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Evidence of adiabatic channels in the singlet photoisomerization of *cis*-1,2-diarylethenes: a fluorimetric study

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Abstract

The deactivation of the first excited singlet state (S_1) of some cis isomers of 1,2-diarylethenes was studied by fluorimetric and photochemical measurements. When at least one of the aryl groups is a large polycyclic group of low S_1 energy (as in the case of pyrenyl and anthryl derivatives) the minimum at 90° (typical of stilbene) in the potential energy curve as a function of the twisting coordinate may disappear. This leads to an unusual fluorescence emission at room temperature and favours the adiabatic $^1cis^* \rightarrow {}^1trans^*$ isomerization mechanism instead of the well-known diabatic pathway, which implies internal conversion to the ground state from the $^1perp^*$ configuration.

INTRODUCTION

Based on the behaviour of the model compound, stilbene (S), the photophysics and photochemistry of 1,2-diarylethenes (DAEs) have been widely investigated in the last decade.

The fluorescent trans isomers have been studied more extensively and were found to generally follow the same photoisomerization mechanism widely accepted for stilbene. Twisting about the central double bond in the first excited singlet state S_1 (with an energy maximum at the perpendicular, 90°, configuration) and an upper excited state S_n (probably, a doubly excited state with a minimum at 90°) leads to an (avoided) crossing which offers the system an activated $^1trans^* \rightarrow {}^1perp^*$ pathway towards the energy minimum at ca. 90° from which $^1perp^* \rightarrow {}^Gperp$ internal conversion to the ground state surface and partitioning to the trans and cis isomers takes place [1]. It has been found that the relative extent of the radiative and reactive deactivation of the S_1 state and the predominance of a singlet or triplet reaction mechanism depend strongly on the size and the nature of the aryl groups linked to the ethenic central bond [2,3].

When the aryl groups have low S_1 and T_1 energies, the energy position of the lowest excited singlet and triplet states ($^{1,3}trans^*$ and $^{1,3}cis^*$) decreases thus making the crossing with the upper S_n curve less probable. As a consequence, the activation energy for twisting increases and the potential energy may pass through a maximum at 90°. Figure 1 shows a qualitative sketch, based on theoretical and experimental data [3], of the potential energy curves for twisting about the central bond in the lowest excited singlet state of some typical

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DAEs. When the barrier is higher than ca.12 kcal/mol, the isomerization to cis in S_1 at room temperature is inhibited and the only way to cis is intersystem crossing (ISC) to ^{3}trans*. In T_1, the energy barriers are generally smaller and the diabatic (^{3}trans* → ^{3}perp* → G_{perp} → G_{trans} + G_{cis}) or adiabatic (^{3}trans* → ^{3}cis* → G_{cis}) mechanisms can be favoured. The trans → cis isomerization becomes completely inhibited ("one way" isomerization, only from cis to trans [4]) when the barrier for twisting is also high in T_1. Thus, by choosing the suitable nature of the aryl groups linked to the ethenic double bond of DAEs, one can gradually tune the trans → cis pathway proceeding from a net singlet to a net triplet mechanism and/or from a high to a negligible quantum yield.

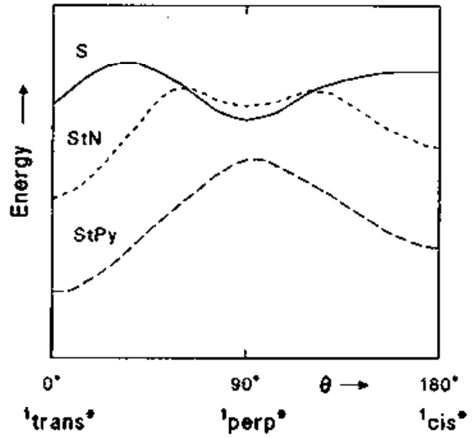

Figure 1. Sketch of the potential energy curves for the twisting around the ethenic double bond of some typical DAEs in the first excited singlet state.

The situation has been investigated less for the cis compounds, which are very short-lived and generally do not emit in fluid solutions at room temperature [1], moreover, they may also photocyclize to polycyclic arenes [5]). The ^{1}cis* → ^{1}perp* twisting, not activated in S [1], may present a barrier in DAEs bearing large polycyclic arenes thus opening the way to ISC and to an easier twisting in T_1. In any case, the torsional energy barriers are always relatively small, compared with those from the trans side. When only a shallow minimum (or no minimum at all) is present at ca. 90°, as mentioned above for the trans compounds, ^{1}cis* (and ^{3}cis* too) has to overcome easy slopes isomerizing directly to ^{1}trans* (or ^{3}trans*) *via* an adiabatic mechanism. Tokumaru's group has demonstrated that adiabatic isomerization of cis isomers in the triplet manifold takes place in the alkyl and aryl derivatives of vinyl-pyrene and vinyl-anthracene [4]. Until recently, little clear evidence of adiabatic isomerization in the singlet manifold could be found in the literature. To explain the observation of a bi-exponential decay, Sandros and Becker [6] proposed that such a mechanism is operative for *cis*-9-styrylanthracene (*cis*-9-StAn) but a different hypothesis of two cisoid species has been proposed by Görner [7]. Recently, Saltiel et al.

[8], using an elegant statistical method (principal component analysis, PCA) succeeded in resolving the emission following excitation of *cis*-S in the cis and trans contributions, thus demonstrating that, in stilbene itself, a very minor part of the cis isomerization (less than 1% of the overall isomerization yield) takes place by a direct photoconversion to ^{1}trans*. This interesting result appears to be at the limits of reliability, even if the parallel photocyclization reaction does not seem to interfere with the fluorescence measurements. Recently, we reported clear evidence of *singlet* adiabatic photoisomerization for *cis*-1-styrylpyrene (*cis*-1-StPy) [9]. On the basis of these results, it seemed justified to assume that this adiabatic photoprocess is a relatively general phenomenon in DAEs. To verify this hypothesis, we examined some DAEs containing the naphthyl (N), phenanthryl (Ph), pyrenyl (Py) and anthryl (An) groups. The results obtained by a fluorimetric and photochemical study show that, in the presence of large aryl groups of low S_1 and T_1 energies, the adiabatic mechanism may become a common isomerization pathway, not only in the triplet [4] but also in the singlet manifold.

RESULTS

Fluorescence emission by *cis*-DAEs has been observed in the past for stilbene [10] and naphthyl-analogues [11] in viscous media at low temperatures when the photoreactivity is inhibited and the singlet lifetime becomes relatively longer. We now extended the investigation to a series of styrylarenes of decreasing S_1 energy. The DAEs investigated were prepared for previous works [3]. Details about the photophysical and photochemical measurements are given elsewhere [9]. The measured ϕ_F and τ_F values have an uncertainty of 6% but the error can be higher for the derived parameters at room T for the intrinsic quantum yields of fluorescence, ϕ_F^c (10%), and singlet adiabatic isomerization, $^1\phi_{c\to t}$ (20%). Table 1 contains some photophysical parameters measured at low temperatures for these compounds in methylcyclohexane/3-methylpentane 9/1 (v/v) (MCH-3MP) and also includes stilbene for comparison purposes. The fluorescence lifetimes are on the order of 4 ns for all the various cis isomers; the only exception is 2-StAn which has a longer lifetime (90 ns). The corresponding quantum yields (ϕ_F^c) are relatively high, but remain substantially below unity, indicating the competition of non-

Table 1
Fluorescence parameters of some *cis*-DAEs in a rigid matrix of MCH-3MP at 77 K.

compound	λ_{max}/nm	ϕ_F^c	τ_F/ns	$k_F/10^8$ s^{-1}
S	435	0.80^a	5.0^b	1.6
1-StN	430	0.75	4.1	1.9
1-StPh	435	0.56	3.8	1.5
1-StPy^c	440	0.58	3.9	1.5
1,1'-NPyE	480	0.56	3.4	1.6
2-StAn	407, 431, 459	0.45	90	0.05
9-StAn	425	0.57	5.4	1.06

^{a} at 85 K (from refs 10,11); ^{b} from ref. 12; ^{c} at 150 K (from ref. 9).

radiative deactivation. S and 1-StN have the highest values while their analogues have smaller yields of radiative decay being characterized by a substantial triplet population. Given the small changes in lifetime and quantum yield, the radiative rate constant k_F lies in the range 1 to 2 (10^8 s^{-1}) except for 2-StAn ($5x10^6$ s^{-1}). This low value and the anthracene-like vibronic structure in the observed emission spectrum at low T (usually broad for cis isomers) indicate that the excitation is largely localized in the anthryl chromophore in this DAE. The k_F values obtained at low temperature were particularly useful since they allowed the intrinsic emission yield at room temperature to be approximately evaluated even in the presence of *singlet* adiabatic processes (see below).

Until very recently, the cis isomers were considered to be non-emitting in fluid solutions at room temperature [1]. Even though fluorescence emission from the cis isomers of S and n-StN at low temperatures and high viscosities was reported long ago [10,11], studies in fluid media at room T were unsuccessful, probably because of the very low yield and the competition of the two photoreactions, isomerization to trans [1] and dehydrocyclization to phenanthrene and benzophenanthrenes [5], respectively. As mentioned above, Saltiel et al. [8] succeeded in resolving the emission following excitation of *cis*-S into cis and trans contributions and estimated that 0.2% of the excited cis molecules isomerize to the trans through an adiabatic pathway. Moreover, the value $k_F = 1.6x10^8$ s^{-1} of Table 1 allowed a rough estimation of $\phi_F{}^c=10^{-4}$ from the recently reported lifetime of ≅ 1 ps at 293 K [13].

Our attempts to show fluorescence emission from the naphthyl and phenanthryl derivatives at room temperature have been unsuccessful so far. In fact, these compounds have a relatively low torsional barrier to $^1perp^*$ where a (shallow) energy minimum favours the diabatic isomerization mechanism. A value $\Delta E_{c\rightarrow t}$=2.7 kcal/mol was derived for 1-StPh from the temperature dependence of the fluorescence quantum yield and even smaller values are expected for StNs which do not emit at room temperature either.

First reports of substantial room T fluorescence appeared recently for 1-StPy [9,14] and 9-StAn [6,7,15] where the photoreactivity was slowed down and the lifetime was longer. Our investigation was then extended to some new compounds in order to gain more insight on the photophysical behaviour of *cis*-DAEs.

The procedure used in the following examples was based on the measurement of the pure cis emission ($\phi_F{}^c$ and τ_F) at low T where the adiabatic process in S_1 was inhibited and the fluorescence spectral shape became T-independent. The k_F could then be calculated from these low-T parameters and assume the same value at room T. From the τ_F value measured at room T, one could thus obtain the intrinsic fluorescence quantum yield of the cis isomer ($\phi_F{}^c$) at the same T. An alternative procedure was the deconvolution of the spectrum of the cis + trans mixture into the separate components, thus evaluating the unknown cis contribution [8].

Pyrenyl derivatives

Table 2 shows some measured and derived parameters for the geometrical isomers of 1-StPy and its naphthyl derivative, the 1-(1-pyrenyl),2-(1'-naphthyl)ethene (1,1'-PyNE) at room temperature. Both trans isomers have a very small photoreactivity; it is practically negligible for 1-StPy because the main deactivation pathway is the radiative one. The observed fluorescence spectrum after excitation of the cis isomer at room temperature is clearly indicative of a two-component emission, showing a substantial contribution of the adiabatically produced trans isomer. The contribution was larger in 1-StPy because of the higher intrinsic emission yield of ^{1}trans* and a larger yield of its production from ^{1}cis*. From the temperature dependence of τ_F, the barrier to twisting was slightly higher for the naphthyl derivative, thus explaining its smaller isomerization yield in the singlet manifold and indicating a higher non-radiative and non-reactive deactivation.

Table 2
Photophysical and photochemical parameters of 1-styrylpyrene and 1,1'-pyrenylnaphthylethene in de-aerated MCH-3MP at 298 K.

parameters	1-StPy		1,1'-PyNE	
	trans[a]	cis[b]	trans[a]	cis
ϕ_F	0.94	0.19	0.85	0.19
τ_F/ns	4.4	1.3	3.6	1.2
$k_F/10^8\ s^{-1}$	2.1	1.5	2.4	1.6
ΔE_{isom}/kcal mol^{-1}	>12	7.7	10.6	9.1
ϕ_{isom}	<0.01	0.5	0.004	0.25
$^1\phi_{c\to t}$		0.58		0.24

[a] From ref. 3; [b] from ref. 9.

cis-1-styrylpyrene. The fluorescence spectrum of pure *cis*-1-StPy in MCH-3MP was detectable at 180 K or below and the corresponding lifetime was 3.8 ns. Above this temperature, the decay became bi-exponential following the equation

$$I_F = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \tag{1}$$

At room temperature (298 K) the following parameters were obtained: τ_1 = 1.3 and τ_2 = 4.4 ns, A_1=-0.09, A_2=0.14. The shorter lifetime, τ_1, assigned to ^{1}cis*, decreased with increasing T because of the competitive isomerization ($\Delta E_{c\to t}$=7.7 kcal/mol) while τ_2 remained essentially constant. The negative pre-exponential factor indicated that the longer-lived species was ^{1}trans* which is directly formed by irradiation of the shorter-lived one through adiabatic isomerization. The trans lifetime was practically independent of temperature because of the high torsional barrier which prevented isomerization to cis ("one-way" isomerization). The decrease of τ_1 above 200 K was accompanied by a change in the shape of the fluorescence spectrum towards the more intense and resolved trans spectrum, thus confirming the occurrence of photoconversion. By $k_F=\phi_F/\tau_F=1.5\times10^8\ s^{-1}$ measured at 180 K, where only the cis emission was observed (one-component system), a $\phi_F{}^c$ value of 0.19±0.03 was estimated for the cis isomer at room temperature by assuming that k_F does not change with T. The experimental $\phi_F{}^{obs}$ value measured in MCH-3MP at 298 K was 0.74, which is the sum of two contributions, from the ^{1}cis* directly excited and the ^{1}trans* produced by adiabatic isomerization in S_1:

$$\phi_F{}^{obs} = \phi_F{}^c + \phi_F{}^t \times {}^1\phi_{c\to t} \tag{2}$$

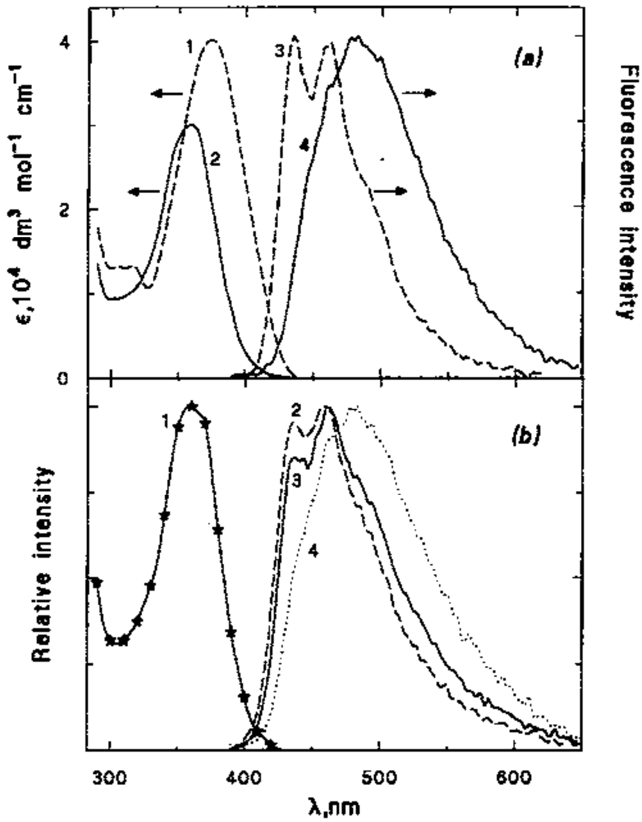

Figure 2. (a) Absorption (1,2) and fluorescence (3,4) spectra of pure trans (– – –) and cis (———) isomers of 1,1'-PyNE in MCH-3MP; (b) Observed fluorescence spectra after excitation of *cis*-1,1'-PyNE at different temperatures (T=354, 295 and 235 K for curves 2, 3 and 4, respectively) in the same solvent. Spectrum 1 (———) is the absorption spectrum of the cis isomer; star symbols show the fit of the fluorescence excitation spectrum at 295 K with the cis absorption (1).

The value $^{1}\phi_{c\to t} = 0.58\pm0.11$ thus obtained overestimates the singlet contribution being higher than the measured overall (singlet + triplet) yield ($\phi_{c\to t}$=0.5±0.02). This is probably due to the uncertainty in the measurements of the intrinsic photophysical and photochemical parameters . However, the value clearly indicates the large contribution of the adiabatic singlet mechanism to isomerization and points out a very small contribution of the triplet mechanism in dilute solutions (at higher concentrations, $^{3}\phi_{c\to t}$ increases because of the chain mechanism induced by ^{3}trans* + G_{cis} → G_{trans} + ^{3}cis* energy transfer [4]).

cis-1,1'-pyrenylnaphthylethene. A similar behaviour was found for *cis*-1,1'-PyNE using the same procedure. Figure 2a shows the spectral characteristics of the two geometrical isomers while 2b shows the two-component emission spectra observed at three temperatures and the excitation spectrum which fits the absorption spectrum of the cis isomer very well. The latter behaviour clearly indicates that the overall cis + trans emission originates from a unique excited state (^{1}cis*). Data in Table 2 show that the intrinsic fluorescence parameters are nearly the same as the phenyl analogue while the photoisomerization yield is markedly lower. The value of 0.19 ± 0.02 obtained for $\phi_F{}^c$ was roughly confirmed by the results obtained convoluting the separate spectra of the two components into that of the mixture at room T. By using eq.2, a quantum yield of 0.24 ± 0.05 was derived for the *singlet* adiabatic isomerization, compared with an overall yield of 0.25 ± 0.01, which includes the consequently small triplet contribution (the triplet yield was found <0.03 [16]). Since the sum $\phi_F{}^c + \phi_{c \rightarrow t}$ (0.19 + 0.25) is substantially below unity, a non-negligible internal conversion yield must be inferred to account for the absorbed quanta. This is probably due to the relatively high torsional barrier found for the singlet isomerization (9.1 kcal/mol) and the relatively scarce triplet population. Little deactivation *via* side photoreactions (e.g., cyclization) was also observed by HPLC.

Anthryl derivatives

The behaviour of n-StAns is significantly different from that described for the pyrenyl derivatives. Due to the low S_1 energy of anthracene, the torsional barriers are expected to be higher and then the *singlet* adiabatic isomerization would not be favoured.

cis-9-styrylanthracene. Table 3 collects the parameters measured in MCH-3MP at room T for the two geometrical isomers, including the optical density (ΔOD) measured for the $T_1 \rightarrow T_n$ transient of the cis compound. The fluorescence spectrum of *cis*-9-StAn was recorded in a rigid matrix of MCH-3MP at 77 K. The corresponding lifetime was 5.4 ns. Under our experimental conditions, no sign of singlet adiabatic isomerization was found at room T, whereas Sandros and Becker [6] estimated a singlet adiabatic yield of 8% in *n*-hexane. The emission decay remained mono-exponential until almost 310 K; above this temperature, clear signs of two decay components were obtained (at 353 K, τ_1=0.46 ns,τ_2=2.72 ns). As in the case of the pyrenyl derivatives, the short, T-dependent, lifetime (τ_1) was assigned to the cis isomer while the longer one was close to that of the trans isomer. We concluded that, at room T, isomerization takes place predominantly in the triplet manifold and that only above room temperature a small fraction of molecules can overcome the high torsional barrier in S_1 thus isomerizing.

However, the situation is complicated in this solvent because a concurrent photoreaction led to a not well identified compound (X, probably a photocyclization product) above 200 K, which became the predominant product above room T. Due to the complications introduced by this photoproduct, we preferred to investigate the behaviour in acetonitrile. There are indications in the literature that the torsional energy barrier in S_1 decreases in polar solvents, probably because of the stabilization of ^{1}perp* which has a zwitterionic character. This should facilitate both the diabatic and adiabatic pathways in S_1. The results obtained in acetonitrile confirmed the expectation. A further advantage of the polar solvent was that the X formation became practically negligible.

Table 3
Photophysical and photochemical parameters of 9-StAn in de-aerated solvents at room temperature.

parameters	trans		cis	
	MCH-3MP	CH_3CN	MCH-3MP	CH_3CN
ϕ_F	0.44	0.45	0.16	
τ_F /ns	3.6	4.3	2.4	0.11
$k_F/10^8\ s^{-1}$	1.2	1.0	0.66	
ϕ_{isom}			0.19	0.41
ϕ_X			0.27	0.04
$^1\phi_{c\rightarrow t}$			<0.02	0.11
ΔOD_{460}			0.08	0.043

An approximate $^1\phi_{c\rightarrow t}$ value of 0.11 was derived from the ratio between the overall $\phi_F{}^{obs}$ (0.05) and the intrinsic value of the trans isomer ($\phi_F{}^t$=0.45) at room T, where the fluorescence spectrum of *cis*-9-StAn is practically overlapped to that of the trans isomer. In acetonitrile, it was not possible to obtain k_F of the cis isomer since at the minimum T which can be reached in this solvent (below 230 K a non-transparent glass was formed) the fluorescence spectrum still showed the presence of both geometrical isomers. In this solvent, the fluorescence emission intensity decreased markedly and an even greater decrease was observed in lifetime while the partially coupled isomerization to trans (the singlet contribution) increased (the overall yield more than doubled while the triplet yield decreased [16]). The fluorescence decay in this solvent was already bi-exponential at 240 K, with a T-dependent short-lived component and a practically constant longer-lived component. The latter was clearly assigned to the ^{1}trans* species on the basis of its lifetime (4.3 ns, equal to the value obtained by direct irradiation of the trans isomer) and of the emission spectral changes.

cis-2-styrylanthracene. Figure 3 shows the spectral behaviour of this compound as a function of T. Above room temperature, the fluorescence spectrum observed by excitation of this isomer is practically coincident with that of the B conformer [17-19] of the trans isomer (spectra 4 and 5 of Figure 3). The lifetime was found to be bi-exponential (τ_1=2 ns, τ_2=64 ns), the longer value corresponding to the lifetime of the B conformer of the trans isomer in the same solvent. For 2-StAn, contrary to 9-StAn, the *singlet* adiabatic isomerization is the predominant deactivation pathway of S_1. A reasonable explanation for such behaviour, unexpected at least in non-polar solvents, lies in the very small k_F value (5×10^6 s^{-1}) which makes the ^{1}cis* → ^{3}cis* and ^{1}cis* → ^{1}trans* processes more competitive with the radiative deactivation. In fact, a high overall isomerization quantum yield (0.43) was found for this compound in MCH-3MP and a similar value was found in acetonitrile. The experimental findings point out a substantial singlet contribution on the basis of the triplet yield experimentally observed (<0.1[16]) and the huge change of τ_F on going from 77 K (90 ns) to room T (2 ns). However, a quantitative separation of the singlet and triplet contributions cannot be achieved at this stage owing to the complexity of the system. In fact, the longer-lived B conformer of the trans isomer produced from ^{1}cis* is characterized by a dual emission from two neighboring (equilibrated) singlet states [20]. A complete fluorimetric analysis of this three-component system in this solvent would then require a rigorous spectral deconvolution based on the PCA method.

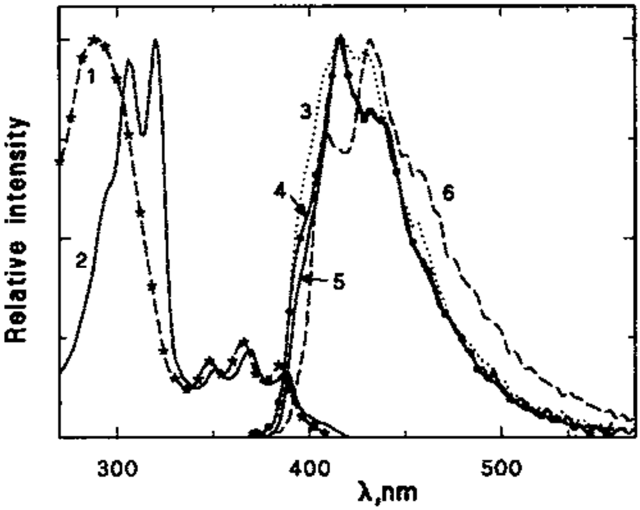

Figure 3. Normalized absorption (1,2) spectra of pure trans (——) and cis (– – –) isomers of 2-StAn in MCH-3MP at room T and corresponding fluorescence spectra at λ_{exc}=290 nm (3, 4 and 6) obtained by excitation of the cis isomer at different temperatures [T=354 K (4), 298 K (3) and 120 K (6)]. Spectrum 5 is the emission spectrum of trans isomer; star symbols show the fit of the fluorescence excitation spectrum at 298 K with the cis absorption (1).

CONCLUSIONS

Adiabatic isomerization appears to be a relatively common phenomenon for *cis*-1,2-diarylethenes. When at least one of the aryl groups of DAEs is a large-size polycyclic group of low S_1 energy, ^{1}cis* lies in an energy minimum. Then, its twisting becomes more or less activated and fluorescence of ns duration becomes detectable even at room T. Moreover, the funnel at the perp configuration may disappear leaving a maximum in the potential energy curve. In such cases, adiabatic isomerization may be favoured in the decay pathway of S_1, possibly competing with the better known diabatic isomerization. The efficiency of the adiabatic process depends on the nature of the aryl groups and the solvent; both can affect the torsional energy barrier and the shape of the curve at 90°.

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