

ADIABATIC PHOTOCHEMICAL ISOMERIZATION OF *cis*-1-(9-ANTHRYL)-2-PHENYLETHYLENES

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Summary

The photochemical *cis*-*trans* isomerization of 1-(9-anthryl)-2-phenylethylenes (9-styrylanthracenes) has been studied by performing steady state and time-resolved fluorescence measurements. It has been found that singlet excited *trans* isomers are formed from their photoexcited *cis* precursors and this is explained in terms of an adiabatic photoreaction. Polar solvents and/or polar substituents on the styrylanthracene markedly enhance the adiabatic isomerization.

1. Introduction

cis-1,2-Diarylethylenes are normally distinguishable from their *trans* isomers by their markedly lower fluorescence quantum yields [1], and the differences between their geometries in the ground and excited state are typically apparent from the shape of their absorption and emission spectra as well as from the magnitude of the Stokes shifts [2 - 6]. Moreover, the differences between their absorption spectra facilitate the photochemical interconversion of *cis*-*trans* isomeric diarylethylenes on choosing the appropriate excitation wavelengths. Concerning the reaction mechanism, the potential energy surfaces for the excited states are normally characterized by a minimum and a photochemical funnel where the ethylene double bond involved in the geometric isomerization is twisted by 90° [7].

In a study dealing with the relationship between the molecular geometry and the excited state reactivity of various 9-anthryl-substituted alkenes, *cis*-1-(9-anthryl)-2-phenylethylene (1a; 9-styrylanthracene) in cyclohexane solution was found to be fluorescent ($\Phi_f = 0.16$), and its photochemical conversion into *trans*-1-(9-anthryl)-2-phenylethylene (2a; $\Phi_f = 0.46$) proceeded in methylene chloride solution with a quantum yield of 0.31 [8]. Remarkably, however, photoexcitation of 2a did not yield any detectable *cis* isomer 1a, although the disappearance of 2a in a low quantum yield process ($\Phi = 0.0014$) leading to some undefined, apparently polymeric product was noticed [9]. We have now found that the excited state properties of

9-anthrylethylenes **2** in terms of quantum yields of isomerization are affected by substituents on the phenyl moiety. Thus, both the 4-(4-phenylsulphonyl) derivative **2b** and the 4-formyl derivative **2c** isomerize photochemically to the corresponding *cis* compounds **1b** and **1c**. The increase in the quantum yield of isomerization of **2b** and **2c** with increasing solvent polarity is paralleled by a decrease in fluorescence quantum yield (*cf.* Tables 1 and 2), suggesting that the excited singlet state involved in the isomerization of **2b** and **2c** is polar in character. The flash photolytic investigation of the *trans* compounds **2a** - **2c** has revealed that the triplet state was populated in all three cases [10]. The low isomerization quantum yield of **2a** is thus not caused by inefficient intersystem crossing. In fact, the steady state *trans*:*cis* ratio on photosensitization with biacetyl is at least 50 for all the three compounds, *a* - *c*, which means that a triplet state isomerization mechanism is insignificant also for **2b** and **2c**.

The photochemical properties of **1a**, but not those of its derivatives **1b** and **1c**, seem to resemble those of certain 2-anthrylethylenes which have been found to undergo adiabatic *cis*-*trans* isomerization [11] in their excited triplet state. In the present paper we report the results of an

TABLE 1

Fluorescence properties of 9-anthrylethylenes in cyclohexane and acetonitrile at 298 K

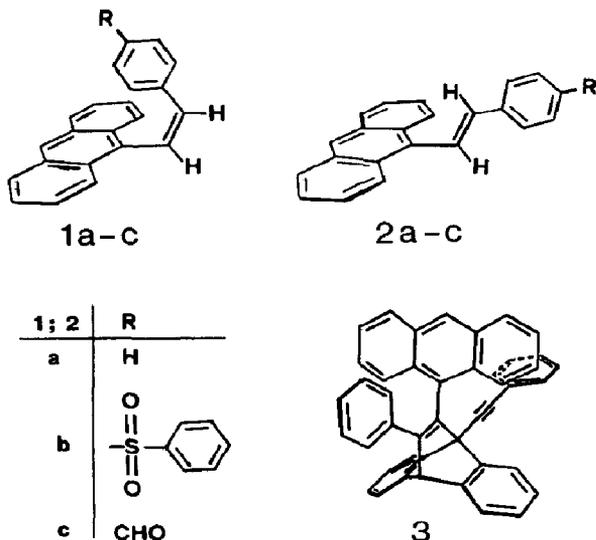
Compound	Stokes shifts (cm ⁻¹)		Fluorescence quantum yields	
	In cyclohexane	In acetonitrile	In cyclohexane	In acetonitrile
1a	4000	4600	0.16	0.040
2a	4600	4600	0.46	0.45
3	850	850	0.50	0.46
1b	5300	6400	0.31	0.002
2b	5300	6400	0.51	0.026
1c	5700	7400	0.33	0.005
2c	5700	7400	0.57	0.045

TABLE 2

Quantum yields of geometric isomerization of 9-anthrylethylenes **1** and **2** in dilute cyclohexane and acetonitrile solutions at 298 K

Solvent	<i>1a</i> → <i>2a</i>	<i>1b</i> → <i>2b</i>	<i>1c</i> → <i>2c</i>
	(<i>2a</i> → <i>1a</i>)	(<i>2b</i> → <i>1b</i>)	(<i>2c</i> → <i>1c</i>)
Cyclohexane	0.22 (<0.01)	0.73 (0.06)	0.70 (0.02)
Acetonitrile	0.41 (0.003)	0.36 (0.37)	0.35 (0.38)

investigation directed towards elucidating the mechanism of the photochemical "one-way" isomerization of 9-anthrylethylene 1a. The study involved both steady state and time-resolved fluorescence measurements with the cis and trans isomers 1a - 1c and 2a - 2c and the model compound 3.



2. Experimental details

Fluorescence spectra were obtained on an Aminco SPF 500 (corrected spectra) instrument, and quantum yields of fluorescence are based on the fluorescence quantum yield of 9,10-diphenylanthracene ($\Phi_f = 0.83$) [12]. Photochemical isomerization quantum yields were measured in an optical bench arrangement and are based on the potassium ferrioxalate actinometer [13]. Fluorescence lifetimes were obtained in air-saturated solutions (excitation wavelength, 356 nm) with a single-photon counting (SPC) instrument described previously [14], and deconvolution of the decay kinetics was carried out by the global reference method with subsequent calculation of the species-associated spectra [15].

The syntheses of 9-anthrylethylenes 1a and 2a have been described previously [8]. Derivatives 1b (melting point, 146 - 148 °C) and 1c (melting point, 103 - 105 °C) were prepared by photochemical isomerization in acetonitrile or methylene chloride of the trans isomers 2b and 2c respectively. Trans isomers 2b (melting point, 254 - 258 °C) and 2c (melting point, 158 - 159 °C) were obtained by Wittig reaction of (9-anthrylmethyl)-triphenylphosphonium bromide and the correspondingly substituted benzaldehydes. Synthetic and nuclear magnetic resonance spectroscopic details will be published elsewhere [16]. The synthesis of model compound 3 has been reported before [17].

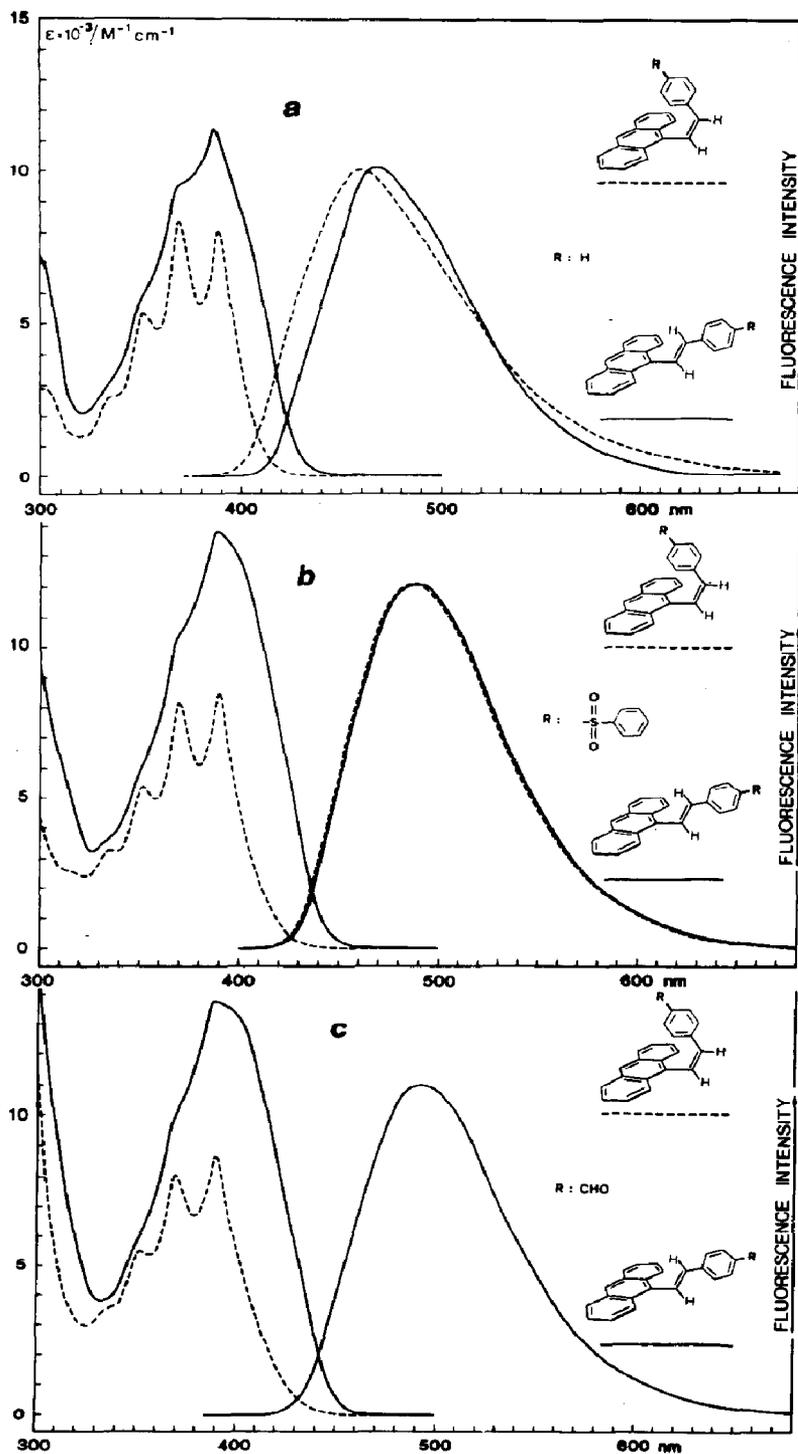


Fig. 1. (a) - (c) Electronic absorption and emission spectra in cyclohexane of 1a - 1c (broken curves) and 2a - 2c (solid curves).

3. Results and discussion

3.1. Electronic absorption and emission spectra

The *cis*-isomeric 9-anthrylethylenes 1a - 1c in cyclohexane solution are absorption-spectroscopically distinguishable from their *trans* isomers 2a - 2c because they exhibit vibrational structure which characterizes the electron spectrum of the anthracene chromophore (see Figs. 1(a) - 1(c)). The conjugation of the anthracene π system with the styryl moiety in the *trans* isomers 2 as a consequence of their less constrained molecular geometry is borne out in the partial loss of fine structure, as had previously been noted for various other 9-anthrylalkenes [8,18], and in an enhanced absorption around 290 nm attributable to the styryl chromophore.

Significantly, the fluorescence spectrum of *cis*-9-anthrylethylene 1a in cyclohexane solution is not strictly related to its absorption spectrum by mirror symmetry but is virtually structureless and is similar in appearance to that of the *trans* isomer 2a (*cf.* Fig. 1(a)). For 1a and 2a the Stokes shifts between the longest-wavelength absorption band and the emission maximum are 4000 cm^{-1} and 4600 cm^{-1} respectively, suggesting similar intramolecular mobility and, consequently, similarly large differences between ground and excited state geometries. Indeed, X-ray structure analyses of crystalline 1a and 2a reveal that the angles between the plane of the anthracene and the plane of the ethylene double bond are as large as 79° and 66° respectively [19]. The corresponding angle is 82° in the *cis*-9-anthrylethylene 3, in which the ethylene double bond is part of a rigid bicyclic system, and the Stokes shift associated with the structured fluorescence spectrum of 3 (*cf.* Fig. 2)

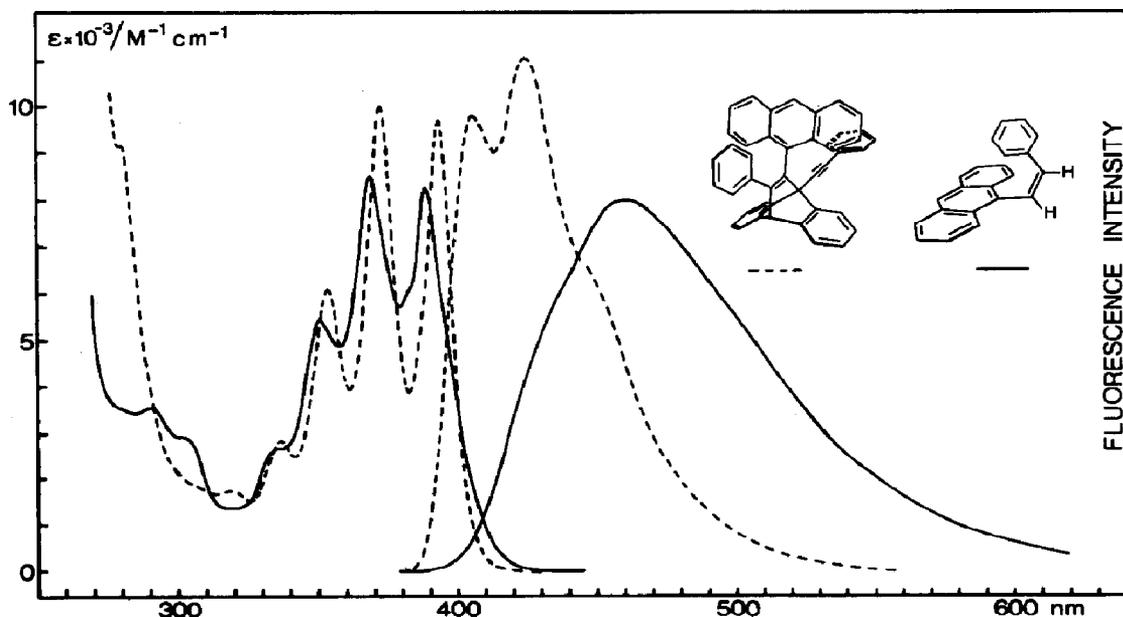


Fig. 2. Electronic absorption and emission spectra of compounds 1a (solid curves) and 3 (broken curves) in cyclohexane.

is as small as 850 cm^{-1} (*cf.* Table 1). The angle between the plane of the ethylene and the plane of the phenyl moiety in compounds 1a and 2a is 7° in each case, but in the bicyclic model compound 3 the corresponding angle is 39° [19].

The absorption spectra of *cis* isomers 1b and 1c in cyclohexane solution generally differ from those of their *trans* isomers 2b and 2c in the same fashion as described above for the parent compounds 1a and 2a. Remarkably, however, the emission spectra of both 1b and 1c are virtually identical with those of their corresponding *trans* isomers 2b and 2c (see Table 1 and Figs. 1(b) and 1(c)). This is also true for solutions of 1b and 1c in acetonitrile, although the quantum yields of emission are reduced in this solvent by about two orders of magnitude. We have ascertained by inspection of the excitation spectra that the "trans-like" emission is not due to the inadvertent presence of the *trans* isomers as impurities, but that it originates indeed solely by excitation of the *cis* isomers. (An intermolecular excitation energy transfer can be excluded as the concentration of *trans* isomer is probably less than 10^{-7} M in the solutions used for the excitation spectra determinations.) The decrease in the fluorescence quantum yields in acetonitrile is much more dramatic for 1b and 1c than it is for the corresponding *trans* isomers 2b and 2c (*cf.* Table 1). As for the parent *cis* isomer 1a its fluorescence quantum yield in acetonitrile is one quarter of the value measured in cyclohexane. In contrast, the fluorescence quantum yields of the *trans* isomer 2a and the 9-anthrylethylene 3 are virtually unaffected by solvent polarity. The quantum yields of fluorescence found for ethylenes 1 - 3 in *n*-hexane at 298 K are virtually identical with those found in cyclohexane (*cf.* Table 1). The fluorescence quantum yield of 1a in hexane shows a normal temperature dependence while those of 1b and 1c decrease with decreasing temperature. The ratios between the yields at 203 K and 298 K are 3.1, 0.36 and 0.43 for 1a, 1b and 1c respectively. Also remarkable is the finding that at lower temperatures the emission spectra from solutions of the isomers of b and c are not identical. This is shown in Fig. 3 for 1b and 2b.

3.2. *Cis-trans* isomerization: solvent and concentration effects

The quantum yields of the photochemical *cis-trans* isomerization for 1a - 1c in dilute cyclohexane solution are 0.22, 0.73 and 0.70 respectively. Thus, for each of the three 9-anthrylethylenes, the *trans* isomer is strongly favoured at the photostationary state (*cf.* Table 2). In acetonitrile solution, in contrast, this is true only for the parent *cis* isomer 1a. In the case of 1a the quantum yield of *cis-trans* isomerization actually increases to 0.41, while that of the reverse reaction in acetonitrile is as low as 0.003. However, for 1b and 1c the isomerization quantum yield in acetonitrile decreases to 0.36 and 0.35 respectively. Significantly, the quantum yields of the photochemical *trans-cis* isomerization for 2b and 2c in acetonitrile are of the same order of magnitude, *i.e.* 0.37 and 0.38 (*cf.* Table 2).

The exceptional photochemical behaviour of the parent 9-anthrylethylene 1a has prompted us to investigate its *cis-trans* isomerization in

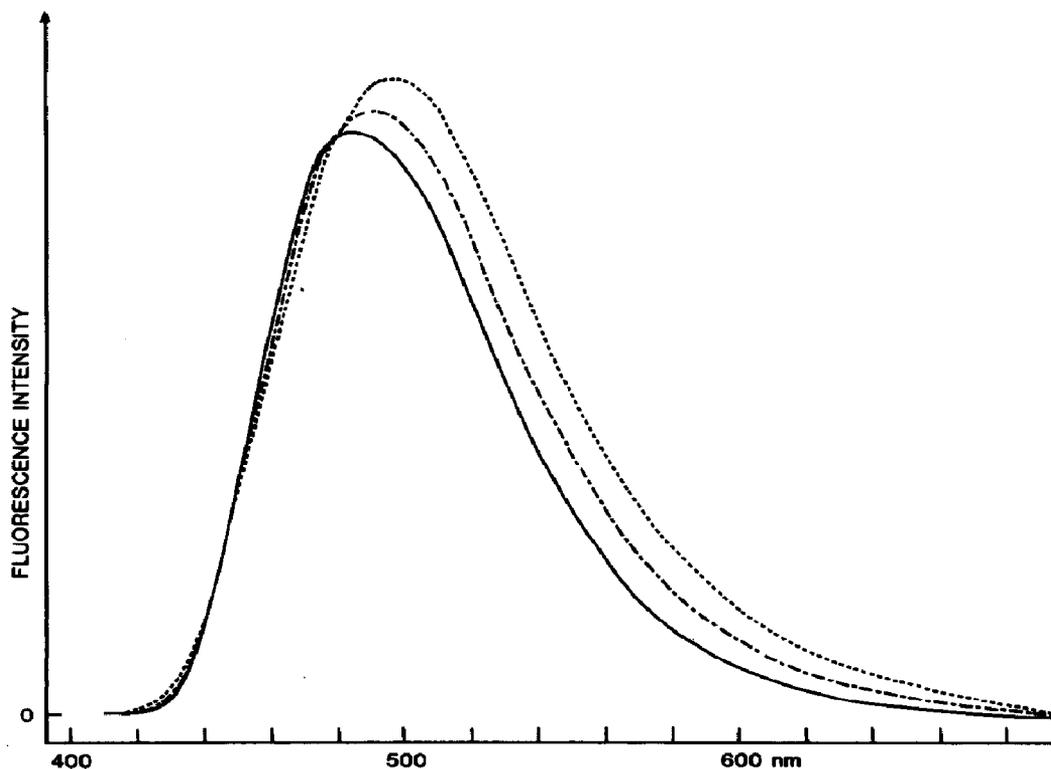


Fig. 3. Fluorescence spectra obtained from hexane solutions of 1b (---) and 2b (—) at 203 K. By adopting Scheme 1 and assuming that the *cis*:*trans* emission ratio of the 1b solution is 44:56 at 485 nm (*cf.* Table 5) a pure emission spectrum for 1b* may be calculated (- - -). The spectra are normalized at 485 nm.

detail. We have found that in both cyclohexane and acetonitrile solution in the absence of oxygen the quantum yield of geometric isomerization increases with increasing concentration of 1a (see Table 3). At a concentration of 0.005 M in cyclohexane, the isomerization of 1a proceeds with a quantum yield of 87%. Significantly, no concentration dependence of the isomerization quantum yields is observed in air-saturated solution. This finding suggests that 1a may undergo a quantum chain process on the excited triplet surface, analogous to that found previously by Karatsu *et al.* for the triplet-sensitized isomerization of certain 2-anthrylethylenes [11]. Indeed, we also find that 9-anthrylethylene 1a smoothly undergoes biacetyl-sensitized *cis*-*trans* isomerization for which the quantum yield in dilute solution, independent of solvent polarity, is unity (*cf.* Table 3). The biacetyl-sensitized isomerization of 1a in more concentrated solution (0.0014 M) was found to proceed with a quantum yield of 1.92, supporting a triplet state chain reaction.

Interestingly, at low concentrations of 1a, the ratio of quantum yields for the *cis*-*trans* isomerization in oxygen-free and air-saturated cyclohexane is 1.00, while the corresponding ratio of fluorescence quantum yields is 1.13.

TABLE 3

Quantum yields of cis-trans isomerization of 9-anthrylethylene 1a: dependence on concentration in cyclohexane and acetonitrile at 298 K

Excitation	Solvent	[1a] (M)	Quantum yield	
			Oxygen-free solution	Air-saturated solution
Direct	Cyclohexane	0.00017	0.22	0.21
	Cyclohexane	0.0049	0.87	0.22
	Acetonitrile	0.00016	0.41	0.41
	Acetonitrile	0.0044	0.50	0.42
Biacetyl sensitized	Cyclohexane	0.00006	1.01	
	Acetonitrile	0.00006	1.02	
	Cyclohexane	0.0014	1.92	

We conclude, therefore, that the lifetime of the excited state undergoing cis-trans isomerization upon direct excitation is shorter than that of the excited state deactivating by fluorescence.

3.3. Fluorescence decay measurements

The results of the SPC experiments in cyclohexane, hexane, acetone and acetonitrile solutions at various temperatures are summarized in Tables 4 - 6. For each of the three cis compounds at room temperature, independent of solvent polarity, the emission was found to follow biexponential decay kinetics. Of the two lifetimes of 1.79 and 2.97 ns found for 1a at room temperature in cyclohexane, the latter is strikingly close to the lifetime of 3.10 ns found for the fluorescence of the trans-isomer 2a under the same conditions. (In oxygen-free solutions of 2a in cyclohexane and in hexane the fluorescence lifetimes at 298 K are 3.64 ns and 3.68 ns respectively.)

TABLE 4

Time-resolved fluorescence measurements on 1a in cyclohexane at 298 K

λ_{em} (nm)	$2a^*$ fluorescence (%)		Remarks
	SPC	Emission spectroscopy	
410	2	2	$\tau(2a^*) = 3.10 \pm 0.04$ ns
450	9	8	
490	10	10 ^a	
600	7	6	

Excitation wavelength, 356 nm.

$\tau(1) = 1.79 \pm 0.02$ ns; $\tau(2) = 2.97 \pm 0.10$ ns.

^aAssumed $2a^*$ contribution to steady state emission spectrum of 1a.

TABLE 5

Temperature dependence of fluorescence properties of *cis*-styrylanthracenes 1a - 1c in *n*-hexane

	T (K)	$\tau(1)$ (ns)	$\tau(2)$ (ns)	" <i>Cis:trans</i> ratio" of emission (λ_{obs})	$\tau(2^*)$ (ns)
1a	323	1.00 ± 0.02	2.80 (fixed)	83:17 (460 nm)	2.80 ± 0.03
	298	1.55 ± 0.02	2.84 (fixed)	92:8	2.84 ± 0.04
	203	4.98 ± 0.05	—	100:0	3.05 ± 0.03
1b	298	0.18 ± 0.01	2.73 ± 0.03	2:98 (485 nm)	2.81 ± 0.04
	203	0.79 ± 0.04	2.84 (fixed)	44:56	2.84 ± 0.04
1c	298	0.18 ± 0.04	3.06 ± 0.04	3:97 (490 nm)	2.97 ± 0.04
	254	0.20 ± 0.06	2.93 ± 0.04	4:96	2.91 ± 0.04
	203	0.36 ± 0.11	2.89 ± 0.04	11:89	2.82 ± 0.04

TABLE 6

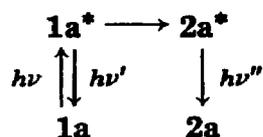
Temperature dependence of fluorescence properties of 1a in acetone and in acetonitrile

T (K)	$\tau(1)$ (ns)	$\tau(2)$ (ns)	" <i>Cis:trans</i> " ratio of emission	$\tau(2a^*)$ (ns)
<i>In acetone</i>				
298	0.29 ± 0.01	3.47 ± 0.06	36:64 ^a	3.43 ± 0.03
273	0.47 ± 0.01	3.47 ± 0.03	60:40	
248	0.71 ± 0.02	3.49 ± 0.11	78:22	
223	1.27 ± 0.02	3.49 (fixed)	92:8	3.49 ± 0.04
198	2.16 ± 0.02	3.49 (fixed)	96:4	
<i>In acetonitrile</i>				
298	0.159 ± 0.002	3.50 ± 0.03	33:67 ^b	3.60 ± 0.03
273	0.223 ± 0.004	3.77 ± 0.05	41:59	3.76 ± 0.06
254	0.303 ± 0.006	3.95 ± 0.10	52:48	3.84 ± 0.05

^a At 460 nm.

^b At 470 nm.

If we assume that the 2.97 ns emission is due to radiative deactivation of $2a^*$, which originates according to the scheme



Scheme 1.

from $1a^*$, which has a fluorescence lifetime of 1.79 ns, the contribution of the $2a^*$ fluorescence to the total emission observed by photoexcitation of 1a is accessible for various wavelengths from the corresponding amplitude

factors of the SPC measurements. Indeed, we find that the contributions of the 2.97 ns emission obtained from SPC experiments for arbitrarily chosen emission wavelengths are in good agreement with the calculated contributions of $2a^*$ fluorescence to the steady state emission spectrum of $1a$ (see Table 4). Significantly, no $2a$ was detected in absorption spectroscopic measurements made before and after the SPC experiments.

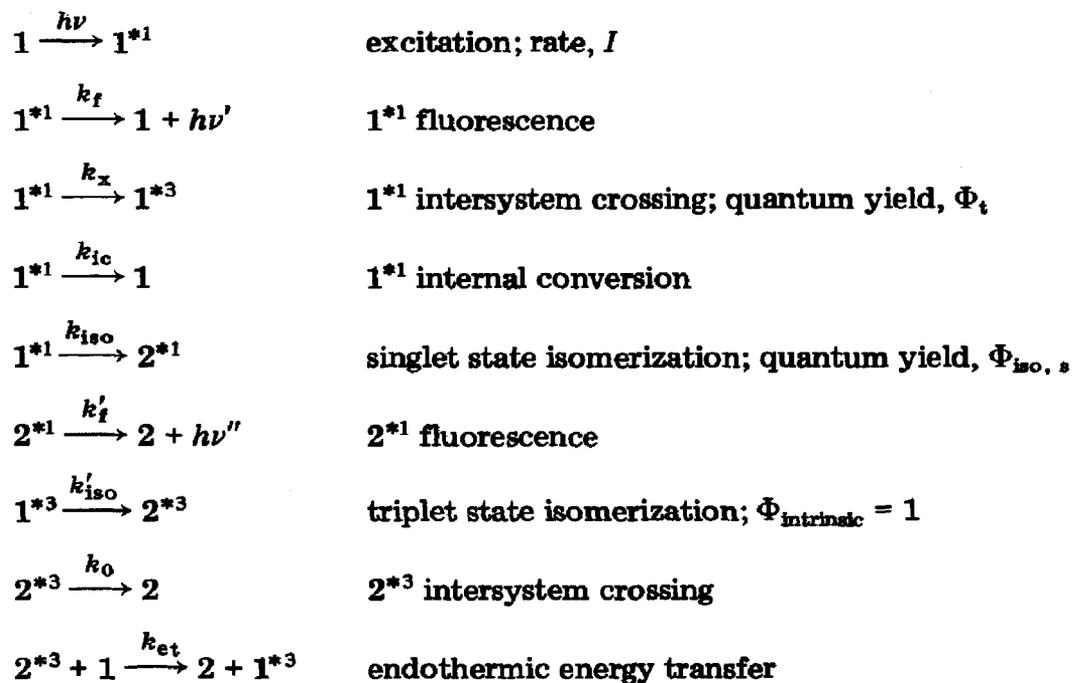
The temperature dependence of the fluorescence resulting from photoexcitation of $1a$ was evaluated in three solvents of different polarity (*cf.* Tables 5 and 6). In hexane solution, $\tau(1)$ attributed to the fluorescence of $1a^*$ increases from 1.00 ns at 323 K to 4.98 ns at 203 K. The contribution of fluorescence from $2a^*$ to the overall emission decreases from 17% at 323 K to 0% at 203 K. Thus, in hexane at 203 K, photoexcitation of $1a$ gives rise to emission from $1a^*$ only. The activation energy associated with the fluorescence of $2a^*$ resulting from photoexcitation of $1a$ may be calculated from the temperature dependence of the $2a^*$ and $1a^*$ emission ratio divided by $\tau(2)$ (assuming the ratio between the radiative rate constants to be temperature independent). Activation energies of 6.6 kcal mol⁻¹, 4.4 kcal mol⁻¹ and 2.7 kcal mol⁻¹ were obtained in hexane, acetone and acetonitrile respectively. The rate constants for the adiabatic isomerization[†] of $1a^*$ at 298 K in hexane, acetone and acetonitrile are 0.18×10^8 s⁻¹, 3.0×10^8 s⁻¹ and 3.7×10^8 s⁻¹. These values are not related to the viscosity, which is virtually the same (0.3 cP) for the three solvents. The obtained activation energies should, therefore, be true measures of the barriers on the excited singlet surfaces. Recent detailed studies show that these barriers may be solvent dependent [20]. In the case of the photoexcited *cis*-styrylanthracenes **1** we find that the polarity of the solvent governs the adiabatic formation of the *trans* isomers 2^* by affecting the height of the barrier which separates 1^* and 2^* . For example, the SPC experiment in acetonitrile at 298 K indicates that 67% of the emission at 470 nm observed by photoexcitation of $1a$ originates from $2a^*$. The effect of polar substituents on the properties of $1b^*$ and $1c^*$ is such as to enhance the emission from $2b^*$ and $2c^*$ respectively, even in non-polar solvents. Thus, the emission observed upon photoexcitation of $1b$ and $1c$ in hexane at room temperature is almost exclusively (98% and 97% respectively) that of the corresponding *trans* isomer. For the biexponential fluorescence decay of these solutions *negative amplitudes* of the first term are obtained in accordance with the proposed mechanism. The values of k_{iso} at 298 K are 4.5×10^9 s⁻¹ and 3.3×10^9 s⁻¹ for $1b^*$ and $1c^*$ respectively. The adiabatic isomerization is the dominating temperature-dependent process, and the activation energies are best estimated from the values of $\tau(1)$. Activation energies of 2.3 kcal mol⁻¹ and 1.0 kcal mol⁻¹ were found for $1b^*$ and $1c^*$.

[†] $k_{iso} = \alpha \Phi_{f, 1a} / \Phi_{f, 2a} (\tau(1))$, where α is the fraction of emission originating from $2a^*$. $\Phi_{f, 1a}$ and $\Phi_{f, 2a}$ are the total fluorescence yields on excitation of $1a$ and $2a$ respectively (*cf.* Table 1). The quantum yields of fluorescence of $1a$ and $2a$ in acetone are 0.060 and 0.44 respectively.

The quantum yields for the adiabatic cis-trans isomerization in the excited singlet state can be calculated for 1b and 1c from the SPC data and the steady state fluorescence yields. For 1b* and 2b* in cyclohexane solution, the fluorescence quantum yields are 0.31 and 0.51 respectively, and the overall quantum yield of cis-trans isomerization is 0.73. If we assume 98% of the emission observed on photoexcitation of the cis compound 1b to originate from its trans isomer 2b*, the quantum yield of adiabatic excited singlet state isomerization is $0.31 \times 0.98/0.51 = 0.59$. For 1c, the overall quantum yield for geometric isomerization is 0.70, and the quantum yield for adiabatic cis-trans isomerization in the excited singlet state is $0.33 \times 0.97/0.57 = 0.56$.

3.4. Mechanism of photochemical cis-trans isomerization of cis-styryl-anthracene 1a

The question as to whether the photochemical isomerization of 1a into the trans compound 2a proceeds adiabatically, as was indicated by the concentration-dependent quantum yields discussed above (see Section 3.2), can be elucidated on the basis of the following kinetically relevant processes.



At steady state

$$\frac{d[2^{*3}]}{dt} = I\Phi_t - k_0[2^{*3}] = 0 \quad (1)$$

For isomerization rate on the triplet surface

$$\frac{d[2]}{dt} = [2^{*3}](k_0 + k_{et}[1]) \quad (2)$$

It follows from eqns. (1) and (2) that

$$\Phi_{\text{iso, t}} = \Phi_{\text{t}} \left(1 + \frac{k_{\text{et}}}{k_0} [1] \right) \quad (3)$$

The total quantum yield is assumed to be

$$\Phi_{\text{iso}} = \Phi_{\text{iso, s}} + \Phi_{\text{iso, t}} \quad (4)$$

The parent *cis*-styrylanthracene 1a in dilute cyclohexane isomerizes upon direct excitation with a quantum yield of 0.22 (at 1.7×10^{-4} M; 0.20 at infinite dilution), and concerning its excited state properties we can conclude from SPC measurements that 9% of the total emission by photoexcitation of 1a in cyclohexane is due to the trans isomer 2a*. Consequently, the quantum yield for the adiabatic isomerization $1a^* \rightarrow 2a^*$ on the excited singlet surface, calculated from the SPC data and steady state fluorescence quantum yields of 1a* (0.16) and 2a* (0.46), is as low as 0.03. The triplet state contribution to the *cis*-*trans* isomerization quantum yield in dilute solution, therefore, should be $0.20 - 0.03 = 0.17$.

From the quantum yield (0.87) for the isomerization found by direct excitation of 1a at high concentration (4.9×10^{-3} M), we obtain

$$0.87 = 0.03 + 0.17 \left(1 + \frac{k_{\text{et}}}{k_0} \times 4.9 \times 10^{-3} \right)$$

and

$$\frac{k_{\text{et}}}{k_0} = 8.0 \times 10^2 \text{ M}^{-1}$$

Since the quantum yields obtained in the triplet-sensitized isomerization of 1a were 1.01 and 1.92 at concentrations of 6×10^{-5} M and 1.4×10^{-3} M respectively, it follows that

$$\Phi_{\text{iso}} = \Phi_{\text{iso, t}} = 0.97 \left(1 + \frac{k_{\text{et}}}{k_0} \times 1.4 \times 10^{-3} \right) = 1.92$$

and

$$\frac{k_{\text{et}}}{k_0} = 7.0 \times 10^2 \text{ M}^{-1}$$

As k_0 has been estimated from time-resolved triplet-triplet absorption measurements [6] at low concentrations to be $2.5 \times 10^4 \text{ s}^{-1}$, the rate constant k_{et} for triplet energy transfer is $1.9 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. For triplet energy transfer in cyclohexane solution, the following relation has been obtained [21]:

$$k_{\text{et}} = 8 \times 10^9 \exp\left(-\frac{\Delta E}{RT}\right)$$

where ΔE is the endothermicity of the energy transfer reaction. The difference between the triplet energies of 1a and 2a was thus estimated to be 3.6 kcal mol⁻¹.

3.5. Kinetic and thermodynamic parameters

Fluorescence rate constants are expected to be almost independent of the temperature. The values of this parameter obtained for the cis emissions at different temperatures might thus serve as a test of the assumed mechanism. As a further test the experimentally determined radiative rate constants can be compared with rate constants calculated from absorption and emission spectra [22]. The results presented in Table 7 strongly indicate that adiabatic isomerization operates on the singlet excited state surface and that $\tau(1)$ may be identified with the lifetime of 1*.

As mentioned earlier the trans-cis isomerization of 2a - 2c occurs to a negligible extent on the triplet state surface. When the quantum yields are low, for the adiabatic singlet excited state isomerization the following relation should be a good approximation:

$$\Phi_{2 \rightarrow 1} = k_{2^* \rightarrow 1^*} \tau_{2^*} (1 - \Phi_{1 \rightarrow 2})$$

where $\Phi_{1 \rightarrow 2}$ is the total cis-trans isomerization yield including the triplet state contribution. Results from hexane solutions at 298 K are given in Table 8. The quantum yields were actually determined in cyclohexane but

TABLE 7

Fluorescence rate constants determined from measurements in air-saturated hexane solutions compared with values calculated from absorption and emission spectra

	T (K)	$\Phi_{f,1}$	$\Phi_{f,1^*}$	$\tau(1)$ (ns)	$k_{f,1^*}$ $\times 10^{-7}$ (s ⁻¹)	$k_{f,calc}$ $\times 10^{-7}$ (s ⁻¹)
1a	298	0.11	0.10	1.55 ± 0.02	6.5 ± 0.1	6.0
	203	0.35	0.35	4.98 ± 0.05	7.0 ± 0.1	
1b	298	0.27	0.007	0.13 ± 0.01	5.4 ± 0.4	6.1
	203	0.10	0.045	0.79 ± 0.04	5.7 ± 0.4	
1c	298	0.30	0.010	0.18 ± 0.04	5.8 ± 1.3	6.3
	203	0.13	0.015	0.36 ± 0.11	4.6 ± 1.4	

TABLE 8

Isomerization data for hexane solutions at 298 K

	$\Phi_{1 \rightarrow 2}$	$k_{1^* \rightarrow 2^*}$ $\times 10^{-7}$ (s ⁻¹)	$E_{a,1^* \rightarrow 2^*}$ (kcal mol ⁻¹)	$\Phi_{2 \rightarrow 1}$	τ_{2^*} (ns)	$k_{2^* \rightarrow 1^*}$ $\times 10^{-7}$ (s ⁻¹)	$\Delta H_{2^* \rightarrow 1^*}$ (kcal mol ⁻¹)
a	0.20	1.8	6.6	0.003	3.68	0.10	1.7
b	0.73	450	2.3	0.061	3.21	7.0	2.5
c	0.70	330	1.0	0.021	3.32	2.1	3.0

the yields were found, within the limits of error, to be identical in the two solvents. The values in the last column of Table 8 are based on the assumption $\Delta S_{2^* \rightarrow 1^*} = 0$.

4. Conclusion

1-(9-Anthryl)-2-phenylethylenes **1** undergo photochemical cis-trans isomerization adiabatically both on the excited singlet and the triplet state surfaces, as shown schematically in Fig. 4 for **1a** and **2a**. The adiabatic conversion on the surface of the excited singlet state is favoured by polar solvents and by polar substituents attached to the phenyl moiety.

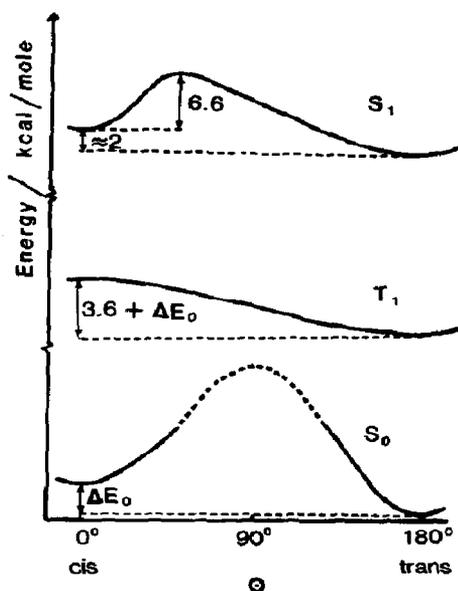


Fig. 4. Schematic representation of potential energy surfaces for ground state (S_0) and excited state (T_1 and S_1) cis-trans isomers **1a** and **2a** in non-polar solvents (θ is the angle of twist about the ethylene double bond).

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