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Excited state behaviour of some *trans*-stilbene analogues bearing thiophene rings

P. Gajdek [1], R.S. Becker [2], F. Elisei, U. Mazzucato *, A. Spalletti

Dipartimento di Chimica, Università di Perugia, 06123, Perugia, Italy

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Abstract

The effect of replacing the phenyl group(s) of *trans*-stilbene with thienyl groups, or polycyclic groups containing a thienyl moiety, on the relaxation properties of the lowest excited states was studied by fluorometric, photochemical and laser flash photolysis techniques, as well as by theoretical calculations, for four trans compounds in non-polar and polar solvents. In some cases, a larger contribution of intersystem crossing and, consequently, a triplet mechanism to trans → cis photoisomerization, with respect to the parent hydrocarbons, was found. Although the compound with a single thienyl group, 2-styrylthiophene, shows reactive relaxation in the singlet manifold as in the case of stilbene, the presence of two heteroaromatic rings in di(2-thienyl)ethene enhances the spin–orbit coupling, thus leading to a mixed singlet–triplet mechanism in non-polar solvents. The presence of polycondensed rings in dibenzothienylethene and thienyl-naphthothienylethene reduces the isomerization yield due to an increase in the torsional barrier for twisting in the singlet manifold. Therefore these compounds deactivate mainly through fluorescence emission and intersystem crossing, which leads to a predominant triplet mechanism for trans → cis photoisomerization. Polar solvents reduce the activation barrier to twisting, thus favouring isomerization in the singlet manifold.

Keywords: Photoisomerization; Thienylethenes; Triplet properties

1. Introduction

The effect of the nitrogen heteroatom on the excited state properties of stilbene-like molecules has been extensively studied in the last two decades [1–4]. For compounds bearing pyridine rings, the proximity effect of the (generally) lowest π,π^* state and a close-lying n,π^* state in the singlet manifold can lead to extensive $S_1 \rightarrow S_0$ internal conversion (IC), thus affecting the relaxation properties of aza-stilbenes. Much less is known about the excited state behaviour of stilbene-like molecules bearing heterocyclic rings containing the sulphur heteroatom. The spectral and photochemical properties of the simplest of these compounds, *trans*-2-styrylthiophene (**1**), have been reported by Millefiori et al. [5] and Costanzo et al. [6] respectively. In the latter study, a clean reversible trans–cis photoisomerization was shown to be operative with a relatively high quantum yield, which increased with increasing excitation energy and was practically independent of the solvent. A triplet mechanism was hypothesized for both the direct and sensitized photoreactions. In a more recent study on this compound, Gennari [7] obtained similar results and studied the λ_{exc} dependence of the quantum yields on the basis of the selective excitation of two rotational isomers (s-trans, s-cis) having slightly different radiative and reactive properties [8]. More recent spectroscopic studies on thienylpyridylethenes [9] and α,ω-dithienylpolyenes [10] have been performed.

This work was undertaken to study the relaxation properties of the lowest singlet and triplet excited states of some *trans*-stilbene analogues where one (or both) phenyl group(s) is (are) replaced by thienyl groups or their benzo and naphtho derivatives.

2. Experimental details

The four compounds investigated (see Scheme 1) were gifts from H. Winberg (Groningen, Netherlands) and were used without further purification. The solvents used were *n*-hexane (*n*-He), a mixture of methylcyclohexane (MCH) and 3-methylpentane (3MP) (9:1, v/v), butyronitrile (BuCN) and acetonitrile (AcCN) (all from Carlo Erba SpA, RP

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* Corresponding author.

[1] Present address: Faculty of Chemistry, Jagiellonian University, Kraków, Poland.

[2] On leave from the Department of Chemistry, University of Arkansas, Fayetteville, AR, USA and Instituto de Tecnologia Química e Biológica, 2780 Oeiras, Portugal.

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grade). The last two were purified by standard procedures before use.

The quantum yields of photoisomerization ($\phi_{t\rightarrow c}$) and fluorescence (ϕ_F) and the fluorescence lifetimes (τ_F) were measured by the methods described elsewhere [11]. For lifetimes in the nanosecond region, the single-photon counting technique was used. The shortest lifetimes were also measured by a Spex Fluorolog-τ2 system, which uses the phase modulation technique (λ_{exc} modulated in the 0.5–330 MHz range; time resolution, approximately 10 ps). The frequency domain intensity decays (phase angle and modulation vs. frequency) were analysed with Globals Unlimited™ (revision 3) global analysis software [12]. The experimental error in both the quantum yield and lifetime measurements (mean deviation of at least three independent experiments) was about 5%.

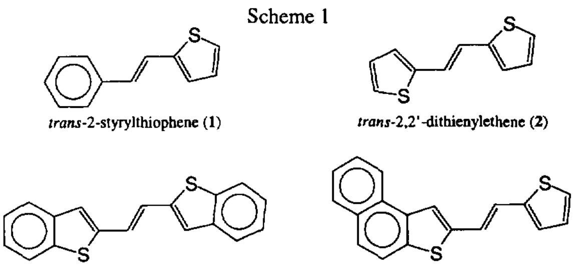
A λ_{exc} value of 347 nm from a ruby laser (J.K., second harmonic) was used in nanosecond flash photolysis experiments (pulse width, approximately 20 ns; energy, less than 5 mJ per pulse) [13]. The transient spectra were obtained by monitoring the optical density change at intervals of 10 nm over the 300–800 nm spectral range and averaging at least ten decays at each wavelength. All measurements were carried out at 22 ± 2 °C; the solutions were saturated by bubbling with argon. For measurements of the yield of singlet oxygen ($O_2(^1\Delta_g)$) production (ϕ_Δ) in aerated solvents, the phosphorescence of singlet oxygen was passed through a cut-off filter at 1050 nm (Oriel, 51362) and three pieces of gelatin cut-off filter at 870 nm (Kodak Wratten, 87C) and was detected by a germanium diode (Judson, J16 SP, 5 mm diameter). After amplification with a two-stage home-built amplifier (bandwidth, approximately 100 MHz; gain, 14 decibels), the output of the diode was fed into a digital signal analyser (Tektronik DSA602) and computer stored and analysed (Tektronik PEP301) [14]. At least ten sets of kinetics were averaged for each solution. The experimental error of the measured parameters was approximately 10% for the triplet lifetimes (τ_T) and about 15% for $\epsilon_T\phi_T$ and ϕ_Δ. A larger error is expected for the derived triplet yields (ϕ_T) due to the assumptions involved (see below).

3. Results and discussion

3.1. Molecular orbital calculations

The lowest energy levels, electronic structures and transition probabilities of compounds **1**–**4** in the stable trans configuration (Scheme 1) were investigated by semiempirical computational methods (MNDO [15] plus ZINDO/S [16]) using HYPERCHEM (version 4.5) software. The presence of different ground state conformations as a consequence of rotation about the aryl–ethene single bonds [7,8] was not taken into account.

Scheme 1


trans-2-styrylthiophene (1)
trans-2,2'-dithienylethene (2)
trans-2,2'-dibenzothienylethene (3)
trans-2-thienyl-2'-naphthothienylethene (4)

The configuration interaction (CI) calculations included 99 singly excited configurations built from the seven highest occupied (HOMO) and seven lowest unoccupied (LUMO) molecular orbitals. The ZINDO-derived HOMOs and LUMOs are shown in Fig. 1 for compound **2**, as an example. The lowest three singlet transitions of the four compounds investigated are reported in Table 1, together with those of the model compound *trans*-stilbene for comparison. As in the latter, the HOMO is largely localized in the central ethene bridge with a substantial involvement of the side aromatic groups. For the two asymmetrical molecules, **1** and **4**, the side electronic distribution involves predominantly the thienyl moiety for **1** and the naphthothienyl moiety for **4**. In the LUMO, there is displacement (usual in stilbene-like compounds) of the charge density from the central ethene bridge

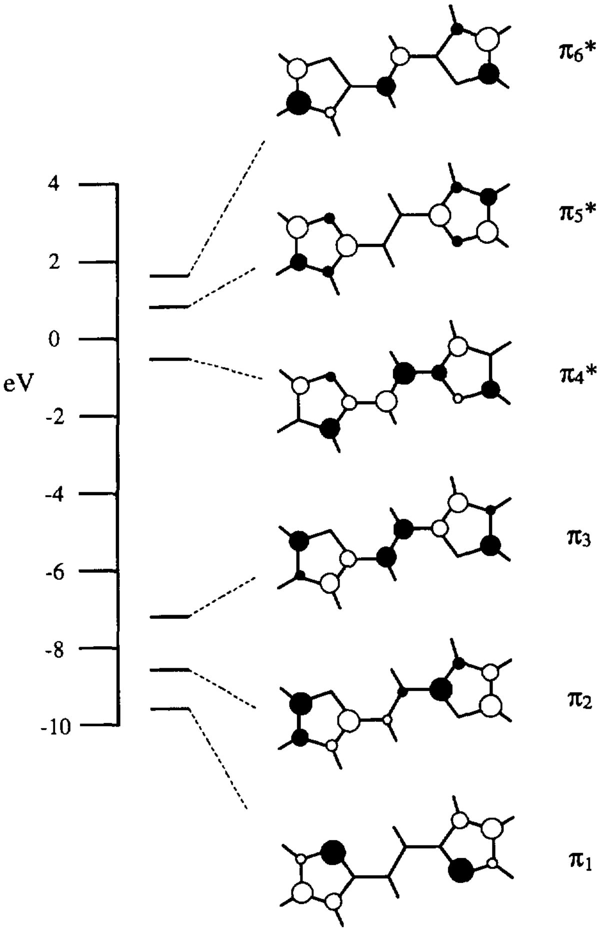


Fig. 1. Frontier molecular orbitals of **2** calculated by the ZINDO/S method.

Table 1
Transitions of π,π^* character for 1–4 calculated by the ZINDO/S-CI semiempirical method after geometrical optimization with MNDO compared with the experimental absorption maxima (λ_{max}) and extinction coefficients (ϵ_{max}) in *n*-He

Compound	Transition	λ (nm)	f	λ_{max} (nm)	ϵ_{max} (10^4 M^{-1} cm^{-1})	CI	
						%	Orbital
Stilbene	$S_0 \rightarrow S_1$	300	1.33	295	2.75	98	$\pi_H \rightarrow \pi_L^*$
	$S_0 \rightarrow S_2$	289	0.029			43	$\pi_H \rightarrow \pi_{L+1}^*$
						27	$\pi_{H-1} \rightarrow \pi_L^*$
	$S_0 \rightarrow S_3$	289	0.0000			44	$\pi_H \rightarrow \pi_{L+2}^*$
						27	$\pi_{H-2} \rightarrow \pi_L^*$
1	$S_0 \rightarrow S_1$	328	1.25	321	2.73	98	$\pi_H \rightarrow \pi_L^*$
	$S_0 \rightarrow S_2$	291	0.003			41	$\pi_H \rightarrow \pi_{L+1}^*$
						25	$\pi_{H-2} \rightarrow \pi_L^*$
	$S_0 \rightarrow S_3$	251	0.006			70	$\pi_H \rightarrow \pi_{L+2}^*$
2	$S_0 \rightarrow S_1$	349	1.26	338	2.70	98	$\pi_H \rightarrow \pi_L^*$
	$S_0 \rightarrow S_2$	267	0.0000			74	$\pi_H \rightarrow \pi_{L+1}^*$
	$S_0 \rightarrow S_3$	249	0.0000			67	$\pi_{H-1} \rightarrow \pi_L^*$
						20	$\pi_H \rightarrow \pi_{L+1}^*$
3	$S_0 \rightarrow S_1$	363	1.84	356	5.60	95	$\pi_H \rightarrow \pi_L^*$
	$S_0 \rightarrow S_2$	304	0.0000			30	$\pi_H \rightarrow \pi_{L+3}^*$
						25	$\pi_{H-3} \rightarrow \pi_L^*$
	$S_0 \rightarrow S_3$	304	0.027			32	$\pi_H \rightarrow \pi_{L+2}^*$
						25	$\pi_{H-2} \rightarrow \pi_L^*$
4	$S_0 \rightarrow S_1$	383	1.49	367	3.48	92	$\pi_H \rightarrow \pi_L^*$
	$S_0 \rightarrow S_2$	333	0.012			37	$\pi_H \rightarrow \pi_{L+1}^*$
						23	$\pi_{H-2} \rightarrow \pi_L^*$
	$S_0 \rightarrow S_3$	297	0.015			82	$\pi_H \rightarrow \pi_{L+1}^*$

towards the quasi-single bonds with the aryl groups responsible for isomerization.

The first transition is of relatively pure and allowed (oscillator strength f ranging from 1.25 for **1** to 1.84 for **3**) HOMO → LUMO ($\pi_H \rightarrow \pi_L^*$) character. An evaluation of the nodal patterns of the π orbitals indicates that the ethene character of the first transition decreases progressively on going from **1** to **4**.

As in the case of *trans*-stilbene, the second and third transitions are forbidden for the symmetrical molecules **2** and **3** and very weak for **1** and **4**.

3.2. Electronic spectra

Fig. 2 shows the absorption spectra of the four *trans*-thienylethenes (**1**–**4**) in *n*-He compared with the calculated oscillator strengths. Table 2 shows the main absorption and emission maxima, which appear to be insensitive to the medium in the three solvents examined.

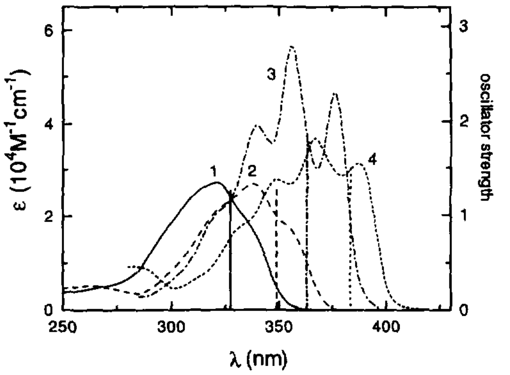


Fig. 2. Absorption spectra of **1** (———), **2** (– – –), **3** (– · –) and **4** (- - -) in *n*-He compared with the oscillator strengths (vertical lines) of the $S_0 \rightarrow S_1$ transitions calculated by the ZINDO/S-CI method.

The spectral behaviour of **1** is similar to that of stilbene, the first intense absorption band at approximately 325 nm corresponding to the $\pi_H \rightarrow \pi_L^*$ transition at about 300 nm, characteristic of stilbene-like molecules. The similarity with stilbene is expected from the similarity between benzene and thiophene, as discussed in theoretical papers [17]. However, the introduction of the heteroaromatic ring increases the conjugation with the styrene moiety compared with the phenyl group, as indicated by a substantial bathochromic shift (approximately 25 nm) with respect to the conjugation band of stilbene. This shift was satisfactorily reproduced by theoretical calculations in our and other [5] laboratories.

The presence of two thienyl rings in **2** leads to similar spectral characteristics, with the main band further red shifted by 15–20 nm. The shift is even more pronounced in the other two compounds, which show structured spectra, the main peaks being red shifted by approximately 35 and 45 nm for **3** and **4** respectively compared with that of **1**.

Fig. 3 shows the normalized fluorescence spectra of compounds **1**–**4** in *n*-He. The spectra are broad for compounds **1** and **2**, but become structured for **3** and **4** due to the decrease in ethene character and increase in the aromatic character during excitation. In polar solvents, the spectra remain broad and are only slightly red shifted for compounds **1** and **2**, but are practically independent of the solvent for the other compounds (Table 2). The spectral behaviour of compounds **3**

Table 2
Absorption (λ_{abs}, nm) and emission (λ_{fl}, nm) maxima of **1**–**4** in different solvents [a]

Compound	*n*-He		BuCN		AcCN	
	λ_{abs}	λ_{fl}	λ_{abs}	λ_{fl}	λ_{abs}	λ_{fl}
1	321	354	324	370	321	380
		368				
2	338	393	340	399	339	395
3	339	387	340	389	338	388
	356	408	358	411	356	409
	377	430	378	435	376	432
4	347	401	350	406	348	405
	367	423	369	427	367	430
	387	448	389	454	387	450

[a] The main maxima of the structured spectra are underlined.

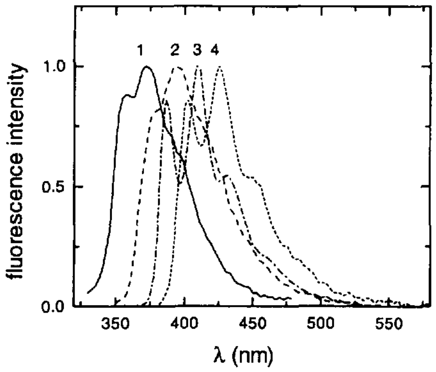


Fig. 3. Fluorescence spectra of **1** (———), **2** (– – –), **3** (– · · –) and **4** (- - -) in *n*-He.

and **4** is in agreement with the calculations of Section 3.1 indicating that, in these compounds, the $\pi\rightarrow\pi^*$ conjugation (stilbene) band has more localized character in condensed ring groups.

3.3. Fluorescence quantum yields and lifetimes

Table 3 shows the photophysical properties of the four compounds investigated in non-polar and polar solvents at room temperature, together with those obtained at 77 K in a non-polar matrix. Contrary to the spectral bands, the quantum yields and lifetimes of radiative relaxation are markedly dependent on the solvent, at least for the larger molecules. The fluorescence quantum yields of **1** and **2** at room temperature are lower than that of the parent hydrocarbon (for stilbene, $\phi_F \cong 0.04$ in *n*-He [18]), particularly in polar solvents. The lifetime of **1** is also shorter than that of stilbene ($\tau_F \cong 70$ ps [3]); the values in polar solvents are below the limits of our instrumentation (less than 10 ps), as expected by the practically barrierless twisting of the ^{1}trans* form towards the perpendicular (^{1}perp*) configuration (see below) and, at least for some compounds, due to the more important competition of $S_1 \rightarrow T_1$ intersystem crossing (ISC), favoured by spin–orbit coupling induced by the heteroatom. The fluorescence yields and lifetimes are markedly higher for **3** and **4**, mainly in non-polar solvents, probably as a result of the higher torsional barriers to twisting due to localization of the excitation energy in the heteroaromatic groups. However, the lifetimes remain much shorter than those of the corresponding hydrocarbons containing naphthyl and phenanthryl groups [19]. The radiative rate constants derived from the ratio ϕ_F/τ_F are similar for compounds **1**–**4** (slightly smaller for sym-

Table 3
Photophysical (fluorescence quantum yields and lifetimes) and photochemical (trans → cis isomerization quantum yields) properties of some 2-thienyl derivatives in different solvents

Compound	Solvent	ϕ_F	τ_F (ps)	k_F (10^8 s^{-1})	$\phi_F(77)$ [a]	$\tau_F(77)$ [a] (ps)	$k_F(77)$ [a] (10^8 s^{-1})
1	*n*-He	0.0087	13	6.7	0.30	430	7.0
	BuCN	0.0067	< 10	> 6.7			
	AcCN	0.0023	< 10	> 2.3			
2	*n*-He	0.050	160	3.1	0.24	600	4.0
	BuCN	0.0090	50	1.8			
	AcCN	0.0050	32	1.6			
3	*n*-He	0.34	440	7.7	0.37	590	6.3
	BuCN	0.16	320	5.0			
	AcCN	0.12	270	4.4			
4	*n*-He	0.35	800	4.4	0.48	1000	4.8
	BuCN	0.13	310	4.2			
	AcCN	0.078	260	3.0			

[a] Measured in an MCH–3MP mixture at 77 K.

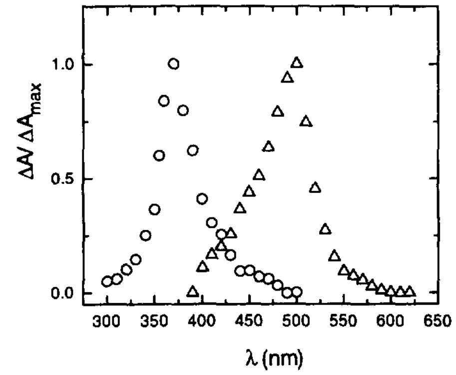


Fig. 4. Normalized triplet–triplet absorption spectra of **1** (circles) and **4** (triangles) sensitized by benzophenone in AcCN (λ_{exc} = 347 nm).

metrical compound **2**) and slightly dependent on the solvent. These values are very close to that obtained from the photophysical parameters reported above for stilbene ($k_F = 5.7 \times 10^8$ s^{-1}). Preliminary measurements of the effect of temperature on the fluorescence yield in non-polar solvents show that the barrier to ^{1}trans* → ^{1}perp* twisting (the activated relaxation process) is very small (less than 2 kcal mol^{-1}) for the asymmetrical (**1**) and symmetrical (**2**) thienyl derivatives, but substantial (greater than 6 kcal mol^{-1}) for the dibenzothienyl derivative (**3**). Measurements of ϕ_F in rigid matrices at liquid nitrogen temperature, where the photoreaction is inhibited, show that, contrary to stilbene ($\phi_F \cong 1$ at 77 K [18]), the yield remains substantially below unity (see Table 3), indicating a more important role of radiationless processes (probably ISC) in the deactivation of the lowest excited singlet state S_1 in comparison with the corresponding hydrocarbons bearing phenyl groups instead of thienyl groups. The fluorescence lifetimes in rigid matrices at 77 K are also shorter (1 ns or less) for **1**–**4** than for the corresponding hydrocarbons [18,19], again indicating a substantial contribution of radiationless (probably ISC) deactivation from the lowest excited singlet state of these molecules. The k_F values calculated at 77 K are in very good agreement with those obtained at room temperature.

3.4. Triplet properties

Laser flash photolysis experiments at an excitation wavelength of 347 nm in n-He and AcCN at room temperature show that the $T_1 \rightarrow T_n$ absorption represents the dominant transient of **3** and **4** in both solvents and of **2** in AcCN. For **2** in n-He and **1**, no transient is observed by direct excitation. The triplet transients appear within the laser pulse and decay by first-order kinetics at low pulse intensities.

Energy transfer experiments involving **1**–**4** were performed by using benzophenone (B) as a high-energy donor; the quenching of the donor triplet was accompanied by the appearance of sensitized triplet–triplet absorption. Fig. 4 shows, as an example, the B-sensitized triplet spectra of **1** and **4** in AcCN.

Table 4 shows the triplet properties for the four compounds in n-He and AcCN. The $T_1 \rightarrow T_n$ spectrum, practically independent of the solvent, has a maximum at 370 nm for **1**, which gradually shifts towards the red for the other compounds, reaching 500 nm for **4** (following the change in transition character from predominantly ethene-like to predominantly aromatic).

The triplet lifetimes (τ_T) on the sub-microsecond timescale (Table 4) were measured at approximately 1 mJ per pulse by direct excitation or by sensitization. The very short lifetimes of both S_1 and T_1 for these molecules prevent the measurement of the extinction coefficient of the triplet (ϵ_T) by energy transfer. A comparison between the ΔA values at λ_{max} of optically matched solutions of **1**–**4** in n-He and AcCN and B in AcCN (linear ΔA vs. laser dose plots were obtained) allows $\epsilon_T\phi_T$ to be obtained using $\epsilon_{520}\phi_T = 6500$ M^{-1} cm^{-1} for B [20] (Table 4). The ϵ_T values, needed to obtain the ϕ_T values, are unknown. However, considering that practically the same ϵ_T values are expected for the four compounds (which have similar ϵ_{max} values of the first absorption band in the singlet manifold), we expect that the trend of $\epsilon_T\phi_T$ will parallel the trend of the triplet yield.

The effect of temperature on the change in the maximum absorbance was evaluated in the 298–77 K range in an MCH–

Table 4
Triplet properties (λ_{max}, τ_T and $\epsilon_T\phi_T$) and quantum yield of singlet oxygen production (ϕ_Δ) for **1**–**4** in n-He and AcCN

Compound	Solvent	λ_{max} (nm)	τ_T (μs)	$\epsilon_T\phi_T$ (M^{-1} cm^{-1})	ϕ_Δ	ϕ_T	k_{ISC} (10^8 s^{-1})
1	n-He			≤100	≤0.01	≤0.01 (≤0.01) [a]	≤7.7 (16) [b]
	AcCN	370 [c]	0.20 [c]	≤80	≤0.01	≤0.005	5
2	n-He	410	0.36	4300	0.15	0.27 (0.14) [a]	17 (13) [b]
	AcCN	410 [c]	0.25 [c]	350	≤0.01	0.02	6.3
3	n-He	440	0.63	11000	0.56	0.70 (0.63) [a]	16 (11) [b]
	AcCN	440	0.63	3900	0.13	0.24	8.9
4	n-He	500	0.70	8100	0.45	0.52	6.5 (5.2) [b]
	AcCN	500	0.57	1500	0.08	0.10	3.8

[a] Values in parentheses obtained from Eq. (1).
[b] Values in parentheses obtained from Eq. (2).
[c] Obtained by sensitization (see text).

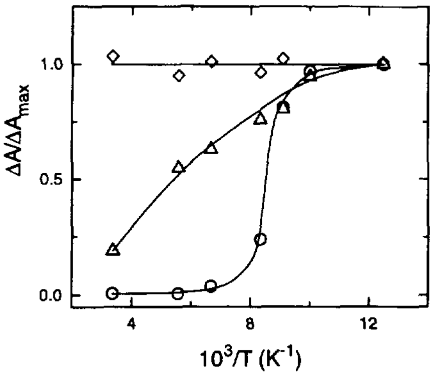


Fig. 5. Effect of temperature on the change in absorbance recorded at λ_{max} (ΔA) for **1** (circles), **2** (triangles) and **3** (diamonds) in an MCH–3MP mixture ($\lambda_{exc}=347$ nm).

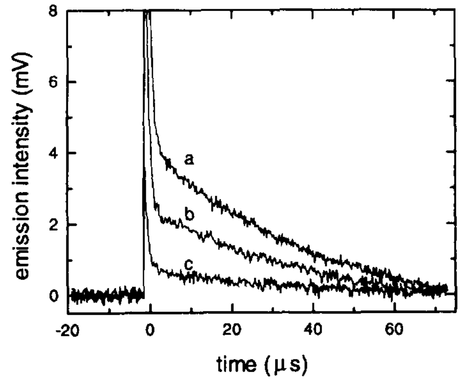


Fig. 6. Decay kinetics of the phosphorescence of $O_2(^1\Delta_g)$ sensitized by phenalenone (a), **4** (b) and **2** (c) in *n*-He ($\lambda_{exc}=347$ nm).

3MP mixture. Three different behaviours are observed (Fig. 5). The triplet population of **1** is practically negligible down to approximately 120 K and then increases significantly at lower temperatures. This usual behaviour reflects the competition between ^{1}trans* → ^{1}perp* rotation and ISC in the singlet manifold. This effect is not expected for compounds having relatively high ISC yields at room temperature. This was experimentally proven for **3**, which displayed a practically constant ΔA value over a large temperature range (298–77 K). An intermediate behaviour is observed for **2**, whose triplet population, already substantial at 298 K, starts to increase just below room temperature. This trend should reflect the competition between two decay processes of S_1 ($S_1 \rightarrow T_1$ ISC and ^{1}trans* → ^{1}perp* rotation) characterized by similar kinetic parameters.

The T_1 state is quenched by molecular oxygen with the formation of singlet oxygen ($O_2(^1\Delta_g)$). For an indirect estimation of the triplet production, the ϕ_Δ values were measured. Although this estimation is very approximate (particularly for **1** and **2** because of their short triplet lifetimes), since the fraction S_Δ of triplet molecules which produce singlet oxygen is unknown, the trend should give a further indication of the triplet yields of these molecules.

Fig. 6 shows the luminescence decay kinetics sensitized by phenalenone and two thienyl derivatives (**2** and **4**) in air-equilibrated *n*-He solutions. The luminescence was detected by a Ge photodiode and is assigned to $O_2(^1\Delta_g)$ phosphorescence, because it decays by first-order kinetics with lifetimes (30 μs in *n*-He and 63 μs in AcCN) very close to those reported for such emission [21] and it is not observed in the absence of the substrate or by bubbling with argon. The emission signal recorded just after the laser pulse (I_0), which is proportional to the concentration of $O_2(^1\Delta_g)$ generated by excitation, depends on the quantum yield of $O_2(^1\Delta_g)$ production (ϕ_Δ) and on the laser energy E_L. After calibrating the experimental set-up using phenalenone as standard in both *n*-He and AcCN ($\phi_\Delta=0.97\pm0.03$) [22], the slopes of the plots gave the ϕ_Δ values reported in Table 4. It is interesting to note that their trend is similar to that of $\epsilon_T\phi_T$, thus confirming that they reflect the trend of the triplet yields. The measured ϕ_Δ value is negligible for **1** in both *n*-He and AcCN and for **2** in AcCN, whereas it is substantial in the other cases and reaches a high value of 0.56 for **3** in *n*-He. In polar solvents, ϕ_Δ is smaller, since the lower torsional barrier in S_1 favours the singlet mechanism (see below) and reduces the ISC quantum yield.

It is interesting to note that, for compound **3**, the high ϕ_Δ value in *n*-He offers a way to estimate the ϕ_T value. If we take into account the fact that the fraction of triplets quenched by oxygen in air-equilibrated *n*-He ($[(\tau_T^{Ar}-\tau_T^{air})/\tau_T^{Ar}]$, where the superscripts Ar and air refer to solutions bubbled with argon and air equilibrated respectively) is found to be 0.8, the triplet yield ($\phi_T=0.70$) is very close to $1-\phi_F$ (0.66). In this way, $\epsilon_T=15\,700$ M^{-1} cm^{-1} is obtained, a value similar to that reported for a styrylbenzo[b]thiophene derivative ($\epsilon_T=20\,000$ M^{-1} cm^{-1}) [23]. By assuming the same ϵ_T value for the four compounds in both solvents, we obtain the ϕ_T data reported in Table 4. Generally, the trend of these ϕ_T values follows that of ϕ_Δ with a high S_Δ (above 0.5). Using a different method, the effect of temperature on ΔA, shown in Fig. 5, allows the ϕ_T values at room temperature to be estimated by assuming that, in a rigid matrix, the only decay processes of S_1 are fluorescence and $S_1 \rightarrow T_1$ ISC

$$\phi_T(298)=\frac{\Delta A(298)}{\Delta A(77)}\times\phi_T(77)$$

$$=\frac{\Delta A(298)}{\Delta A(77)}\times[1-\phi_F(77)] \qquad (1)$$

These values, reported in parentheses in Table 4, are in very good agreement with those of **1** and **3** derived by the first method. For compound **2**, the two methods give different results, the value in parentheses being more probable considering its agreement with ϕ_Δ.

The ISC rate constants are also reported in Table 4. They are generally higher than those of fluorescence, reflecting the spin–orbit coupling induced by the sulphur atom. These k_{ISC} values are in good agreement with those estimated from ϕ_T at 77 K by

$$k_{ISC}(77)=\frac{\phi_T(77)}{\tau_F(77)}=\frac{[1-\phi_F(77)]}{\tau_F(77)} \qquad (2)$$

These results on the triplet properties show that the effect of the sulphur heteroatom is strongly dependent on the structure of the diarylethene. In particular, the triplet yield of **1** is very low, whereas for **3** and **4** it is high in *n*-He and substantial in AcCN. For compound **2**, an intermediate behaviour is found with a non-negligible ϕ_T value in *n*-He but a very low value in AcCN. These remarkable differences in the photophysical behaviour of **1–4** are not due to their k_{ISC} values, which remain almost constant for the four compounds in non-polar and polar solvents.

3.5. Photoisomerization quantum yields

In Table 5, the quantum yields of geometrical photoisomerization ($\phi_{t\rightarrow c}$) for the four trans isomers investigated are reported. The yields are high (larger than 40%) for all compounds in AcCN and for **1** and **2** in *n*-He. The quantum yield decreases, particularly in non-polar solvents, for **3** and **4**, namely for compounds bearing polycyclic condensed groups.

The behaviour of these sulphur-containing compounds can be interpreted taking stilbene as a model system. For the latter, the well-known singlet mechanism for photoisomerization [18] indicates that more than 90% of the excited trans molecules in the singlet manifold (^{1}trans*) twist through a small energy barrier towards the perpendicular configuration (^{1}perp*), cross to the ground state ^{1}perp and finally relax in almost equal parts to the trans and cis isomers ($\alpha \cong 0.5$). In stilbene, almost 5% of the excited molecules decay by fluorescence and only about 1% produce ^{3}trans* through ISC. The triplet state can, in turn, isomerize by twisting to ^{3}perp*, followed by analogous processes as in the singlet manifold.

The behaviour of our thienylethenes can be discussed on the basis of the same pattern, keeping in mind that a higher ISC rate is expected due to the presence of the sulphur heteroatom. The same partitioning factor of stilbene ($\alpha \cong 0.5$) for the molecules reaching the perpendicular configuration in S_1 or T_1 (^{1,3}perp*) can be assumed to hold for these thienyl derivatives.

The simplest of the four compounds in Table 5, compound **1**, has been reported [6] to isomerize with a high yield of approximately 0.5 when sensitized by high-energy triplet donors. This observation and other results obtained in the presence of azulene as quencher have led to the assumption that the triplet state is mainly responsible for isomerization.

Table 5
Direct ($\phi_{t\rightarrow c}$) and sensitized (by biacetyl) photoisomerization quantum yields for 1–4

Compound	$\phi_{t\rightarrow c}$		$\phi_{t\rightarrow c}^{sens}$ (benzene)
	n-He	AcCN	
1	0.42	0.54	0.47
2	0.41	0.43	0.48
3	0.20	0.44	0.45
4	0.13	0.40	0.43

In the present work, the sensitized isomerization yields were measured in benzene using biacetyl as triplet donor and were found to be in the 0.43–0.48 range for the four compounds (Table 5). Although these values confirm that T_1 is the reactive state, the results in previous sections do not seem to confirm the interpretation of Ref. [6]. Indeed, the behaviour of **1** is reminiscent of that of stilbene [18] and many other diarylethenes [2,18,19,24] having a highly reactive triplet state which is negligibly populated by ISC because of fast twisting in the singlet manifold or fast radiative deactivation. In principle, the substitution of the phenyl ring of stilbene with a thienyl ring could modify the competition between the different relaxation channels through faster ISC induced by the heavy atom (Table 4). In fact, looking at the data of Table 3 and Table 5, the fluorescence and photoreaction quantum yields show values similar to those of stilbene, the main difference for **1** being an even lower percentage (less than 1%) decaying radiatively. For this compound, the results obtained indicate that the fast twisting in S_1 prevails over the radiative and ISC processes, despite the high values of the rate constant for the latter. The very small effect of temperature on the fluorescence yield, leading to an activation energy for twisting even smaller than in the case of stilbene, confirms that the singlet mechanism is an efficient pathway, in agreement with the smaller ϕ_F and τ_F values of **1** compared with stilbene. Therefore the contribution of a triplet mechanism for **1**, if any, should be practically negligible.

The fluorescence contribution to the decay increases to approximately 5% in the symmetrical compound **2** in *n*-He. However, for this compound, bearing two heteroatoms, the ϕ_Δ and ϕ_T values shown in Table 4 point to a mixed singlet–triplet mechanism for photoisomerization in non-polar solvents. On the other hand, the behaviour of **2** in AcCN is practically the same as that reported for **1**.

For the other two compounds, containing polycyclic groups, the behaviour is different. As already observed in the parent hydrocarbons [19], localization of the excitation energy in the polycondensed rings increases the torsional barrier for twisting towards the perpendicular configuration in S_1, thus favouring the fluorescence emission and the population of the triplet manifold through ISC. The data in Table 3 and Table 4 show that the fluorescence yield increases to about 35% and that the triplet yield is also substantial (particularly for **3**). The isomerization yield, which decreases to 20% and 13% for **3** and **4** respectively (Table 5), is reasonably explained by a triplet mechanism. The isomerization quantum yields of **3** and **4** are smaller than those expected from the corresponding ϕ_T values (Table 4), if all the triplet molecules twist towards ^{3}perp*. This behaviour can be related to the substantial torsional barrier even in the triplet manifold which slows down the reaction and favours a non-negligible $T_1 \rightarrow S_0$ deactivation.

The effect of polar solvents on compounds **2**, **3** and **4** is reminiscent of that found in many other cases for stilbene-like molecules [19]. Stabilizing the zwitterionic perpendicular configuration, polar solvents reduce the torsional barrier compared with non-polar solvents, thus favouring isomerization in the singlet manifold. This is confirmed by the results obtained for compounds characterized by high barriers and small reaction yields in *n*-He. For compounds **3** and **4**, the isomerization yield reaches high values of more than 40% in AcCN with a parallel decrease in singlet oxygen production in the same solvent.

4. Conclusions

The photophysics and photochemistry of the thienyl derivatives investigated are strongly dependent on the shape of the potential energy curve along the torsional coordinate in both the lowest singlet and triplet states. Comparing the kinetic parameters of the competing relaxation processes, the k_F values are only slightly dependent on the structure and are very close to the value for stilbene. In addition, the k_{ISC} values do not change markedly in the series **1–4** in both solvents ($(4–17)\times 10^8$ s^{-1}), but are markedly higher than the value for stilbene (1×10^8 s^{-1} or less). The photoreaction quantum yields show that the $k_{t\rightarrow c}$ values play an important role in determining the decay channels of S$_1$. In the case of **1**, a practically barrierless twisting is predominant (singlet photoisomerization mechanism), while a high torsional barrier in **3** leads to predominant ISC (triplet mechanism). In the other two cases, a mixed (singlet + triplet) mechanism is operative in non-polar solvents at room temperature. When the torsional barrier is high in *n*-He, the polar solvent reduces the activation energy and increases the fraction of molecules rotating in the singlet manifold.

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