Protonation effect on the excited state behaviour of some aza-analogues of *EE*-distyrylbenzene

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ABSTRACT. The photobehaviour of four aza-analogues of *EE*-distyrylbenzene bearing the heteroatom in the two side rings [1,4-di-(2-pyridylethenyl)benzene] or in the central ring [2,5-di-(phenylethenyl)pyridine, 2,6-di(phenylethenyl)pyridine and the corresponding diene, 2,6-di(phenylbutadienyl)pyridine] has been investigated in aqueous solutions at pH 2 and 9, where the molecules are in mono-protonated and neutral forms, respectively. The type of conjugation, linear for the first two compounds and crossed for the others, is particularly important in determining the spectral and photochemical properties. The main effects of the protic solvent are a reduction of the radiative deactivation, prevalent in the corresponding hydrocarbons, and an increase of the reactive deactivation, very modest in the hydrocarbons. The increase in photoreactivity to detriment of fluorescence, observed in protic medium with respect to non-polar solvents, is drastically emphasized in acid medium where the fluorescence quantum yield decreases by an order of magnitude leading to high values of the EE→ZE photoisomerization quantum yield. The presence of conformational isomerism (two main conformers were detected) has been observed in both basic and acid media for compounds with crossed conjugation and for the linearly conjugated 2,5 substituted pyridine. The results obtained give a picture of the different photobehaviour of the neutral and protonated species and indicate the experimental conditions to favour a specific relaxation pathway.

1. INTRODUCTION

The excited state behaviour of aza-analogues of stilbenoid compounds, where one or two phenyl groups are replaced by pyridyl groups, has been extensively investigated in our [1–8] and other [9–13] laboratories. The fluorescence properties and the photoisomerization mechanism have been interpreted in terms of the competition among the radiative, non-radiative and reactive relaxation processes. The acid-base equilibria and the protonation effect on the photobehaviour in aqueous solutions have been studied in this laboratory for n-styrylpyridines [14–16], naphthyl- and phenanthryl-n-pyridylethenes [17, 18], n,n'-dipyridylethenes [19] and 1,4-di-(n-pyridyl)butadienes (n,n' = 2, 3 and 4) [20].

This paper describes the acid-base equilibria and the protonation effect on the photobehaviour of some aza-analogues of distyrylbenzene, bearing the nitrogen heteroatom in the two side aryl groups or in the central aromatic ring, previously studied in organic solvents [21–23]. The main aim was to compare their excited state properties with those of the corresponding hydrocarbons, 1,4-distyrylbenzene [1,4-(PhE)$_2$B, linear conjugation] and 1,3-distyrylbenzene [1,3-(PhE)$_2$B, crossed conjugation] and the corresponding dienes [21–24]. Replacement of benzene rings with pyridine rings or protonated pyridinium rings in stilbenoid compounds can differently affect the photobehaviour. Generally, the heteroatom has been found to reduce the torsional barrier to

isomerization thus leading to an increase of the photoreaction rate [7, 25, 26]. However, in some cases, the presence of n, π^* states introduced by the nitrogen atom have been found to favour internal conversion (IC), thus reducing both fluorescence and photoreaction. In the latter case, protonation of the pyridyl group is expected to avoid the deactivating effect of the n, π^* states, thus potentially increasing the contribution of the radiative and/or reactive relaxation pathways [16–18].

The results now obtained in aqueous solutions, at basic and acid pH's, are compared to those previously obtained for the corresponding hydrocarbons and for the same aza-analogues in organic solvents. They show that changes in pH may favour a selective relaxation pathways of S$_1$; this can be important since potential applications of these compounds in material science may require, depending on their nature, a predominance of the radiative pathway or the reactive one [24].

2. EXPERIMENTAL

The four EE compounds investigated (Scheme 1) bear the heteroatom in the two side rings [1,4-di-(2-pyridylethenyl)benzene (**1**)] or in the central ring [2,5-di-(phenylethenyl)pyridine (**2**), 2,6-di(phenylethenyl)pyridine (**3**) and 2,6-di(phenylbutadienyl)pyridine (**4**). Conjugation of compounds **1** and **2** is linear while crossed conjugation characterizes compounds **3** and **4** [24]. They were prepared by the Wittig reaction at the Padua laboratory for previous works carried out in organic solvents [21–23].

LINEAR CONJUGATION
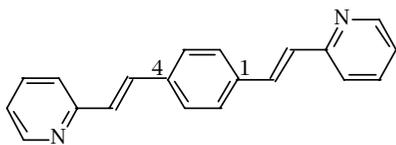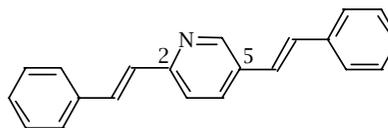
1,4-di-(2-pyridylethenyl)benzene **(1)**   2,5-di-(phenylethenyl)pyridine **(2)**

CROSSED CONJUGATION
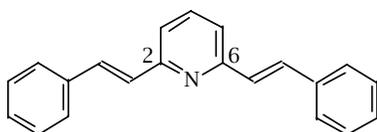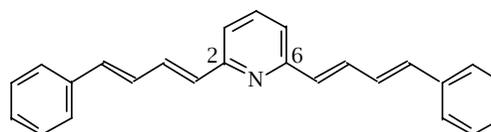
2,6-di-(phenylethenyl)pyridine **(3)**   2,6-di-(phenylbutadienyl)pyridine **(4)**

Scheme 1.

In the present work, a 30/70 (v/v) CH_3CN/H_2O mixture was generally used, the percentage of organic solvent, which reached 40% for compound **4**, being required by the scarce solubility in water.

The absorption measurements were carried out by a Perkin-Elmer Lambda 800 spectrophotometer. The fluorescence spectra were measured by a Spex Fluorolog-2 F112AI spectrofluorimeter. Dilute solutions (absorbance < 0.1 at the excitation wavelength, λ_{exc}) were used for the fluorimetric measurements. Except when otherwise specified, the emission and photoreaction quantum yields were determined at λ_{exc} corresponding to the maximum of the first absorption band (λ_{max}). 9,10-diphenylanthracene was used as fluorimetric standard ($\phi_F = 0.90$ in deareated cyclohexane [27]). 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. A Waters apparatus equipped with analytical Simmetry C18 (4.6×250 mm; 5μm) or Prontosil 200-3-C30 (4.6×250 mm; 3μm) columns and UV detector was used. Fluorescence lifetimes were measured by an Edinburgh Instrument 199S spectrofluorimeter, using the single photon counting method, or by a Spex Fluorolog-τ2 apparatus, based on the phase modulation technique, described elsewhere [26]. The fluorimetric and photochemical mea-

surements were carried out in solutions de-areated by bubbling nitrogen. All parameters reported in the tables are averages of at least three independent experiments with mean deviations of ca. 10% for fluorescence and photoisomerization quantum yields and ca. 15% for the fluorescence lifetimes.

The pK_a values were obtained by spectrophotometric titration, measuring the pH values by a Sargent PXB pH-meter with glass electrode. Britton buffers at constant ionic strength (0.01) were used in the 2–12 pH range, and $HClO_4$ and NaOH solutions for more acid and alkaline pH's, respectively. For the second protonation of the bibasic compound **1**, concentrated H_2SO_4 solutions were used, their acidity being evaluated by the H_0 acidity function. For the weaker base **2**, the small percentage of neutral species still present at pH 2 was found (check at pH 1) to have negligible effect on the radiative and reactive parameters.

Theoretical calculations on the energy levels, electronic structure and transition probabilities were carried out by the ZINDO/S method using Hyperchem (version 6) software and PM3 optimized geometries. The calculations of configuration interaction included 81 (9×9) single excited configurations. The overlap weighting factor was set $f_{p\pi} = 0.585$ for the neutral and biprotonated molecules and $f_{p\pi} = 0.70$ for the monoprotonated species to obtain a good accord with the experimental electronic spectra.
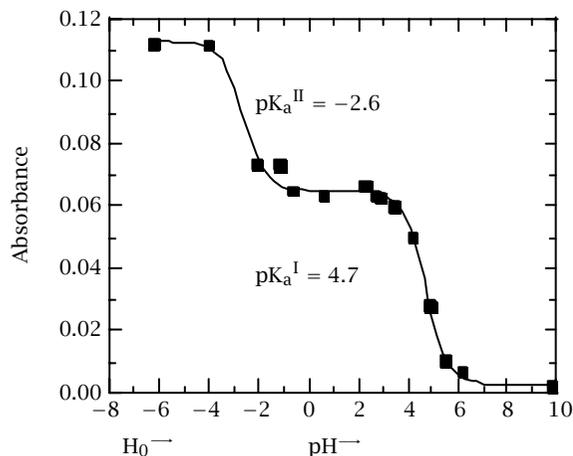
Figure 1. *Spectrophotometric titration curve of* **1** *in* 30/70 *v/v* CH_3CN/H_2O.

3. RESULTS AND DISCUSSION

3.1. Acid-base equilibria. This reaserch work started with the measurements of the acid-base properties of the investigated compounds in order to choose the pH values suitable to study the photobehaviour of the neutral and protonated species. The equilibrium constants (pK_a, where K_a is the dissociation constant of the conjugated acid) of some aza-analogues of *EE*-distyrylbenzene were measured by spectrophotometric titration. Figure 1 shows, as an example, the titration curve of the bibasic compound **1**. Table 1 collects the ground state pK_a's (not far from the known value of pyridine, ca. 5.2 [27]) together with the corresponding values for the first excited singlet state (pK_a^*) calculated by the Förster cycle. The high pK_a^* values (> 8) indicate that these molecules become much stronger bases on excitation, as found for the aza-analogues of several diaryl-ethenes [14–19] and the corresponding dienes [20].

Since these compounds exist in solution as a mixture of different conformers in equilibrium (see below), the spectrometric titration gives pK_a values which can be considered averaged values for the conformer mixtures. However, one can reasonably expect that different conformers have practically the same acid-base properties.

On the basis of these pK_a values, the effect of protonation on the spectral properties and on the photophysical and photochemical behaviour was investigated at pH values of 2 and 9, corresponding to the protonated and neutral species, respectively. For the bibasic compound **1**, pH 2 corresponds to the monoprotonated species; the biprotonated species was investigated at $H_0 = -4.9$.

3.2. Spectral properties and conformational equilibria. Figures 2 and 3 show the absorption and fluo-

Table 1. pK_a *and* pK_a^* *for the investigated compounds in* 30/70 CH_3CN/H_2O *at room temperature, measured by spectrophotometric titration and calculated by the Förster cycle.*

| compound	pK_a	pK_a^* (calc.)
1	4.7	9.2
2	3.8	8.5
3	4.3	10.1
4[a]	4.2	10.8

[a]In 40/60 CH_3CN/H_2O.
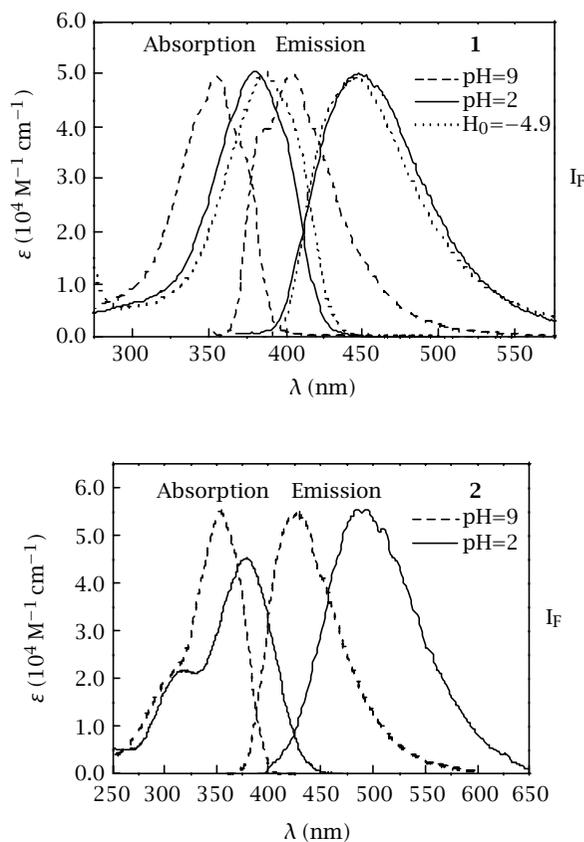
Figure 2. *Spectra of neutral, mono- and bi-protonated* **1** *and neutral and protonated* **2** *in* 30/70 *v/v* CH_3CN/H_2O.

rescence spectra of the neutral and protonated species of the four aza-compounds investigated. Protonation induces a marked red-shift of the spectra with respect to those of the neutral species. For the two compounds with crossed conjugation (**3** and **4**), an inversion of the intensity of the two first absorption bands was found on going from basic to acid medium.

This behaviour can be related to the shift of the conformational equilibrium towards the more elongated rotamer (see below).

MO calculations of the energy levels, transition probabilities and formation enthalpies of the neutral and protonated forms of these aza-compounds
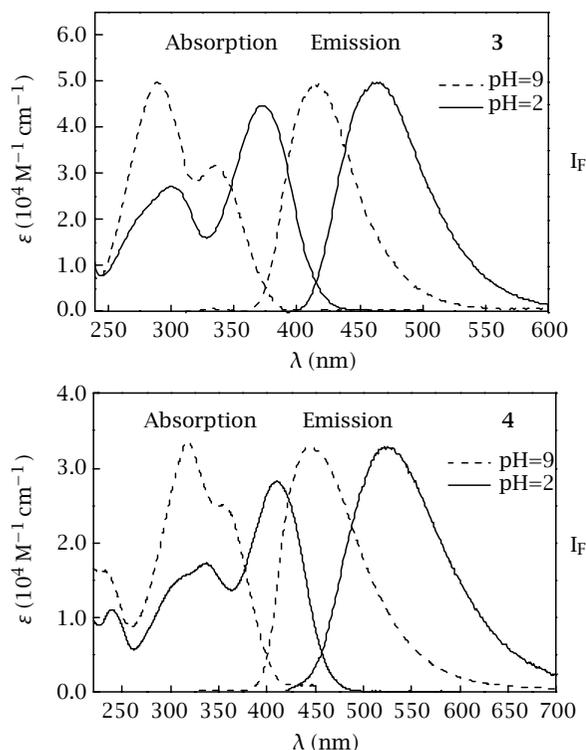
Figure 3. *Spectra of neutral and protonated* **3** *in* 30/70 *v/v* CH_3CN/H_2O *and* **4** *in* 40/60 *v/v* CH_3CN/H_2O.

Figure 4. *Effect of* λ_{exc} *and* λ_{em} *on the emission and excitation spectra of compound* **2** *in* 30/70 *v/v* CH_3CN/H_2O *at different* pHs.

(Tables 2 and 3) led to results in good agreement with the experimental spectra. The computed spectra well reproduce the large red-shift (over than 30 nm) observed after protonation. Those for the second protonation of 1,4-$(2PE)_2B$ remained practically unchanged; only a further small red shift was found in the experimental spectra.

The computed enthalpy difference of the conformers of the neutral species is small (in the range 0.2–0.8 kcal/mol) suggesting the occurrence of a dynamic equilibrium among different conformers in fluid solutions at room temperature. The observed photobehaviour of the compounds with pyridine as central ring clearly confirmed the presence of at least two different conformers [21, 22].

Indeed, as reported for the hydrocarbons [21, 23, 24], the very small effects of the excitation wavelength (λ_{exc}) on the fluorescence spectra of the 1,4-substituted compound **1**, as well as its mono-exponential decay, made the detection of the expected rotamers rather difficult (probably because of very similar spectral and photophysical properties of the existing conformers). A clearer wavelength dependence and a poly-exponential decay were found for the other compounds, particularly for **2** and **3** (see below). Figure 4 shows the wavelength effect on the spectra of compound **2**, as an example.

The results of MO calculations in Tables 2 and 3 refer to the two most different conformers. For the symmetric compound **1**, rotation of the pyridylvinyl group leads to species with practically the same heats of formation and spectral properties, whereas small, but more significant, differences were found by rotation of the side pyridyl groups, which changes the distance of the heteroatom with respect to the ethenic hydrogens. The two conformers reported in Table 2 are then the more elongated ones, with different positions of the heteroatom. On the other hand, for compounds **2**, **3** and **4**, the two most different configurations are those obtained by rotation of the two styryl or arylbutadienyl groups. For compound **2**, data in Table 2 refer to elongated species whereas, for the cross-conjugated compounds **3** and **4**, the most different conformations (I and II in Table 3) are the most elongated and constricted ones.

For compounds **2**, **3** and **4**, spectral changes were also found at pH 2 where a larger enthalpy difference favours the less constricted conformer I which absorbs at shorter wavelengths. This allowed the quasi-pure spectrum of the bathochromic rotamer II to be obtained by selective excitation at the tail of the absorption spectrum (Figure 4).

Table 2. MO *calculations of electronic spectra (transition energy, λ, and oscillator strength, f) and heats of formation (ΔH_f°) for the two most different conformations of neutral and protonated compounds* **1** *and* **2** *(linear conjugation).*
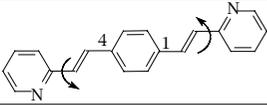
molecule	rotamer	ΔH_f° (kcal/mol)	λ (nm)	f	
1	I	112.66	348.5	2.00	S_1
			296	0.004	S_2
			278	0.058	S_4
	II	113.16	348	1.96	S_1
			296	0.003	S_3
			279	0.15	S_4
1-H$^+$	I	259.97	422	1.76	S_1
			290	0.17	S_2
			281	0.21	S_3
	II	261.44	426	1.67	S_1
			290	0.17	S_2
			281	0.36	S_3
1-H$_2^{++}$	I	444.95	421	1.95	S_1
			307	0.018	S_3
			280	0.13	S_4
	II	448.02	422	1.86	S_1
			307	0.012	S_3
			277	0.275	S_4
2	I	105.45	350	1.86	S_1
			303	0.13	S_2
	II	105.69	353	1.70	S_1
			297	0.37	S_2
			272	0.026	S_3
2-H$^+$	I	250.29	384	1.45	S_1
			312	0.89	S_2
	II	251.58	395	1.24	S_1
			303	0.953	S_2
			295	0.307	S_3
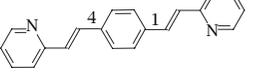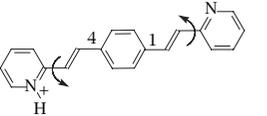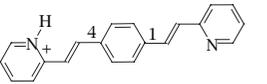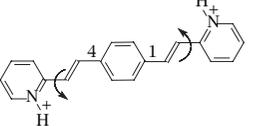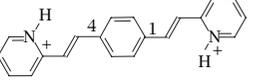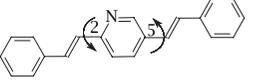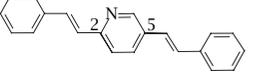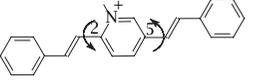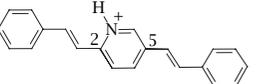
The first transition, characterized by a high value of the oscillator strength, populates an allowed excited singlet state for all compounds investigated. The splitting of the first absorption band into two components, characteristic of aza-compounds with the ethenic bridge in ortho position with respect to the heteroatom [30], is not much evident when the pyridine is the side group, as in compound **1**. A weak hypsochromic band (almost 10 times less intense than the bathochromic one) is observable only for conformer II, having the N atom closer to the ethenic hydrogen, and for the protonated species. A slightly more evident behaviour, particularly at pH 2, was found for compound **2**, with the N atom in the central ring and with linear conjugation. The splitting becomes more important in the cross-conjugated compounds **3** and **4**. The calculations on the neutral and protonated, more constricted, species of these compounds (rotamers II in Table 3) gave the first transition less intense than that of the hypsochromic band in the absorption spectra. This is in nice agreement with the spectra of Figure 2 showing an inversion in the intensity of the first two absorption bands in the protonated species with respect to those of neutral ones, pointing to a prevalence of the hypsochromic (more elongated) conformer I in acid medium. Indeed, the calculated oscillator strength of

Table 3. MO *calculations of electronic spectra (transition energy, λ, and oscillator strength, f) and heats of formation* (ΔH_f°) *for the most two different conformations of neutral and protonated compounds* **3** *and* **4** *(crossed conjugation).*
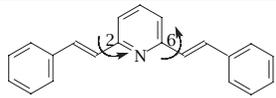
molecule	rotamer	ΔH_f° (kcal/mol)	λ (nm)	f	
3	I	106.05	337	1.25	S_1
			296	0.32	S_2
			276	0.902	S_6
	II	106.58	343	0.75	S_1
			288	0.019	S_2
			287	1.07	S_3
			282	0.072	S_5
			275	0.47	S_6
3-H$^+$	I	247.77	388	1.80	S_1
			293	0.373	S_2
			268	0.033	S_3
	II	250.67	396	1.085	S_1
			291	1.046	S_2
			267	0.41	S_3
4	I	133.86	354	2.28	S_1
			315	0.19	S_2
			293	0.79	S_3
	II	134.72	363	0.834	S_1
			307	2.20	S_2
			293	0.24	S_3
4-H$^+$	I	274.00	434	2.44	S_1
			330	0.25	S_2
			294	0.054	S_3
			275	0.48	S_4
	II	277.33	446	1.03	S_1
			328	1.67	S_2
			295	0.843	S_3
			274	0.114	S_4
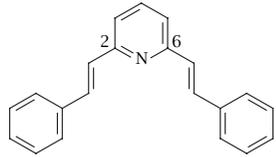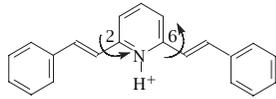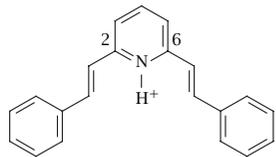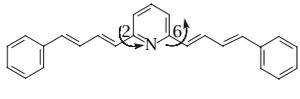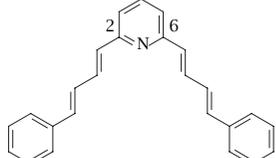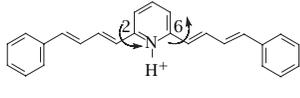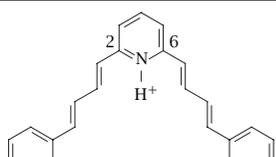
the first two absorption transitions of the protonated **3** compound is very similar for the more constricted rotamer II, but higher for the first transition in the case of rotamer I. A similar behaviour was found for compound **4**. However, it has to be noted that, for the latter, more complicate conformational equilibria exist in solutions since rotation around the quasi-single bonds of the olefin chain can come into play.

The calculated heat of formation for the cross-conjugated compounds points to the elongated species as the most stable one, but the results on the relative stability, in the case of the neutral species, could be

Table 4. *Effect of the nitrogen heteroatom on the photobehaviour of* 1,4-(2PE)$_2$B *(1, with linear conjugation) in non-polar solvent and in* 30/70 CH$_3$CN/H$_2$O *at* pH 9 *and* 2 *and* H$_0$ = −4.9.

solvent	MCH/3MP		aqueous medium		
compound	1,4-(PhE)$_2$B[a]	1[a]	1	1-H$^+$	1-H$_2^{++}$
Φ_F	0.84	0.28	0.13	0.018	0.033
τ_F (ns)	1.7	0.56	0.35	0.12	0.27
k$_F$ (10^8 s^{-1})	4.3	5.0	3.7	1.5	1.2
$\Phi_{EE \to ZE}$	< 0.001	0.25	0.31	0.56	0.64

[a] From ref. [22].

Table 5. *Effect of the nitrogen heteroatom on the photobehaviour of* 2,5-(PhE)$_2$P *(2, with linear conjugation) in non-polar solvent and in* 30/70 CH$_3$CN/H$_2$O *at* pH 9 *and* 2.

solvent	MCH/3MP		aqueous medium	
compound	1,4-(PhE)$_2$B[a]	2[a]	2	2-H$^+$
Φ_F	0.84	0.29	0.32	0.14
τ_F (ns)	1.7	0.43/0.92	0.57/1.1	0.45/1.2
k$_F$ (10^8 s^{-1})	4.3	4.0[b]	4.1[b]	1.8[b]
$\Phi_{EE \to ZE}$	< 0.001	0.046	0.15	0.31

[a] From ref. [22].
[b] derived using a mean τ_F value obtained by a mono-exponential treatment of the fluorescence decay.

uncertain owing to the very small enthalpy differences between the crowded and elongated species of Table 3. Nevertheless, a more refined calculation based on an *ab-initio* method at 3-21G level for the geometry optimization, carried out only for compound **3**, resulted in an inversion of the rotamers stability, in agreement with our previous findings in organic solvent [21].

3.3. Photophysical and photochemical properties.

Linear conjugation (1,4- and 2,5-derivatives). Tables 4 and 5 show the solvent and protonation effect on the relaxation properties of compounds **1** and **2** compared with the parent hydrocarbon, 1,4-(PhE)$_2$B. The prevalent relaxation pathway of the latter is the radiative one, accompanied by a very low isomerization yield, negligible S$_1$ → T$_1$ intersystem crossing (ISC) but non-negligible S$_1$ → S$_0$ internal conversion (IC) [22, 24]. The nitrogen effect in the conjugative position leads to a redistribution of the excitation energy which reduces the order of the isomerizable bonds lowering the torsional barrier and favouring the ZE production to detriment of the radiative deactivation. In fact, the fluorimetric parameters in non-polar solvent [22], reported for comparison, show a net decrease in both ϕ_F and τ_F for the aza-analogue. The radiative kinetic parameter, k$_F$, remains practically unchanged at values above 10^8 s^{-1}, typical of allowed transitions. The competition between radiative and reactive relaxations pointed to a twisting process in the singlet potential energy curve [22, 24]. A diabatic mechanism, common to stilbene and many stilbene-like molecules, is assumed to be operative. It involves IC from the perpendicular configuration in S$_1$ (^{1}perp*) to the ground state ^{1}perp and relaxation to E and Z with a partitioning factor of ∼ 0.5 [31].

For compound **1** (Table 4), the emission quantum yield in aqueous medium, lower than that in organic solvent, is still substantial in the basic solution but decreases markedly for the protonated species. The lifetime has a similar trend. The fluorescence decay is monoexponential within the limits of the experimental error. The drastic reduction in the radiative parameters is accompanied by an increase in the EE→ZE photoisomerization which proceeds with a quantum yield slightly higher than that in organic solvent, at pH 9, and almost doubled in acid media. In fact, the fluorescence yield decreases by a factor of ∼ 50, while the isomerization yield increases by a factor of more than 600, with respect to the parent hydrocarbon, and reaches at pH 2 a value close or higher than the maximum value (50%) expected for a diabatic mechanism. The effect of protonation is then quite important to drive the relaxation of the excited molecule along the reactive pathway.

The photobehaviour of compound **2** (Table 5) is not much different from that of **1**. Howerer, the decrease in ϕ_F and the corresponding increase in $\phi_{EE \to ZE}$ are less marked and a contribution of IC is probably operative. The fluorescence decay is biexponential at both basic and acid pH's, in agreement with the λ_{exc} effect on the spectra (section 3.2). For this asymmetric compound, only the ZE isomer (with the cis double bond in ortho position with respect to the heteroatom) was produced in both basic and acid media. A small production of the other stereoisomer (EZ) was found only by sensitization with a triplet donor [22].

Table 6. *Effect of the nitrogen heteroatom on the photobehaviour of* $2,6$-$(PhE)_2P$ *(**3**, with crossed conjugation) in non-polar solvent and in* $30/70$ CH_3CN/H_2O *at pH* 9 *and* 2.

solvent	MCH/3MP		aqueous medium	
compound	$1,3$-$(PhE)_2B$[a]	3[a]	3	3-H^+
Φ_F	0.28/0.88	0.24/0.72	0.26	0.034
τ_F (ns)	18/7.5	1.5/3.5	1.2/3.1	0.34/1.1
k_F (10^8 s^{-1})	0.16/1.2	1.6/2.1	1.1	0.47
$\Phi_{EE \to ZE}$	0.038	0.14/0.075	0.10	0.72

[a] From ref. [21].

Table 7. *Effect of the nitrogen heteroatom on the photobehaviour of* $2,6$-$(PhBu)_2P$ *(**4**, with crossed conjugation) in non-polar solvent and in* $40/60$ CH_3CN/H_2O *at pH* 9 *and* 2.

solvent	MCH/3MP		aqueous medium	
compound	$1,3$-$(PhBu)_2B$[a]	4[a]	4	4-H^+
Φ_F	0.44/0.71	0.18/0.88	0.30	0.038
τ_F (ns)	26/8.0	1.4/2.8	3.6	0.30
k_F (10^8 s^{-1})	0.17/0.89	1.3/3.1	0.83	1.3
$\Phi_{EEEE \to EZEE}$	0.076	0.031	0.11	0.28
$\Phi_{EEEE \to ZEEE}$	0.068	0.017	0.05	not observed

[a] From ref. [23].

Crossed conjugation (1,3 and 2,6 derivatives). The radiative and reactive properties of compounds **3** and **4** in non-polar and protic solvents and at pH 2 are shown in Tables 6 and 7 where they are compared with those of the parent hydrocarbons, $1,3$-$(PhE)_2B$ and the corresponding butadienyl-derivative. Contrary to the 1,4 analogue, fluorescence remains the main deactivation pathway of these cross-conjugated distyrylbenzenes, at least for one rotamer. As observed in previous works from our [21] and other laboratories [24, 32, 33], the absorption spectrum of $1,3$-$(PhE)_2B$ is similar in position to that of E-stilbene (with almost double intensity) indicating that the cross-conjugation makes the two styryl chromophores practically independent. However, the emission spectrum is red-shifted and originates from a lower lying forbidden state of A_g parentage, at least for one of the two observable conformers (see section 3.2). In compound **3**, the effect of the heteroatom in the central ring does not affect much the fluorescence yield (Table 6) but modifies markedly the spectral properties and the conformational equilibrium (see later). Moreover, the yield of the reactive pathway increases in the aza-analogue, but less than for the linearly conjugated analogues. As suggested by NMR measurements, this behaviour is probably due to a type of intramolecular hydrogen bond interaction in one of the two rotamers, which keeps the molecule in a more rigid and planar conformation, thus reducing the IC efficiency [21]. This working hypothesis is confirmed by the behaviour in aqueous medium where the breaking of intramolecular N··· H bonds restores the trend observed for the 1,4 aza-compound.

The emission quantum yield of **3**, lower than that in organic solvent, is still substantial in the basic solution and decreases further, by a factor of 7, at pH 2. The lifetime, clearly biexponential, as found in organic solvent [21], is also quite smaller, by a factor of ~ 3, in acid medium. The decay was better investigated at different λ_{exc} and λ_{em} values (Table 8). On increasing λ_{exc}, the two lifetimes change only slightly, almost within the limits of the experimental uncertainty, but the weight of the longer component increases and tends towards 100% when exciting at the tail of the absorption spectrum. This confirms the presence of two main ground state rotamers (probably I and II in Table 3), as reported for the same molecules in organic solvent [21], and indicates that the bathochromic one is the longer lived rotamer. A complete fluorimetric analysis of the conformational equilibrium, based on kinetic and statistical methods [34], successfully carried out for similar compounds [35], was out of the scope of the present work. Therefore, the parameters in Table 6 refer to the rotamer mixture excited at the maximum of the first absorption band, corresponding to similar abundances of the two species. Given the relatively small difference between the lifetimes of the two rotamers, the radiative rate constant was calculated by using the lifetime measured with a monoexponential treatment. A similar behaviour was found for compound **2**, as shown in Table 8. Only negligible deviations from mono-exponential decay were observed for compound **4**.

The radiative kinetic parameter of **3** reveals an allowed transition at pH 9, but is rather lower at pH 2,

Table 8. λ_{exc} *effect on the fluorescence decay of neutral and protonated species of linear-*(**2**) *and cross-conjugated* (**3**) *compounds in* 30/70 v/v CH_3CN/H_2O *at room temperature.*

compound		λ_{exc} (nm)	λ_{em} (nm)	τ_I (ns)	τ_{II} (ns)	% (II)
2	pH = 2	380	500	0.43	1.18	46
		380	420	0.45		0
		425	500	0.51	1.18	75
	pH = 9	350	425	0.55	1.10	43
		350	385	0.58	1.25	17
		395	425		0.93	100
3	pH = 2	372	460	0.30	1.11	49
		400	460	0.35	1.14	73
		410	> 420[a]	0.36	1.12	82
	pH = 9	289	408	1.20	3.42	89
		335	408	1.22	3.15	77
		375	408	1.43	3.47	95

[a] Measured by a fluorimetric method based on the phase modulation technique.

as found for the other compounds investigated and already observed for analogous compounds [20]. The EE→ZE isomerization yield of **3** is relatively small for the neutral molecule but, at pH 2, becomes higher (0.72) than the maximum value expected for a diabatic mechanism, as already reported for some styrylquinolines [36]. A tentative explanation of this behaviour could be related to a change in the shape of the S_0 and S_1 potential energy surfaces (different partitioning factor from the perpendicular configuration towards E and Z) caused by protonation.

The behaviour observed for the butadienyl derivative **4** (Table 7) partly reflects that of the ethenyl analogue. In the hydrocarbon and its aza-analogue in organic solvent, the photoreaction leads to two isomeric photoproducts, namely EZEE (rotation of the double bond adjacent to the central ring) and ZEEE (rotation of the double bond adjacent to the side ring). In this case, the introduction of the heteroatom in the central ring leads to a decrease in the isomerization yield in non-polar solvent, probably due to the intramolecular N···H interaction, which produces a more rigid and photostable structure. However, in protic solvent, a normal photoreactivity [7, 8, 37] was again observed, with a prevalence of the twisting around the double bond adjacent to the pyridine ring; at pH 2, EZEE becomes the unique photoproduct.

At pH 2, the strong decrease in the fluorescence yield is similar to the ethenyl derivative whereas the increase in reactivity is smaller since the longer chain favours non-radiative and non-reactive deactivation through the IC process. The lifetime of **4** offers a pattern of difficult interpretation owing to a larger number of possible conformers.

In the cross-conjugated compounds, an important difference between compounds having a central benzene or pyridine ring lies in the k_F value of the longer-

lived rotamer, which is markedly lower than that of the other rotamer, in the case of the hydrocarbons. This indicates that the emitting state of the longer-lived rotamer of 1,3-$(PhE)_2B$ and of the corresponding diene has a forbidden character. On the other hand, in compounds **3** and **4**, the observed reduction in the fluorescence lifetime of the neutral species is mainly related to the higher k_F values, which indicate an allowed emitting state.

4. CONCLUSIONS

The position of the N atom in the side or central ring, the kind of conjugation and the pH of the solutions are important factors in determining the relaxation pathways of the excited state. The behaviour of the neutral molecules in the protic solvent was found similar to that in non-polar organic solvent, with a slight tendency to an increase in the yield of the reactive pathway to detriment of the radiative one. This behaviour is drastically emphasized in acid medium where the fluorescence quantum yield decreases by an order of magnitude for protonated compounds leading to high values of the photoreaction yield.

The presence of two main conformers, already observed in organic solvent for compound **2** [22] and for cross-conjugated compounds [21, 23], remains also in aqueous solution making the study more interesting but also more complicated.

The intermolecular interaction of these aza-compounds with the protic solvent breaks the intramolecular N-H interaction observed in non-protic solvent, particularly for the crossed compounds. Since this interaction has been reported to affect the conformational equilibrium (favouring the compressed rotamer) [21, 23, 35] and to reduce the photoreactivity (which increases very little with respect to the

hydrocarbon) [21–23], the protic solvent allows a substantial increase in the isomerization yield to be again observed.

An interesting effect was observed in the butadienyl derivative **4** where the basic species leads to two isomeric photoproducts whereas the acid medium, in addition to the general increase in the isomerization yield, selectively leads the EZEE isomer with the cis bond adjacent to the central pyridine ring.

The present results offer a picture of the different behaviour of the neutral and protonated species and indicate the experimental conditions suitable for a selective choice of a preferred relaxation pathway.

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