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Photoisomerization mechanism of the *cis* isomers of 1,2-distyrylbenzene and two hetero-analogues

S. Ciorba[a], G. Bartocci[a], G. Galiazzo[b], U. Mazzucato[a], A. Spalletti[a,*]

[a] *Dipartimento di Chimica and Centro di Eccellenza Materiali Innovativi Nanostrutturati (CEMIN), Università di Perugia, 06123 Perugia, Italy*
[b] *Dipartimento di Scienze Chimiche, Università di Padova, 35131 Padova, Italy*

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Abstract

The radiative and reactive excited state relaxations of the ZE and ZZ geometrical isomers of 1,2-distyrylbenzene [1,2-$(PhE)_2B$] and two hetero-analogues, where the side phenyl groups were replaced by 4′-pyridyl or 2′-thienyl groups, were studied and compared with the photobehaviour of the EE isomers previously investigated.

The ZE and ZZ isomers of the hydrocarbon photoisomerize by a predominant adiabatic mechanism (a "one photon – two bonds" process is also operative in the case of ZZ) whereas the contribution of the adiabatic pathway is reduced for the thienyl-analogues, which isomerize by a mixed (diabatic/adiabatic) mechanism, whereas a prevalent diabatic mechanism characterizes the behaviour of the pyridyl analogue.

Keywords: 1,2-Distyrylbenzene; Thio-1,2-distyrylbenzenes; Photoreaction mechanism

1. Introduction

The photobehaviour of *E,E*-1,*n*-distyrylbenzene [*EE*-1,*n*-$(PhE)_2B$, with $n = 2$, 3 or 4] has been widely investigated in the last decade because of the interest in their photoisomerization mechanism and potential applications, f.i., as laser dyes, scintillators and building blocks of polyphenylenevinylene materials used in optoelectronics [1–3]. Most information concerns the compounds bearing the two styryl substituents in the para ($n = 4$, linear conjugation) and meta ($n = 3$, crossed conjugation) positions. Both series of compounds with $n = 3$ and 4 display a very low photoisomerization yield and decay predominantly by the radiative pathway. For them, the presence of conformational equilibria and their role on the photobehaviour have been also investigated (for some representative articles, see Refs. [1,4–9]. The non-conjugated ortho-positional isomer, *EE*-1,2-$(PhE)_2B$, has been relatively less investigated. Its photobehaviour has been mainly studied under severe experimental conditions (light dose, concentration) [10] whilst only scattered information are available under mild experimental conditions [4,11,12].

The effect of replacement of the side phenyl rings with 4′-pyridyl (4P), 2′-thienyl (2T) and 2′-furyl (2F) rings on the competitive radiative/reactive relaxations of the EE geometrical isomers of 1,2-$(PhE)_2B$ has been recently investigated in our laboratory [12]. On the line of the previous study, the photobehaviour of the corresponding *cis* isomers (ZE and ZZ) of 1,2-$(PhE)_2B$ and its 4P and 2T analogues has been here investigated.

Due to the lack of conjugation, the main relaxation pathways of these *cis* compounds is internal conversion (IC) accompanied by substantial geometrical photoisomerization to EE (from ZE) and to ZE (from ZZ), whilst the radiative deactivation was hardly observable at low temperature only. Important adiabatic contributions to the photoreaction have been evidenced, which are of the "one photon – two bonds" type in the case of the ZZ → EE process. A comparison with the results previously obtained on the EE isomers allowed a general description of the photobehaviour of this series of compounds to be obtained.

2. Experimental

The compounds investigated are shown in Scheme 1. They were synthesized at the Padua laboratory for previous works. The geometrical isomers were separated from the synthesis mixture

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

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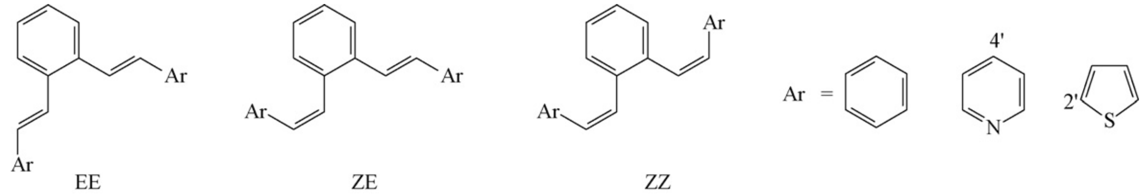


Scheme 1. Geometrical isomers of the investigated compounds.

and carefully purified by preparative HPLC. The EE isomers were characterized by ^{1}H NMR spectrometry [11,12].

The solvent used was a mixture of 9/1 (v/v) methylcyclohexane/3-methylpentane (MCH/3MP) from Fluka, spectrophotometric grade, except otherwise specified for solubility reasons. The solvents were further purified by standard procedures.

A Perkin-Elmer Lambda 800 spectrophotometer was used for the absorption measurements. The fluorescence spectra were carried out by a Spex Fluorolog-2 F112AI spectrofluorimeter and the fluorescence lifetimes by an Edinburgh Instrument 199S spectrofluorimeter, using the single photon counting method. 9,10-diphenylanthracene in de-aerated cyclohexane was used as fluorimetric standard ($\phi_F = 0.90$ [13]).

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 analytical Simmetry C18 (4.6 × 250 mm; 5 μm) and Prontosil 200-3-C30 (4.6 × 250 mm; 3 μm) columns and UV detector. Further details on the experimental measurements are reported elsewhere [12].

All measurements were carried out in de-aerated solutions by purging with nitrogen. The parameters reported in the Tables are averages of at least three independent experiments with mean deviations of ca. 15% and 10% for fluorescence quantum yields and lifetimes, respectively, and ca. 10% for the photoisomerization quantum yields. A larger uncertainty is expected for the derived adiabatic contribution to the overall photoisomerization quantum yield.

The theoretical calculations were performed using the HyperChem computational package (version 6.1). The heats of formation and dihedral angles between the ethenic bridge and the central aromatic ring were obtained for the geometries optimized by the PM3 method. The electronic spectra (transition energy and oscillator strenght) were calculated by ZINDO/S.

3. Results and discussion

3.1. Spectral and photophysical behaviour

The spectral behaviour of the three geometrical isomers of the hydrocarbon at room temperature is shown in Fig. 1A. It is reasonably well described by the theoretical calculations reported in Table 1 that collects the spectral properties (transition energy and oscillator strength), heats of formation and other structural information for the most stable (according to PM3 calculations)

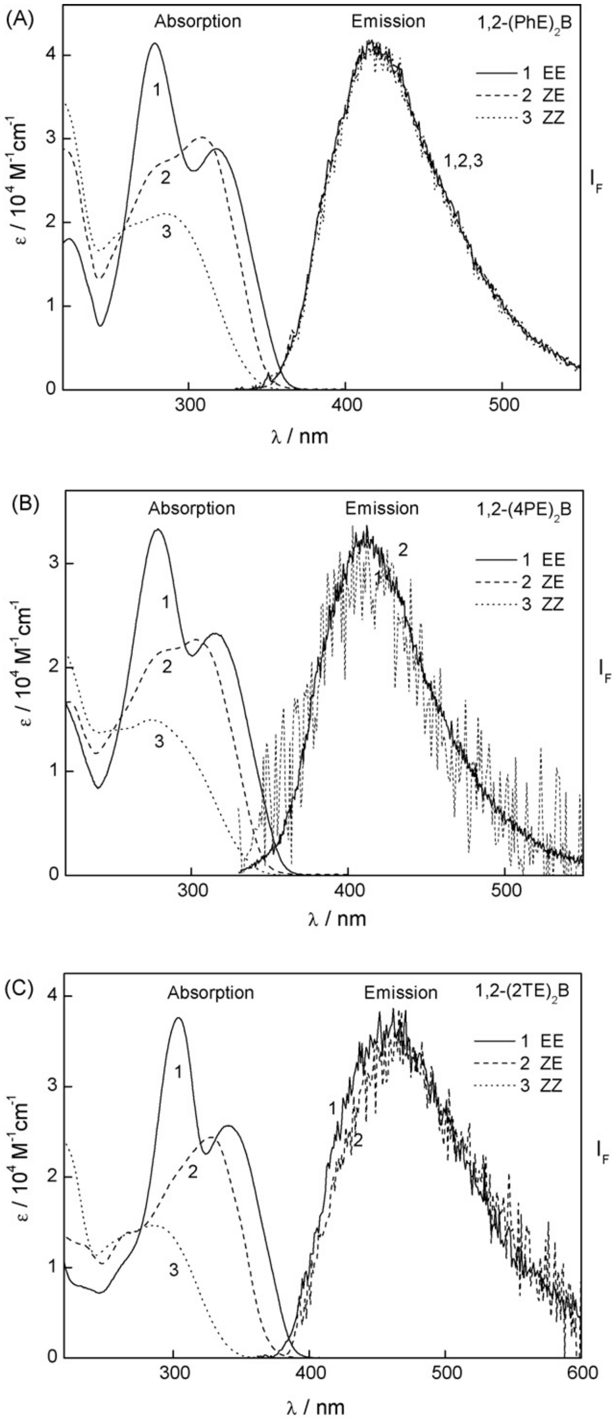


Fig. 1. Absorption and emission spectra of the geometrical isomers of 1,2-(PhE)$_2$B and two heteroanalogues in MCH/3MP at room temperature.

Table 1
Calculated spectral properties, heats of formation (ΔH_f^0) and dihedral angles between the styryl (or etheroaryl-ethenyl) moieties and the central ring for the most stable rotamer of the three isomers of the investigated compounds

Compound	Isomer	Angles (°)	ΔH_f^0 (kcal/mol)	λ	*f*	S_n
1,2-$(PhE)_2B$	EE	−0.34/0.88	99.12	334	1.11	S_1
				285	0.33	S_3
				284	1.00	S_5
	ZE	−39.4/10.2	103.88	316	1.04	S_1
				305	0.17	S_2
				280	0.23	S_4
				278	0.30	S_5
	ZZ	−60.2/96.9	106.52	282	0.01	S_1
				267	0.57	S_4
				235	0.17	S_5
1,2-$(4PE)_2B$	EE	−0.23/1.03	113.31	331	1.11	S_1
				282	1.29	S_3
	ZE	−39.7/10.0	117.91	314	1.01	S_1
				302	0.16	S_2
				280	0.36	S_3
	ZZ	−33.2/87.3	121.24	278	0.007	S_1
				258	0.51	S_6
				219	0.13	S_{12}
1,2-$(2TE)_2B$	EE	0.15/0.34	116.72	372	1.04	S_1
				325	0.16	S_2
				312	1.15	S_3
	ZE	−7.15/37.12	121.47	353	1.16	S_1
				321	0.21	S_2
				317	0.23	S_3
	ZZ	−73.5/43.8	124.13	312	0.21	S_1
				288	0.21	S_2
				284	0.75	S_3

conformer (see below). The first band, at 318 nm for EE and hypsochromically shifted at 309 nm for ZE, is rather intense ($f > 1$). The second band at ∼280 nm (related to two very close energy levels, according to calculations) is also intense for EE, less for ZE. The first band of ZZ is weaker and shifted to even shorter wavelengths (286 nm), as expected for *cis* geometries. The second band is partially overlapped and observed as a shoulder at 262 nm in Fig. 1. The better resolution of the spectra recorded at 80 K (see below) led to a complete separation of the two components, the second band showing there a net maximum at ∼280 nm.

The room temperature absorption spectra of the compounds bearing 4P and 2T groups are shown in Fig. 1B and C. The two first bands of the EE and ZE isomers of the 4P derivative are similar (only slightly blue-shifted) to those of the hydrocarbon whilst those of the 2T derivative are red shifted by ∼25 nm, as common for compounds bearing 2T groups [14]. In the case of ZZ, the bathochromic shift was no longer observed for the 2T derivative (286 and 265 nm) whilst the 4P one has again a blue-shifted spectrum (276 and 254 nm). According to calculations, the first transition of ZZ is partially allowed for 2T but forbidden in both the hydrocarbon and its 4P derivative. For the ZE isomer of the three compounds investigated at room temperature, the same fluorescence spectrum as found for EE was obtained and the fluorescence excitation spectra overlapped the absorption spectra of the irradiated compounds. This clearly indicated the occurrence of adiabatic photoisomerization producing the excited EE isomers (see below). Also under irradiation of the ZZ isomer of the hydrocarbon, the measured fluorescence spectrum overlapped that of EE.

The presence of conformational equilibria in the ground or excited singlet states of these molecules could affect both their photophysical and photochemical behaviour. However, no excitation wavelength effect on the emission spectra was found thus suggesting that one of the possible conformers predominates in solution, the ground-state conformational equilibrium being largely shifted towards the most stable one [15], as already reported for the EE isomers [12]. The occurrence of conformer interconversion in the excited state could offer an alternative hypothesis [15]. In this case, the photophysical and photochemical properties and the derived parameters should be considered mean values of the different conformations which can be specifically involved in the relaxation processes of these excited geometrical isomers. A more detailed study as a function of temperature and viscosity is in progress to clarify the role of conformation in the excited states.

Fig. 2A shows the spectra recorded under irradiation of the three geometrical isomers of the hydrocarbon in MCH/3MP at 80 K. Only at the high viscosity of the rigid matrix, when the photoreaction is expected to be inhibited, did the intrinsic emission spectrum of *ZE*-1,2-$(2PhE)_2B$ become detectable whereas irradiation of ZZ displayed a spectrum which did not completely overlap, but was similar to that of ZE. For the corresponding hetero-derivatives (Fig. 2B and C), irradiation of ZE gave an emission spectrum very similar to that of EE even at low temperature. The ZZ isomers practically do not emit; the weak

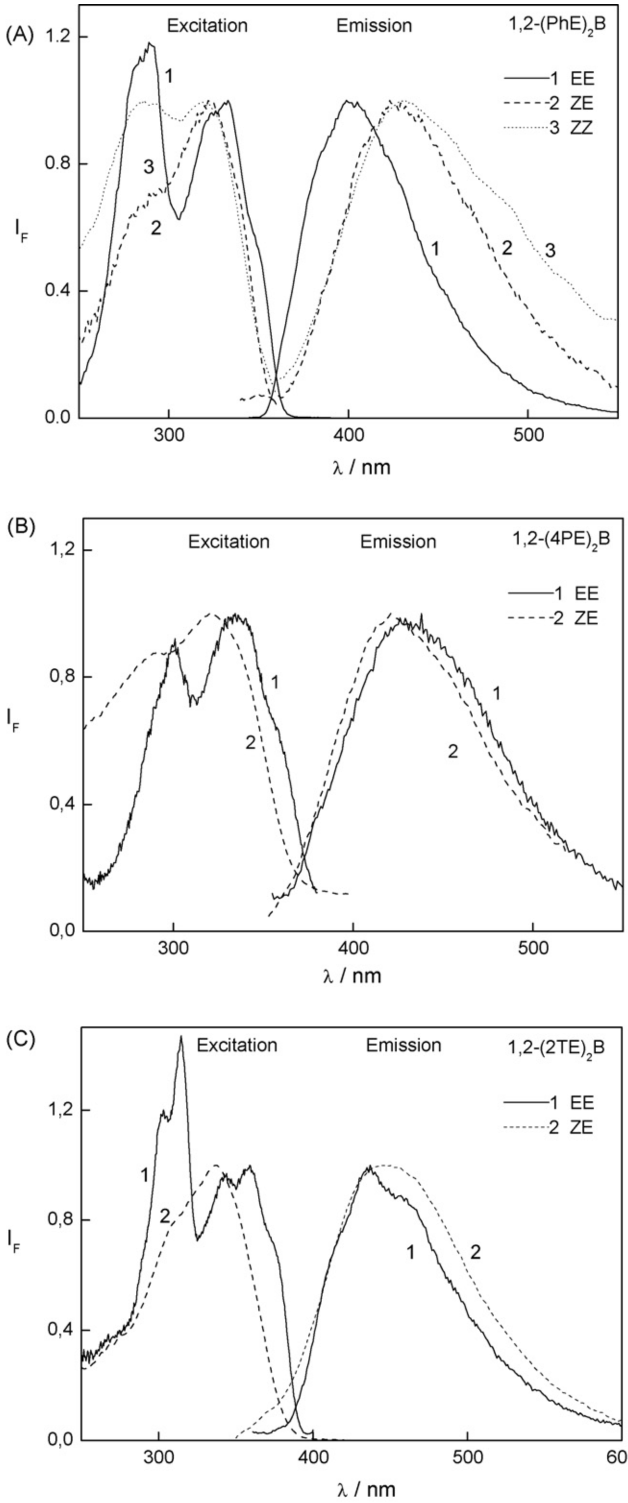


Fig. 2. Fluorescence excitation and emission spectra of the geometrical isomers of 1,2-$(PhE)_2B$ and two hetero-analogues in a rigid matrix of MCH/3MP at 80 K.

luminescence observed under irradiation of the 2T derivative being too weak to allow a meaningful assignment.

The fluorescence parameters measured under irradiation of the three isomers of each compound investigated are collected in Table 2. The fluorescence decay following excitation of the *cis* compounds at room temperature was monoexponential with the same lifetime as EE, confirming the spectral information of adiabatic production of the fluorescent EE isomer. The emission yields measured under irradiation of the compounds bearing *cis* double bonds at room temperature (Table 2) are then apparent, being assignable to $^1EE^*$ adiabatically produced; the yield is drastically reduced by the presence of the heteroatoms, in this case being detectable for ZE only.

Table 2
Photophysical and photochemical parameters obtained under irradiation of the three isomers of 1,2-$(PhE)_2B$ and its 4P and 2T derivatives in MCH-3MP at room temperature

Compound	Isomer	ϕ_F	τ_F (ns)	ϕ_{ISO}	ϕ_{dis}
1,2-$(PhE)_2B$	EE[a]	0.29	26	0.05 (EE → ZE)	0.15
	ZE	0.17	26.2	0.40 (ZE → EE)	
	ZZ	0.04	22.7	0.09 (ZZ → ZE) 0.08 (ZZ → EE)	
1,2-$(4PE)_2B$	EE[a]	0.026	1.8	0.30 (EE → ZE)	0.40
	ZE	0.0008	1.7	0.23 (ZE → EE)	
	ZZ	–	–	0.31 (ZZ → ZE) 0.016 (ZZ → EE)	
1,2-$(2TE)_2B$	EE[a]	0.04	4.4	0.09_5 (EE → ZE)	0.10
	ZE	0.008	4.4	0.33 (ZE → EE)	
	ZZ	–	–	0.30 (ZZ → ZE) 0.05 (ZZ → EE)	

[a] From Ref. [12].

3.2. Photochemical behaviour

The measured isomerization quantum yields (ϕ_{ISO}) of the three isomers of 1,2-$(2PhE)_2B$ and its two hetero-analogues are shown in Table 2. Since the photoisomerization of the EE isomers has been reported to be accompanied by non-negligible side photoreactions [12], the values of the disappearance quantum yield (ϕ_{dis}) are also reported in Table 2. On the contrary, the ZE → EE photoisomerization was found to be clean if the irradiation was performed in mild conditions, as indicated by the maintenance of isosbestic points until a certain degree of photoconversion ($\leq$30%). Under longer irradiation times, formation of side photoproducts was detected, indicating that the EE isomer initially produced is the responsible of further photoreactivity [12].

No photoproduction of ZZ was found under irradiation of both EE [12] and ZE, as previously reported for the 1,4 and 1,3 analogues [1,7a,11,16]. The substantial reduction in the fluorescence yield measured under irradiation of the ZE hetero-analogues was not accompanied by an increase of their photoreactivity whereas a marked increase in reactivity, particularly in the yield of ZE production, was found under irradiation of ZZ. An increase in the isomerization yield has been reported for the EE hetero-isomers, particularly for the 4P derivative [12], due to a reduction in the torsional barriers in S_1. It can also be observed that the contribution of decay by IC, induced by low-lying (deactivating) n,π* states in 4-styrylpyridine and other aza-stilbenes [17,18], does not play any role here since the n,π* states are located at higher energies.

Whilst the isomerization of the EE isomers of the compounds investigated have been reported to occur by the common diabatic mechanism (implying $S_1 \rightarrow S_0$ IC or $T_1 \rightarrow S_0$ ISC at the perpendicular configuration, ${}^{1,3}\mathrm{EE}^* \rightarrow {}^{1,3}\mathrm{PE}^* \rightarrow {}^{1}\mathrm{PE} \rightarrow \alpha{}^{1}\mathrm{ZE} + (1-\alpha){}^{1}\mathrm{EE}$, where the partitioning factor α is ~0.5 [19]), the present results indicate that for the *cis* compounds the alternative adiabatic mechanism (${}^{1,3}\mathrm{ZE}^* \rightarrow {}^{1,3}\mathrm{EE}^*$, directly in a unique potential energy surface [20]) becomes operative.

Using the experimental radiative and reactive parameters, the contribution of the adiabatic mechanism in S_1 to the overall isomerization could be estimated by the equation:

$$ {}^{1}\phi^{\mathrm{ad}}_{\mathrm{ZE}\rightarrow\mathrm{EE}} = {}^{1}\phi^{\mathrm{ad}}_{\mathrm{ZE}^*\rightarrow\mathrm{EE}^*} \times {}^{1}\phi_{\mathrm{G,EE}} = \frac{\phi_{\mathrm{F,ZE}}}{\phi_{\mathrm{F,EE}}} \times {}^{1}\phi_{\mathrm{G,EE}} \qquad (1) $$

where $\phi_{\mathrm{F,ZE}}$ is the fluorescence quantum yield measured under excitation of ZE, $\phi_{\mathrm{F,EE}}$ is the intrinsic fluorescence yield of EE, ${}^{1}\phi^{\mathrm{ad}}_{\mathrm{ZE}^*\rightarrow\mathrm{EE}^*}$ is the formation quantum yield of ${}^{1}\mathrm{EE}^*$ through the adiabatic isomerization mechanism in S_1 under excitation of ZE, and ${}^{1}\phi_{\mathrm{G,EE}} = (1-\phi_{\mathrm{dis}})$ is the overall quantum yield of the non-reactive deactivation to the ground state for the EE isomer.

Replacing ZE with ZZ and using relationships analogous to Eq. (1), the yield of the ZZ → EE isomerization through “one photon – two bonds” adiabatic mechanism can be derived. The adiabatic contribution to the ZZ → ZE isomerization could be estimated by the adapted Eq. (1) and/ or by Eq. (2):

$$ {}^{1}\phi^{\mathrm{ad}}_{\mathrm{ZZ}\rightarrow\mathrm{ZE}} = {}^{1}\phi^{\mathrm{ad}}_{\mathrm{ZZ}^*\rightarrow\mathrm{ZE}^*} \times {}^{1}\phi_{\mathrm{G,ZE}} = \frac{\phi_{\mathrm{ZZ}\rightarrow\mathrm{EE}}}{\phi_{\mathrm{ZE}\rightarrow\mathrm{EE}}} \times {}^{1}\phi_{\mathrm{G,ZE}} \qquad (2) $$

where $\phi_{\mathrm{ZZ}\rightarrow\mathrm{EE}}$ and $\phi_{\mathrm{ZE}\rightarrow\mathrm{EE}}$ are the experimental isomerization quantum yields of the process leading to the EE isomer under excitation of ZZ and ZE, respectively, ${}^{1}\phi^{\mathrm{ad}}_{\mathrm{ZZ}^*\rightarrow\mathrm{ZE}^*}$ is the yield of production of ${}^{1}\mathrm{ZE}^*$ through the adiabatic mechanism under excitation of ZZ, and ${}^{1}\phi_{\mathrm{G,ZE}} = (1-\phi_{\mathrm{ZE}\rightarrow\mathrm{EE}})$ is the overall yield of deactivation to the ground state under direct excitation of ZE.

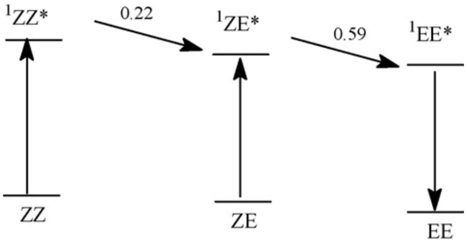
The yield of ${}^{1}\mathrm{ZZ}^* \rightarrow {}^{1}\mathrm{EE}^*$ two-fold adiabatic process can be also derived by Eq. (3):

$$ {}^{1}\phi^{\mathrm{ad}}_{\mathrm{ZZ}^*\rightarrow\mathrm{EE}^*} = {}^{1}\phi^{\mathrm{ad}}_{\mathrm{ZZ}^*\rightarrow\mathrm{ZE}^*} \times {}^{1}\phi^{\mathrm{ad}}_{\mathrm{ZE}^*\rightarrow\mathrm{EE}^*} \qquad (3) $$

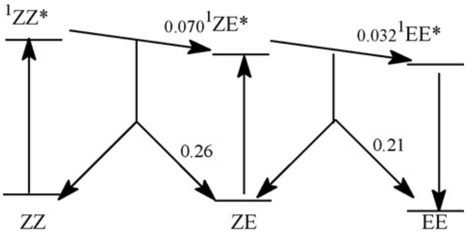
The adiabatic contribution to the ZZ → EE photoisomerization quantum yield was then calculated by Eq. (4):

$$ {}^{1}\phi^{\mathrm{ad}}_{\mathrm{ZZ}\rightarrow\mathrm{EE}} = {}^{1}\phi^{\mathrm{ad}}_{\mathrm{ZZ}^*\rightarrow\mathrm{EE}^*} \times {}^{1}\phi_{\mathrm{G,EE}} \qquad (4) $$

For 1,2-$(\mathrm{PhE})_2\mathrm{B}$, the adiabatic contributions thus derived (Table 3) overcome at different extents (20%–30%) the experimental value of Table 2. This apparent discrepancy between the estimated adiabatic contributions and the overall experimental yields can be reasonably ascribed to the uncertainty in the measured yields which can be magnified by error propagation in the treatment using Eqs. (1)–(4). In any case, the derived values clearly indicate that the photoconversion of the ZE and ZZ isomers of 1,2-$(\mathrm{PhE})_2\mathrm{B}$ takes place by a largely prevalent (or unique) adiabatic mechanism, implying, in the case of the ZZ → EE process, a “one photon – two bonds” mechanism. These results are resumed in Scheme 2 that shows the processes in the *cis* → *trans* direction.



Scheme 2. Qualitative sketch of the photoisomerization mechanism of the ZE and ZZ isomers of 1,2-$(\mathrm{PhE})_2\mathrm{B}$ showing the quantum yields of the derived values for the adiabatic processes.

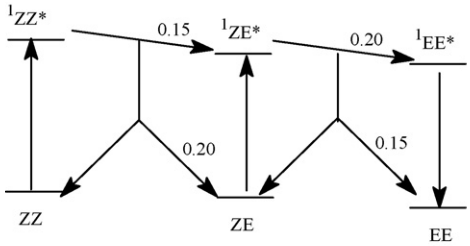


Scheme 3. Qualitative sketch of the photoisomerization mechanism of the ZE and ZZ isomers of 1,2-$(\mathrm{4PE})_2\mathrm{B}$ showing the derived quantum yields for the competitive diabatic/adiabatic contributions.

Application of the same treatment to the two hetero-derivatives led to smaller adiabatic contributions to the overall photoreaction (Table 3). Since the EE compounds were found not to have detectable triplet production [12], it was reasonable to neglect isomerization in T_1 even for the compounds with *cis* double bonds. Therefore, the yield of the diabatic contribution to photoisomerization in S_1 (${}^{1}\phi^{\mathrm{d}}$) could be simply estimated by difference between the measured overall quantum yield and the derived adiabatic contributions (Table 3 and Schemes 3 and 4).

Table 3
Adiabatic contributions to the photoisomerization quantum yields of the investigated compounds, as derived by Eqs. (1) and (2)

Compound	X	${}^{1}\phi_{\mathrm{G,X}}$	${}^{1}\phi^{\mathrm{ad}}_{\mathrm{X}^*\rightarrow\mathrm{EE}^*}$	${}^{1}\phi^{\mathrm{ad}}_{\mathrm{X}\rightarrow\mathrm{EE}}$	${}^{1}\phi^{\mathrm{ad}}_{\mathrm{X}^*\rightarrow\mathrm{ZE}^*}$	${}^{1}\phi^{\mathrm{ad}}_{\mathrm{X}\rightarrow\mathrm{ZE}}$	${}^{1}\phi^{\mathrm{d}}_{\mathrm{X}\rightarrow\mathrm{EE}}$	${}^{1}\phi^{\mathrm{ad}}_{\mathrm{X}\rightarrow\mathrm{ZE}}$
1,2-$(\mathrm{PhE})_2\mathrm{B}$	EE	0.85						0.05
	ZE	0.60	0.59	0.50				
	ZZ	0.83	0.13	0.11	0.22	0.13		
1,2-$(\mathrm{4PE})_2\mathrm{B}$	EE	0.60						0.30
	ZE	0.77	0.032	0.019			0.21	
	ZZ	0.67	0.0022	0.0013	0.070	0.054	0.015	0.26
1,2-$(\mathrm{2TE})_2\mathrm{B}$	EE	0.90						0.09_5
	ZE	0.67	0.20	0.18			0.15	
	ZZ	0.65	0.03	0.027	0.15	0.10	0.023	0.20



Scheme 4. Qualitative sketch of the photoisomerization mechanism of the ZE and ZZ isomers of 1,2-$(2TE)_2B$ showing the derived quantum yields for the competitive diabatic/adiabatic contributions.

A different behaviour, compared to that of the hydrocarbon, was found for the 4P derivative where only a very small fraction of excited *cis* molecules undergo the adiabatic pathway whilst most of them isomerize by the diabatic mechanism. This can be explained by a stabilization of the twisted configurations in S_1 induced by the pyridyl substituent, particularly at the perpendicular configuration ($^1PE^*$ and $^1ZP^*$), thus producing a net minimum in the potential energy curve (the well known "funnel", in the case of stilbene [19]). As a consequence, the torsional energy barrier decreases (net increase of the EE → ZE isomerization yield) and the $S_1 \rightarrow S_0$ IC at 90°, responsible for the diabatic mechanism, becomes the prevailing reaction pathway for the *cis* compounds (Scheme 3).

An intermediate situation was found for the 2T derivative where the weights of the diabatic and adiabatic mechanisms are comparable (Scheme 4).

Previous work on the EE isomers had shown that the main effect of the heteroatom on the behaviour of the hydrocarbon was a drastic decrease in the radiative relaxation compensated by a relevant increase in the reactive pathway ($\phi_{ZE\rightarrow EE} = 0.30$) for the 4P analogue only [12]. The present results on the ZE and ZZ compounds show that the 4P and 2T groups affect very little (slight decrease) the $\phi_{ZE\rightarrow EE}$ values whereas the photoreaction yield of the ZZ isomers is almost trebled with respect to the hydrocarbon. This increase favours the production of ZE compared with that of EE, whilst the two contributions are almost equal in the hydrocarbon.

The discussion of the heteroatom effect in these non-conjugated 1,2 compounds can be extended by a comparison with the corresponding linearly-conjugated 1,4 compounds [7a,9]. It is interesting to note that, despite the marked structural difference between the two series of compounds, the photobehaviour is not much different. In fact, in both series the following similarities were observed: (i) the photoisomerization of the *cis* compounds occurs by a unique adiabatic mechanism in both hydrocarbons; (ii) the heteroatom produces a drastic decrease in the emission yield of EE compensated by increased ZE production, particularly for the 4P compound; (iii) the overall reactivity of ZE is little affected by the heteroatom (small increase for the 1,4 and small decrease for the 1,2 compounds) whilst that of ZZ increases substantially, particularly towards ZE; and (iv) the adiabatic contribution to the overall isomerization yield of both ZE and ZZ decreases markedly in the presence of the heteroatoms, particularly for the 4P derivative.

Moreover, for both 1,4 and 1,2 compounds, an intramolecular migration of the excitation energy towards one of the ethenic isomerizable double bonds seems to be favoured and the rotation of the second double bond is found in the direction of EE only but never in the opposite direction ("one-way").

References

[1] H. Meier, Angew. Chem. Int. Ed. Engl. 31 (1992) 1399–1540 (and references therein).
[2] S. Wang, W.J. Oldham Jr., R.A. Hudack Jr., G.C. Bazan, J. Am. Chem. Soc. 122 (2000) 5695–5709.
[3] J.L. Segura, N. Martin, J. Mater. Chem. 10 (2000) 2403–2435 (and references therein).
[4] D. Oelkrug, K. Rempfer, E. Prass, H. Meier, Z. Naturforsch. 43a (1988) 583–590.
[5] Y. Ito, Y. Uozu, T. Dote, M. Ueda, T. Matsuura, J. Am. Chem. Soc. 110 (1988) 189–198.
[6] K. Sandros, M. Sundahl, O. Wennerström, U. Norinder, J. Am. Chem. Soc. 112 (1990) 3082–3086;
M. Sundahl, O. Wennerström, K. Sandros, T. Arai, K. Tokumaru, J. Phys. Chem. 94 (1990) 6731–6734.
[7] (a) E. Marri, D. Pannacci, G. Galiazzo, U. Mazzucato, A. Spalletti, J. Phys. Chem. A 107 (2003) 11231–11238;
(b) E. Marri, G. Galiazzo, A. Spalletti, Photochem. Photobiol. Sci. 2 (2004) 205–210;
(c) E. Marri, F. Elisei, U. Mazzucato, D. Pannacci, A. Spalletti, J. Photochem. Photobiol., A: Chem. 177 (2006) 307–313.
[8] L. Giglio, U. Mazzucato, G. Musumarra, A. Spalletti, Phys. Chem. Chem. Phys. 2 (2000) 4005–4012.
[9] G. Ginocchietti, G. Galiazzo, U. Mazzucato, A. Spalletti, Photochem. Photobiol. Sci. 4 (2005) 547–553.
[10] F. Dietz, M. Scholz, Tetrahedron 24 (1968) 6845–6849;
W.H. Laarhoven, Th.J.H.M. Cuppen, R.J.F. Nivard, Rec. Trav. Chim. Pays-Bas 87 (1968) 687–698;
W.H. Laarhoven, Th.J.H.M. Cuppen, R.J.F. Nivard, Tetrahedron 26 (1970) 1069–1083;
W.H. Laarhoven, Recl. Trav. Chim. Pays-Bas 102 (1983) 241–254;
W.H. Laarhoven, Pure Appl. Chem. 56 (1984) 1225–1240.
[11] E. Marri, G. Galiazzo, U. Mazzucato, A. Spalletti, Chem. Phys. 312 (2005) 205–211.
[12] S. Ciorba, G. Galiazzo, U. Mazzucato, M. Šindler-Kulyk, I. Škorić, A. Spalletti, J. Photochem. Photobiol., A: Chem. 187 (2007) 325–331.
[13] G. Bartocci, F. Masetti, U. Mazzucato, A. Spalletti, I. Baraldi, F. Momicchioli, J. Phys. Chem. 91 (1987) 4733–4743.
[14] G. Bartocci, G. Galiazzo, G. Ginocchietti, U. Mazzucato, A. Spalletti, Photochem. Photobiol. Sci. 3 (2004) 870–877;
I. Baraldi, G. Ginocchietti, U. Mazzucato, A. Spalletti, Chem. Phys. 337 (2007) 168–176.
[15] U. Mazzucato, F. Momicchioli, Chem. Rev. 91 (1991) 1679–1719;
G. Bartocci, A. Spalletti, U. Mazzucato, in: J. Waluk (Ed.), Conformational Analysis of Molecules in Excited States, Wiley-VCH, New York, 2000 (Chapter 5 and references therein).
[16] G. Ginocchietti, G. Galiazzo, D. Pannacci, U. Mazzucato, A. Spalletti, Chem. Phys. 331 (2006) 164–172.
[17] D.G. Whitten, M.T. McCall, J. Am. Chem. Soc. 91 (1969) 5097–5103.
[18] U. Mazzucato, Pure Appl. Chem. 54 (1982) 1705–1721 (and references cited therein).
[19] J. Saltiel, Y.-P. Sun, in: H. Dürr, H. Bouas-Laurent (Eds.), Photochromism: Molecules and Systems, Elsevier, Amsterdam, 1990, pp. 64–162 (and references therein).
[20] G. Bartocci, G. Galiazzo, E. Marri, U. Mazzucato, A. Spalletti, Inorg. Chim. Acta 360 (2007) 961–969.