonitrile (MeCN) from Fluka and chloroform (CH) from J.T. Baker.

Perkin-Elmer Lambda 800 and Varian Cary 4E spectrophotometers were used for the absorption measurements. The fluorescence spectra were measured in dilute solutions (absorbance <0.1 at the excitation wavelength, λ_{exc}) by a Spex Fluorolog-2 F112AI spectrofluorimeter. The emission quantum yields were determined at λ_{exc} corresponding to the maximum of the first absorption band (λ_{max}) using 9,10-diphenylanthracene in cyclohexane as fluorimetric standard ($\phi_F = 0.90$ in de-aerated solvent [13]). For photochemical measurements (potassium ferrioxalate in water as actinometer), a 150 W high pressure xenon lamp coupled with a monochromator was used. The trans → cis photoreaction (solute concentrations $\sim 10^{-4}$ M) was monitored by HPLC using a Waters apparatus equipped with an analytical (Phenomenex Jupiter C18; 250 × 4.6 mm, 5 μm) column and a UV detector. Water/MeCN mixtures were used as eluents. The monitoring wavelength was at the isosbestic point. The conversion percentage was held at below 8% to avoid the competition from the back photoreaction. The photostationary state (pss) composition, shifted towards the cis isomer for the compounds with one double bond, was found to be reversed for **5** and **6** with two isomerizable double bonds. The [cis]/[trans] ratio at pss was very low and made rather difficult the measurements of the quantum yields of the direct ($\phi_{t\rightarrow c}$) photoprocess of these two compounds. In the case of **6**, it prevented to isolate the cis isomer; its yield was then evaluated from the pss composition at the isosbestic point through the relationship $[\text{cis,trans}]/[\text{trans,trans}] = (\varepsilon_{\text{trans,trans}}/\varepsilon_{\text{cis,trans}}) \times (\phi_{\text{trans,trans}\rightarrow\text{cis,trans}}/\phi_{\text{cis,trans}\rightarrow\text{trans,trans}})$. The quantum yields reported in Table 2 for **6** have to be taken with caution.

Fluorescence lifetimes (obtained for compound **5** only, owing to the very low emission yields of the others) were measured by a Spex Fluorolog-τ2 apparatus, based on the phase modulation technique.

All measurements were carried out in de-aerated solutions by purging with nitrogen. The parameters reported in the Tables are averages of at least three independent experiments with mean deviations of *ca.* 15% and 10% for fluorescence and photoisomerization quantum yields, respectively. The uncertainty of the latter is higher for **6** (see above). Other details on the experimental measurements are reported elsewhere [14].

The tests on the binding of the ethenic compounds to salmon DNA (from Sigma–Aldrich) were carried out by measuring the changes of the absorption spectra under successive additions of an aqueous buffered (ETN, 0.01 M NaCl, pH 7.0) solution of DNA to an initial $\sim 2 \times 10^{-5}$ M concentration of ligand in the same buffer. The complexation constants (K) were obtained by absorption/concentration plots according to the equation of McGhee and von Hippel [15]. The experiments, repeated at least two times, also varying in some cases the monitoring wavelength, had a reproducibility within 30% owing to the rather small changes in absorbance and additional errors associated to corrections for dilution.

Theoretical calculations of the electronic spectra, conformational equilibria [16] and heats of formation of the cations (see Appendix A) were carried out using the HyperChem computational package (version 7.5). The computed transition energies and oscillator strengths were obtained by ZINDO/S using optimized geometries (according to PM3 method) with 9 × 9 configuration interaction.

Table 1
Spectral properties of the iodide salts **1**–**8** in buffered (ETN) water and solvatochromic properties [red-shift from water (W) to chloroform (Ch)].

Compound	λ_{ab}^{max} in W (nm)	λ_{F}^{max} (nm)	Stokes shift (cm^{-1})	λ_{ab}^{max} in Ch (nm)	$-\Delta\lambda_{(Ch-W)}$ (cm^{-1})
1	333	440	7300	347	1210
2	365[a]	480[a]	6560	382	1220
3	367	460	5510	384	1210
4	412[a]	510[a]	4660	442	1650
5	402	530	6010	421	1120
6	447	585	5280	483	1670
7	359	458	6020	372	970
8	368	470	5900	380	860

[a] From Ref. [10].

3. Results and discussion

3.1. Spectral properties

The spectral data of the six compounds investigated are collected in Table 1 while Fig. 1 shows their absorption spectra in buffered (ETN) water. After a careful check, some λ_{ab}^{max} values in Table 1 were now corrected with respect to those previously reported [4a,11]. Replacement of the phenyl group of **1** by pentatomic groups leads to a net red-shift of the absorption/emission spectra (see Section 3.4). An even higher bathochromic shift was observed for compounds with two ethenic bonds, two side donor groups and a central acceptor group (D–E–A–E–D, **5** and **6**).

No sign of dimerization or association was observed in the dilute solutions examined. The computed spectral properties (see Appendix A Supplementary Data) were in reasonable agreement with the experimental positions and intensities of the absorption bands. In all compounds, the first band corresponds to a π,π^* HOMO → LUMO electronic transition with partial CT character.

As to the very weak fluorescence spectra, a strong Stokes shift with respect to the corresponding absorption bands was observed, indicating that the emitting state has a relaxed geometry rather different from that of the Franck–Condon state reached by absorption. Contrary to the absorption spectrum, which shifts to the blue, the emission spectrum does not shift or shifts slightly to the red in polar solvents. This behaviour points to an excited state of very small dipole moment in agreement with the result of a deep investigation [17] on the fluorescence behaviour of the 4-pyrydinium analogue of our compound **4** in 20 solvents of varying solvent polarity parameter, $E_T{}^N$ [18].

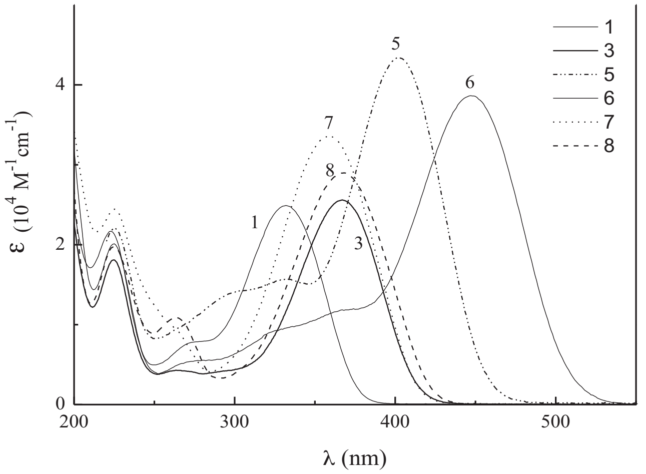
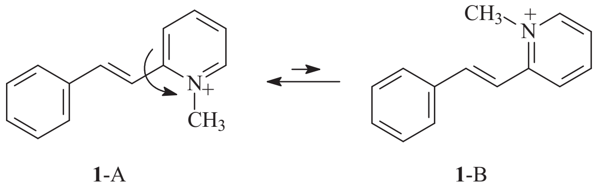


Fig. 1. Absorption spectra of compounds **1**, **3**, **5** and **6**–**8** in buffered (ETN) water at room temperature.



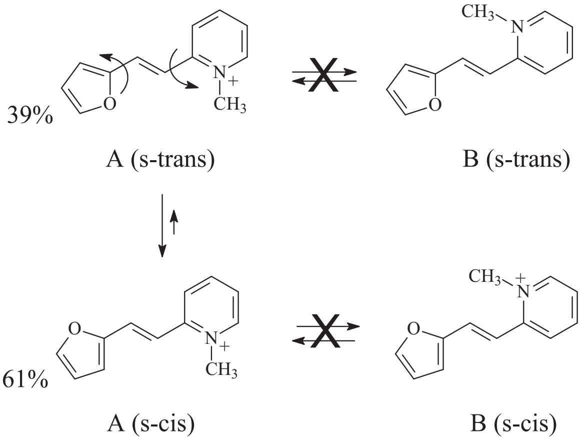
Scheme 2. Conformational equilibrium of compound **1**.

3.2. Conformational equilibria

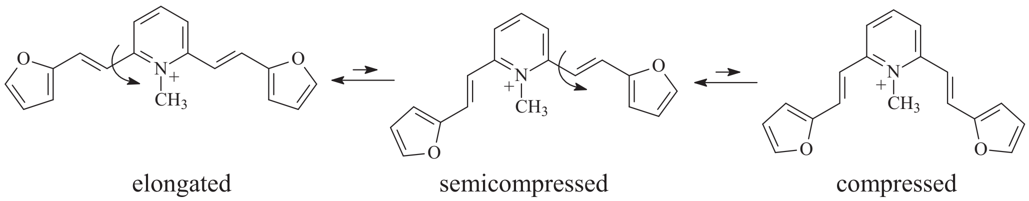
The compounds investigated are expected to exist in solution as mixtures of different conformations [16]. The conformer equilibrium for the reference compound **1** is shown in Scheme 2. The calculations (Appendix A) indicated that the conformer A has the smallest formation enthalpy difference ($\Delta H_f{}^\circ$) and is the prevalent species in solution.

Also in compounds **2**–**4** (four possible conformers, see the case of compound **3**, as an example, in Scheme 3), the most stable species are those of the A type, with a prevalence of the s-cis species (produced by rotation around the quasi-single bond with the pentatomic ring), as previously reported for the thienyl (**2**) and pyrrolyl (**4**) derivatives [10].

In the case of compounds **5** and **6** with two ethenic bonds (10 possible conformers), the computed $\Delta H_f{}^\circ$ values indicated a prevalence of the three elongated species with a largest abundance for the s-cis, s-cis species, particularly for **6** (86%). Rotation around the quasi-single bond adjacent to the pyridinium group leads to species of much higher energy, strongly deviating from planarity (see semi-compressed and compressed species in Scheme 4 for compound **5**, as an example). Finally, for compounds **7** (four conformations) and **8** (two possible species), the s-cis conformer is largely prevalent.



Scheme 3. Possible conformers of compound **3**.



Scheme 4. Conformers of compound **5** produced by rotation around the bond with the central pyridinium group.

Table 2
Quantum yields of the radiative and reactive relaxation of the iodide salts of trans-2-styryl-(1-methylpyridinium) and some hetero-analogues in buffered (ETN) water.

Compound	ϕ_F ($\times 10^4$)	$\phi_{t\to c}$	$\phi_{c\to t}$
1	3	0.40	0.20
2[a]	1.2	0.60	0.22
3	4	0.52	0.13
4[a]	4.0	0.37	0.46
5	60	0.04	0.26
6	4	~0.01	~0.5
7	7	0.44	0.16
8	8	0.49	0.25

[a] From Ref. [10].

The fluorescence excitation spectra did well overlap the corresponding absorption spectra (see two examples in Fig. 2) as expected from the calculations that support the prevalence of one conformer in solution. In our experimental conditions, the fluorescence lifetime ($\tau_F = 0.12$ ns) was measurable for **5** only, which has the highest ϕ_F value. The monoexponential decay indicates that the prevalent elongated conformers (quasi-isoenergetic) have undistinguishable emission properties.

3.3. Radiative and reactive relaxation quantum yields

Table 2 shows the quantum yields of the radiative and reactive relaxation of the compounds investigated. The main deactivation pathway of the compounds of the diarylethene series is trans → cis photoisomerization, similarly to the related neutral molecules [19]. The photobehaviour of our reference compound, 1-methyl-2-styrylpyridinium iodide (**1**) in buffered (ETN) water is similar to that previously reported for the protonated compound ($\phi_F = 0.003$, $\phi_{t\to c} = 0.55$ and $\phi_{c\to t} = 0.28$) in 50/50 water/ethanol at pH 2 [19b]. The presence of a pentatomic group (2T, 2F, 2Py) in compounds **2**–**4**, **7** and **8** affects the fluorescence/isomerization competition at a negligible extent. Their common characteristic is a high trans → cis photoisomerization quantum yield, which, according to the diabatic mechanism, which implies a trans → perp quantum yield almost the double of the trans → cis yield, approximately accounts for the absorbed quanta. In fact, the competitive radiative relaxation pathway is very weak, its yield being <0.001 (except for compound **5** with $\phi_F = 0.006$) with a consequent scarce help of the usually informative fluorescence properties for the interpretation of the relaxation mechanism. The photoreactivity (rotation of one double bond, trans,trans → cis,trans) of the two compounds of the di-(arylethenyl)pyridinium series, **5** and **6**, is very small, again similarly to the corresponding neutral molecules [20], but with a modest compensation of the usually coupled radiative deactivation whose yield remains small, even if, for **5** (bearing two side furan rings), it increases by more than one order of magnitude. In any case, internal conversion is the main deactivation channel of these quadrupolar molecules.

As to the back photoisomerization quantum yield from cis to trans ($\phi_{c\to t}$ values reported in Table 2), it is of the same order than the direct one ($\phi_{t\to c}$) for compound **4** only; for the others it is smaller but still substantial. An efficient radiationless pathway contributes to the deactivation of the S_1 state of the cis isomers. Interestingly, irradiation of the trans, cis isomer of **5** led prevalently to trans, trans but a small yield (~0.7%) of the cis,cis isomer was also detected. The photochemical formation of cis,cis is rather unusual in the series of distyrylbenzene analogues [21].

The quantum yield of the reactive deactivation was measured also in MeCN. Generally, it tends to increase in the non-protic solvent, particularly for the pyridinium salts bearing the furyl group, **3** and **5**. The $\phi_{t\to c}$ value goes from 0.52 to 0.75 for **3** and from 0.05 to 0.25 for **5**. This behaviour, reported also for the 4-pyridinium positional isomer of our 2-pyridinium derivative (**4**) mentioned above [17], could be tentatively explained by the interaction of water with the oxygen of the furan ring which opposes the twisting around the double bond leading to isomerization.

3.4. Intramolecular charge transfer effects

Asymmetrical 1,2-diarylethenes where the two side aryl groups have different D/A properties are generally characterized by high polarizability and hyperpolarizability and can behave as NLO systems. An exhaustive investigation carried out on stilbene-like molecules bearing quaternized azine groups (mainly of the triflate salts of 4-methylpyridinium analogues) demonstrated that

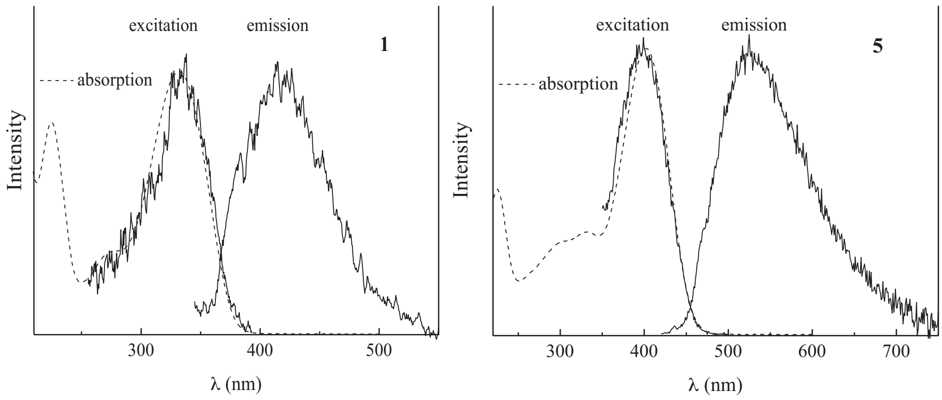


Fig. 2. Fluorescence emission and excitation spectra of **1** and **5** in buffered (ETN) water at room temperature (absorption spectra shown for comparison).

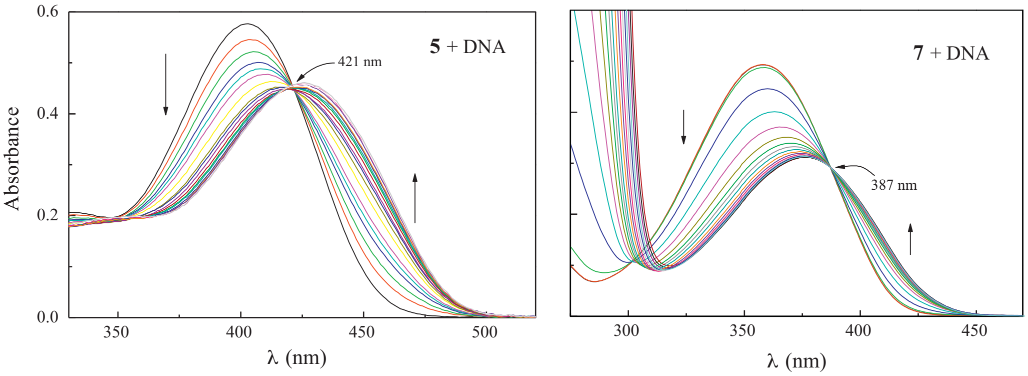


Fig. 3. Absorption spectra of compounds **5** and **7** (corrected for dilution) recorded after successive addition of a DNA solution up to 8×10^{-4} M.

the spectral shifts induced by an increase in the donating properties of D, the quaternization and the solvent polarity can be useful parameters indicating them as suitable candidates for components of materials having interesting two-photon absorption properties and frequency up-converted lasing activity [1,22].

A comparison of the spectral behaviour of diarylethenes **2**–**4**, **7** and **8** with that of the corresponding phenyl derivative **1** (Table 1) shows that the red shift induced by the heterocyclic group (see Section 3.1) is substantial for all compounds and greatest for the pyrrolyl-derivative **4**, which has the best donor properties. The shift becomes even larger in the quadrupolar compounds **5** and **6** with a 2,6-disubstituted pyridinium group. This indicates that these compounds can display interesting NLO properties [1,22]. An evaluation of the interaction between the two D/A heterocycles and consequent ICT effects in the present compounds was roughly obtained by measuring the dependence of the absorption spectrum on the solvent polarity. Solubility problems drastically limits the range of the solvent to be investigated. In any case, measurements in Ch, MeCN and water showed that the absorption maximum shifts to shorter wavelengths and the absorption coefficient $\varepsilon_{\max}$ decreases on increasing the solvent polarity. It has to be noted that different solvents may also affect the equilibrium between conformers discussed in Section 3.1. The negative solvatochromism shown in Table 1 for all of our compounds indicates a lower dipole moment in the excited state, due to the CT character of the electronic transition. This behaviour is in agreement with the dipole moment of the excited state roughly estimated by calculations (see Appendix A). The hypsochromic shift in water with respect to Ch confirms the push–pull character of the compounds investigated. The shift increases in compounds bearing the best accepting pyrrole ring (**4** and **6**).

3.5. Interactions with DNA

Spectrophotometric measurements showed that all the trans isomers investigated interact with DNA, as evidenced by the red-shift and the intensity decrease of their absorption maximum under successive additions of DNA to a constant olefin concentration ($\sim 2 \times 10^{-5}$ M). For compounds **1** and **3** the spectral shift was very small indicating that the complex formation involves relatively weak interactions. Much more evident spectral changes were found for **5** and **6**. Two examples of the spectral evolvement due to the formation of trans-diarylethene-DNA complexes are shown in Fig. 3 for compounds **5** and **7**.

By increasing substantially the DNA concentration, a final spectrum was obtained which was assumed to correspond to an equilibrium completely shifted towards the complexed form. Its maximum is shifted towards the red by about 20 nm in both cases.

Table 3
Complexation constants of compounds **1**, **3** and **5**–**8** with DNA in buffered (ETN) water at room temperature.

Compound	K (M^{-1})	n
1	2700	6.5
3	5700	7.5
5	13,600	3.0
6	58,500	1.1
7	58,000	3.4
8	119,000	1.6

A treatment of the absorbance changes according to the equation of McGhee and von Hippel [15]:

$$\frac{\nu}{c} = K(1 - n\nu)\left(\frac{1 - n\nu}{1 - (n-1)\nu}\right)^{n-1}$$

where c is the concentration of the free ligand and ν is the binding density (*i.e.* the ratio between the bound ligand and DNA) allowed the complexation constant (K) and the number of the binding sites excluded when the ligand is bound to DNA (n) to be estimated (Table 3). An example of the treatment for compound **8** is shown in Fig. 4.

The K values reported [10] for compounds **2** and **4** were of the order of 3500 M^{-1}; the little reproducible n values were not reported there.

The ligand–DNA complexation constants are in the range $3–6 \times 10^3$ in the case of the pyridinium derivatives with one ethenic bond (**1**–**4**). These values are probably too low for therapeutic application (K values reported for analogous compounds are higher by one order of magnitude or more [2]). The K value increases to the

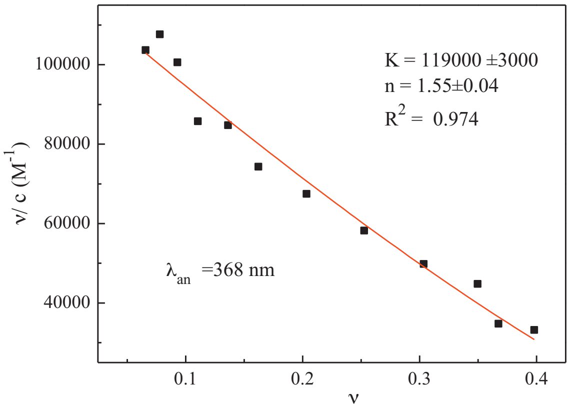


Fig. 4. Plot to obtain the association constant of the system **8**-DNA according to the equation of McGhee and von Hippel [15].

Table 4
Spectral properties and fluorescence quantum yields of the complexes with DNA in buffered (ETN) water.

Compound	λ_{ab}^{max} (nm)	ε^{max} (M^{-1} cm^{-1})	λ_{F}^{max} (nm)	λ_{isosb} (nm)	ϕ_F ($\times 10^4$)
1	340	20,800	440	349	4.0
3	372	21,400	455	386	3.0
5	425	34,700	515	420	200
6	476	16,600	569	474	130
7	376	9100	464	387	46
8	381	13,000	474	400	30

range 1–6 ($\times 10^4$) for the di-substituted compounds, **5** and **6**, and is even higher for the imidazole derivatives, **7** and **8**. The high K values found for the compounds with two ethenic bonds (**5** and **6**) and those halogen-substituted (**7** and **8**) are interesting and can be related to the observation that the presence of three aromatic rings and of halogen substituents might increase the anti-proliferative activity [4b]. Indeed, the latter, tested against two tumor cell lines (breast and prostate carcinomas) following the method described elsewhere [3], has been reported to be particularly high for these compounds. The n value in Table 3 is near to 1 (typical of intercalated complexes [15]) for two compounds only, indicating that intercalation of the ligand is probable for **6** and **8**, whereas in the other cases groove binding is favoured in our experimental conditions.

3.6. Photobehaviour of the complexes with DNA

When styrylpyridinium ligands are organized on the DNA, the photophysical and photochemical relaxations of the excited state can change substantially with respect to that of the free molecule, depending on the aryl moiety properties of the ligand and its DNA-binding mode [2].

In our previous work on the thienyl (**2**) and pyrrolyl (**4**) derivatives, characterized by rather small K values (of the order of few thousands M^{-1}), it was found that the emission yield of the complexes remained almost unchanged for **2** but increased markedly for **4** [10]. Table 4, which collects the spectral properties and emission yields of the new compounds investigated (**1**, **3** and **5**–**8**), shows that the radiative relaxation is always (more or less) favoured by complexation (compared with data in Table 2). The complexes of compounds **5** and **6** with two quadrupolar systems (three heterocyclic groups) display the largest bathocromic absorption/emission shift and, interestingly, the highest fluorescence yields, probably due to an increase of planarity of the ligand in the complex. The observed fluorescence enhancement, particularly efficient for **5**–**8**, reflects a reduced flexibility of the complexed ligands which could affect both the reactive and non-reactive radiationless deactivations. However, it should be noted that the quanta involved in the emission process remain a too small fraction to involve sizable effects on the competitive processes (see below).

An example of the changes in the fluorescence yield is shown for compound **5** in Fig. 5.

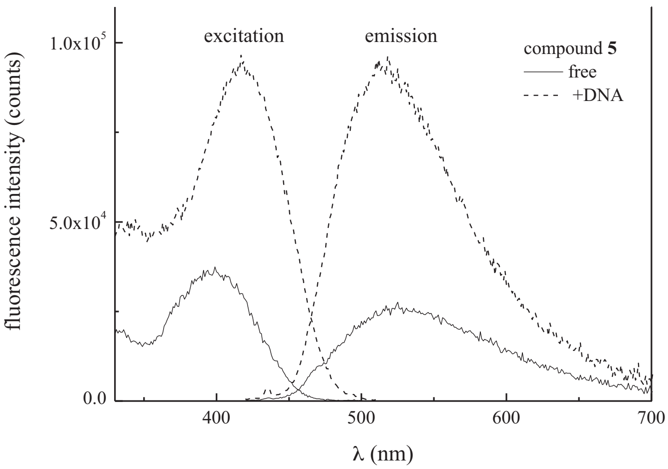


Fig. 5. Fluorescence intensity of the free and DNA-complexed compound **5** in buffered (ETN) water at room temperature.

As to the reactive relaxation, it has been reported that DNA affects the photostationary state (pss) composition through its preference in binding affinity towards trans or cis isomers [2]. In the diluted ligand solutions used in this work ($\sim 10^{-5}$ mol dm^{-3}), irradiation gave only a mixture of the two geometrical isomers without formation of cyclobutane photodimers, which were often detected in styrylpyridinium salt photochemistry [2]. In our previous paper on compounds **2** and **4**, it was found that complexation did not alter the photobehaviour substantially. In the case of compound **2**, both the *pss* ([Z]/[E]) composition and E → Z quantum yield decreased with respect to the free ligand while a quite larger red-shift of the absorption spectrum but a negligible decrease of $\phi_{E\rightarrow Z}$ was reported for compound **4**. It has to be noted that both the K and ϕ_F values of these compounds were characterized by a large incertitude and no clear coupling between the radiative/reactive relaxation was found in the case of these two compounds [10].

We have here investigated the effect of the interaction with DNA on photoisomerization for two compounds having a small K value and high n value (compound **3**) and viceversa (compound **8**). It was not possible to investigate compound **6** (with $n = 1.1$) since it practically did not isomerize even in the absence of DNA (Table 2). The results obtained were $\phi_{E\rightarrow Z} = 0.47$ and 0.55 for **3** and **8**, respectively. The changes found with respect to the free ligands were of the order of magnitude of the experimental uncertainty thus indicating that the interaction (both intercalation and groove binding modes) leaves the reaction center enough space to undergo twisting of the double bond. In the case of intercalation, prevalent for **8**, this behaviour should imply an incomplete insertion of the ligand into the intercalation pocket so that the protruding part of the ligand has enough space to isomerize.

A detailed investigation on the photoreactivity of these complexes will be the subject of a next paper.

4. Conclusions

The information obtained gives a general description of the S_1 relaxation of this series of salts. The stilbene analogues display a photobehaviour similar to that of stilbene, that is a largely prevalent relaxation by essentially diabatic isomerization and an even smaller competition by fluorescence. On the contrary, the photobehaviour of the two distyrylbenzene analogues (**5** and **6**) is quite different from that of the corresponding neutral compounds (2,6-distyrylpyridine and 1,3-distyrylbenzene) where the prevalent deactivation path is the radiative one and the photoreactivity is very low or quite negligible. In the present case, both main relaxation processes are little efficient and internal conversion becomes the prevalent deactivation process.

The complexation with DNA did not change much the photobehaviour of this series of free ligands. In any case, a general tendency to favour the very small yield of the radiative decay and to decrease the yield of the reactive pathway was observed but the coupling of the radiative/reactive relaxation, typical of stilbenoid compounds, was not clearly verified in these poorly emitting complexes. However, it is probable that the decay is complicated by a different contribution of the internal conversion in the relaxation of the complexed ligands.

The results obtained indicate that the structure/property relationship (spectral and DNA-complexation properties) are in some way related to other properties useful for material applications. Solvatochromism indicators can be used as probes of the ICT and its potential applications in the field of two photon pumping and frequency up-converted lasing activity [1,22]. On the other hand, the complexation constants with DNA can provide a probe for potential antitumor activity [2,4b]. The promising results obtained so far need gaining deeper insight into the ground state properties and the photobehaviour of this series of compounds.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2010.09.007

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