Effect of thienyl groups on the photoisomerization and rotamerism of symmetric and asymmetric diaryl-ethenes and diaryl-butadienes †

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Five symmetric (bis-substituted) and asymmetric (mono-substituted) analogues of *E*-stilbene and *EE*-1,4-diphenylbutadiene, where one or both the side aryls are 2′-thienyl or 3′-thienyl groups, have been studied by stationary and pulsed fluorimetric techniques, laser flash photolysis, conventional photochemical methods and theoretical calculations. The results obtained for these compounds and the comparison with those previously reported for three other compounds of the same series, allowed the effects of the position of the heteroatom and of the extension of the olefin chain on the excited state relaxation properties to be understood. The presence of one or two thienyl groups and their positional isomerism affect the spectral behaviour, the relaxation properties (radiative/reactive competition), the photoisomerization mechanism (singlet/triplet) and the ground state rotamerism. For the dienes containing the 3′-thienyl substituent(s), two rotamers were evidenced whose radiative and photochemical properties were obtained by selective excitation.

1 Introduction

The excited state properties of some diarylpolyenes, where one or both the side aryls were *n*′-thienyl (*n*′ = 2′ or 3′) groups, have been studied in previous works in this[1–4] and other laboratories.[5–9] The photobehaviour of the asymmetric [1-(2′-thienyl),2-phenyl]ethene[1,5–7] and some symmetric longer chain compounds [α,ω-di-(2′- or 3′-thienyl)-polyenes, with diene, triene and tetraene chains],[3,9] has been particularly investigated. Generally, the sulfur heteroatom was found to induce a relevant population of the triplet state thus opening additional pathways to isomerization with respect to the corresponding hydrocarbons. Interesting effects of the position of the unsaturated chain with respect to the heteroatom have been described dealing with the relative position of the two lowest excited singlet states of A_g and B_u parentage, the competition among their parallel (radiative, reactive) relaxation processes, the equilibria between different conformers and the role of an upper excited singlet state in the relaxation processes.[1,3] The present work describes the effect of the positional isomerism (*n*′ = 2′ or 3′) on the photobehaviour and ground state rotamerism[10] of five symmetric (bis-thienyl-substituted) and asymmetric (mono-thienyl-substituted) derivatives of 1,2-diphenylethene, (Ph)₂E, and 1,4-diphenylbutadiene, (Ph)₂Bu, namely [1-(2′-thienyl),4-phenyl]butadiene and four analogous compounds bearing one or two 3′-thienyl groups. In order to discuss all together the complete series of these compounds, the properties of three members of the same series previously studied (the asymmetric 2′-styrylthiophene and the symmetric di-(2′-thienyl)-ethene and di-(2′-thienyl)-butadiene),[1,3] are also reported for comparison. The results of this experimental study, supported by theoretical calculations, point out how the presence and position of the sulfur heteroatom may affect the excited state properties and ground state rotamerism of this
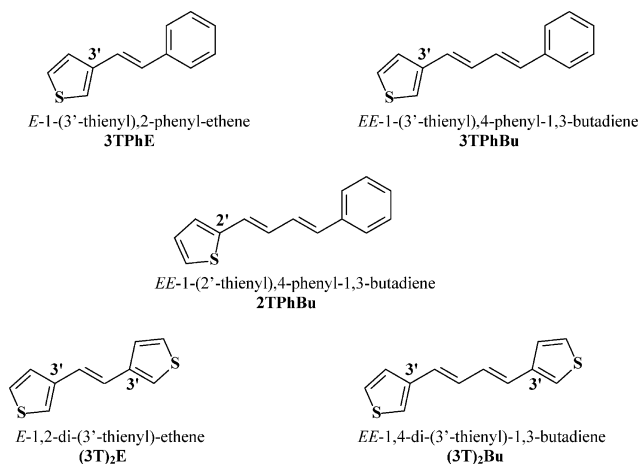
series of eight short-chain diarylpolyenes bearing 2′-thienyl (2T) or 3′-thienyl (3T) rings.

2 Experimental

2.1 Materials and experimental measurements

The compounds investigated (Scheme 1) were prepared at the Padua laboratory by standard procedures and characterized by NMR. A Wittig reaction between benzyltriphenylphosphonium bromide and the appropriate *n*-thienylaldehyde was applied, which gives a mixture of *E* and *Z* ethene derivatives, then separated by column chromatography. Likewise, for the butadiene derivatives, the synthesis from cynnamyl-triphenylphosphonium bromide in *E* configuration and the appropriate *n*-thienylaldehyde was used leading to a mixture of *EE* and *ZE* stereoisomers where the *E* configuration of the starting salt is retained. In some cases, a further purification of the stereoisomers by preparative HPLC was necessary.

The solvents used were 9/1 (v/v) methylcyclohexane/3-methylpentane (MCH/3MP), benzene and acetonitrile

E-1-(3′-thienyl),2-phenyl-ethene
3TPhE

EE-1-(3′-thienyl),4-phenyl-1,3-butadiene
3TPhBu

EE-1-(2′-thienyl),4-phenyl-1,3-butadiene
2TPhBu

E-1,2-di-(3′-thienyl)-ethene
(3T)₂E

EE-1,4-di-(3′-thienyl)-1,3-butadiene
(3T)₂Bu

Scheme 1

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† Electronic supplementary information (ESI) available: (1) Calculated electronic spectra (transition energy and oscillator strength) and ground state total energy of the rotamers of the *trans* isomers; (2) Absorption and emission spectra. See http://www.rsc.org/suppdata/pp/b4/b408241a/.

Table 1 Spectral properties[a] of all-*trans* isomers of symmetric and asymmetric thienyl-derivatives of (Ph)$_2$E and (Ph)$_2$Bu in MCH/3MP at room temperature

Compound	λ^{abs}/nm	ε^{abs}_{max}/M^{-1} cm^{-1}	λ^{fluo}/nm	Stokes shift/cm^{-1}
2TPhBu	330.5, *344*, 360	50300	383^{sh}, *405*, 417	
3TPhE	*293*, 303, 317	28800	323, *338.5*, 356	589
3TPhBu	313, *326*, 343	50700	351^{sh}, *368.5*, 386^{sh}	665
(3T)$_2$E	281, *292*, 304, 320^{sh}	32500	*347*	
(3T)$_2$Bu[b]	306, *319*, 335	51300	347^{sh}, *360*, 377.5	696
2TPhE[b]	*321*, 337^{sh}	27300	354	
(2T)$_2$E[c]	326.4^{sh}, *339*, 354^{sh}	27000	377^{sh}, *392.5*, 413.5^{sh}	1700
(2T)$_2$Bu[c]	326^{sh}, 341.5, *357.2*, 377	51000	400^{sh}, *428*, 458^{sh}	1500

[a] The main maximum is in italics. [b] From ref. 1. [c] From ref. 3.

(AcN); for NMR analyses, deuterated benzene and dimethyl-sulfoxide (DMSO) were used.

The absorption and emission spectra were recorded by a Perkin-Elmer Lambda 800 spectrophotometer and a Spex Fluorolog-2 F112AI spectrofluorimeter, respectively. Dilute solutions (absorbance < 0.1 at the excitation wavelength, λ_{exc}) were used for fluorimetric measurements. The emission and photoreaction quantum yields were generally determined at λ_{exc} corresponding to the maximum of the first absorption band (λ_{max}). 9,10-diphenylanthracene in cyclohexane was used as fluorimetric standard (ϕ_F = 0.90 in de-aerated solvent[11]) and potassium ferrioxalate in water as actinometer for photochemical measurements. For irradiation, a 150 W high pressure xenon lamp coupled with a monochromator was used. The photoreaction (solute concentrations $\approx 10^{-4}$ M) was monitored by HPLC using a Waters apparatus equipped with analytical Simmetry C18 (4.6 × 250 mm; 5 μm) or Prontosil 200–3–C30 (4.6 × 250 mm; 3 μm) columns and UV detector. Sensitized experiments were carried out using biacetyl in benzene as triplet donor.

Fluorescence lifetimes were measured by an Edinburgh Instrument 199S spectrofluorimeter, using the single photon counting method, and a Spex Fluorolog-τ2 apparatus, based on the phase modulation technique.

The triplet state was investigated by nanosecond laser flash photolysis. For direct excitation a Continuum Surelite II Nd:YAG laser (λ_{exc} = 355 nm) and a Lambda Physik LPX 105 excimer laser (λ_{exc} = 308 nm) were used. The sensitized experiments were carried out using benzophenone (λ_{exc} = 355 nm) and biacetyl (λ_{exc} = 420 nm); in the latter case, a parametric oscillator, OPO, pumped by the Nd:YAG laser, was used.

All measurements were carried out in de-aerated solutions by purging with nitrogen. The parameters reported in the tables are averages of at least three independent experiments with mean deviation of *ca.* 15% for fluorescence quantum yields and lifetimes and *ca.* 10% for the photoisomerization quantum yields. Further details on spectrophotometric, fluorimetric and laser flash photolysis measurements are reported elsewhere.[1]
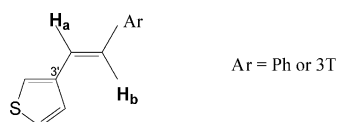
2.2 NMR analysis

The compounds were characterized by one- and two-dimensional ^{1}H-NMR spectra using a Bruker AC 400 spectrometer and TMS as reference. The following chemical shifts [δ (ppm)] and coupling constants (*J*/Hz) were obtained for the ethenic hydrogens.
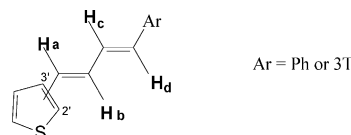
E isomers

3TPhE (deuterated DMSO) δ: 7.08 (1H, d, J_{ab} = 16.3 Hz, H$_a$), 7.26 (1H, d, J_{ba} = 16.4, H$_b$).

(3T)$_2$E (C$_6$D$_6$) δ: 6.77 (2H, s, H$_a$, H$_b$).

EE isomers

2TPhBu (MeOD) δ: 6.58 (1H, d, J_{dc} = 15.5, H$_d$), 6.67 (1H, dd, J_{cd} = 15.4, J_{cb} = 10.3, H$_c$), 6.79 (1H, d, J = 15.28, H$_a$), 6.89 (1H, dd, J_{ba} = 15.5, J_{bc} = 10.1, H$_b$).

3TPhBu (MeOD) δ: 6.58 (1H,d, J_{dc} = 15.4, H$_d$), 6.65 (1H, d, J_{ab} = 15.2, H$_a$), 6.78 (1H, dd, J_{cd} = 15.2, J_{cb} = 10.3, H$_c$), 6.89 (1H, dd, J_{ba} = 15.4, J_{bc} = 10.3, H$_b$).

(3T)$_2$Bu (C$_6$D$_6$) δ: 6.39 (2H, m, H$_b$), 6.61 (2H, m, H$_a$).

2.3 Theoretical calculations

These were performed using the HyperChem computational package (version 6.1). The calculated electronic spectra (transition energy and oscillator strength) were obtained by ZINDO/S using PM3 optimized geometries (see ESI†). Calculations of the configuration interaction included 81 (9 × 9) single excited configurations. *Ab initio* calculations on the possible rotamers of the isomers in *trans* configurations were also performed. After a complete optimization of geometry at 3-21G level, the total molecular energy was obtained using the same basis set. The correlation effects at MP2 level were taken into account.

3 Results and discussion

3.1 Absorption and emission spectra

The spectral properties of the five compounds investigated (*trans* geometries) are collected in Table 1. In order to have a general picture of the all series of symmetric (bis-substituted) and asymmetric (mono-substituted) thienyl derivatives of ethenes and dienes, the properties of three other compounds previously investigated[1,3] are also reported.

The absorption spectra of the five new compounds are presented in Fig. ESI-1.† The first absorption band of the ethenes lies in the range 260–340 nm. The corresponding dienes (280–380 nm) show the expected red-shift, a more pronounced vibronic structure (with a progression of ≈ 1300 cm^{-1}) and a marked increase of the absorption coefficient with respect to the corresponding ethenes. The 3T derivatives show an hypsochromic shift with respect to the 2T analogues. This blue-shift, already observed for longer chain dithienylpolyenes,[3] probably reflects electronic factors (as also indicated by quantum mechanical calculations, see below) even if the role of more distorted geometries in the 3T derivatives cannot be excluded.[3] The high intensity of the first band points to an allowed (of $^1A_g \longrightarrow {}^1B_u^*$ type) transition. The small Stokes-shifts indicate that the emitting state is the same as, or very close to, that populated by absorption. The fluorescence spectra (Fig. ESI-2) display the same trend observed for the absorption spectra.
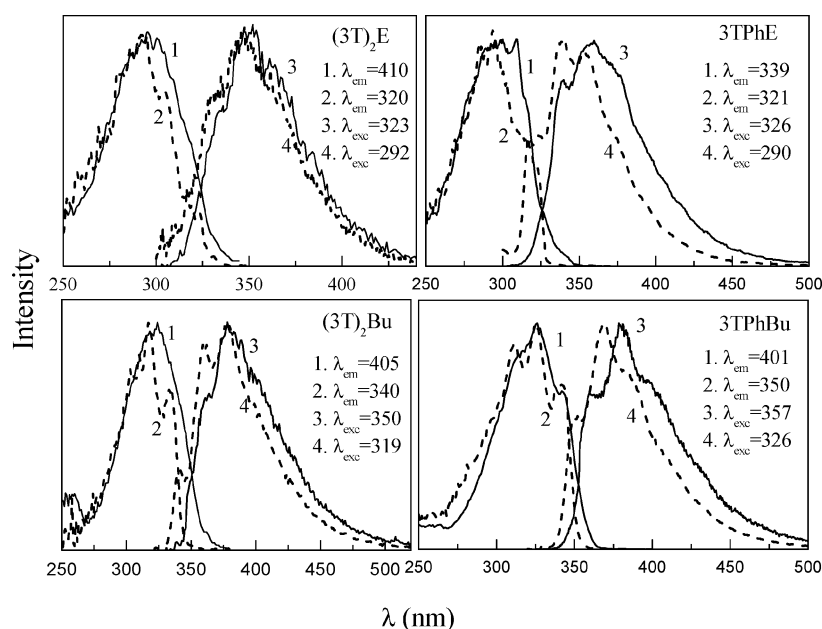
Fig. 1 The most different emission and excitation spectra of all-*trans* isomers of the 3′-thienyl derivatives investigated at selective wavelengths (λ_{exc} and λ_{em} in nm) in MCH/3MP at room temperature.

In the case of the 3T derivatives, the shape of the fluorescence emission and excitation spectra was found to depend on the excitation and emission wavelengths (λ_{exc} and λ_{em}, respectively) while the excitation spectrum did not coincide with the absorption spectrum. The changes in the spectral shape became more significant when the spectra were recorded at λ_{em} corresponding to the origin of the emission spectrum and at λ_{exc} on the red tail of the absorption spectrum. These spectral changes (Fig. 1), which indicate the existence of conformational isomers[10] in solutions of 3T compounds (see below), as reported for all-*trans*-di-(3′-thienyl)hexatriene,[3] tend to disappear when decreasing temperature. The temperature effect on the spectral properties of (3T)₂E clearly indicated the hypsochromic and short-living (A) rotamer as the most stable one. The shoulder around 320 nm in the absorption spectrum at room temperature gradually disappears with decreasing temperature. The structured emission spectrum at 77 K showed the same maxima found for the hypsochromic rotamer by photoexcitation at 200 K (Fig. 2). The same photobehaviour was found for the asymmetric 3TPhE.
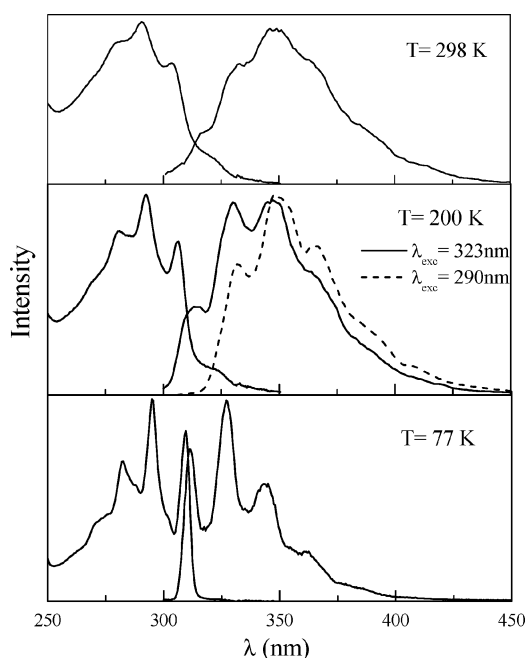
The spectra change drastically at low temperatures. Fig. 3 shows the strong effect observed in the absorption and emission spectra of the investigated compounds. The effect is reasonably explained by the contribution of sets of different geometries to the spectra in fluid solutions whereas planar forms predominate at the low temperature and high viscosity of the rigid matrix, as reported for flexible molecules of this type.[12] This explains also the red-shift of the absorption spectrum and the increase in the

Fig. 2 Normalized absorption and emission spectra of *E*-(3T)₂E in MCH/3MP at different temperatures.
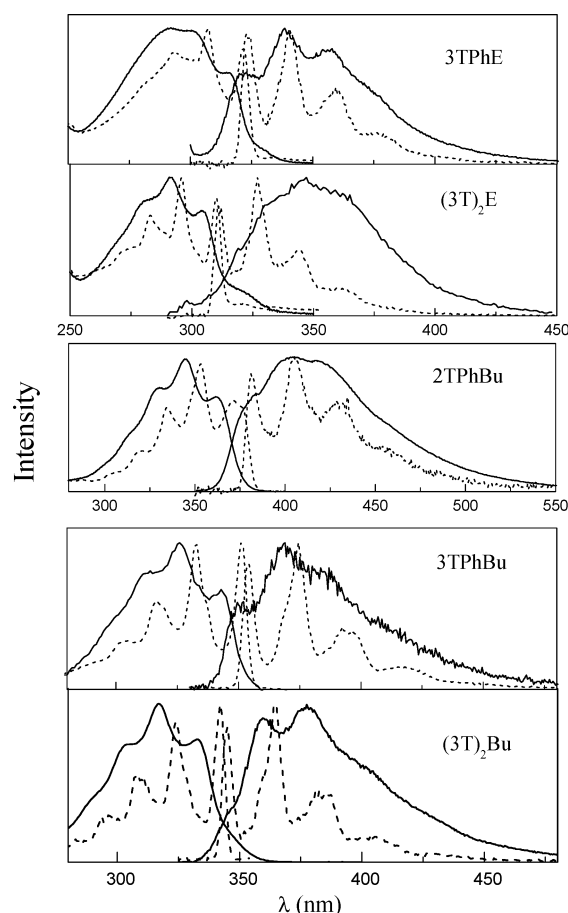

Fig. 3 Fluorescence emission and excitation spectra of all-*trans* isomers of five *n*′-thienyl derivatives in MCH/3MP at 293 (——) and 77 K (· · ·).

vibronic progression (from ≈1300 to ≈1700 cm^{-1} for 3TPhBu) on going from 293 to 77 K. It has to be noted that a temperature effect on the relative population of conformers (for 3'-thienyl derivatives) and on the B_u/A_g singlet excited state mixing (for butadienes) could also contribute to the observed spectral changes (see later).

3.2 Theoretical calculations

The results of MO calculations on different conformers of the *trans* isomers investigated were found useful to explain their conformational and spectral behaviour.

The calculated spectral properties of the conformational isomers are reported in Table ESI-1.† Only one important transition is present in the wavelength region above 220 nm: it has a HOMO–LUMO character (≈ 70%) and an oscillator strength characteristic of allowed transitions. The calculated spectra well reproduce the large difference between the absorption maxima of 2T and 3T derivatives. Indeed, the replacement of a phenyl group with a 2'-thienyl group produced a net red shift (20–30 nm) while the introduction of a 3'-thienyl group left the spectrum practically unchanged with respect to the corresponding hydrocarbon (a careful examination allowed very small blue shifts to be observed). The introduction of a second 2T group caused a further red shift of the spectra (20–30 nm), whereas the absorption maxima of the symmetric 3T derivative moved towards shorter wavelengths, the long-wavelength tails remaining practically unchanged. The difference in the spectral behaviour of 2T and 3T compounds is probably related to the different electron density at the two positions.[13] Indeed, our calculations showed that the sulfur atom in the 2T derivatives contributes to the HOMO less than in the 3T derivatives, whereas the electronic density map of LUMO looks very similar in 2T and 3T compounds. Therefore, a major stabilization of HOMO with respect to LUMO is induced in 3T compounds, as suggested by the energies of the two orbitals for the asymmetric ethene derivatives (see the example in Scheme 2). These energy values indicate that the HOMO is more stabilized in 3T with respect to 2T derivatives, whereas the contrary holds for the LUMO.
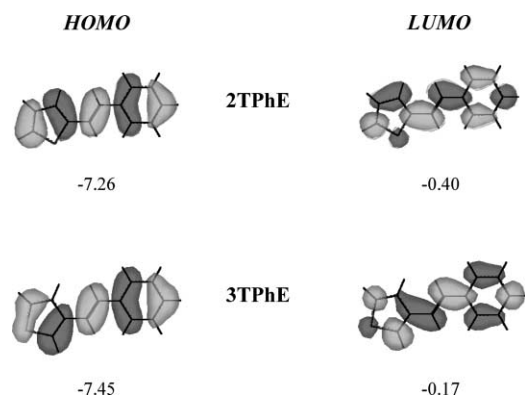
Scheme 2 Calculated frontier molecular orbitals and corresponding energies (eV) for 2'- and 3'-styrylthiophene.

The rotation of the *n*'-thienyl group around the quasi single bond with the ethenic bridge also produces rotamers with different spectral properties. Shifts ≥ 10 nm are expected from the calculations and experimentally observed (see below).

The calculations showed that the first transition, characterized by a high value of the oscillator strength, leads to an allowed excited singlet state for all the investigated compounds, in agreement with the high k_F values in Table 2 (see below). All these results support the experimental findings showing that the presence of the sulfur heteroatom produces positional and conformational isomers with markedly different spectral properties, much more evident than in the corresponding aza-derivatives.[10,14]

Table 2 Fluorimetric and kinetic parameters of all-*trans* isomers of five symmetric and asymmetric thienyl-derivatives in MCH/3MP at room temperature. The parameters of three other thienyl derivatives and of the corresponding hydrocarbons are also reported for comparison

Compound	ϕ_F	τ_F/ns	$k_F/10^8$ s^{-1}	$k_F^{\circ}/10^8$ s^{-1}
2TPhBu	0.18	0.77	2.3	9.6
3TPhE	0.016	0.070	2.3	8.9
3TPhBu	0.21	0.22/0.89	4.6^a	11.0
(3T)$_2$E	0.022	0.14	1.5	9.9
(3T)$_2$Bu	0.18	0.18/0.96	2.8^a	11.6
2TPhE^b	0.0087	0.013	6.7	
(2T)$_2$E^c	0.05	0.16	3.1	6.0
(2T)$_2$Bu^c	0.29	3.3	0.89	8.7
(Ph)$_2$E^d	0.04	0.09	4.4	
(Ph)$_2$Bu^e	0.42	0.60	7.0	

^{a} Values derived by using a mean τ_F (0.46 and 0.65 ns for 3TPhBu and (3T)$_2$Bu, respectively) as obtained by a mono-exponential treatement of the fluorescence decay. ^{b} From ref. 1. ^{c} From ref. 3. ^{d} From ref. 16. ^{e} From ref. 17.

The calculated enthalpy difference among different rotamers was 0.8–0.9 kcal mol^{-1} in the case of the two most stable conformers of 3T compounds and higher (1.6–2.0 kcal mol^{-1}) for 2T compounds, in agreement with the experimental evidence of dynamic conformational equilibria in fluid solutions at room temperature for the 3T compounds only. Then, the rotation of the 3'-thienyl group around the quasi-single bond with the ethenic bridge produces at least two conformers with similar abundances whereas the equilibrium is shifted towards the most stable species in the case of the 2'-thienyl compounds. Also in the dienic derivatives, similar heats of formation were found for the 3T conformers only. For these compounds, the calculations for the conformers originated by rotation around the quasi-single bond between the two double bonds predicted that the boat conformations are much less stable than the chair ones ($\Delta H > 3$ kcal mol^{-1} with respect to the most stable conformer). These results are in line with what reported for the corresponding hydrocarbon, 1,4-(Ph)$_2$Bu, which behaves as one-component system except when excited in the extreme red onset region of its absorption spectrum.[15] A high enthalpy difference between the boat and chair rotamers (≈2 kcal mol^{-1}) was calculated also in this case, in agreement with the experimental findings.[15]

3.3 Radiative decay

The relaxation properties of the lowest excited singlet state S_1 change on going from ethenes to dienes and from 2T to 3T compounds (Table 2). Comparison with the corresponding hydrocarbons (stilbene, (Ph)$_2$E, and diphenylbutadiene, (Ph)$_2$Bu) shows that the replacement of phenyl groups by thienyl groups produces a general reduction in the fluorescence quantum yields, which are in the range 1–5% for ethenes and 20% for dienes.

For 3T derivatives, the fluorescence quantum yield was found to depend on λ_{exc}. The photoexcitation at the red tail of the absorption spectra produced a more fluorescent species (*e.g.*, ϕ_F increases up to 0.04 for 3TPhE and 0.07 for (3T)$_2$E by exciting at 326 and 323 nm, respectively). The fluorescence lifetime, very short for ethenes (of the order of 100 ps and even lower, ≈13 ps, for 2TPhE) becomes longer for dienes (several hundreds of ps) and reaches 3.3 ns for (2T)$_2$Bu. Only for 3TPhBu and (3T)$_2$Bu, the fluorescence decay was well fitted by a bi-exponential function with similar amplitudes of the two A and B components (A and B refer to the short and longer living rotamers, respectively). For the two compounds above, a study of the conformational equilibria by selective photoexcitation was carried out (see below). The fluorescence rate parameters (k_F), derived from the ratio ϕ_F/τ_F, are in the range 1 to 6/10^8 s^{-1}. In

the case of the ethene derivatives, smaller k_F values were found for the 3T compounds with respect to the 2T analogues. This could indicate a less planar geometry, as reported for the corresponding hexatriene, also on the basis of PM3 semiempirical calculations.[3]

On the other hand, the decrease in k_F observed for the 2T derivatives on going from ethenes to dienes, contrary to what expected [see the increase on going from $(Ph)_2E$ to $(Ph)_2Bu$], could indicate that the emitting state assumes a partial covalent nature in the diene.

The k_F^o values, calculated by the Strickler–Berg relationship, were in the range 9 to $11/10^8$ s^{-1}. The lower values of the experimental parameters could be due to the forbidden character of the low lying state of A_g parentage, even if the latter steals intensity from the closely located B_u state of allowed nature.

As a matter of fact, measurements carried out in a rigid matrix of MCH/3MP at 77 K, when the twisting is inhibited, showed a large increase in ϕ_F (which reached almost unity for $(3T)_2Bu$) and k_F for all compounds (see Table 3, where the data for 3T derivatives refer to the most stable rotamer, see section 3.5). In the case of dienes, this behaviour could be explained by the fact that the increase in polarizability at low temperature stabilizes specifically the state of B_u parentage thus leading to an emitting state of ionic nature. Therefore, the radiative deactivation becomes the most important relaxation pathway at low temperature, particularly for the symmetrical dienes.[3]

3.4 Triplet properties

The triplet spectra were obtained by direct and biacetyl- or benzophenone-sensitized irradiation (Fig. 4). The triplet properties are reported in Table 4. The presence of thiophene groups generally induces an increase in the triplet quantum yield (ϕ_T) to the detriment of fluorescence, with respect to the corresponding hydrocarbon (ϕ_T is < 0.01 for stilbene[18] and 0.02 for $(Ph)_2Bu$[19]). In the case of the thio-analogues, the triplet yield is negligible (<0.01) for the two asymmetric ethenes only, while it becomes substantial for the dienes, particularly for the symmetric compounds containing two thienyl groups. An efficient quenching of triplet benzophenone was observed by adding $(3T)_2E$, but no transients assigned to the triplet state of the quencher were found, probably because of a triplet lifetime shorter than the resolution of our apparatus (< 30 ns). Only in

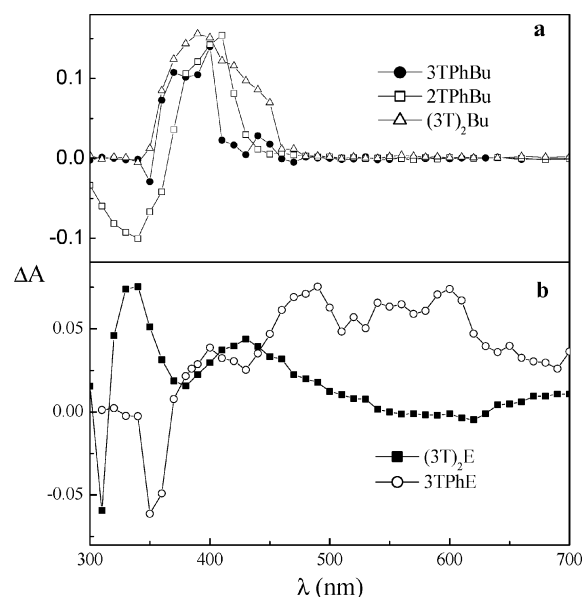**Fig. 4** $T_1 \longrightarrow T_n$ absorption spectra of (a) thienyl butadienes in benzene (direct excitation at room temperature) and (b) $(3T)_2E$ in MCH/3MP (direct excitation at 77 K) and 3TPhE in AcN (sensitized by benzophenone at room temperature).

rigid matrices at 77 K, where photoisomerization and collisions with the solvent are inhibited, it was possible to record the $T_1 \longrightarrow T_n$ spectrum of $(3T)_2E$ reported in Fig. 4b and to measure the triplet lifetime (500 μs). Considering that the triplet yields at room temperature seem not to depend on the positional isomerism (quite similar values for each 2T/3T pair), the yield of $(3T)_2E$ was assumed to be equal to that measured for $(2T)_2E$ (Table 4).

The triplet lifetimes are short for ethenes (< 1 μs), as found for several diaryl derivatives[20] isomerizing in the triplet manifold (when the planar configuration is equilibrated with the perpendicular one), as also indicated by high values (≈ 0.5) of the isomerization yields sensitized by biacetyl (see below).

For dienes, the triplet lifetimes are slightly longer (1 to 7 μs), and the sensitized yields are smaller, but still substantial, indicating a less reactive triplet state. Since the flash photolysis experiments on dienes were carried out at λ_{exc} = 355 nm, where only the bathochromic rotamer absorbs, the triplet parameters practically refer to the B rotamer. Interestingly, in the case of asymmetric dienes, isomerization in T_1 involves both double bonds leading to both *ZE* and *EZ* stereoisomers, with prevalence of *ZE* for 2TPhBu and *EZ* for 3TPhBu. Only for the latter, twisting around both double bonds was also observed under direct excitation (see later). The ISC parameter is higher in the symmetric compounds with two thienyl groups (enhanced induction of triplet population by internal heavy atom effect) and decreases on going from ethenes to dienes (the lengthening of the chain reduces the effect of the side aryl groups).

Table 3 Photophysical and kinetic parameters of all-*trans* isomers of five symmetric and asymmetric thienyl-derivatives in MCH/3MP at 77 K

Compound	ϕ_F	τ_F/ns	$k_F/10^8$ s^{-1}
2TPhBu	0.50	1.0	5.0
3TPhE (A)	0.36	0.59	6.1
3TPhBu (B)	0.70	0.80	8.7
$(3T)_2E$ (A)	0.25	0.35	7.1
$(3T)_2Bu$ (A)	0.98	0.52	19

Table 4 Spectral and photophysical properties of the triplet state of all-*trans* isomers of symmetric and asymmetric thienyl-derivatives in benzene at room temperature.[a]

Compound	λ_{max}/nm	τ_T/μs	ε_T^{max}/M^{-1} cm^{-1}	ϕ_T	$k_{ISC}/10^8$ s^{-1}
2TPhBu	410	3.6	25800	0.20	2.6
3TPhE	490, 600[b]	—	—	<0.01[c]	≤1.4
3TPhBu (B)	400	1.4	18000	0.30	3.4
$(3T)_2E$[d]	*335*, 430	500	—	0.27[e]	19
$(3T)_2Bu$ (B)	390	1.1	8400	0.40	4.2
2TPhE[f]	370	0.20	—	≤0.01	≤8
$(2T)_2E$[f]	410	0.36	16000	0.27	17
$(2T)_2Bu$[g]	410, *425*	7.5	30000	0.69	2.1

[a] λ_{exc} = 355 nm for butadienyl derivatives and λ_{exc} = 308 nm for ethenyl derivatives. [b] In AcN. [c] The same value was found in MCH/3MP. [d] In MCH/3MP at 77K. [e] Assumed to be equal to ϕ_T of $(2T)_2E$ in cyclohexane, from ref. 3 (see text). [f] In *n*-hexane, from ref. 1. [g] In cyclohexane, from ref. 3.

3.5 Conformational equilibria

As said in Section 3.1, the emission and excitation fluorescence spectra of both the symmetric and asymmetric 3T derivatives were found to change with λ_{exc} and λ_{em}, respectively. Too short lifetimes prevented us to separate the two components of ethene rotamers at room temperature. Approximate lifetimes of ≈14 and 250 ps were estimated for the symmetric ethene derivative. A clear biexponential decay was found in the region 240–170 K. An increase in the percentage of the short living and hypsochromic rotamer on decreasing temperature was observed for both ethene derivatives indicating that these species are the most stable ones, in agreement with the calculated results. Below 150 K, the decay becomes monoexponential.

The lifetimes of the longer-lived (B) rotamers remain practically constant in the temperature range explored ($\tau_{F,B}$ ≈ 0.5 ns for 3TPhE and (3T)$_2$E) pointing to a substantial energy barrier for rotation around the double bond in S$_1$ that prevents isomerization in the singlet manifold and opens a triplet pathway to photoreaction. On the contrary, the most stable and short living (A) rotamers have a temperature dependent lifetime. The Arrhenius treatment of these data showed the presence of a very small energy barrier (ΔE ≈ 2.5 kcal mol^{-1}) with a frequency factor A ≈ 5 × 10^{12} s^{-1} for photoisomerization in S$_1$. In Fig. 5, the trend of the lifetime of the short living rotamer as a function of temperature and the corresponding Arrhenius-type plot are reported for E-3TPhE, as an example.
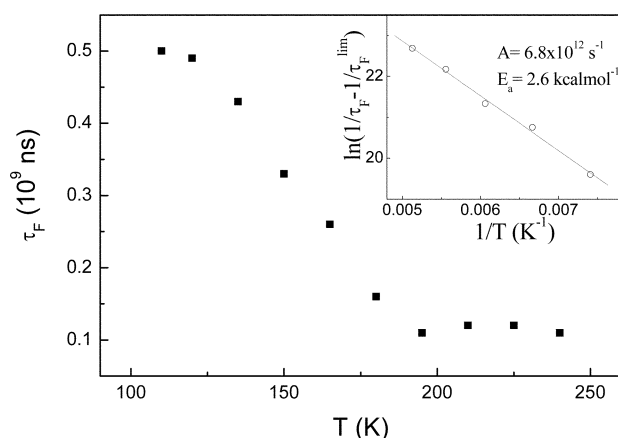

Fig. 5 Temperature effect on the lifetime of the short-lived component of E-3TPhE in MCH/3MP. Inset: Arrhenius-type plot.

The different energy barriers of twisting in S$_1$ are responsible for the big difference (more than one order of magnitude) between the lifetimes of the two rotamers at room temperature. In a rigid matrix at 77 K, where the twisting is inhibited, the lifetime of the most stable species increases and almost reaches the value of the other conformer.

The radiative parameters of dienes, measured as a function of λ_{exc} (Table 5), show that at λ_{exc} ≥ 350 nm, the measured spectrum and lifetime are assignable to the quasi-pure bathochromic component (B). At shorter wavelengths, the contribution of the hypsochromic short living A component (w_A) to the total decay decreased with decreasing temperature in the case of 3TPhBu [$\tau_{F,A}$ = 0.28 (80%), $\tau_{F,B}$ = 0.83 (20%) at 353 K, $\tau_{F,A}$ = 0.22 (57%), $\tau_{F,B}$ = 0.89 ns (43%) at 295 K] and became practically monoexponential with τ_F = 0.85 ns below 200 K in MCH/3MP at λ_{exc} = 326 nm. It should be noted that the calculations generally predicted a greater stability for the hypsochromic component between the two most stable conformations of the 3T derivatives; only for 3TPhBu the prediction was not confirmed by the experimental finding.

Instead, the hypsochromic species of (3T)$_2$Bu was proved to be the most stable one. The following decay parameters were

Table 5 Photophysical parameters of *EE* isomers of 3TPhBu and (3T)$_2$Bu in MCH/3MP at room temperature as a function of λ_{exc}

Compound	λ_{exc}/nm	ϕ_F	$\tau_{F,A}$/ns	$\tau_{F,B}$/ns	w_B (%)	f_B
3TPhBu	300	0.26	0.22	0.89	36	0.73
	326	0.21	0.22	0.89	43	0.72
	354	0.33		1.0	100	1.0
(3T)$_2$Bu	295	0.20	0.20	0.94	63	0.40
	319	0.18	0.18	0.96	71	0.41
	335	0.20	0.36	1.1	63	0.41
	350	0.31		1.1	100	1.0

Table 6 Photophysical and photochemical parameters of the two rotamers of *EE*-3TPhBu and *EE*-(3T)$_2$Bu in MCH/3MP at room temperature

Parameter	3TPhBu A	B	(3T)$_2$Bu A	B
ϕ_F	0.20	0.33	0.11	0.31
τ_F/ns	0.22	0.93	0.24	1.0
k_F/10^8 s^{-1}	9.1	3.7	4.6	3.1
$\phi_{EE \longrightarrow ZE}$	0.12	0.044	0.19	0.12
$\phi_{EE \longrightarrow EZ}$	0.15	0.065		

found: $\tau_{F,A}$ = 0.2 ns, $\tau_{F,B}$ = 0.96 ns, w_B = 59% at 293 K and $\tau_{F,A}$ = 0.35 ns, $\tau_{F,B}$ = 1.0 ns, w_B = 28% at 230 K. Below 150 K, a monoexponential decay was found when exciting at λ_{max} and monitoring the decay at λ_{em} = 364 nm (τ_F = 0.53 ns), but, at λ_{em} = 400 nm, the presence of a small contribution of the longer lived component was found [$\tau_{F,A}$ = 0.51 ns, $\tau_{F,B}$ = 1.4 ns, w_B = 26% at 150 K]. These findings are in agreement with the calculated results that predicted a small enthalpy difference between the two most stable rotamers (0.9 kcal mol^{-1}). This implies the presence of a small amount of the bathochromic, less stable, rotamer even at low temperature (5% at 150 K).

In a solid solution at 77 K, the spectra became wavelength independent, the excitation spectrum overlapped the absorption spectrum and the fluorescence decay became monoexponential. In these conditions, only one rotamer, the most stable species, was present in the matrix.

In Fig. 1, the quasi-pure emission spectra of the B component (measured at the red tail of the absorption spectra) and the excitation spectra of the A rotamer (monitored at the onset of the emission spectra) are reported. The fraction of excited molecules belonging to the B rotamer, $f_B(\lambda_{exc})$, was derived by eqn. (1),

$$f_B(\lambda_{exc}) = [\phi_F(\lambda_{exc}) \times w_B(\lambda_{exc})]/\phi_{F,B} \qquad (1)$$

where $\phi_{F,B}$ is the quantum yield of the B rotamer obtained by selective excitation (λ_{exc} ≥ 350 nm), $\phi_F(\lambda_{exc})$ is the measured quantum yield of the conformer mixture at any λ_{exc} and w_B is the fractional contribution of the B rotamer to the overall fluorescence at any λ_{exc}. The fluorescence quantum yield of the A rotamer was then calculated by eqn. (2) (at λ_{exc} where both rotamers absorb).

$$\phi_{F,A} = \phi_F(\lambda_{exc}) [1 - w_B(\lambda_{exc})]/[1 - f_B(\lambda_{exc})] \qquad (2)$$

Table 6 collects the radiative and photochemical parameters of the two distinct rotamers of the two 3T dienes. They show that for both of them the bathochromic and longer-lived B rotamer is the less reactive species with a slightly higher fluorescence yield and smaller k_F. In the case of the 3T-substituted ethenes, the intrinsic emission yields of the rotamers, obtained by rotation of the 3′-thienyl group around the quasi-single bond with the ethenic bridge, could not be derived owing to the fact that the decay was fitted by a monoexponential function (see above).

Table 7 Direct[a] (ϕ) and sensitized[b] (ϕ^{sens}) photoisomerization quantum yields of all-*trans* isomers of symmetric and asymmetric thienyl-derivatives at room temperature

Compound	$\phi_{E \longrightarrow Z}$	$\phi_{EE \longrightarrow ZE}$	$\phi_{EE \longrightarrow EZ}$	$\phi^{sens}_{E \longrightarrow Z}$	$\phi^{sens}_{EE \longrightarrow ZE}$	$\phi^{sens}_{EE \longrightarrow EZ}$
3TPhE	0.33[c]			0.50		
(3T)$_2$E	0.41[c]			0.40		
2TPhBu		0.16[c]			0.11	0.015
3TPhBu		0.066[c]	0.090[c]		0.095	0.15
		0.044[d]	0.065[d]			
(3T)$_2$Bu		0.16[c]			0.28	
		0.12[e]				
2TPhE[f]	0.42			0.47		
(2T)$_2$E[g]	0.41			0.48		
(2T)$_2$Bu[g]		0.068			0.10	

[a] In MCH/3MP. [b] By biacetyl in benzene at $\lambda_{exc} = 435$ nm, concentrations in the order of 10^{-3} M. [c] $\lambda_{exc} = 313$ nm. [d] $\lambda_{exc} = 357$ nm. [e] $\lambda_{exc} = 348$ nm. [f] From ref. 1. [g] From ref. 3.

3.6 Photoisomerization

Table 7 collects the quantum yields of *trans* → *cis* photoisomerization for the five compounds investigated together with the same parameters for the three compounds previously studied, for comparison.

No sign of adiabatic $E \longrightarrow Z$ photoisomerization (directly, from one to the other excited isomer on the same potential energy surface) was found in the direct photoreaction. Moreover, no clear evidence of the acceptor concentration (in the range investigated, up to 2×10^{-3} M) was observed in the sensitized experiments, as previously reported for analogous compounds.[21] Therefore, these thienyl derivatives were assumed to isomerize by the well known diabatic mechanism of stilbene (twisting to the perpendicular configuration at 90°, followed by internal conversion to the ground state in the same configuration and then almost 50 : 50 relaxation to the *trans* and *cis* isomers), as usually found for isomerization in the *trans* → *cis* direction.[18] The results obtained showed a decrease in the reactivity of dienes compared with ethenes, as reported for (Ph)$_2$Bu[22] and other diarylbutadienes.[4]

In principle, two photoproducts (*ZE* and *EZ*) can be formed by irradiation of the asymmetric *EE* compounds. Indeed, both were found in the case of 3TPhBu only (with a slight prevalence of *EZ*, the isomer with the *cis* bond adjacent to the phenyl ring), while a single photoproduct (*ZE*) was found in the case of 2TPhBu, as previously found for other asymmetric diarylbutadienes.[4] For dienes containing the 3T group, the isomerization yield (ϕ_{ISO}) was found to depend on the excitation wavelength, indicating a different reactivity for the two conformers. The measured quantum yield is then the weighted average of the intrinsic values of the two conformers except for values measured at $\lambda_{exc} \geq 350$ nm which could be related to B, that is the only species absorbing at these wavelengths. The corresponding yield of the A species can then be obtained at shorter wavelengths by eqn. (3).

$$\phi_{ISO,A} = [(\phi_{ISO}(\lambda_{exc}) - f_B(\lambda_{exc}) \times \phi_{ISO,B}]/f_A (\lambda_{exc}) \quad (3)$$

The values thus obtained (Table 6) show that A is more reactive whereas B has a higher radiative quantum yield pointing to a higher degree of planarity for the latter rotamer.

The triplet sensitized isomerization yields are also shown in Table 7. The ethenes have a quantum yield near to the maximum value of 0.5, reported for many diarylethenes isomerizing by a diabatic mechanism with a *ca.* 50 : 50 partitioning at the perpendicular configuration.[18] The dienes display lower yields, probably because of higher torsional barriers and/or lower frequency factors, as found for other diarylbutadienes[23] and dithienylpolyenes.[3] In this case, the two asymmetric dienes gave two photoproducts, *ZE*, *EZ*, with a clear prevalence of the former for the 2T derivative.

Using the sensitized yields, the relative weight of the singlet and triplet mechanisms could be derived as

$$^3\phi_{ISO} = \phi_T \times \phi^{sens}_{ISO} \quad (4a)$$

$$^1\phi_{ISO} = \phi_{ISO} - {}^3\phi_{ISO} \quad (4b)$$

Data derived by this procedure showed that for 3TPhE the photoreaction proceeds in the singlet manifold ($\phi_{ISO} \cong {}^1\phi_{E \longrightarrow Z}$), as reported for 2TPhE,[1] whereas, for (3T)$_2$E, singlet and triplet isomerization yields of 0.30 and 0.11, respectively, were obtained. For dienes, isomerization occurs in the triplet manifold for (3T)$_2$Bu, as reported for (2T)$_2$Bu,[3] whereas a mixed mechanism was found for the two other dienes, with a prevalence of the singlet contribution for 2TPhBu and of the triplet contribution for 3TPhBu.

It has to be noted that, since some parameters (triplet and sensitized yields) were measured in benzene, while the direct isomerization yields are in MCH/3MP, the data derived by eqn. (4) are not without question. We believe that the values obtained for ethenes are reliable, since ϕ_T values in saturated hydrocarbons are available (see Table 4) and an important solvent effect on the sensitized yield, due to changes in polarizability, is not expected. The situation is different for dienes, where the solvent can affect the mixing between the two lowest excited singlet states, thus changing the photoreactivity in the two manifolds of different multiplicity. However, we believe that the results obtained for the formation of the *ZE* stereoisomers give an estimate, even if rough, of the separate singlet/triplet contributions to the photoreaction. This interpretation receives support by the experimental findings. In fact, the predominant contribution of the singlet mechanism for 2TPhBu is in agreement with the fact that only the *ZE* isomer was formed under direct irradiation while the triplet sensitized photoreaction led to both *ZE* and *EZ* isomers, with a small yield of the latter. The 3T group has the main effect of favouring the triplet mechanism as expected by the rather high triplet yields. The prevalence of the triplet mechanism for 3T derivatives of dienes is in agreement with the finding that the fluorescence lifetime of the B rotamer is practically temperature independent in a wide range (230–350 K).

4 Conclusions

The results described in the present work allowed a clear picture of the excited state properties of symmetric and asymmetric thienyl derivatives of ethenes and butadienes to be obtained. The increase in k_{ISC} induced by one or, even better, by two thienyl groups leads to a change in the photoisomerization mechanism from singlet (3TPhE) to mixed [(3T)$_2$E and asymmetric dienes] and to triplet [(3T)$_2$Bu]. The direct and sensitized reactivity decreases in dienes and is lower for 3T derivatives.

The length of the unsaturated chain and its position with respect to the heteroatom have a substantial effect on the energy order of the two lowest excited singlet states of A_g and B_u parentage. The two states are so close in the dienes that the experimental conditions (solvent polarizability, temperature, etc.) or structural factors (2T and 3T positional isomers) can change their ordering. In solvents of high polarizability and/or at low temperature, state inversion may occur and S_1 acquires a nature of B_u parentage. In fact, k_F at 77 K almost reaches the k_F° values calculated by the integrated absorption spectra (10^8 to 10^9 s^{-1}).

This study also allowed the separate properties of two main conformers of the 3T dienes, due to restricted rotation around the C–C quasi-single bonds between the thienyl group and the diene chain, to be obtained.

Acknowledgements

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