

# Fluorescence/photoisomerization competition in *trans*-aza-1,2-diarylethenes

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Received: 1 August 2008 / Accepted: 23 February 2009 / Published online: 31 March 2009  
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**Abstract** The effect of the presence and position of the nitrogen heteroatom on the photobehaviour of a series of symmetric and asymmetric 1,2-diarylethenes, where one or both the one-, two- or three-membered aryl groups, linked to the ethene bridge, contain(s) nitrogen heteroatoms, has been investigated by fluorimetric and photochemical techniques. The yield of the radiative pathway is generally reduced with respect to the corresponding hydrocarbons, due to a smaller energy barrier for *trans*→*cis* (E→Z) photoisomerization in the singlet state, which often can be slightly favoured in the aza-compounds. All compounds investigated exist in solution as mixtures of two or more conformers, which can have different spectral and kinetic properties. Attempts to separate the intrinsic properties by selective photoexcitation, at a wavelength where the light is mainly absorbed by one conformer, allowed in some favourable cases the spectra and decay times of the largely prevalent (quasi-pure) conformer to be obtained. In two cases, the formation of intramolecular (hydrogen-bond-type) interactions between the nitrogen atom and the nearest hydrogen atom of the ethene bridge (proved by NMR measurements and confirmed by theoretical calculations) were found to stabilize a specific conformer thus affecting a selective relaxation of the excited molecule.

**Keywords** Aza-1,2-diarylethenes · Fluorescence · Photoisomerization · Heteroatom effects

## Introduction

The effect of the introduction of nitrogen heteroatoms on the photobehaviour of 1,2-diarylethenes, where one or both the side phenyl groups of stilbene were replaced by aza-aryl groups, has been widely investigated by various laboratories in the last decades (for some representative papers, see refs. [1–16]).

The present work is the outcome of a joint collaboration between two groups having different interests in the photobehaviour of aza-derivatives of 1,2-diarylethenes. The Dalmine laboratory has synthesized a series of *trans* (E) compounds, where the aryl groups are two-terms or three-terms polycyclic groups, with the main scope of photoproducing the *cis* (Z) forms and studying the experimental and theoretical factors responsible for the consecutive photocyclization to monoaza and diaza[5] helicenes [15, 16]. On the other hand, the Perugia laboratory has investigated this series of compounds in the framework of a long-term project on the photoisomerization of 1,2-diarylethenes and related compounds and on the effect of the introduction of the nitrogen heteroatom (by replacing one of the side aryl groups with pyridyl, quinolyl or phenanthridyl groups) on the relaxation pathways of the lowest electronically excited states of singlet and triplet multiplicities [6–11].

In principle, the presence of the heteroatom may markedly affect the relative weight of the radiative and reactive relaxations, therefore this research work is mainly aimed to evaluate the role of the nitrogen position in driving the decay of the excited *trans* isomers of a series of

**Electronic supplementary material** The online version of this article (doi:10.1007/s10895-009-0472-0) contains supplementary material, which is available to authorized users.

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aza-diarylethenes towards either fluorescence emission or conversion to the *cis* geometrical isomers.

Aza-diarylethenes with nitrogen in both aryl groups (such as 1,2-dipyridylethenes [1, 9]) or two nitrogen atoms in the same ring (such as pyrazyl and quinoxalyl derivatives [12, 13]) have also been investigated. The interesting behaviour of compounds where the nitrogen atom occupies positions that favour intramolecular N $\cdots$ H interactions and stabilize specific conformations, thus affecting the photo-physical and photochemical properties, has been reported for 1,2-diarylethenes containing pyridine [17, 18], quinoline and isoquinoline [3, 5] or indole and pyrrole groups [19, 20]. The nitrogen effect in aza-diphenylbutadienes [17] and aza-distyrylbenzenes [18, 21, 22] has also been investigated.

In a qualitative attempt to rationalize the photobehaviour of several series of aza-1,2-diarylethenes [14], it was concluded that it reflects mostly the properties of the aryl group bearing the heteroatom, which, in turn, depend on the relative energy of the  $n,\pi^*$  and  $\pi,\pi^*$  singlet states, which is generally conserved in the aza-diarylethene. However, the effect of the position of the heteroatom was not discussed in detail.

The pyridyl-derivatives, deeply investigated in previous works, had shown a marked decrease of the radiative relaxation with respect to the corresponding hydrocarbons when the heteroatom was in a conjugative position to the ethene bridge, whilst smaller energy barriers for twisting in the singlet state of the aza-compounds could favour photoisomerization [9, 10]. In some cases, the  $n,\pi^*$  states introduced by the nitrogen atom could play a deactivating role, mainly through vibronic coupling and consequent internal conversion (IC) to the ground state [1, 9].

Intersystem crossing (ISC) to the triplet manifold in the absence of oxygen was found to be negligible in most cases [11, 23–25], therefore the triplet reactivity was often studied under sensitized population of  $T_1$  only. However, it has to be noted that  $T_1$  was reported to be substantially responsible for photoisomerization of pyrazinyl- and quinoxalyl-derivatives [12, 13] but to also contribute to the torsional process in styrylquinolines [2, 14].

In the present work the photobehaviour of a series of symmetric and asymmetric 1,2-diarylethenes, where one or both the one-, two- or three-membered groups, linked to the ethene bridge, contain(s) nitrogen heteroatoms, has been investigated by fluorimetric and photochemical techniques. The dependence of the emission spectra and quantum yields on the excitation wavelength ( $\lambda_{\text{exc}}$ ) and the polyexponential decay indicated the presence of a dynamic equilibrium between different conformers of these flexible diarylethenes [26–28]. In a few cases, the spectral measurements carried out using  $\lambda_{\text{exc}}$  prevalently absorbed by one conformer,

allowed the intrinsic properties of that most abundant (quasi-pure) conformer to be selectively obtained.

## Experimentals

### Materials and experimental measurements

The trans (*E*) compounds investigated (Scheme 1) were prepared at the Dalmine laboratory for previous works; their synthesis and characterization are described elsewhere [15, 16]. The purity was checked by HPLC.

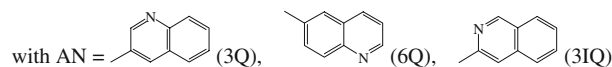
The solvent was 9/1 (v/v) methylcyclohexane/3-methylpentane (MCH/3MP). A Perkin-Elmer Lambda 800 spectrophotometer was used for the absorption measurements. The fluorescence emission spectra were measured by a Spex Fluorolog-2 F112AI spectrofluorimeter. The emission quantum yields were determined at various  $\lambda_{\text{exc}}$ 's in dilute solutions (absorbance < 0.1 at  $\lambda_{\text{exc}}$ ) using 9,10-diphenylanthracene in cyclohexane as fluorimetric standard ( $\phi_{\text{F}}=0.90$  in de-aerated solvent [29]). For photochemical measurements (potassium ferrioxalate in water as actinometer), a 150 W high pressure xenon lamp coupled with a monochromator was used. The photoreaction (solute concentrations  $\sim 10^{-4}$  M) was monitored by HPLC using a Waters apparatus equipped with an analytical Phenomenex Juppiter C18 300A (4.6  $\times$  250 mm; 5  $\mu\text{m}$ ) column and UV detector. Water/acetonitrile mixtures (with 0.1% v/v trifluoroacetic acid) were used as eluents. The monitoring wavelength was at the isosbestic point between the *E* and *Z* isomers (when possible), otherwise corrections for different absorption coefficients were introduced.

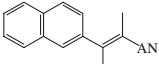
Since all the compounds investigated exist in solution as mixtures of two or more conformers, which can have more or less different spectral and kinetic properties, the measured quantum yields should be considered as mean values related to a specific  $\lambda_{\text{exc}}$ . The conversion percentage was held at below 10% to avoid the competition from the back photoreaction. Fluorescence lifetimes were measured by an Edinburgh Instruments 199S spectrofluorimeter, using the single photon counting method.

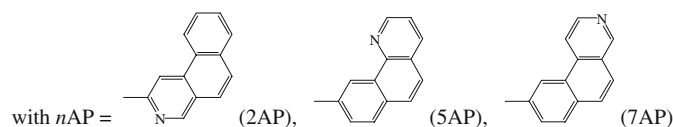
All measurements were carried out in de-aerated solutions by purging with nitrogen. The mean deviations of the measured parameters were of *ca.* 10% for fluorescence quantum yields and *ca.* 15% for the photoisomerization quantum yields and fluorescence lifetimes.

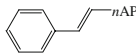
In two cases the role of H-bond type interactions was studied by one- and two-dimensional (COSY and NOESY)  $^1\text{H-NMR}$  spectra in non-polar (deuterated benzene) and in protic (deuterated methanol) solvents using a Bruker DRX 400 spectrometer and TMS as reference.

**Scheme 1** Compounds investigated

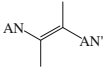
**a** 1-(azanaphthyl),2-(2'-naphthyl)ethenes (AN-E-2N)


Formula	AN	Name and abbreviation	
	3Q	1-(3'-quinolyl),2-(2'-naphthyl)ethene	3Q-E-2N
	6Q	1-(6'-quinolyl),2-(2'-naphthyl)ethene	6Q-E-2N
	3IQ	1-(3'-isoquinolyl),2-(2'-naphthyl)ethene	3IQ-E-2N

**b** 3-styryl-*n*-azaphenanthrenes (3St-*n*AP)


Formula	<i>n</i> AP	Name and abbreviation	
	2AP	3-styryl-2-azaphenanthrene	3St-2AP
	5AP	3-styryl-5-azaphenanthrene	3St-5AP
	7AP	3-styryl-7-azaphenanthrene	3St-7AP

**c** 1,2-di-(aza-2'-naphthyl)ethenes (AN-E-AN') with AN, AN' = 3Q, 6Q, 3IQ

Formula	AN	AN'	Name and abbreviation	
	3Q	3Q	1,2-di-(3'-quinolyl)ethene	3Q-E-3Q
	6Q	6Q	1,2-di-(6'-quinolyl)ethene	6Q-E-6Q
	3IQ	3IQ	1,2-di-(3'-isoquinolyl)ethene	3IQ-E-3IQ
	3Q	6Q	1-(3'-quinolyl),2-(6'-quinolyl)ethene	3Q-E-6Q
	6Q	3IQ	1-(6'-quinolyl),2-(3'-isoquinolyl)ethene	6Q-E-3IQ

**Theoretical calculations**

These were performed using the HyperChem computational package (version 6.1). The calculated electronic spectra (transition energies and oscillator strengths) were obtained by ZINDO/S using optimized geometries (according to PM3 method). Calculations of the configuration interaction included 81 (9×9) single excited configurations. The heats of formation of various conformations of the compounds investigated were also computed (see Supporting Information). More refined *ab initio* calculations were carried out using 3–21G basis set for compounds that revealed an anomalous behaviour ascribed to H-bond type interactions (see below).

**Results and discussion**

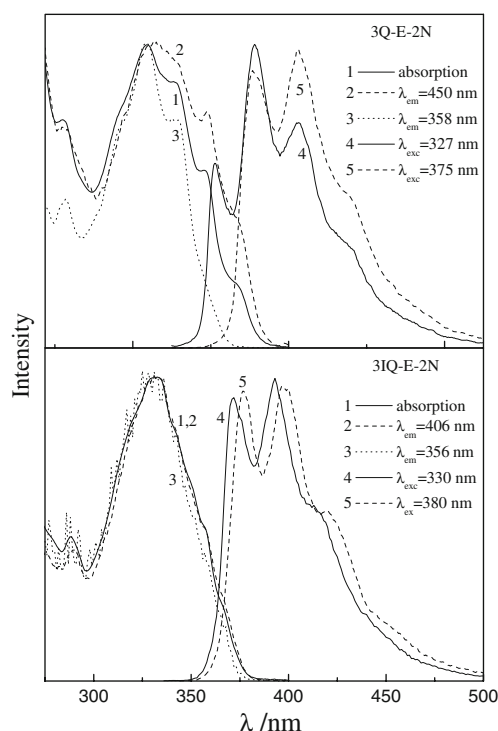
The photobehaviour of the *E*-1,2-diarylethenes investigated will be described by grouping them in three sections: i) monoaza-dinaphthylethenes, with a nitrogen atom in one ring (naphthyl-quinolyl and naphthyl-isoquinolyl derivatives), ii) monoaza-3'-styrylphenanthrenes (phenyl-phenanthrydyl-derivatives), and iii) diaza-dinaphthylethenes with a nitrogen atom in both rings (diquinolyl, di-isoquinolyl and

quinolyl-isoquinolyl derivatives). The new results are compared with information already reported in the literature on related compounds in order to have a more extended picture of the heteroatom effect in these series of compounds.

**Spectral behaviour (experiments and calculations)**

The absorption and fluorescence (emission and excitation) spectra of the compounds investigated are shown in Figs. 1, 2, 3.

Theoretical calculations of transition energies, oscillator strength and formation enthalpies (see [Supplementary Information](#)) gave the following indications: i) the presence of the heteroatom increases the oscillator strength of the first  $S_0 \rightarrow S_1$  transition which is always allowed, contrary to the case of the corresponding 3-styrylphenanthrene (3-StP) [29] and 1,2-di-(2'-naphthyl)ethene (2N-E-2N) hydrocarbons [30], where it is forbidden (at least for one conformer), but acquires intensity by the proximity of the allowed  $S_2$  state; ii) the expected conformational isomers [26–28] are almost isoenergetic or have comparable energies (with two notable exceptions, see below); iii) the species having *s-cis* or *s-cis,s-cis* conformation are the most stable ones and are generally bathochromic, thus suggesting



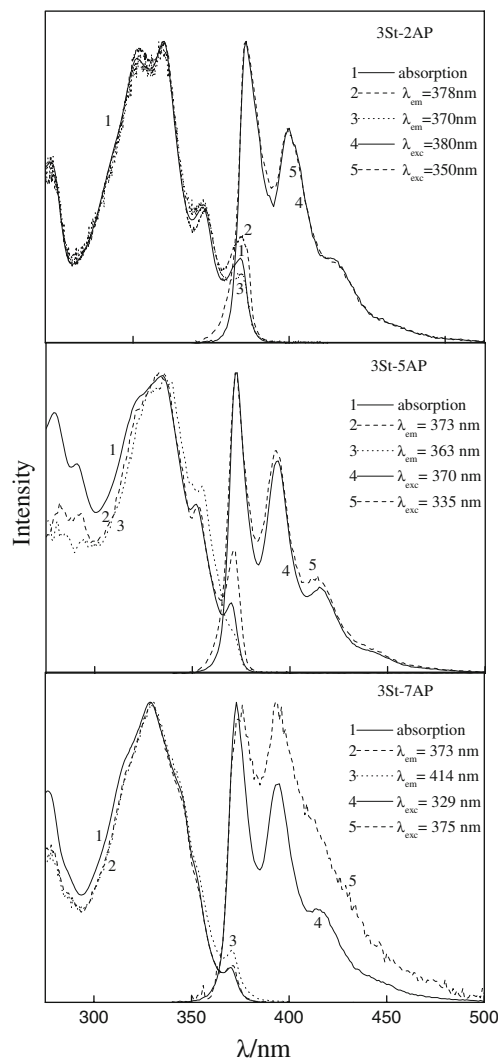
**Fig. 1** Absorption and fluorescence excitation/emission spectra of two *E*-monoaza-1,2-dinaphthylethenes in MCH/3MP

the possibility of measuring, in favourable cases, the separate properties of the bathochromic compound by exciting at the extreme red edge of the absorption spectrum or at a  $\lambda_{\text{exc}}$  where the light is mainly absorbed by one conformer.

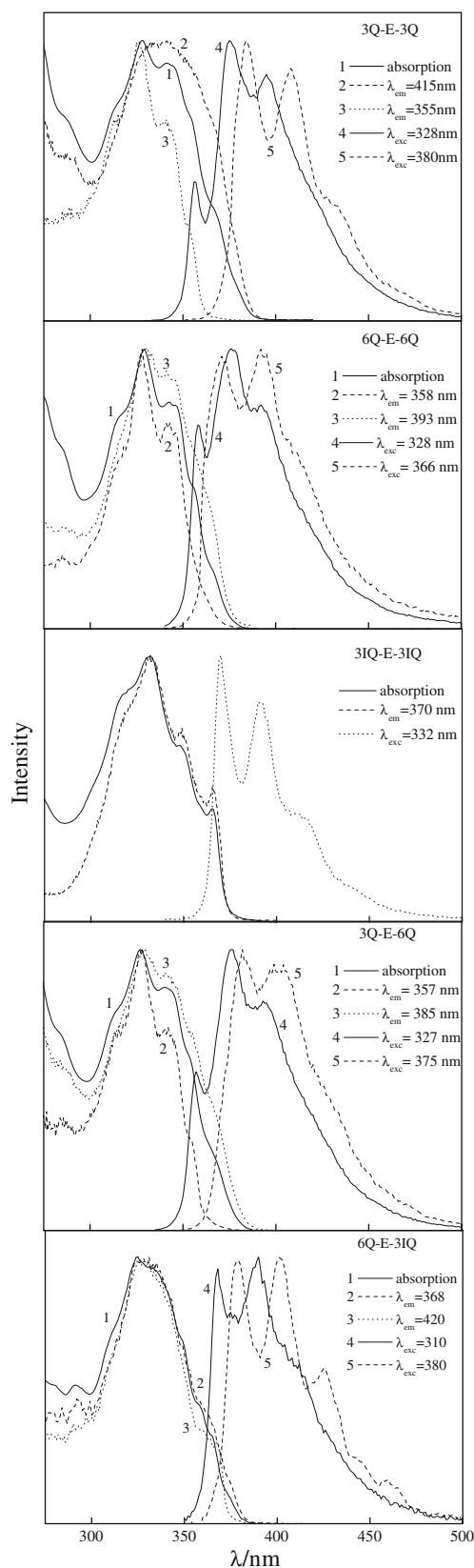
The dependence of the emission spectra and quantum yields on  $\lambda_{\text{exc}}$  and the polyexponential decay, generally observed, confirmed the presence of a dynamic equilibrium between different conformers, as foreseen by the theoretical results. An accurate investigation of the conformational equilibria was carried out in a previous work on one of the present compounds (6Q-E-2N [31]). Since a similar study for all the compounds here investigated was out of the scope of the present work, the photophysical and photochemical properties were generally measured by exciting at the maximum of the first absorption band. Therefore, they are mean values for the mixture of conformers with the exceptions of the few cases where it was possible to obtain the properties of the most abundant (quasi-pure) conformer by selective excitation. It has to be noted that the knowledge of the different intrinsic properties of each conformer in both *E* and *Z* geometries is important because the conformation can selectively favour a specific relaxation pathway, as found for both “conformer-specific” photoisomerization and photocyclization of some *Z* isomers where the parallel formation of dihydrophenanthrenes-type photoproducts can compete with the twisting process [32–35].

## Mono-aza-derivatives of *E*-1,2-di-(2'-naphthyl)ethene

The effect of a nitrogen heteroatom on the photobehaviour of *E*-1,2-DAEs was firstly investigated by replacing one of the naphthyl groups of 2N-E-2N with 3'-quinoline (3Q), 6'-quinoline (6Q) or 3'-isoquinoline (3IQ) groups. For this series of compounds and for the other ones here investigated, a diabatic reaction mechanism is assumed to be operative, as generally applied to the  $E \rightarrow Z$  photoisomerization of diarylethenes [36], namely twisting of  $^1E^*$  towards the perpendicular configuration at  $90^\circ$  ( $^1P^*$ ), followed by internal conversion to the ground state ( $^1P$ ) and equipartitioned (almost 50:50%) decay to the quasi-planar *E* and *Z* isomers. This implies that the quantum yield for rotation around the double bond in  $S_1$  ( $^1E^* \rightarrow ^1P^*$ ) is twice  $\phi_{E \rightarrow Z}$ .



**Fig. 2** Absorption and emission spectra of three *E*-aza-3-styrylphenanthrenes in MCH/3MP



**Fig. 3** Absorption and fluorescence excitation/emission spectra of five *E*-diaza-1,2-dinaphthylethenes in MCH/3MP

It can be recalled that previous studies on aza-styrylnaphthalenes bearing the same three groups (StX with X=3Q, 6Q and 3IQ), using  $\lambda_{exc}$  corresponding to the maximum of the first absorption band in cyclohexane, had shown that the radiative pathway prevails for the 3IQ compound and decreases with 6Q and even more with 3Q (the yields of the latter depend markedly on  $\lambda_{exc}$ ) whereas the competitive  $E \rightarrow Z$  yield displays, as usual, an opposite behaviour [4, 5]. It was found that when the heteroatom was in the styryl-substituted ring of quinoline (positions 2, 3 or 4), the photobehaviour was similar to that of styrylpyridines (reduced reactivity and quasi-absence of fluorescence in positions 2 and 4, and behaviour similar to that of stilbene, namely predominant reactivity, in position 3). However, when the N atom was in the other condensed ring (positions 6, 7 or 8), the photobehaviour was less dependent on the nitrogen position and resembled that of styrylnaphthalenes (scarce reactivity and predominant radiative relaxation [37]).

The results here obtained with the aza-analogues of 2N-E-2N, where a 2'-naphthyl (2N) group replaces the phenyl group, are shown in Table 1, which collects the fluorescence and photoisomerization parameters in an inert solvent. In all these compounds the ethenic bridge is attached to the  $\beta$  positions of the two-membered arenes, analogously to the hydrocarbon. They show slightly red-shifted absorption spectra, reduced fluorescence quantum yields, similar lifetimes and slightly increased photoreactivity with respect to 2N-E-2N.

The nitrogen effect follows a trend similar to that of aza-styrylnaphthalenes. The compound with the 6Q group behaves more similarly to the hydrocarbon if one considers that the sum of the quantum yields of the radiative and reactive deactivation pathways practically accounts for all the absorbed quanta for these two compounds ( $\phi_F + 2\phi_{E \rightarrow Z} \cong 1$ ) indicating that  ${}^1E^* \rightarrow {}^1E$  internal conversion is not operative. A different behaviour was found for the isomers with the 3Q and 3IQ groups. For them, the sum of the two quantum yields remains clearly below 1 and a substantial yield of internal conversion contributes to the relaxation. In any case, the effects of N on the radiative/reactive competition are really very small, indicating that such competition is little affected by the nitrogen position. The fluorescence decay is poly-exponential indicating the presence of different conformers. As found for the hydrocarbon, the fraction of excited rotamers changes with  $\lambda_{exc}$ . Generally, the short living rotamer is bathochromic, therefore the mixture of the excited molecules is enriched in this species when moving  $\lambda_{exc}$  towards the red. Even 3Q-E-2N, whose decay is practically mono-exponential at all  $\lambda_{exc}$ 's, shows small changes of the emission spectrum with  $\lambda_{exc}$  indicating also for this compound the presence of conformers, probably with very similar lifetimes.



**Table 1** Fluorescence and photoisomerization properties of some *E*-monoaza-1,2-dinaphthylethenes measured in MCH/3MP at different  $\lambda_{\text{exc}}$ 's

Compound	$\lambda_{\text{exc}}/\text{nm}^{\text{a}}$	$\phi_{\text{F}}$	$\tau_{\text{F}}/\text{ns}^{\text{b}}$	$\phi_{\text{EE} \rightarrow \text{ZE}}$
2N-E-2N <sup>c</sup>	313	1.0		0.04
	<i>330</i>	0.89	1.4 (0%), 2.1 (20%), 7.2 (80%)	
	374	0.70	1.4 (61%), 2.1 (39%) 7.2 (0%)	0.14
3Q-E-2N	327	0.39	2.4	0.14
	366	0.61	1.9	0.11
6Q-E-2N <sup>d</sup>	<i>330</i>	0.57	1.9 (18%), 3.3 (32%), 3.9 (50%)	0.22
	366	0.71	1.9 (40%), 3.3 (60%), 3.9 (0%)	0.15
3IQ-E-2N	<i>330</i>	0.46	1.3 (15%), 3.9 (85%)	0.10
	375	0.50	1.5 (39%), 3.3 (61%)	0.10

The values for the hydrocarbon are also reported for comparison

<sup>a</sup> The  $\lambda_{\text{exc}}$  value corresponding to  $\lambda_{\text{max}}$  is in italics.

<sup>b</sup> The fractions of excited rotamers belonging to each species is shown in parenthesis.

<sup>c</sup> From ref. [30]

<sup>d</sup> From ref. [31]

### Mono-aza-derivatives of E-3-styrylphenanthrene

The results obtained for some aza-3-styrylphenanthrenes are shown in Table 2. Even in this series of compounds, the main effect of the heteroatom was a slight reduction in both fluorescence quantum yield and lifetime, little dependent on the N position in the phenanthryl group. The reduction in the radiative parameters is compensated by an increase in reactivity for the 7AP derivative only. Changes in the position of the ethene bridge at the aza-phenanthrene group [29] or the introduction of the heteroatom in the phenyl ring [8] had been found to affect more substantially the measured parameters. In the latter case, the most important effect was the depression of the radiative channel when the styryl group was attached at the conjugative positions (2 or 4) of the pyridyl ring likewise in styrylpyridines [1, 9] and naphthylpyridylethenes [6].

For the 5AP and 7AP derivatives, the fluorescence decay is biexponential, as reported for the corresponding hydrocarbon [29, 38] and expected from the small computed enthalpy difference between the two conformers (see [Supplementary Information](#)). Their lifetime decreases markedly with respect to the hydrocarbon and depends on  $\lambda_{\text{exc}}$ . By exciting 3St-5AP at the tail of the absorption spectrum, the abundance of the short-living conformer increases. At  $\lambda_{\text{exc}}=375$  nm, its decay fits well a monoexponential curve ( $\tau_{\text{F}}=3.4$  ns), therefore the measured photophysical properties pertain to the quasi-pure short-living (bathochromic) conformer ( $\phi_{\text{F}}=0.43$ ,  $k_{\text{F}}=1.3 \times 10^8$  s<sup>-1</sup>). On the other hand, for 3St-7AP, the decay is biexponential at  $\lambda_{\text{exc}}=370$  nm but becomes monoexponential at  $\lambda_{\text{exc}}=316$  nm if the monitoring wavelength is around 370 nm. The properties of the quasi-pure longer-

living (hypsochromic) conformer can be measured when exciting at the maximum of the absorption spectrum where the contribution of the other rotamer is very small. For this compound, the calculations indicated that the lowest S<sub>1</sub> state is forbidden for both rotamers, thus explaining the lower radiative rate constant obtained for the hypsochromic rotamer ( $k_{\text{F}} \cong 4.5 \times 10^7$  s<sup>-1</sup>).

Contrary to the other compounds, where a net enrichment in the bathochromic rotamer was achieved under irradiation at the red tail of the absorption spectrum, for the 7AP derivative the behaviour was less evident because the abundance of the short-living bathochromic rotamer is always rather small. Considering that the rotamer lifetimes

**Table 2** Fluorescence and photoisomerization properties of three *E*-3-styryl-*n*-azaphenanthrenes excited in MCH/3MP at different  $\lambda_{\text{exc}}$ 's

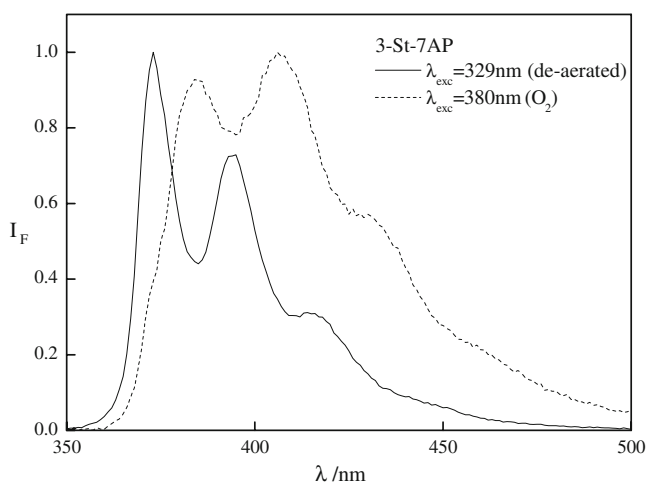
Compound	$\lambda_{\text{exc}}^{\text{a}}$	$\phi_{\text{F}}$	$\tau_{\text{F}}/\text{ns}^{\text{b}}$	$\phi_{\text{EE} \rightarrow \text{ZE}}$
3StP <sup>c</sup>	335	0.58	7.5 (48%), 18.2 (52%)	0.16
	370	0.45	7.6 (83%), 18.6 (17%)	
3St-2AP	335	0.44	4.0	0.16
	350	0.44	4.0	
	375	0.46	3.8	
3St-5AP	335	0.31	3.4 (43%), 5.7 (57%)	0.25
	375	0.43	3.4	
3St-7AP	316		7.8	0.16
	329	0.35		
	370	0.40	1.5 (37%), 7.5 (63%)	
	375	0.53		

The values for the hydrocarbon are also reported for comparison.

<sup>a</sup> The  $\lambda_{\text{exc}}$  value corresponding to  $\lambda_{\text{max}}$  is in italics

<sup>b</sup> The rotamer abundance is shown in parenthesis

<sup>c</sup> From ref. [38]



**Fig. 4** Fluorescence spectra of the two quasi-pure rotamers of 3-styryl-7-azaphenanthrene in MCH/3MP

are sufficiently different, we tried to enrich the rotamer mixture in the short-living component by using the method of selective quenching. On going from the deaerated solution to that where oxygen was bubbled instead of nitrogen, the fluorescence quantum yield at  $\lambda_{\text{exc}}=375$  nm decreased markedly, from 0.53 to 0.33. The effect of selective quenching is even more evident in Fig. 4 which shows the emission spectra of the two quasi-pure rotamers of 3St-7AP obtained in deaerated solution at  $\lambda_{\text{exc}}$  329 nm and in the presence of oxygen at  $\lambda_{\text{exc}}$  380 nm. Decay measurements using  $\lambda_{\text{exc}}$  375 nm and monitoring at 410 nm in oxygen-equilibrated solutions showed a bi-exponential trend with an increased abundance of the short-living bathochromic rotamer (~75%).

**Table 3** Fluorescence and photoisomerization properties of some *E,E*-aza-1,2-dinaphthylethenes measured in MCH/3MP at different  $\lambda_{\text{exc}}$ 's

Compound	$\lambda_{\text{exc}}/\text{nm}$	$\phi_{\text{F}}$	$\tau_{\text{F}}/\text{ns}$	$\phi_{\text{EE} \rightarrow \text{ZE}}$
6Q-E-6Q	328	0.28	1.4 (29%), 3.3 (71%)	0.14
	366	0.33	1.4 (84%), 3.3 (16%)	
	369	0.36		
6Q-E-3Q	327	0.31	2.0	0.18
	365	0.43		
	370	0.48		
6Q-E-3IQ	320	0.39	3.3	0.31
	325	0.43		
	330	0.41		
	350	0.34		
3IQ-E-3IQ	332	0.45	4.3	Undetectable
	366	0.45		
	370	0.48		
3Q-E-3Q	315	0.38	1.9	0.28
	328	0.40		
	355	0.45		
	370	0.60		
	380	1.5		

The  $\lambda_{\text{exc}}$  value corresponding to  $\lambda_{\text{max}}$  is in italics.

A peculiar behaviour was found for the 2AP derivative whose emission spectrum was practically independent on  $\lambda_{\text{exc}}$  and the fluorescence decay was monoexponential. An explanation of such behaviour is presented below (“Effect of intramolecular hydrogen bonding”).

#### Di-aza-derivatives of 2,2'-dinaphthylethene

Modest effects with respect to the mono-aza analogues were observed in compounds containing two N heteroatoms (Table 3). The symmetric 6Q-E-6Q compound preserves a relatively good fluorescence yield which slightly increases by shifting  $\lambda_{\text{exc}}$  towards the red. Its decay is biexponential and the abundance of the excited short-living component increases from 25% to 84% when  $\lambda_{\text{exc}}$  passes from 328 to 366 nm.

Unexpectedly, the other aza-compounds of Table 3 show a monoexponential decay, even if the measured lifetimes tend to slightly decrease at high  $\lambda_{\text{exc}}$  values indicating that at least two species with close lifetimes play a role.

Also the two symmetric compounds with 3Q and 3IQ groups were found to have rather high emission yield. However, whilst the 3Q derivative has a high photoisomerization yield, the 3IQ derivative is not reactive. Its monoexponential decay recalls the behaviour of 3St-2AP cited above and is even more evident (see “Effect of intramolecular hydrogen bonding”). Also the asymmetric compounds bearing 3Q and 3IQ groups display substantial emission yield and good reactivity.

Comparison of the parameters of the di-aza compounds in Table 3 with those of the mono-aza analogues in Table 1,

**Table 4** Relative energy values and corresponding abundances of the conformers of the two compounds showing N···H interactions, compared to two related compounds which do not show such interactions, as obtained by *ab initio* calculations

Compound	Conformer	$\Delta E_{\text{rel}}$ (kcal/mol)	Abundance (%)
3IQ-E-3IQ	s-trans,s-trans	0	99.9
	s-trans,s-cis	5.9	<0.1
	s-cis,s-cis	3.9	0.1
3Q-E-3Q	s-trans,s-trans	0	56.3
	s-trans,s-cis	0.44	26.5
	s-cis,s-cis	0.69	17.2
3St-2AP	s-trans	0	95.5
	s-cis	3.1	0.5
3St-7AP	s-trans	0	66.5
	s-cis	0.4	33.5

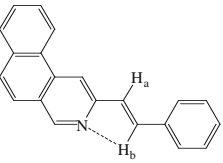
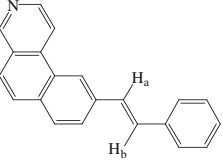
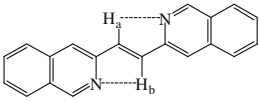
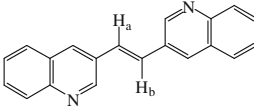
shows that the reactive relaxation towards the Z isomer is slightly increased to detriment of the radiative pathway which is further reduced with respect to the hydrocarbon but remains substantial. However, these parameters are here quite similar each other and the nitrogen effect tends to be flattened.

### Effect of intramolecular hydrogen bonding

The unexpected behaviour of 3-St-2AP (absence of  $\lambda_{\text{exc}}$  effect on the fluorescence spectrum and mono-exponential fluorescence decay), and particularly that of 3IQ-E-3IQ, where the same fluorescence behaviour is accompanied by absence of photoreactivity, resemble those reported for analogous compounds with the N atom in ortho position to the ethenic bridge (such as 1-styrylisoquinoline [3], 1-(2'-pyridyl)-2-phenylbutadiene [17], 2,6-distyrylpyridine [18] and 1-(2'-pyridyl),2-(2''-indolyl)ethene [19]) and can be analogously explained by the formation of intramolecular (hydrogen-bond-type) interactions between the nitrogen atom and the nearest hydrogen atom of the ethenic bridge. Such N···H interaction is expected to force the excited molecule into a transoid conformation [3, 39] which decays by IC in inert solvents. In protic solvents, stronger intermolecular N···H bonds are favoured which destabilize the conformer responsible for the intramolecular H-bond.

Theoretical *ab initio* calculations, used to optimise the geometries of the different conformers of these two compounds, provided the relative energy values reported in Table 4, which confirmed that the conformation proper for the interaction (*s-trans*) is largely stabilized with respect to the other ones and practically the only expected species

**Table 5** Chemical shift ( $\delta$ ) and coupling constants ( $J$ ) in protic and inert solvents for the olefinic hydrogens of two aza-DAEs (3St-2AP and 3IQ-E-3IQ) showing intramolecular hydrogen-bond-type interaction (the shifted peaks are underlined), compared with two positional isomers where the interaction is not possible

Compound	Deuterated methanol	Deuterated benzene
	$\delta$ (ppm)	$\delta$ (ppm)
 3St-2AP	7.55 (H <sub>a</sub> , d) 7.85 (H <sub>b</sub> , d) $J_{\text{ab}}=16.2$ Hz	7.40 (H <sub>a</sub> , d) <u>8.50</u> (H <sub>b</sub> , d) $J_{\text{ab}}=16.9$ Hz
 3St-7AP	7.52 (H <sub>a</sub> , H <sub>b</sub> ) AB system <sup>a</sup>	7.31 (H <sub>a</sub> , H <sub>b</sub> ) AB system <sup>a</sup>
 3IQ-E-3IQ	7.90 (H <sub>a</sub> , H <sub>b</sub> , s)	<u>8.70</u> (H <sub>a</sub> , H <sub>b</sub> , s)
 3Q-E-3Q	7.76 (H <sub>a</sub> , H <sub>b</sub> , s)	7.00 (H <sub>a</sub> , H <sub>b</sub> , s)

<sup>a</sup>The spin system is referred to as AB if the chemical shifts are quite close each other.



in solution (>95%). On the contrary, the two reference compounds, where the interactions are not present, display a normal behaviour with a wide distribution of the various conformers. The calculations also showed that only in the *s-trans* conformations the values of the N $\cdots$ H distances (2.44 and 2.49 Å) and CHN angles (93.3° and 97.3°), for 3-St-2AP and 3IQE3IQ, respectively, are closer to those expected for a real H-bond interaction [40], particularly for the 3IQ derivative.

This explanation was confirmed by the effect of protic solvents on the  $^1\text{H-NMR}$  spectra which showed a net shift to higher  $\delta$  values (de-shielding effect) of the peak assigned to the H atom responsible for the intramolecular interaction on going from methanol to benzene. Table 5 shows the chemical shifts of the two compounds compared with two positional isomers where the interaction is not possible.

In the case of 3St-2AP, the two doublets of  $\text{H}_a$  and  $\text{H}_b$  have a resonance absorption at similar field values in methanol while in benzene  $\text{H}_a$  shows a normal shift towards higher field and  $\text{H}_b$  an opposite trend with a  $\delta$  increase of 0.65 ppm. The coupling constant between the two  $\text{H}_a$  and  $\text{H}_b$  doublets has a value typical of the transoid geometry. This behaviour was compared with that of an analogous compound (3St-7AP), whose N atom occupies a different position, where the interaction is no longer possible. Its spectrum in benzene was rather complicated but clearly showed that the  $\delta$  value has a normal trend (slight decrease on going from methanol to benzene for both ethenic hydrogens). The NMR analysis of this compound was also carried out by NOESY and COSY bidimensional techniques thus allowing an easier signal interpretation. The ethenic protons are two practically overlapped doublets (AB system), therefore the J constant was not measurable.

In the case of the symmetric 3IQ-E-3IQ, the double interaction leads to an even stronger increase (0.80 ppm) of the  $\delta$  value of the singlet ethenic peak in benzene. Such stronger stabilization of the *s-trans,s-trans* conformer makes it particularly planar and rigid, thus explaining the absence of photoisomerization. Even in this case, the  $\delta$  increase on going from methanol to benzene was not observed for the 3Q-E-3Q analogue, where the intramolecular interaction is not possible.

## Conclusions

The results described in this work indicates that the relatively strong effect of the heteroatom on the radiative and reactive relaxation parameters, previously found for the mono-aza- and, even more, for the di-azastilbenes (pyridyl derivatives), tends to decrease by replacing one or both phenyl groups of stilbene with two- and three-membered aryl groups. A reduction of fluorescence and an increase

of photoisomerization is always found in the presence of nitrogen but the effect becomes flat in the compounds of Tables 2 and 3. The nitrogen effects are substantial only in the cases where N $\cdots$ H interactions stabilize one component of the conformational equilibrium. When the intramolecular interaction are particularly strong in inert solvents, as in the case of 3IQ-E-3IQ, the torsional process is practically forbidden and the excited E isomer decay by fluorescence and internal conversion.

**Acknowledgements** The authors are grateful to Dr. Elena Marri for her assistance in the first part of this research and to Mr. Danilo Pannacci for his skilful technical collaboration in the HPLC measurements.

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