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Triplet-sensitized photobehaviour of the three stereoisomers of 1,4-distyrylbenzene and some aza-analogues

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Abstract

The triplet spectral properties of the three stereoisomers (EE, ZE and ZZ) of 1,4-distyrylbenzene and some symmetric *EE*-aza-analogues, bearing a nitrogen heteroatom in the side (2′-pyridyl, 4′-pyridyl or 2′-quinolyl) or in the central (2,5-pyridine) arene rings, have been investigated by laser flash photolysis in different solvents and compared with those of the parent hydrocarbon. The quantum yields of the triplet-sensitized photoisomerization have also been measured. Adiabatic formation of the excited $^3EE^*$ isomer by irradiation of the other geometrical isomers has been detected by transient spectroscopy. The effect of the substrate concentration on the sensitized photoisomerization quantum yield revealed the occurrence of a quantum chain process, as known for similar arylolefins.
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1. Introduction

As an extension of our long-term research project on the photobehaviour of stilbenoid compounds, we have recently addressed our attention to molecules with more than one isomerizable double bond. The photobehaviour of distyrylbenzenes and analogous compounds, in which two aryl(heteroaryl)-ethenyl substituents are attached at a central arene group, has been extensively investigated in the last two decades [1] because of their interest as scintillators, laser dyes and building blocks of polyphenylenevinylene materials having potential applications in optoelectronics [2].

The parent hydrocarbon, distyrylbenzene, $(PhE)_2B$, exists in three isomeric structures depending on whether the two styryl substituents are in the para (1,4, linear conjugation), meta (1,3, crossed conjugation) or ortho (1,2, sterically hindered conjugation) positions of the central benzene ring. The 1,4-$(PhE)_2B$, particularly the compound which bears alkyl-substituted side phenyl groups, has been investigated by several laboratories [1,3–7]. The two-fold (diabatic/adiabatic) mechanism for the triplet-sensitized *cis–trans* photoisomerization has been interpreted on the basis of the results obtained by quantum yield measurements and laser flash photolysis [5].

The introduction of heteroatoms into these hydrocarbons, e.g., by replacing the side phenyl groups with pyridyl or thienyl groups, may markedly affect their excited state properties [8–12]. Our interest in distyrylbenzene aza-analogues started with a study of the photobehaviour of some pyridine derivatives, 2,6-disubstituted with arylethenyl groups [9]. More recently, our attention has been addressed to some symmetric aza-analogues of distyrylbenzene [10–12]. The study of the properties of the lowest excited singlet states of some linearly conjugated (1,4-substitued) compounds [10] has shown that the heteroatom in the side rings generally induces a net decrease in the yield of the radiative deactivation and a corresponding increase in the reactive pathway, which is favoured by lower torsional barriers in the singlet manifold. The population of the triplet state was rather scarce and its implication in the photoreaction seemed to be negligible. The effect of the heteroatom in the central ring, already

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reported for the cross-conjugated 2,6-distyrylpyridine [9], was also investigated for the isomeric 2,5-distyrylpyridine [2,5-$(PhE)_2P$] [10] which maintains a linear conjugation, and found to be less important than that of nitrogen in the side rings.

The aim of the present work was to study more deeply the triplet properties and the triplet sensitized photoreactivity of distyrylbenzene and its aza-analogues with 2′-pyridyl (2P), 4′-pyridyl (4P) and 2′-quinolyl (2Q) side groups. Since the information available in the literature on 1,4-$(PhE)_2B$ is scattered and mainly related to compounds bearing alkyl substituents at the side phenyl groups [4,5,7], all stereoisomers (EE, ZE and ZZ) of the parent unsubstituted hydrocarbon were revisited. Adiabatic formation of the excited $^3EE^*$ by irradiation of the other isomers and the occurrence of an energy transfer chain process were evidenced by the concentration effect on the yield of the sensitized isomerization.

2. Experimental

The studied compounds (Scheme 1) were synthesized for previous works [10]. The solvents used were benzene, acetonitrile (MeCN) and 9/1 v/v methylcyclohexane/3-methylpentane (MCH/3MP). All solvents were of the highest purity degree from Fluka; MCH and 3MP were purified before use by standard methods.

The triplet behaviour was investigated by laser flash photolysis at 355 nm, using the third harmonic of a Continuum (Surelite II) Nd:YAG laser, and at 425 nm, using a parametric oscillator, OPO, pumped by the same laser. The triplet spectra and the absorption coefficients (ε_T) were obtained in sensitized experiments using benzophenone ($\lambda_{exc} = 355$ nm; $\varepsilon_T^{max} = 7220$ and $6250\,M^{-1}\,cm^{-1}$ in benzene and MeCN, respectively) or biacetyl ($\lambda_{exc} = 425$ nm; $\varepsilon_T^{max} = 5160\,M^{-1}\,cm^{-1}$ in benzene) [13] as triplet energy donor. While the values of the product between the absorption coefficient and the triplet quantum yield ($\varepsilon_T \times \phi_T$) were obtained with good reproducibility (±10% in three independent experiments), a much larger uncertainty (±30%) was found for the separate values of the triplet absorption coefficients and quantum yields. In any case their measured values allowed to roughly evaluate the intersystem crossing rate parameters, k_{ISC}. The triplet lifetimes were obtained with an uncertainty of ±10%.

The triplet sensitized photoreaction was carried out in benzene and MeCN using biacetyl as triplet donor ($\lambda_{irr} = 435$ nm). For the photochemical measurements a 150 W high pressure Xenon lamp coupled with a monochromator was used. The photoisomerization was monitored by HPLC with Prontosil 200-3-C30 (4.6 mm × 250 mm; 3 μm) and Yupiter phenomenex C18 (4.6 mm × 250 mm; 5 μm) columns. A photodiode array spectrophotometer was used as detector and water/MeCN mixtures as eluant. In all measurements the solutions were deoxygenated by purging with nitrogen. The reported quantum yields are averages of at least three independent measurements (uncertainty: 10%).

3. Results and discussion

3.1. Triplet spectral behaviour

Fig. 1 shows the transient spectra of the EE isomers of the five compounds investigated obtained in sensitized experiments by benzophenone. Table 1 collects the λ_{max} values of the EE isomers of the investigated compounds in three solvents together with other triplet properties. The values of λ_{max} and τ_T of the hydrocarbon in MCH/3MP are close to those reported for the same compound bearing 3,5-di-tert-butyl substituents at the side phenyl groups in cyclohexane ($\lambda_{max} = 505$ nm, $\tau_T = 3.5$ μs) [5].

The $T_1 \rightarrow T_n$ intense bands are centred around 500 nm. Direct irradiation produced very low intensity spectra with

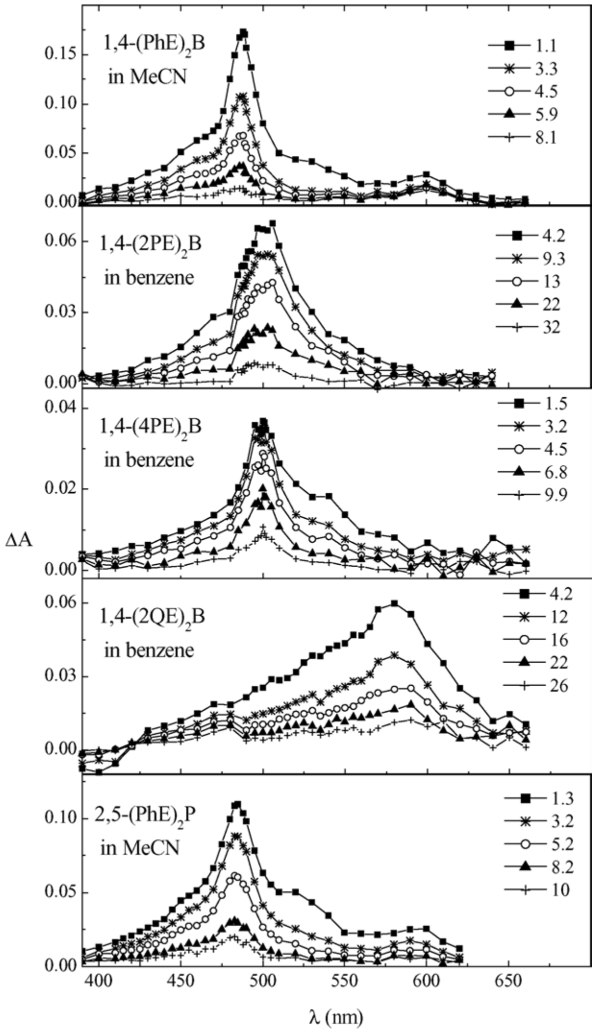
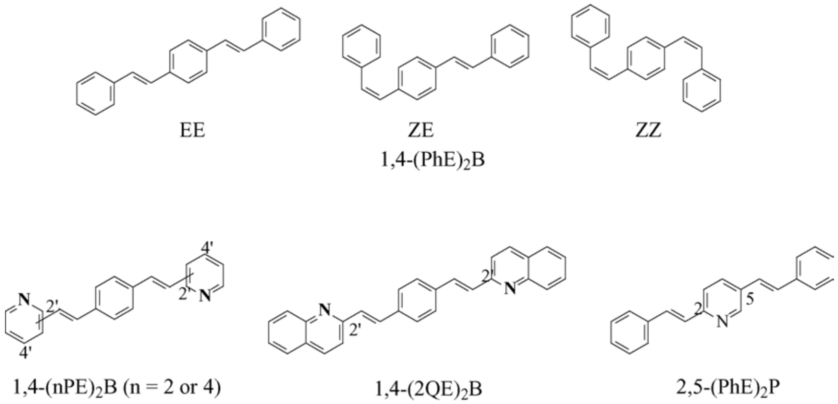


Fig. 1. $T_1 \rightarrow T_n$ absorption spectra of the EE isomers of 1,4-$(PhE)_2B$ and four aza-analogues, obtained in sensitized experiments by benzophenone at different delay times (in μs).



Scheme 1.

Table 1
Spectral and reactivity parameters for the triplet state of *EE*-1,4-(PhE)$_2$B and some aza-analogues in three solvents

Compound	Solvent	λ_{max} (nm)	τ_T (μs)	ε_T (10^4 M^{-1} cm^{-1})	ϕ_T ($\times 10^2$)[a]	ϕ^{sens}
1,4-(PhE)$_2$B	MCH/3MP	485	3		0.45	
	Benzene	500	6	2.3		0.46
	MeCN	487	10	2.1	2.9	0.18
1,4-(2PE)$_2$B	MCH/3MP	485	25		0.47	
	Benzene	506	25	3.95	0.55	0.075
1,4-(4PE)$_2$B	MCH/3MP	484	11		2.2	
	Benzene	500	6	2.5	0.65	0.26
1,4-(2QE)$_2$B	MCH/3MP	565	24		6.8	
	Benzene	580	35	3.7	6.5	0.040
2,5-(PhE)$_2$P	MCH/3MP	490	4		4.6	
	MeCN	485	12	1.9	4.9	
	Benzene			2.2		0.025 (ZE); 0.098 (EZ)

[a] The values in MCH/3MP were derived using the absorption coefficients measured in benzene.

the same maxima. The 2Q derivative showed a marked red shift with respect to the other compounds, as in the case of the $S_0 \rightarrow S_n$ absorption [10]. The weak band, centred at 600 nm, observed for the hydrocarbon (not observed in previous works on the alkyl-substituted compound in cyclohexane [5]) and 2,5-(PhE)$_2$P in MeCN, was assigned to the corresponding radical cations, probably formed by photoionization. This assignment was based on the oxygen effect and the results found in the presence of chloranil (CA) as electron acceptor. Oxygen quenched efficiently the bands centred at 490 nm, assigned to the $T_1 \rightarrow T_n$ absorption, but did not affect at all the kinetics of the transient that absorbs at ~600 nm (as an example, its lifetime was 18 μs both in air-equilibrated and de-aerated solutions of 1,4-(PhE)$_2$B in MeCN). The transient spectra of 2,5-(PhE)$_2$P in MeCN, recorded at different delays after the laser pulse in the presence of CA, are shown in Fig. 2. The intense band centred at 510 nm, recorded at a delay of 0.08 μs, was assigned to the CA triplet. Its decay was accompanied by the growth of two bands, the well-known absorption of the radical anion of CA at 440 nm ($\varepsilon = 9700$ M^{-1} cm^{-1} in MeCN) [14] and the absorption at 610 nm, assigned to the radical cation of *EE*-2,5-(PhE)$_2$P formed in the same electron transfer process. The maximum absorption coefficients of the radical cations (~12,500 M^{-1} cm^{-1} for both compounds in MeCN) were evaluated by comparing the maximum intensities of the bands assigned to the radical anion and cation, respectively.

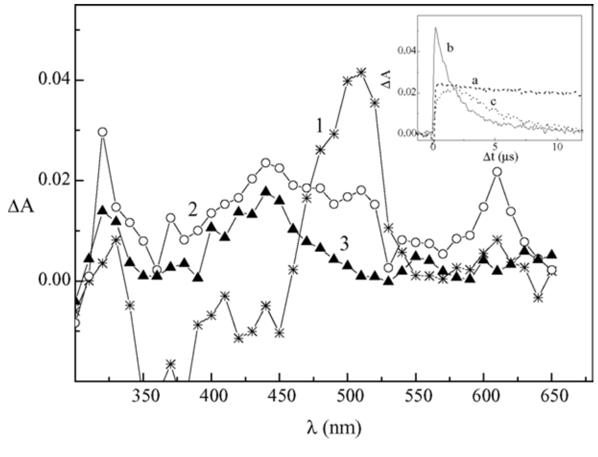


Fig. 2. Transient spectra of *EE*-2,5-(PhE)$_2$P (5.9×10^{-6} M) in the presence of chloranil ($A_{355} = 0.75$) in MeCN at different delays: 1, (*) 0.08 μs; 2, (○) 2 μs; 3, (▲) 17 μs. The inset shows the decay kinetics at different wavelengths: a (- - -) 440 nm; b (—) 510 nm; c (· · ·) 610 nm.

Table 2
Photoisomerization quantum yields of the three isomers of 1,4-$(PhE)_2B$ sensitized by biacetyl in two solvents at room temperature as a function of the isomer concentration

Isomer	Benzene			MeCN		
	Concentration (10^{-3} M)	ϕ^{sens}		Concentration (10^{-3} M)	ϕ^{sens}	
EE		$\phi^{sens}_{EE\to ZE}$	$\phi^{sens}_{EE\to X}$		$\phi^{sens}_{EE\to ZE}$	$\phi^{sens}_{EE\to X}$
	0.9	0.46	0.01	0.3	0.18	0.07
	1.6	0.40	0.01			
ZE		$\phi^{sens}_{ZE\to EE}$			$\phi^{sens}_{ZE\to EE}$	
	0.5	0.58		0.7	0.73	
	0.84	0.70		1.1	0.87	
	1.1	0.83		2.2	1.3	
	1.7	1.0		2.7	1.5	
	2.5	1.3		3.1	1.8	
	4.2	1.6				
	5.2	2.2				
	6.2	2.3				
ZZ		$\phi^{sens}_{ZZ\to ZE}$	$\phi^{sens}_{ZZ\to EE}$		$\phi^{sens}_{ZZ\to ZE}$	$\phi^{sens}_{ZZ\to EE}$
	1.1	0.38	0.50	1.4	0.24	0.60
	1.4	0.38	0.53	3.6	0.21	0.64
	2.8	0.39	0.65	5.8	0.23	0.72
	3.2	0.37	0.70			
	6.3	0.38	0.88			

3.2. *Photobehaviour of the hydrocarbon stereoisomers*

The quantum yield of triplet formation reported in Table 1 for *EE*-1,4-$(PhE)_2B$ is very small. The triplet parameters were thus obtained from sensitized experiments by benzophenone and biacetyl. The sensitized $T_1 \rightarrow T_n$ absorption spectra of all stereoisomers (EE, ZE and ZZ) of 1,4-$(PhE)_2B$ in de-aerated MeCN (Fig. 3) showed the same shape with a maximum at 490 nm and the same decay time, pointing to a common triplet state, similarly to what previously reported for the same isomers alkyl-substitued at the side phenyl rings in cyclohexane [5].

In Table 2 the sensitized isomerization quantum yields for the three stereoisomers are reported. All of them display a high reactivity. The values measured at low olefin concentration in benzene are in very good agreement with those reported for the alkyl-substituted compounds in cyclohexane [5]. As in the case of the reactivity under direct excitation [10], photoisomerization of EE and ZE occurs in both directions. ZZ was not produced in sensitized experiments. A side photoproduct (X) with very low quantum yield was found in the sensitized experiments of EE. It was assigned to an oxygenated compound, probably formed by interaction with the reactive singlet oxygen produced in competitive energy transfer from biacetyl, on the basis of the electronic and gas-mass spectra. The latter showed the main peak at 298, corresponding to the mass of the parent molecule with a gain of an oxygen atom, while the UV spectrum appeared to be very similar to that of alkyl-substituted *E*-stilbenes [15], pointing to a structure where the extended distyrylbenzene conjugation is interrupted. The scarce solubility of EE in MeCN prevented us to measure its sensitized yield at higher concentrations where the competition of the oxidation process should be less important.

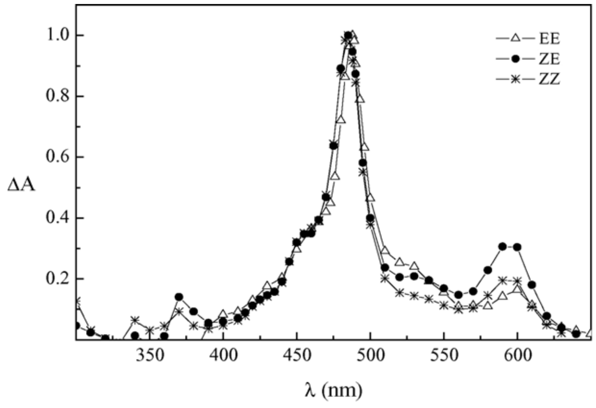


Fig. 3. Normalized $T_1 \rightarrow T_n$ absorption spectra (recorded with a delay of ~1 μs after the pulse) obtained by sensitization from benzophenone of the EE, ZE and ZZ stereoisomers of 1,4-$(PhE)_2B$ (~5×10^{-5} M) in MeCN.

The sensitization of ZZ gave both ZE and EE, the latter implying a “one photon-two bond” isomerization mechanism. Formation of EE by sensitization of ZZ is a proof of at least one adiabatic step ($^3ZZ^* \rightarrow {}^3ZE^*$) in the overall isomerization. The study of the effect of the concentration of the starting isomer on the sensitized isomerization supported the involvement of adiabatic pathways. Practically, no concentration effect was found for $^3EE^* \rightarrow ZE$ and $^3ZZ^* \rightarrow ZE$. On the contrary, the isomerization quantum yield increased with the concentration in the case of $^3ZE^* \rightarrow EE$ and $^3ZZ^* \rightarrow EE$, reaching values even higher than unity. This behaviour indicates the occurrence of a quantum chain process by the known mechanism firstly proposed by Arai and Tokumaru for diarylethenes [16], that in this case implies energy transfer from $^3EE^*$, adiabatically formed from $^3ZE^*$, to the ground

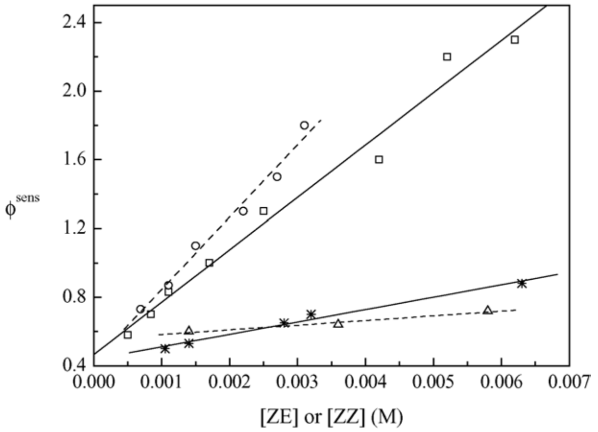


Fig. 4. Plot of the sensitized isomerization quantum yields as a function of the starting isomer concentration: ZE → EE in MeCN (○) and benzene (□); ZZ → EE in MeCN (△) and benzene (*).

state of ZE or ZZ. As a matter of fact, $^3EE^*$ is the chain driver and the independence of concentration observed for $\phi^{sens}_{ZZ\to ZE}$ is due to a balance between the decrease in the $^3EE^* \to ZE$ yield, expected when $^3EE^*$ is quenched by the bimolecular energy transfer process, and the increase due to the chain process, which leads to a recovery of $^3EE^*$ by the adiabatic $^3ZE^* \to {}^3EE^*$ isomerization.

The plots of ϕ^{sens} as a function of the starting isomer concentration are shown in Fig. 4; some parameters are reported in Table 3. The good correlation for the linear fit is in agreement with a largely prevalent adiabatic mechanism. In fact, the relationship describing the dependence of $\phi^{sens}_{ZE\to EE}$ on [ZE], based on the kinetic scheme reported in reference [17], at high concentration reduces to:

$$\phi^{sens}_{ZE\to EE} = {}^3\phi^{ad}_{ZE\to EE^*}({}^3\phi_{G,EE} + k_{et}\tau_{T,EE}[ZE]) \qquad (1)$$

where k_{et} is the rate constant for the energy transfer process ($^3EE^* + ZE \to {}^3ZE^* + EE$). An analogue relationship could be derived in the case of ZZ, assuming a very fast $^3ZE^* \to {}^3EE^*$ process. This assumption implies that the formation of ZE occurs only by diabatic isomerization (see Scheme 2) through $^3EE^* \to {}^3pE^* \to {}^1pE \to \alpha EE + (1-\alpha)$ ZE, where α is the partition factor, assumed ∼0.5, as for stilbene [18]. The intercept is the sensitized isomerization quantum yield in limiting conditions (ϕ^{sens}_{lim}), when the quantum chain process is no longer operative. It is possible to calculate the quantum yield for the adiabatic formation of the excited triplet state of EE from the ZE or ZZ isomers ($^3\phi^{ad}_{IS\to EE^*} = \phi^{sens,lim}_{IS\to EE}/{}^3\phi_{G,EE}$), if $^3\phi_{G,EE}$ is known (IS = ZE or ZZ). The value of this parameter, which is the overall quantum yield for the return to the ground state after sensitization of EE by triplet energy donors [17], can be derived by Eq. (2):

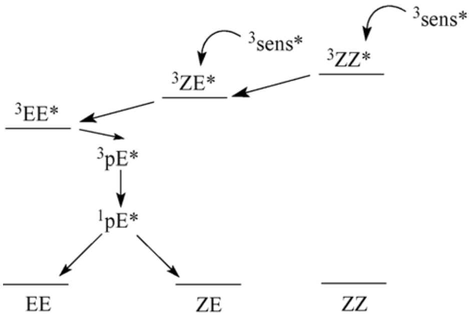
$$^3\phi_{G,EE} = [1 - (\phi^{sens}_{EE\to ZE} + \phi^{sens}_{EE\to X})] \qquad (2)$$

A value of 0.53 was obtained in benzene for *EE*-1,4-(PhE)$_2$B.

Table 3

Components of the sensitized photoisomerization quantum yields of the ZE and ZZ isomers of 1,4-(PhE)$_2$B in two solvents obtained by the plots of Fig. 3, according to Eq. (1)

Isomer	Solvent	ϕ^{sens}_{lim}	Slope	r	$^3\phi^{ad}_{IS\to EE^*}$	k_{et} (10^7 M^{-1} s^{-1})
ZE	Benzene	0.47	305	0.991	0.89	5.7
	MeCN	0.43	420	0.991		
ZZ	Benzene	0.44	72	0.992	0.83	1.4
	MeCN	0.56	27	0.982		



Scheme 2. Sketch of the proposed mechanism for the photosensitised isomerization of 1,4-(PhE)$_2$B in the triplet manifold.

The $^3\phi^{ad}_{IS\to EE^*}$ values were found to be rather high, in agreement with the assumption that the adiabatic isomerization was the main process in the deactivation of the triplet state. As a matter of fact, an almost unitary value was found for $^3\phi^{ad}_{ZZ\to ZE^*}$, derived by the ratio $\phi^{sens,lim}_{ZZ\to EE}/\phi^{sens,lim}_{ZE\to EE}$. The different slopes found for the plots of ϕ^{sens} as a function of [ZE] and [ZZ] were expected considering the higher energy of the triplet state in the case of ZZ. Only for ZE did ϕ^{sens} reach values higher than unity in the explored concentration range.

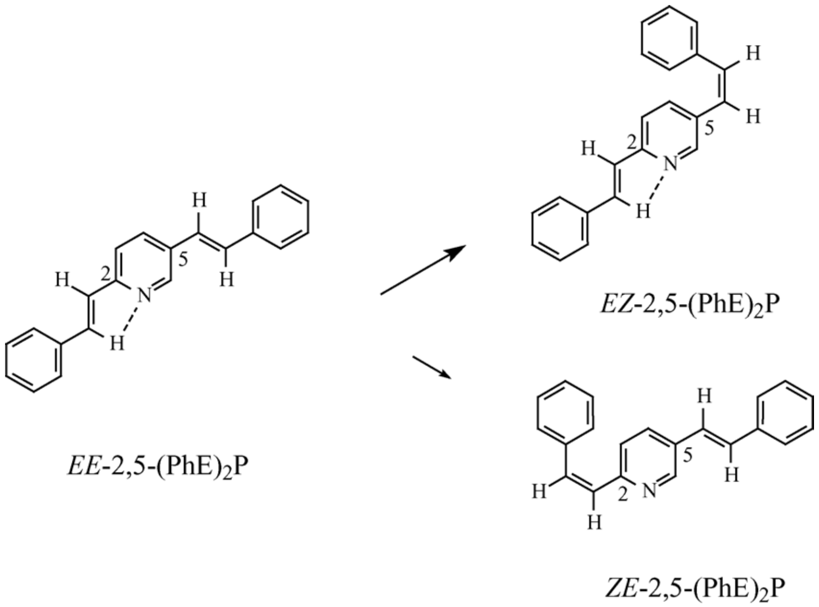
The rather low k_{et} values, derived from the slopes, using the triplet lifetime of EE reported in Table 1, pointed to endothermic energy transfer processes in both cases. A simple kinetic treatment, using the known equation [19]:

$$k_{et} = \frac{k_{diff}}{1 + e^{-\Delta G/RT}} \qquad (3)$$

where k_{diff} is the diffusional rate constant (1×10^{10} M^{-1} s^{-1} in benzene at 20 °C) [20]. Neglecting the entropy terms, $^3ZE^*$ and $^3ZZ^*$ resulted to lie 3 and 3.8 kcal/mol, respectively, above $^3EE^*$.

3.3. *Photobehaviour of the aza-analogues*

The quantum yield of triplet formation reported in Table 1 for the aza-compounds are all very small, in agreement with the low intersystem crossing rate constants (their order of magnitude, 10^7 s^{-1}, as derived by the corresponding fluorescence lifetimes [10], is markedly lower than that of the corresponding fluorescence rate constants), as generally found for diarylpolyenes and their aza-derivatives [21]. The ε^{max}_T values, determined by energy transfer from benzophenone or



Scheme 3. Structures of the two stereoisomers produced in the sensitized isomerization of *EE*-2,5-(PhE)$_2$P.

biacetyl, were in the 20,000–40,000 M^{-1} cm^{-1} range. The measured parameters were little affected by the solvent.

The yield of the sensitized isomerization was substantial for the 4-aza-derivative. It decreased for *EE*-2,5-(PhE)$_2$P and even more for the 2P and 2Q derivatives. The very small ϕ^{sens} values for these two latter compounds are expected from the longer triplet lifetimes (τ_T) reported in Table 1. In the asymmetric compound, *EE*-2,5-(PhE)$_2$P, two different photoproducts, due to rotation around both double bonds (ZE and EZ, see Scheme 3), were obtained in the sensitized experiments.

In our previous study on the effect of the nitrogen atom on the competition between the radiative and reactive relaxations of *EE*-1,4-distyrylbenzene in S_1 [10], it was found that the nitrogen in the side rings induced a net decrease in the yield of the radiative deactivation and a corresponding increase in the reactive pathway. In the 2P and 4P compounds, the rotation around the double bonds experienced lower torsional barriers, whereas the isomerization quantum yield of 2Q remained one order of magnitude smaller. The perpendicular configurations appeared to be stabilized in the aza-compounds thus favouring the diabatic pathways in the ZZ → ZE and ZE → EE isomerizations.

The effect of the heteroatom on the T_1 photochemistry of distyrylbenzenes with linear conjugation appears to be unlike of that reported for the singlet manifold [10]. In fact, in T_1, a substantial isomerization yield was found for 4P only, whereas both 2P and 2Q isomerize with very small yields. This behaviour of 4P and 2Q is similar to that found in the singlet manifold, but differs for 2P whose sensitized yield was found to be rather small. The scarce reactivity when the N atom is in the ortho position with respect to the ethene bridge is generally explained by the formation of intramolecular N···H hydrogen-type bonds, which stabilize the molecule in more planar conformations, thus inhibiting the rotation around the double bond [10,22]. The finding that the yield of the direct photoisomerization of the 2P derivative is substantial whereas the sensitized one is less than 8%, could indicate that the N···H interaction is more important in the triplet than in the singlet manifold.

The results obtained for 2,5-(PhE)$_2$P with the heteroatom in the central ring showed a substantial increase of deactivation through internal conversion to S_0 for this compound whose reactivity in S_1 increases only slightly with respect to the hydrocarbon [10]. The very small sensitized yield is an evidence of an important role played, even in this case, by the intramolecular hydrogen bonds which stabilize the transoid triplet decaying to S_0 through a radiationless and non-reactive deactivation. It is to be noted that the quantum yield to EZ is about four times that to ZE thus confirming that the ethenic group in the ortho position with respect to the heteroatom is less reactive because of the favoured N···H interaction (see Scheme 3).

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