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Excited state behaviour of some thio-analogues of 1,3-distyrylbenzene☆

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Abstract

The excited state properties of 1,*n*-distyrylbenzene (*n* = 2, 3 or 4) and hetero-analogues have being investigated in the authors' laboratory by fluorimetry, nanosecond and femtosecond laser flash photolysis, and conventional photochemical techniques as well as by the help of theoretical calculations. The aim of the present article is to survey recent results of the study on the internal rotation around double bonds, i.e. *cis–trans* photoisomerization (*cis* and *trans* are indicated in the text by *Z* and *E*, respectively) and single bonds (i.e. conformational equilibria) in some thio-analogues of *E*,*E*-1,3-distyrylbenzene where the central or side benzene rings were replaced by thiophene rings. Some peculiarities in the photobehaviour of these compounds will be thus evidenced.

The main effect of the sulphur heteroatom in the side rings is a decrease in the radiative relaxation and an increase in the *E*,*E* → *Z*,*E* photoisomerization yield caused by decreased torsional barriers in S_1 and/or increased triplet yields, which opens the way to isomerization in the triplet manifold. On the other hand, when sulphur is in the central ring, the fluorescence decrease favours non-reactive and non-radiative deactivations. In the case of 2,5-distyrylthiophene with a central thiophene ring, the photobehaviour of the stereoisomers with one or both *cis* double bonds (*Z*,*E* and *Z*,*Z*) showed diabatic/adiabatic formation of the *E*,*E* isomer in both lowest excited states of singlet and triplet multiplicities. In the case of *Z*,*Z*, the adiabatic process (directly from Z,Z^* to E,E^*) is characterized by a "one photon–two bonds" mechanism.

The presence of conformational equilibria in solutions of distyrylbenzenes was found to play a role in their relaxation properties since different conformers can have different deactivation channels, specifically in the case of the 1,3 compound with side 3′-thienyl groups. The results obtained by selective irradiation, as a function of the excitation wavelength and temperature, and supported by theoretical calculations, evidenced uncommon rotamer interconversion during the short S_1 lifetime of this compound.

Keywords: Thio-1,3-distyrylbenzenes; Photoisomerization mechanism; Fluorescence; Isomerism and rotamerism

1. Introduction

The photophysics and photochemistry of 1-*n*-distyrylbenzenes (*n* = 2, 3 or 4), where a central benzene ring bears two styryl substituents, have been widely investigated in the last two decades [1] because of their interest as laser dyes, scintillators and building blocks of photoconductive materials [2]. Introduction of heteroatoms in these compounds can markedly affect the relaxation properties of their excited states, favouring the reactive or non-radiative/non-reactive deactivation pathway, depending on the type of substitution at the central ring (*n*) and the position of the heteroatom. The effect of the introduction of heteroaromatic groups, such as pyridine or thiophene rings, has being deeply investigated in our laboratory [3–6].

The aim of the present work is to survey the photophysical and photochemical properties of the *all-trans* (*E*,*E*) geometrical isomers of the cross-conjugated 1,3-distyrylbenzene [or 1,3-di-(phenylethenyl)benzene, 1,3-$(PhE)_2B$] and three thio-analogues of general formula $(Ar–CH=CH–)_2Ar'$, where a 2,5-disubstituted thiophene ring replaces the central benzene ring (Ar') and 2'-thienyl (2T) or 3'-thienyl (3T) groups replace the side (Ar) phenyl groups (Scheme 1).

For one compound, 2,5-$(PhE)_2T$, the photobehaviour of the stereoisomers with one or both *cis* double bonds (*Z*,*E* and *Z*,*Z*, respectively) are compared with those of the corresponding *E*,*E* isomers.

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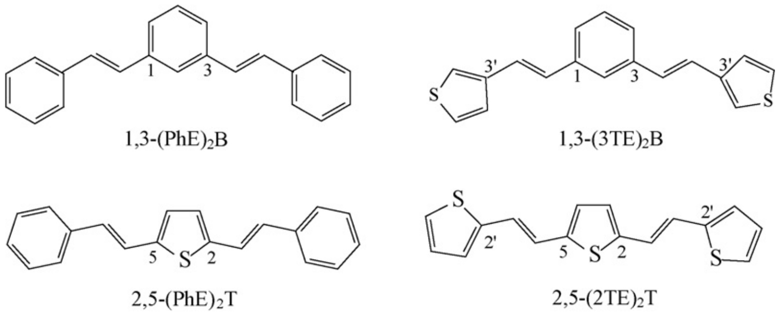


Scheme 1.

Interestingly, the results obtained allowed to evidence some peculiar properties in the photobehaviour of these compounds that will be here reviewed. The kinetic competition between the radiative and reactive relaxation channels in the singlet manifold, the reactivity in the triplet state, populated through the sulphur-induced intersystem crossing (ISC) or by sensitization, the involvement of diabatic/adiabatic photoisomerization mechanisms and, in the case of 1,3-di-(3′-thienylethenyl)benzene, the unusual rotamer interconversion in the lowest excited singlet state will be described. The mechanistic implications of recent achievements will be discussed.

2. Experimental

The preparation of the compounds investigated (Scheme 1) is described elsewhere. The compounds were purified by HPLC and characterized by ^{1}H NMR spectra [3,6]. The solvents used were 9/1 (v/v) methylcyclohexane/3-methylpentane (MCH/3MP), benzene and toluene.

Details on the experimental methods and conditions used in this work are reported in previous papers [6–8]. The parameters reported in the tables are averages of at least three independent experiments with mean deviations of ca. 15% for fluorescence quantum yields and lifetimes and ca. 10% for the photoisomerization quantum yields. The theoretical calculations were performed by the HyperChem computational package (Version 6.1). The calculated electronic spectra (transition energies and oscillator strengths) were obtained by ZINDO/S using optimized geometries (according to PM3 method). Calculations of the configuration interaction included 81 (9×9) single excited configurations.

3. Results and discussion

3.1. Spectral behaviour

The maxima of the absorption and emission spectra recorded under excitation of the four cross-conjugated *E*,*E* isomers investigated and of the *Z*,*E* and *Z*,*Z* isomers of 2,5-(PhE)$_2$T are reported in Table 1.

Spectral data for the parent hydrocarbon, 1,3-(PhE)$_2$B, are in good agreement with those reported for this compound in nonpolar solvents [9]. The replacement of phenyl by 3′-thienyl (3T) groups leaves the spectrum practically unchanged. A marked red shift (~90 nm) was observed in the 2,5 compounds with a central thiophene ring. The red shift increases further (~110 nm) in the 2,5-(2TE)$_2$T, which bears three thiophene groups linked to the ethene bridges in the *ortho* positions, as usually found for compounds bearing 2T substituents [10,11]. The experimental data are well predicted by theoretical calculations of the transition energy and oscillator strength, as shown in Table 1.

The absorption spectrum shifts to the blue and loses intensity and structure on increasing the number of *Z* double bonds, as found for the analogous 1,4 hydrocarbon and its aza-derivatives [4]. This is again in agreement with the theoretical calculations, that predict distorted structures for *Z*,*E* and mainly for *Z*,*Z* isomers, while the *E*,*E* isomers display a spectral behaviour characteristic of quasi-planar geometries [7]. At room temperature, the fluorescence spectra were obtained for the *E*,*E* isomers only. It was practically impossible to detect the intrinsic emission of the *Z*,*E* and *Z*,*Z* isomers since it is very low and probably hidden by the stronger emission of the *E*,*E* isomer, adiabatically produced under irradiation (see below).

Table 1
Absorption and emission spectral data of the four *E*,*E* isomers investigated and of the *Z*,*E* and *Z*,*Z* isomers of 2,5-(PhE)$_2$T in MCH/3MP and toluene for the 1,3- and 2,5-compounds, respectively

Compound	$\lambda_{\max}^{\text{abs}}$ (nm)	$\varepsilon_{\max}^{\text{abs}}$ (10^4 M^{-1} cm^{-1})	$\lambda_{\max}^{\text{calc}}$ (nm)	f	$\lambda_{\max}^{\text{F}}$ (nm)
E,*E*-1,3-(PhE)$_2$B	300	5.3	310/305	0.16/2.14	370
E,*E*-1,3-(3TE)$_2$B	301	4.7	310/303	0.05/1.45	373
E,*E*-2,5-(PhE)$_2$T	392	4.1	396	1.81	461
Z,*E*-2,5-(PhE)$_2$T	368	2.7	363	1.15	467[a]
Z,*Z*-2,5-(PhE)$_2$T	347	1.4	328	0.73	
E,*E*-2,5-(2TE)$_2$T	414	4.9	430	1.84	490

The calculated absorption maximum and oscillator strength refer to the most stable rotamer, according to PM3 calculations (from Refs. [6,7]).

[a] In MCH/3MP at 77 K.

Table 2
Fluorescence parameters and photoisomerization quantum yields of the four *E*,*E* isomers investigated in MCH/3MP at room temperature (from Refs. [6,8])

Compound	ϕ_F	τ_F (ns)	k_F (10^8 s^{-1})	$\phi_{EE\to ZE}$	$\phi^{sens}_{EE\to ZE}$ [a]
E,*E*-1,3-$(PhE)_2B$[b]	0.88/0.28	7.5/18	1.2/0.16	0.038	0.48
E,*E*-1,3-$(3TE)_2B$	0.54/0.21	4.3/11.7	1.3/0.18	0.22	0.50
E,*E*-2,5-$(PhE)_2T$	0.30	0.85	3.5	0.03	0.027
E,*E*-2,5-$(2TE)_2T$	0.04	1.8	0.2	<0.001	<0.001

[a] In benzene.
[b] From Refs. [3,12].

3.2. Radiative/reactive relaxation

The quantum yields of fluorescence and photoisomerization of the four *E*,*E* isomers investigated are collected in Table 2. The pairs of values reported for the fluorescence parameters of the 1,3 compounds refer to the two most abundant A and B conformers (see below). The fluorescence emission is an important deactivation channel of their S_1 state (particularly for the short-living A conformers).

The radiative rate constant of the longer-lived B species of the 1,3-derivatives is one order of magnitude smaller than that of A, indicating that the emission originates from a forbidden state (in agreement with data previously reported [1]), at least for B [3,12]. This also holds for *EE*-2,5-$(2TE)_2T$ which displays emissive parameters characteristic of a forbidden transition.

The reactive pathway is negligible, becoming substantial for the 3T derivative only, where the spin–orbit coupling, favoured by the sulphur heteroatom, induces the formation of a highly isomerizable triplet state.

The introduction of three sulphur atoms in *EE*-2,5-$(2TE)_2T$ causes a net decrease in the fluorescence yield. Interestingly, both 2,5 compounds have negligible isomerization yield even in sensitized experiments with benzophenone as triplet donor, indicating that T_1 does not isomerize, probably because stabilization of the *all-trans* geometry causes a too high energy barrier to twisting in the *E*,*E* → *Z*,*E* direction (see below).

3.3. Transient spectroscopy

The nanosecond flash photolysis measurements showed a substantial population of the triplet state through ISC induced by the heavy heteroatom (see Table 3 and Fig. 1) for the compounds with a thiophene central ring only. The $T_1 \rightarrow T_n$ spectrum of 1,3-$(PhE)_2B$ at 485 nm was observed only under sensitization, the triplet quantum yield under direct irradiation, ϕ_T, being less than 1% [12]. The triplet spectrum was not detectable for the 3T derivative by both direct and sensitized photolysis. Since the triplet benzophenone, used as energy donor in the sensitized experiments in benzene, was found to be normally quenched by 1,3-$(3TE)_2B$, one can argue that the triplet is too short lived because of a fast equilibration with the perpendicular configuration responsible for the photoreaction [6].

As to the 2,5 compounds of Table 3, the ϕ_T value was higher in the case of *EE*-2,5-$(PhE)_2T$ in agreement with its higher yield for the formation of singlet oxygen [6]. The transient absorption spectra obtained by photolysis of the *Z*,*E* and *Z*,*Z* isomers overlap the $T_1 \rightarrow T_n$ spectrum of the corresponding *E*,*E* isomer. The finding that the same triplet spectrum (recorded about 100 ns after the laser pulse) and the same lifetime were measured for the three stereoisomers clearly indicate that also $^3Z,E^*$ and $^3Z,Z^*$ fastly isomerize to $^3E,E^*$ through an adiabatic pathway (see below).

Some experiments were carried out by ultrafast techniques [13] in order to evidence the possible role of upper excited states and/or primary steps involving precursor transients. Only the $S_1 \rightarrow S_n$ transient was observed in the 500–700 nm region, with a decay rate corresponding to the fluorescence lifetime. The examples in Fig. 1 show that, in the case of *EE*-2,5-$(PhE)_2T$, the decay of the transient is accompanied by the appearance of a new band around 470 nm (the dashed curve refers to the spectrum recorded with a delay of ∼1 ns after the laser pulse), in the region where the triplet state of *E*,*E* absorbs. This band grows at the same rate of the $S_1 \rightarrow S_n$ transient decay and does not change in the explored temporal range indicating a fast ISC to the triplet state. The same behaviour could not be observed for *EE*-2,5-$(2TE)_2T$ owing to the overlap of various transitions in the region where the triplet state absorbs and to the lower triplet yield measured for this compound (Table 3). As a matter of fact, a second band around 550 nm was observed when the side phenyl groups were replaced by 2′-thienyl groups as in the case of 1,4-distyrylbenzenes [11,13]. For *EE*-2,5-$(2TE)_2T$, the ultrafast measurements showed the presence of a short-living transient (≅70 ps) assigned to an upper excited singlet state (S_2) reached by an allowed transition. S_2 deactivates to S_1 through IC and directly to the ground state through stimulated emission.

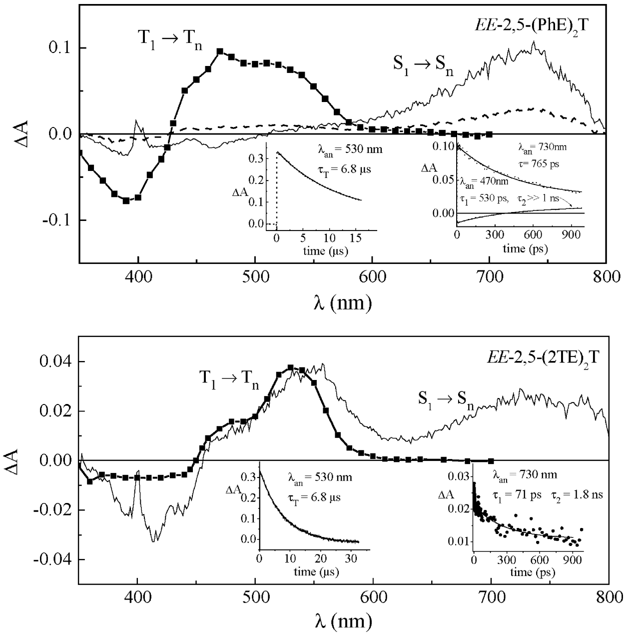


Fig. 1. Transient absorption spectra of the *E*,*E* isomers of 2,5 compounds by nanosecond (■, $T_1 \rightarrow T_n$) and femtosecond (—, $S_1 \rightarrow S_n$) laser flash photolysis in toluene at room temperature. The insets show examples of decay kinetics in both series of experiments.

Table 3
Transient state properties of the *E*,*E* isomers of 2,5-(PhE)$_2$T and 2,5-(2TE)$_2$T in non-polar solvents at room temperature (from Refs. [6,13])

Compound	$T_1 \to T_n$					$S_1 \to S_n$	
	λ_T^{max}(nm)	τ_T (μs)	ε_T^{max}(10^4 M^{-1} cm^{-1})	ϕ_T	k_{ISC} (10^7 s^{-1})	λ_S^{max}(nm)	τ_S (ps)
2,5-(PhE)$_2$T	470	10.5	3.5	0.40	47	740	765
2,5-(2TE)$_2$T	480, 530	6.8	5.0	0.15	8.3	550, 730	60, 1900

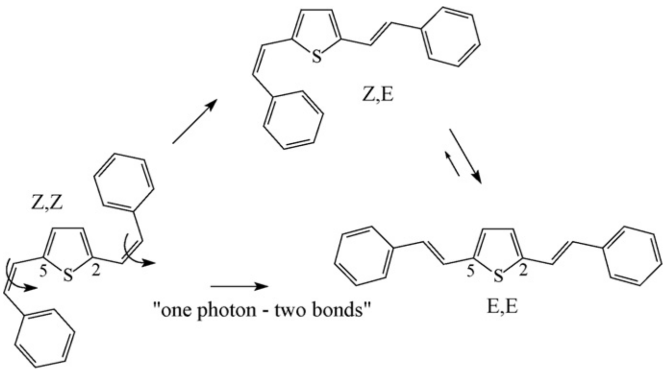
In the stationary experiments the involvement of such an upper state was evidenced by the presence of a hypsochromic shoulder in the fluorescence spectrum, due to emission from S_2, thermally populated by S_1 [13].

3.4. Photobehaviour of geometrical isomers

The quantum yields reported in Table 4 for the isomers with isomerizable double bonds in *cis* configuration show a high production of *E*,*E* from *Z*,*E* and *Z*,*E* from *Z*,*Z*. By excitation of *Z*,*E* and *Z*,*Z* at room temperature, a weak emission was observed with spectrum and lifetime characteristic of *E*,*E*. Therefore, the data reported in parentheses in Table 4 are not the intrinsic yields of the irradiated isomers but mostly refer to the adiabatically formed *E*,*E* isomer.

Only in a rigid matrix of MCH/3MP at 77 K, when the high viscosity of the medium inhibits rotation around the double bond, the intrinsic emission spectrum of *Z*,*E* became detectable and showed a bell-shaped band. This behaviour is in agreement with the presence of an adiabatic pathway for isomerization in S_1 at room temperature, that produces $^1E,E^*$ by irradiation of *Z*,*E*. No emission clearly attributable to *Z*,*Z* was detected even at low temperature, the very weak emission spectrum measured at 77 K being very similar to that of the corresponding *Z*,*E* isomer [7]. The relatively high yield of photoisomerization towards *E*,*E* supports the above hypothesis of a highly activated twisting starting from *E*,*E* in both S_1 and T_1. Therefore, the *E*,*E* isomers of the 2,5 compounds mainly decay by non-radiative and non-reactive relaxation whereas the back photoreaction towards *E*,*E*, starting from the *cis* compounds, is favoured. It has to be noted that the detection of *E*,*E* fluorescence under irradiation of *Z*,*Z* clearly indicates the occurrence of isomerization of both double bonds by absorption of one photon (Scheme 2).

The triplet-sensitized $ZE \to EE$ photoisomerization yield increases with *ZE* concentration (a value of 2.12 was reached at $[ZE] \cong 10^{-3}$ M) indicating a chain mechanism (energy transfer from the excited photoproduct, adiabatically produced, to the starting isomer, as found for many stilbene-like compounds [14]).



Scheme 2. Photoreactivity of the three geometrical isomers of 2,5-(PhE)$_2$T.

All together, these results point to the occurrence of adiabatic pathways (in addition to the diabatic ones, implying $S_1 \to S_0$ internal conversion or $T_1 \to S_0$ ISC at the perpendicular configuration, $^{1,3}P^* \to {}^1P$ [15]), both in the lowest singlet and triplet states. The adiabatic contribution to the overall yield of formation of *EE* is small and can be derived by appropriate treatments. In the case of *ZE*, assuming that all the fluorescence measured under direct excitation at room temperature originates from the adiabatically formed $^1EE^*$, the yield of the adiabatic contribution in S_1 to the overall $ZE \to EE$ photoisomerization can be derived by Eq. (1)

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

where $^1\phi_{G,EE} = 1 - \phi_{EE\to ZE}$ and $\phi_F(ZE)$ refers to the emission observed by excitation of *ZE* but pertaining to $^1EE^*$. By analogous relationships, the same information can be derived for the $ZZ \to ZE$ and $ZZ \to EE$ processes.

For the process in the triplet manifold the contribution of the adiabatic mechanism could be derived using the parameters measured in sensitized experiments. The relationship used for

Table 4
Fluorescence parameters and photoisomerization quantum yields of the three geometrical isomers of 2,5-(PhE)$_2$T in MCH/3MP at room temperature (from Ref. [7])

Compound	ϕ_F	ϕ_{ISO}	$^1\phi^{ad}_{ISO}$	ϕ^{sens}_{ISO}	$^3\phi^{ad}_{ISO}$ [a]
E,*E*-2,5-(PhE)$_2$T	0.30	0.03 (*ZE*)	~0 (*ZE*)	0.03 (*ZE*)	~0 (*ZE*)
Z,*E*-2,5-(PhE)$_2$T	(0.024)	0.47 (*EE*)	0.08 (*EE*)	~1(*EE*)	~1 (*EE*)
Z,*Z*-2,5-(PhE)$_2$T	(0.004)	0.49 (*ZE*) 0.09 (*EE*)	0.09 (*ZE*) 0.08 (*EE*)	<0.03 (*ZE*) ~1(*EE*)	~0 (*ZE*) ~1 (*EE*)

[a] In benzene.

the $^3ZZ^* \rightarrow ZE$ process is

$$^3\phi^{\mathrm{ad}}_{ZZ^*\rightarrow ZE} = {}^3\phi^{\mathrm{ad}}_{ZZ^*\rightarrow ZE^*} \times {}^3\phi_{\mathrm{G},ZE} = \frac{\phi^{\mathrm{sens}}_{ZZ\rightarrow EE}}{\phi^{\mathrm{sens}}_{ZE\rightarrow EE}} \times {}^3\phi_{\mathrm{G},ZE} \qquad (2)$$

where ${}^3\phi_{\mathrm{G},ZE} = 1 - \phi^{\mathrm{sens}}_{ZE\rightarrow EE}$.

The quantum yields thus derived for the adiabatic contribution to the overall isomerization (ϕ_{ISO}) show that they are rather small in the singlet state (${}^1\phi^{\mathrm{ad}}_{\mathrm{ISO}}$). Only when the triplet state is populated by sensitization, the adiabatic mechanism (${}^3\phi^{\mathrm{ad}}_{\mathrm{ISO}}$) prevails and becomes the only pathway for the photoreaction. Unit-yields were found in dilute solutions when the chain mechanism mentioned above is not yet operative.

3.5. Conformational equilibrium

The fluorescence decay of 1,3-$(PhE)_2B$ and its 3T analogue is bi-exponential indicating the presence of at least two rotamers in solution [16]. Contrary to the case of the 2,5 compounds, where different conformers are characterized by a relatively large enthalpy difference and then one of them largely prevails in the rotamer mixture, a small enthalpy difference among different conformers was found by calculations on the 1,3 compounds, predicting similar abundances of at least two rotamers, in agreement with the observed dependence of the fluorescence emission and excitation spectra on the excitation (λ_{exc}) and emission (λ_{em}) wavelength, respectively. The λ_{exc} effect on the emission spectra (particularly on exciting at the long wavelength tail of the absorption spectrum) allowed the separated contributions of the two species to the fluorescence quantum yield to be evaluated [3,8]. In the hydrocarbon, the radiative decay of the short-living A rotamer largely prevails (Table 2) whereas its photoisomerization quantum yield is very small.

In the 3T derivative, an additional contribution to conformational equilibria can be given by rotation of the side thiophene groups. Even in this case the short-living rotamer (which, according to calculations, has the compressed *s-cis*,*s-cis* conformation) decays mainly radiatively but the photoreaction also is substantial ($\phi_{EE\rightarrow ZE} = 0.22$). As reported in Section 3.2, the longer-lived rotamer (elongated *s-trans*,*s-trans* geometry) has a small radiative rate constant ($k_{\mathrm{F}} = 1.8 \times 10^7\ \mathrm{s}^{-1}$) indicating a partially forbidden transition. The rotamerism of *EE*-$(3TE)_2B$ has been studied by the help of the fluorimetric method [16] based on the λ_{exc} and temperature effects on fluorescence spectra, quantum yields and decay profiles [17]. The results obtained [8] allowed the excited state properties of the two most abundant conformers to be derived (Table 2).

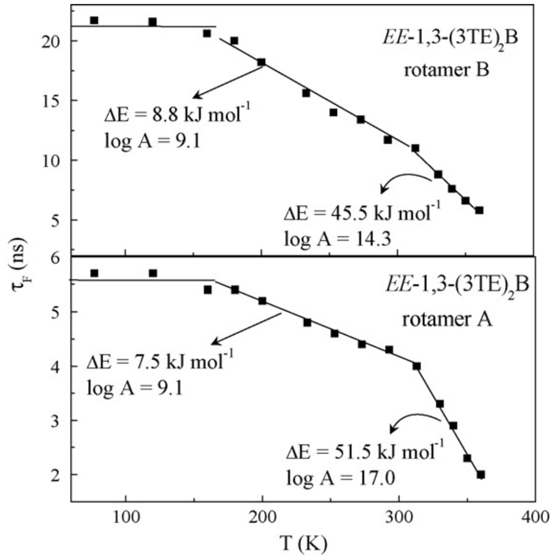
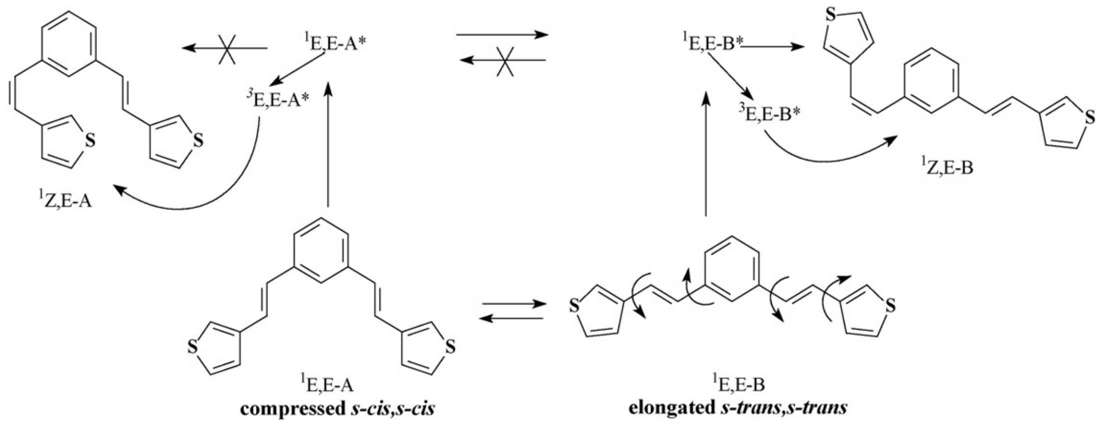


Fig. 2. Temperature effect on the lifetimes of A and B rotamers of *EE*-1,3-$(3TE)_2B$ (the Arrhenius parameters are also reported).

Interestingly, the temperature effect on the fluorescence lifetime (Fig. 2) revealed the presence of two activated steps for both rotamers. The process evidenced at low temperatures with similar activation energies was assigned to an activated ISC, responsible for the photoreaction in T_1, while above room temperature the torsional barriers refer to geometrical isomerization in S_1 for the B rotamer and to $A^* \rightarrow B^*$ interconversion in the excited state for the short-living A rotamer. This unusual process, against the “non equilibration of excited rotamers” (NEER) principle [18], becomes operative at high temperatures only, when the activated rotation around the quasi-single bond starts to compete with the relaxation processes of S_1, namely fluorescence, IC and ISC (see Scheme 3).



Scheme 3. Relaxation mechanism of the A and B rotamers of *EE*-$(3TE)_2B$ including their interconversion in the excited state against the NEER principle.

A support to this interpretation of the temperature effect came by the analysis of the pre-exponential factors of the two components of the fluorescence decay. It showed that the ratio of the fractions of the excited rotamers (f_A/f_B) decreases markedly above room temperature, more than what expected by ground state enthalpy difference ($1.08\,\mathrm{kJ\,mol^{-1}}$) indicating that $^1A^*$ interconverts to $^1B^*$ during its lifetime [8].

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