

Heteroatom effect on the radiative and reactive photobehaviour of *E,E*-1,2-distyrylbenzene

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Abstract

The heteroatom effect on the radiative and reactive relaxations of *E,E*-1,2-distyrylbenzene (DSB) has been studied by stationary and time-resolved techniques on three compounds where the side phenyl (Ph) groups were replaced by 4'-pyridyl (4P), 2'-thienyl (2T) and 2'-furyl (2F) groups. Contrary to the case of the hydrocarbon, whose photoisomerization is accompanied by substantial degradation, the *E,E* → *Z,E* photoisomerization prevails in the hetero-analogues, particularly in the thienyl derivative. The lack of conjugation in these 1,2-substituted benzenes leads to a decrease in the fluorescence yield with respect to their 1,4 and 1,3 analogues (particularly in the presence of the heteroatoms), which is accompanied by an increase of the photoreaction quantum yield for the pyridyl- (significant) and thienyl- (very small) derivatives, whilst internal conversion is the prevalent deactivation pathway of the furyl derivative.

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1. Introduction

The photochemistry of stilbene-like compounds has been thoroughly investigated in the last decades because of their interest from the point of view of both mechanistic photochemistry and potential use in applied research. The photobehaviour of compounds containing repeating phenylenevinylene units has received wide attention since delocalization of π electrons in their electronically excited states can induce new properties which can have implications in the field of material science and particularly in optoelectronics [1].

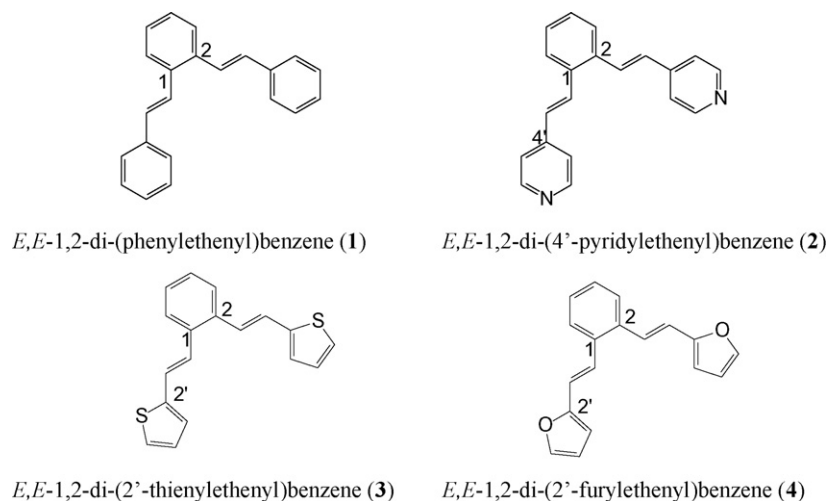
Distyrylbenzene (DSB) can be considered as a model compound for such systems [2]. The photoisomerization of the *para*-substituted 1,4-DSB (linear conjugation) [3,4] and of the *meta*-substituted 1,3-DSB (crossed conjugation) [5–7] has been particularly investigated. The effect of nitrogen and sulphur heteroatoms in the side and central rings has been the object of

an extensive study in our laboratory [4,5,7,8]. More scattered data on the photobehaviour of the sterically crowded *ortho*-substituted 1,2-DSB have been reported [2,5,9].

The present paper describes the results of an investigation on the heteroatom effect on the radiative and reactive relaxations of *E,E*-1,2-DSB. In the compounds investigated (Scheme 1), the side phenyl groups are replaced by pyridyl, thienyl and furyl groups. Previous investigation on the behaviour of the hydrocarbon under prolonged irradiation has shown that the *E,E* → *Z,E* photoisomerization is accompanied by large formation of cyclization and degradation products [9]. Our results, obtained in mild conditions, whilst confirming the substantial formation of side photoproducts for the hydrocarbon, showed that geometrical isomerization is the prevalent reactive relaxation of the hetero-analogues, particularly for the thienyl compound.

The lack of conjugation in these 1,2-substituted benzenes leads to a decrease in the fluorescence yield with respect to their 1,4 and 1,3 analogues (particularly in the presence of the heteroatoms), which is accompanied by an increase of reactivity for the pyridyl- (significant) and thienyl- (very small)

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Scheme 1.

derivatives, whilst the furyl derivative mainly relaxes by internal conversion.

Although the present study was mainly addressed to the photobehaviour of the *E,E* stereoisomers, some preliminary results on the back *Z,E* → *E,E* photoisomerization are also reported.

2. Experimental

The compounds investigated are shown in Scheme 1. The phenyl- (Ph) and 4'-pyridyl- (4P) derivatives (prepared for previous works [5] and the 2'-thienyl (2T) derivatives were synthesized by one of us (G.G.) at the Padua laboratory by application of a two-fold Wittig reaction to difunctional reactants, benzyltriphenyl-phosphonium chloride (appropriately changing the reagents, for the hetero-derivatives) and 1,2-dicarboxyaldehyde. The 2'-furyl- (2F) derivative was synthesized by one of us [10] also by Wittig reaction but starting from *o*-xylen-diphosphonium salt and two equivalents of 2-furancarboxaldehyde. The isomers were separated and carefully purified by preparative HPLC and then characterized by ¹H NMR spectrometry (see Appendix A, supplementary data for compound 3, Ref. [5] for 1 and 2 and Ref. [10] for 4).

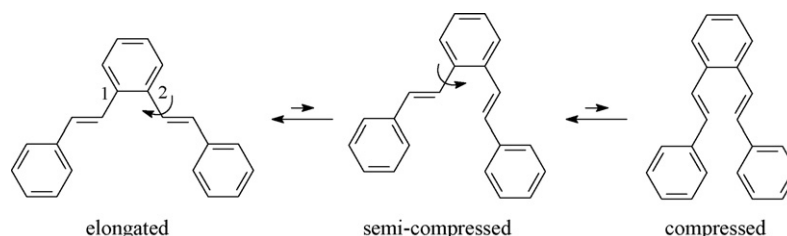
The solvents were 9/1 (v/v) methylcyclohexane/3-methylpentane (MCH/3MP), benzene and acetonitrile from Fluka, spectrophotometric grade.

A Perkin-Elmer Lambda 800 spectrophotometer was used for the absorption measurements. 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 fluorimetric measurements. The emission and photoreaction quantum yields were determined at λ_{exc} corresponding to the maximum of the first absorption band (λ_{max}), except when otherwise indicated. 9,10-Diphenylanthracene in cyclohexane was used as fluorimetric standard ($\phi_{\text{F}}=0.90$ in de-aerated solvent [11]).

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 or Jupiter C18 (4.6 mm × 250 mm; 5 μm) and ProntoSil 200-3-C30 (4.6 mm × 250 mm; 3 μm) columns and UV detector. Water/acetonitrile mixtures were used as eluents. The monitoring wavelength was at the isosbestic point; otherwise corrections for different absorption coefficients were introduced. The disappearance quantum yield (ϕ_{dis}) was measured using thioxant-9-one in acetonitrile as internal standard. The conversion percentage was held at below 8% to avoid the competition from the back photoreaction. Sensitized experiments were carried out using biacetyl in benzene or 2,3-dithienylketone in cyclohexane as triplet donors.

Fluorescence lifetimes were measured by an Edinburgh Instrument 199S spectrofluorimeter, using the single photon counting method. The triplet state was investigated by nanosecond laser flash photolysis ($\lambda_{\text{exc}}=355$ nm) using a Continuum Surelite II Nd:YAG laser.

Scheme 2. Conformational equilibria of *E,E*-1,2-distyrylbenzene.

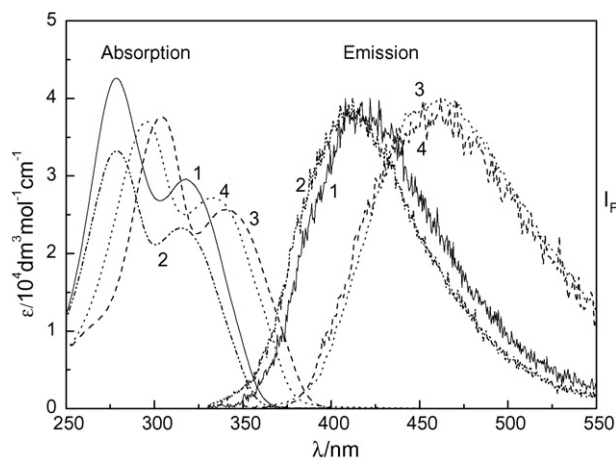


Fig. 1. Absorption and fluorescence (normalized) spectra of the four compounds investigated in MCH/3MP at room temperature (spectra of **1** and **2** are from Ref. [5]).

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 deviation of ca. 10% for fluorescence quantum yields and lifetimes and ca. 12% for the photoisomerization quantum yields.

The theoretical calculations were performed on the different rotamers of the investigated compounds (Scheme 2 shows those of the hydrocarbon, as an example) 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 strength) were calculated by ZINDO/S.

3. Results and discussion

3.1. Absorption and fluorescence properties

Fig. 1 and Table 1 show the absorption and fluorescence spectra of the *E,E* isomers of 1,2-distyrylbenzene and their hetero-analogues in MCH/3MP.

The spectral properties of the hydrocarbon were found in good agreement with those reported in the literature in different solvents [2,5]. Both the absorption and emission spectra of the hetero-analogues maintain the same shape but a marked red-shift was found for the 2F and, even more, for the 2T derivative. The absorption spectrum of the 4P derivative shows a small blue-shift compared to the hydrocarbon [5], as also observed for styrylpyridines [12].

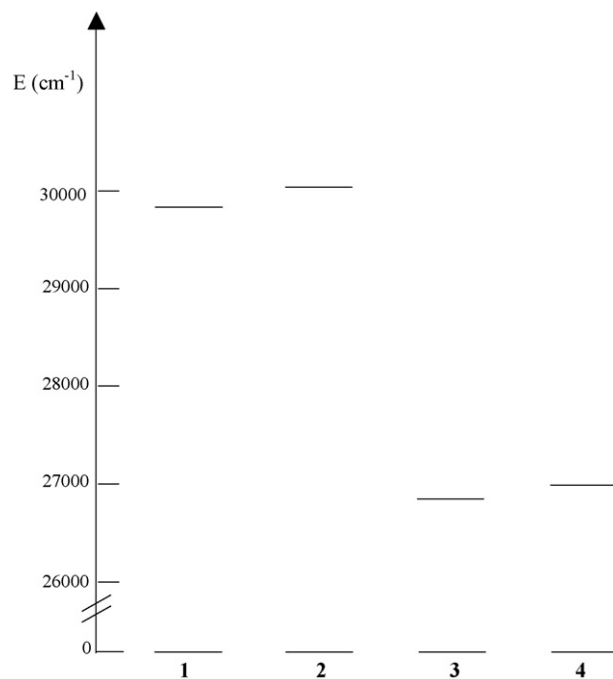


Fig. 2. Schematic diagram of the computed transition energies of the allowed absorption of the elongated (most stable) rotamers of the four compounds investigated.

The large Stokes shift indicates that the emitting state is not that reached by absorption (allowed transition) and that the fluorescence corresponds to a forbidden transition, as previously reported for the hydrocarbon [2]. All these findings were nicely predicted by ZINDO/S calculations (see a sketch of the transition energies in Fig. 2).

In these compounds, rotation of the styryl moiety around the quasi-single bond with the central benzene ring can produce conformers with different spectral properties, as generally evidenced for diarylethenes by the λ_{exc} effect on the emission spectrum and by poly-exponential fluorescence decay [13]. However, contrary to the case of the 1,3 analogues [2,4,5], the conformational equilibrium is practically undetectable for these 1,2 compounds being almost completely shifted towards the most stable conformer for steric reasons (see Scheme 2). This is in agreement with the rather larger differences between the formation enthalpies calculated for the rotamers of the 1,2 compounds (Table 2) indicating the prevalence of the most stable elongated species in the conformer mixture. In fact, the strong deviation of the styryl groups from planarity in the compressed conformers (dihedral angles of $\sim 40^\circ$) decreases their stability and points to a negligible contribution to the conformational

Table 1
Absorption and emission spectral properties of the four compounds investigated in MCH/3MP at room temperature

Compound	λ_{abs}^{max} (nm) ^a	ϵ_{abs}^{max} ($10^4 M^{-1} cm^{-1}$)	λ_F^{max} (nm)	Stokes shift (cm^{-1})
1	<u>278</u> , 318	4.26, 2.96	420	7600
2	<u>279</u> , 316	3.33, 2.33	413	7400
3	<u>305</u> , 342	3.76, 2.56	465	7700
4	<u>296</u> , 333	3.70, 2.72	463	8400

^a The main maxima are underlined.

Table 2

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 elongated and compressed rotamers of the *E,E* isomers of the four compounds investigated

Rotamer	Angles (grades)	ΔH_f^0 (kJ/mol)	λ (nm)	f	
Compound 1	Elongated	−0.34/0.88 ^a	414.72 ^a	334	1.11
				284	1.00
Semi-compressed	8.57/33.49 ^a	426.31 ^a	330	0.73	
			278	1.55	
Compressed	46.56/45.91 ^a	433.92 ^a	329	0.34	
			302	0.21	
			272	1.11	
Compound 2	Elongated	−0.23/1.03 ^a	474.09 ^a	331	1.11
				282	1.29
Semi-compressed	7.01/35.09 ^a	484.97 ^a	326	0.72	
			277	1.09	
Compressed	51.16/50.56 ^a	490.99 ^a	316	0.38	
			296	0.23	
			271	0.84	
Compound 3 ^b	Elongated	0.33/0.84	488.40	373	1.00
				313	1.18
Semi-compressed	4.7/37.4	499.86	363	0.72	
			307	1.31	
Compressed	55.19/55.20	506.31	336	0.46	
			307	0.89	
Compound 4 ^b	Elongated	0.15/0.33	187.82	371	1.05
				314	0.98
Semi-compressed	2.25/38.74	199.16	362	0.69	
			308	1.20	
Compressed	55.72/55.20	205.23	338	0.41	
			307	0.91	

^a From Ref. [5].

^b Calculations refer to the *s-cis,s-cis* conformations (the corresponding *s-cis,s-trans* and *s-trans,s-trans* species resulted to be less stable in our calculations).

equilibrium. This behaviour is reflected in the monoexponential decay of their fluorescence (see later).

In the case of 2T and 2F derivatives the rotation of the heteroaromatic group around the quasi-single bond with the ethene bridge produces additional different rotamers (*s-cis,s-cis*, *s-cis,s-trans* and *s-trans,s-trans*) that could have, in principle, different spectral, photophysical and photochemical properties.

Table 3

Photophysical and photochemical parameters of dilute solutions of the four compounds investigated in MCH/3MP at room temperature

Compound	ϕ_F	τ_F (ns)	k_F (10^7 s ^{−1})	$\phi_{E,E \rightarrow Z,E}$	ϕ_{dis}	$\phi_{E,E \rightarrow Z,E}^{sens}$ ^b
1	0.28 ^a	26 ^a	1.1	0.05	0.15	0.20
2	0.026 ^a	1.8 ^a	1.4	0.30	0.40	0.11
3	0.04	4.4	0.91	0.09 ₅	0.10	0.37
4	0.04	9.0	0.44	0.01 ₅	0.03	0.43

^a From Ref. [5].

^b Sensitized by biacetyl in benzene, concentration of the *E,E* isomer $\cong 5 \times 10^{-4}$ M.

The independence of the fluorescence spectra on the excitation wavelength and the monoexponential decay found also for these compounds indicates that the various species have practically indistinguishable properties or that one of them prevails in the conformer mixture. As a matter of fact, the fluorescence excitation spectrum does not overlap well the absorption spectrum [2], but the effect is not sufficient to allow the intrinsic properties of the different conformers to be separated by selective excitation, as already reported for **1** and **2** [5].

3.2. Flash photolysis measurements

The triplet state was investigated by nanosecond laser flash photolysis. It seems not to play a significant role in the direct photoreaction, as already reported for **1** and **2** [5,6]. No clear sign of triplet formation was detected in the direct experiments, even for **3** and **4**, indicating that the triplet yield is negligible for these compounds too. Experiments carried out in the presence of biacetyl as a triplet donor showed that the triplet absorption of the sensitizer is quenched by the olefin with formation of only very weak absorptions around 400 nm, probably because of low absorption coefficients of T₁. In the case of the 2F and 2T derivatives, a weak transient absorption centered around 550 nm with a lifetime of the order of 5 μ s (unaffected by oxygen) was detected under direct excitation at 355 nm in acetonitrile. It was assigned to a radical cation since the same transient was obtained by energy transfer from an electron acceptor such as chloranil.

3.3. Photophysical and photochemical parameters

The photophysical and photochemical parameters of the compounds investigated are collected in Table 3. The fluorescence quantum yield, substantial for the hydrocarbon, is drastically reduced (by almost one order of magnitude) for the hetero-analogues. The fluorescence decay was always monoexponential indicating that one conformer is largely prevalent in solution at room temperature (see above). The emission lifetime also, quite long for the hydrocarbon, decreases markedly for **2** but increases again for **3** and even more in the case of **4**. The resulting kinetic parameter is rather low, of the order of 10^7 s^{−1}, as expected for a forbidden transition from the emitting state [2].

Irradiation of the four *E,E* isomers in our mild conditions (monochromatic light, dilute solutions, low light dose, short irradiation times) produces the *Z,E* isomers whilst no sign of *Z,Z* was detectable in the irradiated mixture. However, no clear isosbestic points were observed during the photoreaction, even

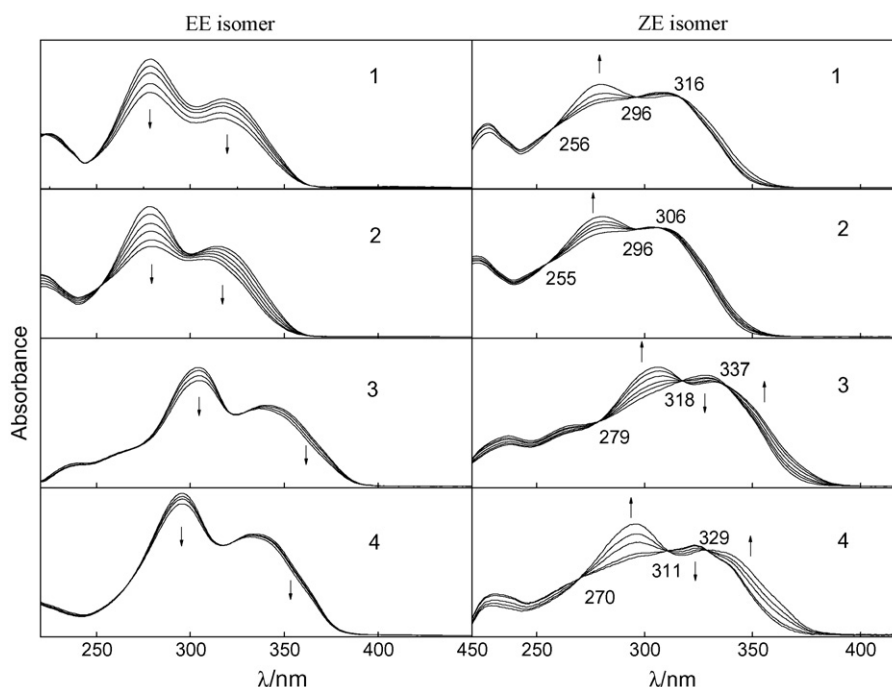


Fig. 3. Spectral evolution under irradiation of the *E,E* and *Z,E* isomers of the four compounds investigated in de-aerated MCH/3MP. For the *Z,E* isomers, the evolution was followed until the maintenance of isosbestic points whose wavelength (nm) is reported.

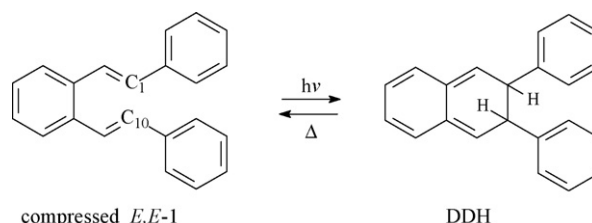
at the initial stages, particularly for the hydrocarbon, indicating that the *E,E* → *Z,E* isomerization is accompanied by the formation of at least another photoproduct. The HPLC analysis showed the formation of small amounts of various side photoproducts. Gas-mass chromatography of the irradiated mixture of the hydrocarbon allowed to recognize stilbene, whose formation has been already reported [9]; moreover, after irradiation of aerated solutions, detection of an atomic weight higher (+14) than that of the starting material indicated the probable formation of an addition product with oxygen accompanied by water elimination. A similar behaviour was found by some of us in the photochemistry of *o*-vinylstyrylfurans [14].

Measurements of the photoisomerization quantum yields were then accompanied by those of the *E,E* disappearance. Perusal of both values reported in Table 3 shows that the photodegradation accompanying photoisomerization is particularly substantial for the hydrocarbon (disappearance quantum yield of about 15%, to be compared with an isomerization yield of about 5%) whereas the presence of the heteroaromatic groups reduces its contribution, particularly for the 2T derivative whose disappearance and isomerization yields are practically the same. Fig. 3 shows the different photobehaviour of the hydrocarbon and its hetero-analogues.

The nature of the photoprocesses accompanying photoisomerization in 1,2-distyrylbenzene is a puzzling subject, not yet clarified despite deep investigations [9]. The analysis is complicated by the fact that primary unstable photoproducts can be in turn implied in photochemical and thermal reactions, including dimerization, cyclization and bond cleavage, leading to small amounts of a variety of final products [9]. It has to be noted that those experiments were often performed in more severe conditions (dose, concentration). In fact, only in rela-

tively mild conditions was the isomerization process prevailing, whereas after prolonged irradiation other photoproducts were found [9b,c]. The high sensitivity of the photoconversion of 1,2-distyrylbenzenes and similar compounds to minor variations in the spatial structure has been deeply discussed [15]. In those works, the authors proposed a photoreaction mechanism of *E,E* isomer of **1** giving dimers, the cyclization product which follows the *E,E* → *Z,E* isomerization (picene), and stilbene as a side photoproduct. The latter was supposed to form through a cyclized intermediate (2,3-diphenyl-2,3-dihydronaphthalene, DDH) originated from the compressed rotamer of **1** (Scheme 3), but was never detected. From the calculations, this rotamer is the less stable in the ground state but could play a role in the excited state. In the present work, together with some amount of stilbene, we found that the disappearance of the *E,E* isomer of **1** was accompanied by the formation of a compound absorbing in the range around 420 nm, typical of the dihydrophenanthrene-like compounds (Fig. 4).

Due to the metastability of this photoproduct, we were unable to accumulate an amount sufficient to its characterization. However, it was reasonably assigned to DDH formed by cyclization of the compressed rotamer of **1**, as hypothesized in previous



Scheme 3.

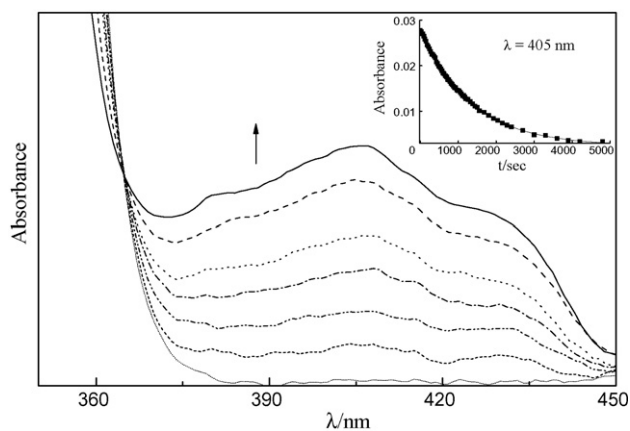


Fig. 4. Evolution of the absorption spectrum around 400 nm under irradiation of the *E,E* isomer of **1** in MCH/3MP at room temperature. The inset shows a typical decay kinetics in aerated solution.

works [9,15]. In our experimental conditions, no sign of the presence of such species was found in the case of **3** and **4**, whilst a very low absorption could be detected for **2**. This evidence is in agreement with the calculated distance between the two reaction centers (C_1 and C'_{10} in Scheme 3): 3.17, 3.25, 3.38 and 3.39 Å for **1**, **2**, **3** and **4**, respectively.

The DDH has a lifetime which strongly depends on the experimental conditions. It decays thermally (lifetime of the order of 20 min in aerated solutions), but the bleaching kinetics became slower in de-aerated solutions and faster under visible irradiation. In the latter case, the bleaching could lead to fragmentation, which explains the presence of stilbene. The ϕ_{dis} of *E,E*, unlike $\phi_{E,E \rightarrow Z,E}$, was also found to be strongly affected by the oxygen concentration and irradiation times. As a matter of fact, similar ϕ_{dis} and $\phi_{E,E \rightarrow Z,E}$ were found by bubbling nitrogen and stopping the experiment at small conversion percentage ($\leq 2\%$).

Another experiment was particularly interesting to investigate the reaction mechanism. Whereas a 20 min irradiation at 313 nm of a solution ($\cong 6 \times 10^{-5}$ M in MCH/3MP) of the *E,E* isomer of **1** led to 3.1% of *Z,E* formation and 5.7% of *E,E* disappearance, a parallel experiment carried out in four 5 min steps (after each step, the solution was left in the dark until complete bleaching of DDH) led to an unchanged yield of *Z,E* (3.2%) and a smaller disappearance yield (3.6%), quite similar to the isomerization yield in this case. These experimental findings indicate that the irradiated DDH is responsible for the formation of the degradation photoproducts, whilst the prevalent reaction in the dark is the cleavage of the $C_1-C'_{10}$ bond recovering *E,E*-**1**.

The results of the flash photolysis measurements (see above) suggest that the direct photoisomerization of the four *E,E* isomers (Table 3) occurs in the singlet manifold, even if a small triplet contribution cannot be excluded, particularly for the 2T derivative where the sulphur heteroatom is expected to favour ISC.

An important effect of the heteroatom on the *E,E* \rightarrow *Z,E* quantum yield was found. Its value, rather small (of the order of 5–10%) for the hydrocarbon and the 2T derivative, decreases further for 2F, whereas it increases to 30% for the 4P derivative, only in this case compensating the strong decrease observed in

Table 4

Spectral data of the *Z,E* isomers of the four compounds investigated in MCH/3MP at room temperature

Compound	λ_{abs}^{max} (nm) ^a	ϵ_{abs}^{max} (10^4 M ⁻¹ cm ⁻¹)
1	279 ^{sh} , 309	3.61
2	278 ^{sh} , 303	2.27
3	267 ^{sh} , 304 ^{sh} , 329	2.77
4	262 ^{sh} , 298 ^{sh} , 323, 340 ^{sh}	2.86

^a The superscript 'sh' means shoulder.

the emission yield. A similar behaviour has been found for the corresponding 4P derivative of the linearly conjugated 1,4 compound [4] indicating that the electron acceptor properties of the two side pyridyl groups lead to a decrease in the bond order of the central double bond and then to lower torsional energy barriers. In any case, the sum of the radiative and reactive deactivation pathways remains rather small indicating that internal conversion to the ground state plays an important role in these sterically crowded compounds, particularly for the 2F derivative. The photoreactivity remains low even in the triplet manifold for **1** and **2**, since the photosensitized isomerization has quantum yields substantially smaller than the limiting value of 50%, generally found for the diabatic mechanism of the *E*-diarylethenes (internal conversion from the perpendicular configuration to the ground state with equipartition to the quasi-planar isomers) [16]. However, the sensitized quantum yield is substantially higher for **3** and **4** indicating a faster equilibration of T_1 with the $^3perp^*$ configuration. In any case, the comparison of the direct and sensitized quantum yields seems to confirm a prevalence of the singlet mechanism for the direct photoisomerization. In conclusion, this study has shown that the three heteroaromatic groups investigated have a noticeable quenching effect on the radiative decay channel of *E,E*-**1**. On the other hand, they display different effects on photoisomerization: the thienyl group produces only small increase of the reactivity, whereas the pyridyl group leads to an important decrease in the torsional energy barrier in S_1 , thus favouring isomerization, and the furyl group displays an opposite effect favouring internal conversion.

The spectral properties of *Z,E* isomers (separated by preparative HPLC) are shown in Table 4. Their absorption spectra are hypochromic and hypsochromic with respect to those of *E,E*, as generally found for analogous compounds. The photoreactivity of the *Z,E* isomers was also investigated. When irradiation was performed in mild conditions, the *Z,E* \rightarrow *E,E* photoisomerization is clean, as indicated by the maintenance of three isosbestic points until a certain degree of photoconversion ($\sim 30\%$, at least, and even higher for **4**). After that, formation of side photoproducts was detected, indicating that the *E,E* isomer initially produced is the responsible for further photoreactivity, as seen above. It has to be noted that, also by irradiation of *Z,E*, no formation of *Z,Z* was found.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2006.10.031.

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