Excited-State Behavior of Some *all-trans*-α,ω-Dithienylpolyenes

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Abstract: The photophysics and photochemistry of *all-trans*-α,ω-di(2-thienyl)polyenes (with chain length *n* = 2, 3, 4) and α,ω-di(3-thienyl)polyenes (with *n* = 3, 4) have been extensively studied by stationary and pulsed spectrometry. Fluorometric and laser flash techniques were used to measure the quantum yields and lifetimes of the lowest excited states of singlet and triplet multiplicity in nonpolar and polar solvents at different temperatures. The trans−cis photoisomerization was also investigated, at least for the shorter oligomers. The kinetic parameters of the radiative, nonradiative, and reactive relaxation pathways were evaluated and discussed by comparison with the parent compound having *n* = 1 (*trans*-1,2-dithienylethene) and the better known α,ω-diphenylpolyenes.

Introduction

The photophysics and photochemistry of polyenes and α,ω-diphenylpolyenes (DPhPs) have been extensively studied by both theoretical and experimental approaches.[1−6] Most interest lies in their role as models for conformational properties and photoisomerization reactions about a polyene double bond in the biological functions of proteins.[7] Particular attention has been given to the ordering of the first excited states of A_g and B_u character which is correlated with the length of the polyene chain. Much less is known for the corresponding thiophene derivatives (α,ω-dithienylpolyenes, DTPs). A series of 2-thienyl derivatives, with *n* = 2, 3, 4, has been synthesized and investigated spectroscopically by Birnbaum et al. in *n*-alkane solutions at liquid helium temperature.[8] In these experimental conditions, the $^1A_g*$ state is the lowest excited state for *n* ≥ 3, while for *n* = 2, the covalent $^1A_g*$ and ionic $^1B_u*$ states are almost degenerate. The fine structure of the spectra has been carefully described,[8] but only scattered data have been reported for the photophysical parameters (quantum yields, lifetimes) measured in different experimental conditions, and no information has been reported on their photoreactivity.

Chart 1

di(2-thienyl)ethene (D2TE)

di(2-thienyl)butadiene (D2TB)

di(2-thienyl)hexatriene (D2TH)

di(2-thienyl)octatetraene (D2TO)

di(3-thienyl)hexatriene (D3TH)

di(3-thienyl)octatetraene (D3TO)

The aim of this paper is a detailed investigation of the radiative, nonradiative, and reactive relaxation pathways and the photokinetic behavior of the first oligomers (up to *n* = 4) of DTPs bearing the 2-thienyl and 3-thienyl side groups (D2TPs and D3TPs, respectively) in solvents of different polarity and polarizability at different temperatures. In addition to the effect of the chain length, the effect of the position of the chain (2 or 3, with respect to the heteroatom) has been carefully examined. Two peculiar cases of rotamerism[9] and emission from upper excited states[10] are reported.

Experimental Section

The compounds investigated (see Chart 1) were gifts from H. Winberg (Groningen, Netherlands). Their purity was checked by HPLC. The solvents used were a mixture of methylcyclohexane/3-methylpen-

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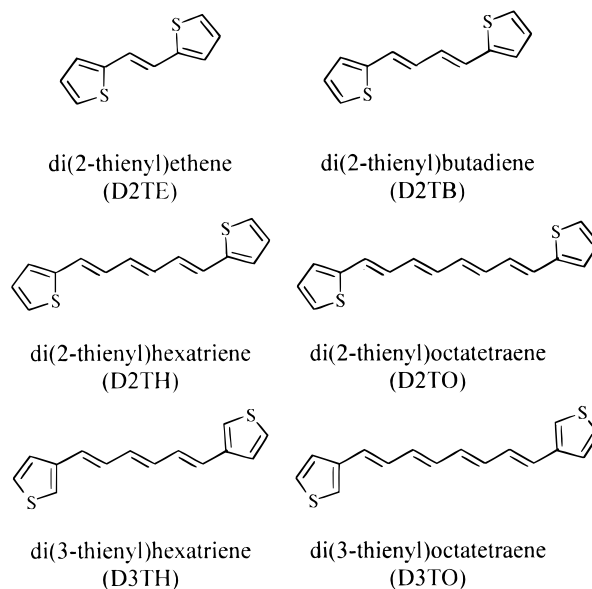
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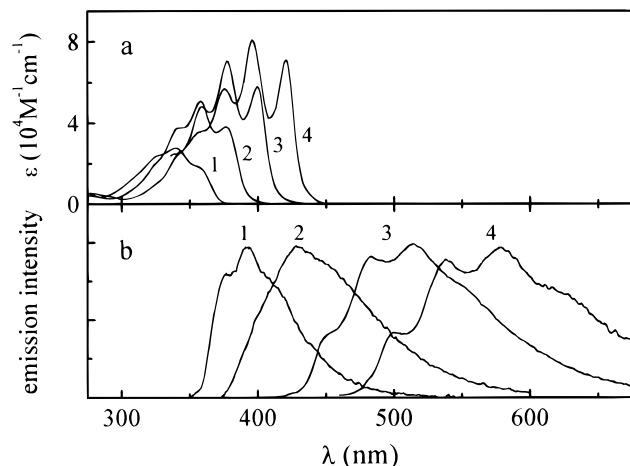
Figure 1. Absorption (a) and normalized emission (b) spectra of D2TE (1), D2TB (2), D2TH (3), and D2TO (4) in MCH/3MP at room temperature.

tane (MCH/3MP, 9:1, v/v), acetonitrile (AcCN) and butyronitrile (BuCN); some measurements were also carried out in benzene (B), cyclohexane (CH), isopentane (IP), dodecane (Do) and carbon disulfide. Except for the two solvents of the mixture (from Carlo Erba, RPE grade, purified before use by standard methods) and Do (from Aldrich), the other solvents were from Fluka, spectrograde.

The absorption measurements were carried out by a Perkin-Elmer Lambda 16 spectrophotometer. The fluorescence spectra were measured by a SPEX Fluorolog-2 F112AI spectrofluorometer. The corresponding quantum yields were determined using 9,10-diphenylanthracene in CH as standard ($\phi_F = 0.90$).[11] The values in the tables are averages of three independent experiments with a mean deviation of ~5%. The fluorescence lifetimes (τ_F, mean deviation of three independent experiments, ~5%) were measured with both an Edinburgh Instrument 199S spectrofluorometer (using the single-photon counting method) and a SPEX Fluorolog-τ2 system (using the phase modulation technique).

For photochemical measurements, a 150-W high-pressure xenon lamp coupled with a monochromator was used. The reactions were monitored by absorption spectrometry and by HPLC. The trans → cis photoisomerization quantum yields (ϕ_{iso}) were measured by a ferri-oxalate actinometer.

The triplet properties were measured by laser flash photolysis at 355 nm using the third harmonic of a Continuum (Surelite II) Nd: YAG laser (pulse width ~7 ns and laser energy <5 mJ/pulse). The T−T extinction coefficients (ϵ_T) were obtained by energy transfer from benzophenone in B (7200 M^{-1} cm^{-1} at 520 nm)[12] and AcCN (6500 M^{-1} cm^{-1} at 520 nm)[12] and from phenanthrene (25 000 M^{-1} cm^{-1} at 480 nm)[12] and to β-carotene (240 000 M^{-1} cm^{-1} at 520 nm) in CH. The latter value was measured by energy transfer from phenanthrene (this work).

For chromatographic measurements, a Waters apparatus was used equipped with a Symmetry C_{18} column (4.6 × 200 mm) and a UV detector coupled with an integrator (eluent, AcCN/water mixtures).

A cryostat (Oxford Instruments DN 1704) was used to control temperature in the 77−350 K range. For the ϕ_F measurements as a function of temperature, the value at 293 K was used as reference, taking into account the changes in absorbance and refractive index with temperature. For all measurements, the solutions were deoxygenated by purging with nitrogen.

Results and Discussion

Absorption and Emission Spectra. The absorption and emission spectra of the six *all-trans*-DTPs investigated in MCH/3MP are shown in Figures 1 and 2. Their spectral maximums, extinction coefficients, and Stokes shifts in nonpolar and polar
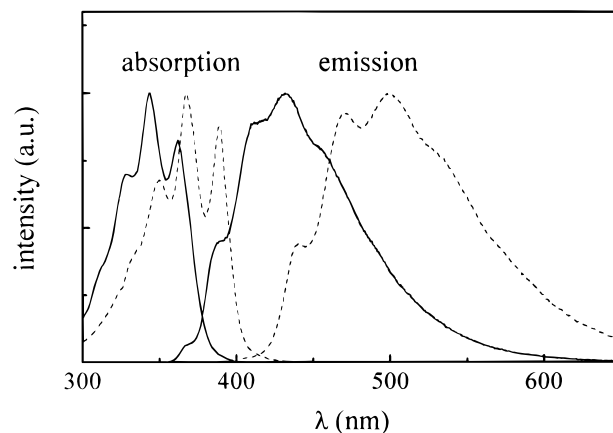
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Figure 2. Absorption and normalized emission spectra of D3TH (full lines) and D3TO (dashed lines) in MCH/3MP.

solvents are collected in Table 1. In addition to the well-known shift toward the red, an increase of vibronic structure and absorption intensity was observed when the number of the conjugated double bonds increased (ϵ_{max} in MCH/3MP goes from 27 000 to 82 000 M^{-1} cm^{-1} on passing from $n = 1$ to $n = 4$ in the series of the 2-thienyl derivatives). The strong absorption intensity is due to the symmetry-allowed HOMO−LUMO ($^1A_g \rightarrow \, ^1B_u^*$) transition, which hides the symmetry-forbidden $^1A_g \rightarrow \, ^1A_g^*$ transition. Also, the Stokes shift increases with *n*, indicating that states of different nature are responsible for the absorption and emission transitions, at least for $n \geq 2$. The spectra of the two 3-thienyl derivatives (with $n = 3, 4$) are substantially blue-shifted (probably because of a more distorted geometry related to steric interactions in the ground and excited states, as also indicated by quantum-mechanical calculations for S_0; see Figure 3) with respect to the 2-thienyl analogues. It is generally reported that the side aromatic groups have less effect on the electronic excitation in long-chain systems.[3,8,13]

The spectral shape is nearly the same in nonpolar and polar solvents, apart from a very small red-shift in BuCN, which decreases in the longer chain compounds when the prevalent nature of the lowest excited-state becomes $^1A_g^*$. More substantial is the temperature effect on the spectra. For D2TB in MCH/3MP (see Figure 4), in addition to a normal reduction of the bandwidth and a probable further decrease of the already small presence of conformers (see below), the decrease of temperature leads to more structured excitation and emission spectra. The fluorescence excitation spectrum, which reproduces the absorption spectrum, shifts toward the red; the vibronic progression of its C=C stretch mode increases from ~1380 to ~1550 cm^{-1} on going from 293 to 77 K, and a change in the intensity distribution of the vibronic component is also found. Meanwhile, the emission spectrum does not change its position. This behavior, already observed for *trans*-stilbene[14] and its monoaza-derivatives,[15] has been explained on the basis of excitation of sets of different ground-state species more or less deviating from planarity, as also shown by the little structured absorption spectra which reflect an overlap of $S_0 \rightarrow S_n$ transitions of different geometries.[14] A temperature decrease and a viscosity increase favor the planar or quasi-planar forms and lead to red-shifted and more resolved spectra and to a larger vibronic progres-

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Table 1. Spectral Properties of *all-trans*-Di(2-thienyl)- and *all-trans*-Di(3-thienyl)polyenes at Room Temperature in MCH/3MP and BuCN

compd	solvent	$\lambda_{abs}{}^a$ (nm)	$\epsilon_{max}{}^b$ (M^{-1} cm^{-1})	$\lambda_{fluo}{}^a$ (nm)	Stokes shift (cm^{-1})
D2TE	MCH/3MP	326.4^{sh}, *339.0*, 354.0^{sh}	27 000	376.7^{sh}, *392.5*, 413.5^{sh}	1700
	BuCN	340.0	28 000	399.0	
D2TB	MCH/3MP	326.0^{sh}, 341.5, *357.2*, 377.0	51 000	400.0^{sh}, *428.0*, 458^{sh}	1500
	BuCN	343.0, *358.0*, 374.0	52 000	432.0	
D2TH	MCH/3MP	342.5, 359.0, *377.0*, 399.4	77 000	452.8, 482.3, *514.2*	2950
	BuCN	343.4^{sh}, 361.8, *378.1*, 399.7	72 000	456.0^{sh}, 484.0, *515.0*, 552.3^{sh}	
D2TO	MCH/3MP	358.0^{sh}, 375, *396.7*, 420.8	82 000	501.0, 538, *578.2*, 625^{sh}	3800
	BuCN	357.8^{sh}, 376.0, *396.7*, 420.0	86 000	502.7, 540.8, *580.1*, 626.0	
D3TH	MCH/3MP	312.4, 327.3, *342.3*, 362.4	78 000	365.0^{sh}, 385.0^{sh}, 413.9^{sh}, *431.9*, 454.6	1620
	BuCN	332.0^{sh}, *344.8*, 362.9	79 000	389.8^{sh}, *431.4*, 457.8	
D3TO	MCH/3MP	348.4, *366.7*, 387.8		439.9, 470.8, *500.2*, 531.3^{sh}	3000
	BuCN	350.0, *367.7*, 388.9		440.7, 470.8, *501.2*, 532.2^{sh}	

^{a} The main maximum is in italics. ^{b} Extinction coefficients measured at the main maximum.
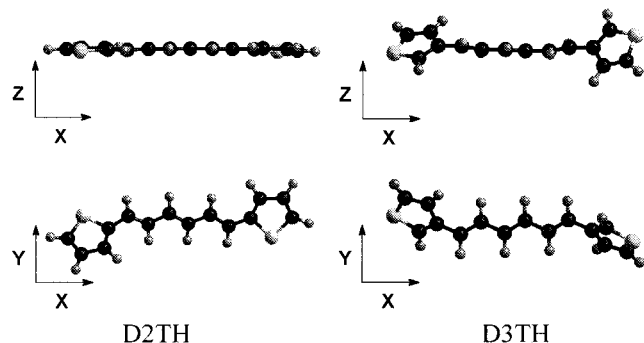
Figure 3. Perpendicular views of the ground-state geometry of D2TH and D3TH optimized by MNDO semiempirical calculations.
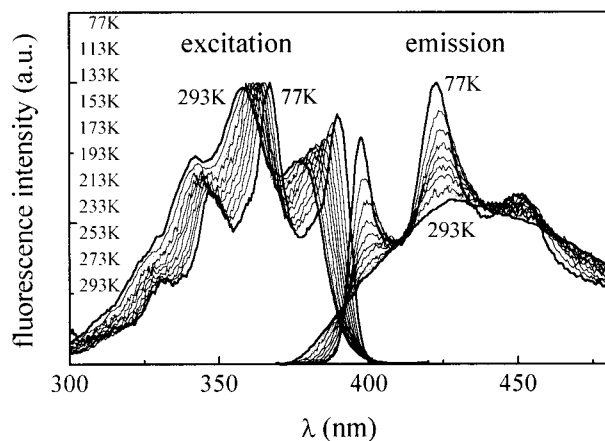
Figure 4. Normalized excitation and emission spectra of di(2-thienyl)-butadiene in MCH/3MP as a function of temperature.

sion.[14,15] In isoviscosity conditions ($\eta \sim 1.5$ cP, as in D$_o$ and MCH/3MP at 293 and 233 K, respectively), a red shift of the absorption spectrum of D2TB was also observed in the solvent of higher polarizability (MCH/3MP at 233 K), thus indicating that a polarizability effect on the energy of the allowed $^1A_g \rightarrow {}^1B_u{}^*$ transition cannot be excluded. The effect of the solvent polarizability on the energy and order of the lowest excited singlet states of different nature (^1A_g or ^1B_u) in DTPs is analyzed in the last section on the solvent effects.

Differently from the absorption spectrum, no red-shift in the fluorescence spectrum was observed by decreasing temperature. This points to an emission from a relaxed quasi-planar S_1 state, probably of A_g nature. However, the temperature decrease produces important changes in the spectral shape. In fact, the spectra become more and more structured with a parallel reduction in both the bandwidth and the intensity of an emission component in the 375−390-nm region, which disappears below 140 K. The latter observation can be explained by the presence

Table 2. Fluorescence Quantum Yield (ϕ_F), Lifetime [τ_F (ns)] and Radiative [k_F (10^7 s^{-1})] and Nonradiative [k_{NR} (10^7 s^{-1})] Rate Constants of Dithienylpolyenes at Room Temperature in MCH/3MP and BuCN

compd	MCH/3MP				BuCN			
	ϕ_F	τ_F	k_F	k_{NR}	ϕ_F	τ_F	k_F	k_{NR}
D2TE	0.05	0.16	31.2	594	0.009	0.050	18.0	1980
D2TB	0.29	3.3	8.9	21.5	0.049	0.51^a	9.6	186
D2TH	0.077	7.6^a	1.0	12	0.089	7.0^a	1.3	13
D2TO	0.0031	1.0^a	0.3	99	0.0041	1.2^a	0.4	83
D3TH	0.46	9.7	4.8	5.6	0.20	8.7/1.7	5.6^b	22^b
D3TO	0.11	9.3^a	1.2	9.6	0.15	12.0^a	1.3	7.1

^{a} Longer lifetime ($\geq$93%). ^{b} Value calculated by τ_F obtained with a monoexponential treatment (3.6 ns).

of a $S_2 \rightarrow S_0$ transition from an upper excited singlet state of B_u nature next to the A_g one (see below).[10] A similar, but much less evident, behavior was observed for the 2-thienyl derivatives with longer chain length.

Fluorescence Properties. Table 2 shows the fluorescence quantum yields and lifetimes of the compounds investigated in nonpolar and polar solvents and the kinetic parameters for the competitive relaxation pathways. The nonradiative rate parameters include the singlet contribution to isomerization, the $S_1 \rightarrow T_1$ intersystem crossing (ISC), and the $S_1 \rightarrow S_0$ internal conversion (IC) processes. The emission decays, measured by exciting at λ_{max} without an exit monochromator, are generally monoexponential. For some compounds (see Table 2), the biexponential fitting was evidence for the contribution of more than one emitting species, probably because of the presence of at least two conformers in the solutions.[9] When the weight of such contribution was < 7%, the lifetimes reported in Table 2 refer only to the more abundant species (>93%). Only for D3TH in a polar solvent was the weight of the second shorter-lived (1.7 ns) component substantial (~30%) so that its conformational equilibrium was investigated by selective photoexcitation (see below).

In the nonpolar solvent, the fluorescence parameters (quantum yield and lifetime) are reminiscent of what is known for the corresponding hydrocarbons[3] even if the trend with the chain length is not exactly the same. For DPhPs, both ϕ_F and τ_F increase for the first three members of the series and only with $n = 4$ do both parameters start to decrease because of the competition of radiationless and nonreactive processes.[3] In the present case, the behavior is different and differs also between the 2- and 3-thienyl derivatives. In the 2-thienyl compounds, the lifetime increases on going from $n = 1$ to $n = 3$ and then decreases for $n = 4$, while it is slightly longer for $n = 4$, compared with $n = 3$, in the 3-thienyl compounds. On the other hand, the quantum yield of the 2-thienyl series increases from $n = 1$ to $n = 2$ only and then decreases progressively for $n =$

3 and $n = 4$. For the 3-thienyl compounds, since the shorter chain members were not available, we could only observe the decrease of ϕ_F from $n = 3$ to $n = 4$.

In the polar solvent BuCN, the behavior is more reminiscent of that of the hydrocarbon analogues.[3] In fact, both experimental fluorescence parameters increase with the chain length up to $n = 3$ and then start to decrease when $n = 4$, while the radiative rate parameter always decreases. Their values are practically the same in both solvents, indicating that the vibronic coupling between the two lowest excited states is little affected by the solvent polarity.

In the absence of a parallelism between ϕ_F and τ_F, one can get more information from the dependence of the fluorescence rate parameters (derived from $k_F = \phi_F/\tau_F$) on the chain length. The difference in k_F between the first two members of the series indicates that the lowest state starts changing from allowed to forbidden in the diene, even if its still high k_F value suggests that this member retains some allowed character in both solvents. The decrease in k_F is relatively modest on going from $n = 3$ to $n = 4$, suggesting that the two lowest excited states are relatively far apart. For the 3-thienyl compounds, where the two states are closer, relative to the corresponding 2-thienyl analogues, k_F decreases markedly from the triene to the tetraene.

The value of k_F for D2TE is the highest in the series (3.1×10^8 s^{-1} in nonpolar solvent) and is characteristic of an allowed transition ($^1B_u^* \rightarrow {}^1A_g$, as for stilbene[4]). Its value gradually decreases with the increase in chain length, reaching a value 2 orders of magnitude smaller for D2TO, indicative of a forbidden transition. This behavior, already observed for DPhPs,[3] is due to the presence of the two lowest excited singlet states of different symmetry, whose relative stabilization depends on the extent of conjugation at different chain lengths and then affects the nature of the lowest excited state. The fluorescent state S_1 has then a net ionic (B_u) character when $n = 1$, with the covalent (A_g) S_2 state lying at higher energies. The two states become almost degenerate when $n = 2$, and their relative position depends on the experimental conditions (temperature and/or solvent polarizability; see later). A smaller energy gap occurs, leading to an increase in the oscillator strength of the $S_1 \rightarrow S_0$ transition if S_1 has an A_g nature. For polyenes[6] and DPhPs,[3] an inversion of states is operative in hexatriene, where the mixed nature of the lowest excited state has a relevant A_g contribution. In the present case, the behavior is different and the inversion of states is already observed in D2TB. The $S_1 - S_2$ energy gap increases, but more and more slightly, with an increase in the chain length. It becomes large enough for DTO, whose lowest excited state has a net A_g nature.

Except for D2TB, whose S_1 character drastically depends on solvent polarizability, the present results are in agreement with the order and nature of the two lowest excited states of *all-trans*-D2TPs derived by their excitation and emission spectra in solid solutions of *n*-alkanes at liquid helium temperature.[8] The k_F rate constants of the longer chain 3-thienyl derivatives are higher than those of the 2-thienyl analogues, which reflects a smaller energy gap between S_1 and S_2 of A_g and B_u nature, respectively. This is probably due to the more distorted geometries of S_1, as above indicated by the spectra. The consequent stronger mixing between the two states explains why their k_F decreases markedly from the triene to the tetraene.

Triplet Properties. Table 3 collects the information on the triplet state obtained by laser flash photolysis. The $T_1 \rightarrow T_n$ spectra in a polar solvent are shown in Figure 5. This absorption shifts toward the red with increasing chain length, as expected. For the 2-thienyl derivatives, the longer chain compounds have

Table 3. Spectral and Photophysical Properties of the Triplet State of Dithienylpolyenes at Room Temperature

compd	solvent	λ^a (nm)	τ_T (μs)	ϵ_T^b (M^{-1}cm^{-1})	ϕ_T
D2TE	CH	410	0.36	16 000	0.27
	AcCN	410	0.25	17 500	0.02
D2TB	CH	410, *425*	7.5	30 000	0.69
	B	410, *425*	4.8	23 000	0.37
	AcCN	405^{sh}, *425*	8.6	23 000	0.07
D2TH	CH	420^{sh}, *445*	9.1	41 000	0.16
	B	420, *445*	9.4	34 000	0.11
	AcCN	420, *445*	12.2	36 000	0.14
D2TO	CH	445, *465*	13.8	53 000	$\leq$0.006
	B	440, *465*	1.9	46 000	0.01
	AcCN	440, *465*	4.4	43 000	$\leq$0.005
D3TH	CH	410	18	10 500	0.27
	AcCN	405	33	8 600	0.24
D3TO	CH	420	4.8	14 000	0.14
	AcCN	420	42	10 000	0.12

^{a} The main maximum is in italics. ^{b} Extinction coefficient at the main maximum.
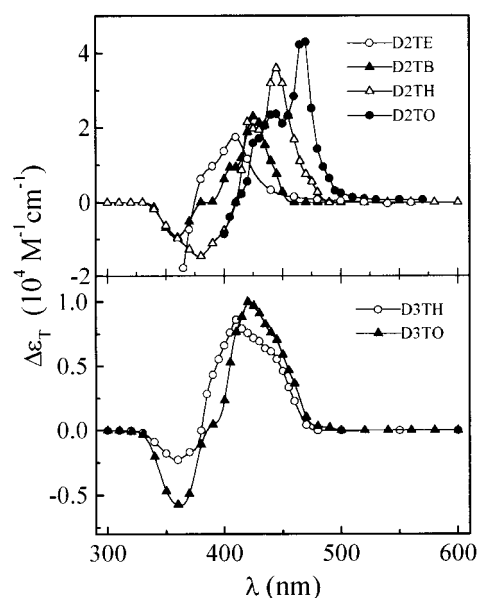

Figure 5. $T_1 \rightarrow T_n$ absorption spectra of dithienylpolyenes in AcCN at room temperature.

more structured spectra while the 3-thienyl derivatives have little structured and blue-shifted spectra compared with the 2-thienyl counterparts, as observed for the $S_0 \rightarrow S_n$ absorption. A similar behavior was found in nonpolar solvents (MCH/3MP and CH).

The triplet quantum yield ϕ_T was found to be substantial for D2TE and D2TB and to decrease for longer chains. Similar results, with higher ϕ_T values, were obtained for the 3,3'-derivatives. In any case, the triplet yields were found to be substantial, with the notable exception of D2TO, for all compounds investigated, unlike the corresponding DPhPs whose triplet yields are often negligible, particularly for longer chains.[16] Moreover, a clear decrease of ϕ_T in the polar solvent was found for D2TE and D2TB only.

The triplet lifetimes are in the range 4−40 μs, except for D2TE ($\sim$0.3 μs), and become longer in more polar solvents. These long lifetimes are peculiar of nontwisting states and then point to high torsional barriers in T_1 and to prevalent radiationless relaxation, as found for styrylanthracenes.[17]

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Table 4. Temperature Effect on the Photophysical Parameters [ϕ_F and τ_F (ns)] and on the Radiative Rate Constant [k_F (10^7 s^{-1})] of Di(2-thienyl)polyenes in MCH/3MP

T (K)	D2TE			D2TB			D2TH			D2TO		
	ϕ_F	τ_F	k_F	ϕ_F	τ_F	k_F	ϕ_F	τ_F	k_F	$\phi_F{}^a$	τ_F	k_F
354	0.020			0.22	2.57	8.6	0.064	6.9	0.93	0.0032		
333	0.027			0.26	2.87	9.1	0.068	7.1	0.96	0.0034		
313	0.033			0.28	3.08	9.1	0.070	7.1	0.99	0.0030		
293	0.050	0.16	31	0.29	3.30	8.9	0.077	7.6	1.1	0.0031	1.0	0.3
273	0.073	0.27	27	0.34	3.28	10	0.083	7.3	1.1	0.0035		
253	0.099	0.27	37	0.39	3.17	12	0.088	7.1	1.2	0.0039		
233	0.123	0.29	42	0.41	3.22	13	0.099	7.0	1.4	0.0041		
213	0.147	0.34	43	0.45	3.13	14	0.10	7.1	1.4	0.0040		
193	0.169	0.38	45	0.48	2.97	16	0.10	7.1	1.4			
173	0.182	0.41	44	0.51	2.77	18	0.098	7.8	1.3			
153	0.182	0.43	42	0.53	2.70	20	0.094	9.8	1.0			
133	0.188	0.47	40	0.55	2.49	22	0.090	9.6	1.0			
77	0.251	0.60	42	0.95	1.86	51	0.092	11	0.84			
$^1\Delta E_{act}$ (kcal mol^{-1})		3.0			10.4							
$\log{}^1A_{act}$		11.9			14.4							

^{a} ϕ_F only in the 354−213 K range because of low solubility.

Temperature Effect on Photophysical Parameters. The presence of activated processes in the S_1 relaxation was investigated by measuring the temperature effect on the fluorescence parameters. While small effects were found for the longer chain compounds, a marked dependence of ϕ_F and τ_F on temperature was found for $n = 1$ and $n = 2$ in MCH/3MP (see Table 4).

The reaction scheme proposed for the deactivation of the lowest excited states of DTPs is the following:

$$^1P \xrightarrow{h\nu} {}^1P* \tag{1}$$

$$^1P* \xrightarrow{k_F} {}^1P + h\nu' \tag{2}$$

$$^1P* \xrightarrow{{}^1k_{act}} {}^1perp* \tag{3}$$

$$^1P* \xrightarrow{k_{IC}} {}^1P + heat \tag{4}$$

$$^1P* \xrightarrow{k_{ISC}} {}^3P* + heat \tag{5}$$

$$^3P* \xrightarrow{{}^3k_{act}} {}^3perp* \tag{6}$$

$$^3P* \xrightarrow{k'_{ISC}} {}^1P + heat \tag{7}$$

where P indicates the polyene, perp represents the twisted geometry at 90°, and the superscripts 1 and 3 refer to the singlet and triplet multiplicity. The rate constants of the activated torsional pathways toward ^{1,3}perp*

$$^{1,3}k_{act} = {}^{1,3}A_{act} \exp(-^{1,3}\Delta E_{act}/RT) \tag{8}$$

can be derived by the Arrhenius parameters obtained by the temperature effect on the fluorescence quantum yields and lifetimes through the Arrhenius-type equations

$$\ln\left[\frac{\phi_F^{lim}}{\phi_F} - 1\right] = \ln(\tau_F^{lim\,1}A_{act}) - \frac{^1\Delta E_{act}}{RT} \tag{9}$$

$$\ln\left(\frac{1}{\tau_F} - \frac{1}{\tau_F^{lim}}\right) = \ln{}^1A_{act} - \frac{^1\Delta E_{act}}{RT} \tag{10}$$

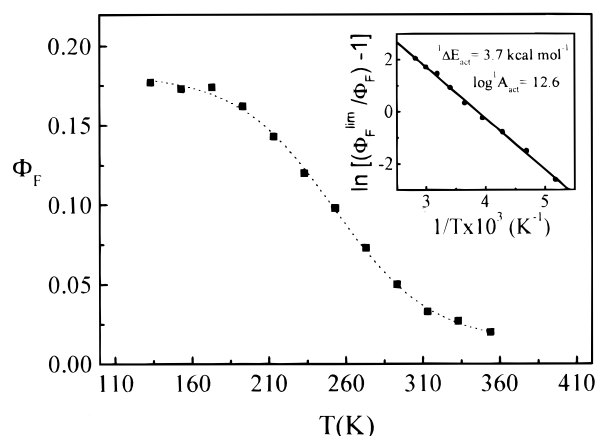based on the stationary-state approximation applied to the

Figure 6. Fluorescence quantum yield of di(2-thienyl)ethene in MCH/3MP as a function of temperature. The inset shows the Arrhenius plot.

reaction scheme above. The τ_F^{lim} and ϕ_F^{lim} values refer to the lifetimes and quantum yields measured at low temperatures where, being the reactive process inhibited, the only relaxation pathways of S_1 remain the radiative and nonradiative (ISC and IC) ones. The trend of ϕ_F with temperature and the corresponding Arrhenius-type plot are shown in Figure 6 for D2TE in MCH/3MP, as an example. The parameters thus obtained were $^1\Delta E_{act} = 3.7$ and 2.3 kcal mol^{-1} and $^1A_{act} = 4 \times 10^{12}$ and 1.6×10^{11} s^{-1}, by using eqs 9 and 10, respectively. The average values are reported in Table 4. They allowed $^1k_{act} = 4.6 \times 10^9$ s^{-1} to be obtained at 293 K.

The quasi-degeneracy of the two lowest excited states of D2TB can produce a peculiar photobehavior since their mixing is very sensitive to temperature and solvent perturbations. In fact, an anomalous trend of the fluorescence lifetime with temperature was found for this compound. The τ_F value decreased with temperature (from 3.3 to 1.9 ns, on going from 293 to 77 K) against the expectations that would foresee an independence of temperature or, possibly, an opposite behavior (increase in lifetime) if activated paths were present in the nonradiative deactivation of S_1. Such behavior produced an anomalous increase in k_F (up to 6 times) on going from 293 to 77 K. Since the kinetic scheme above was based on the assumption that the radiative parameters were independent of temperature, as generally found, it could not be used to describe the behavior of D2TB. Therefore, to evaluate the torsional barrier in S_1 for this compound, the measurement of the ^{1}(trans,

trans)* → ¹(trans,perp)* twisting rate constant as a function of temperature became necessary. The $^1k_{act}$ values for this activated process could be obtained at each temperature by the equation

$$^1k_{act}(T) = 1/\tau_F(T) - k_F(T) - k_{ISC} - k_{IC} \qquad (11)$$

assuming that the ISC and IC rate constants are independent of temperature. From the experimental parameters (ϕ_F, τ_F, and ϕ_T, measured at 293 K, and τ_F^{lim} and ϕ_F^{lim}, measured at 133 K) it was possible, by using the equations

$$k_{ISC} \cong \phi_T/\tau_F \qquad (12)$$

$$k_{IC} \cong 1/\tau_F^{lim} - (k_F^{lim} + k_{ISC}) \qquad (13)$$

to derive $k_{ISC} = 2.1 \times 10^8$ s^{-1}, while k_{IC} was found to be negligible. Introducing these values in eq 11, the $^1k_{act}$ values were obtained at different temperatures. The kinetic parameters thus obtained were $^1A_{act} = 2.7 \times 10^{14}$ s^{-1}, $^1\Delta E_{act} = 10.4$ kcal mol^{-1}, and $^1k_{act} = 4.7 \times 10^6$ s^{-1} at 293 K. The latter value is 3 orders of magnitude smaller than that obtained for D2TE. An increase in the torsional barrier on going from $n = 1$ to $n = 2$ has also been reported for DPhPs ($^1\Delta E_{act}$ of about 3 and 5 kcal mol^{-1} for stilbene[18] and 1,4-diphenylbutadiene (DPhB),[19,20] respectively).

Conformational Equilibria in Solutions of *all-trans*-D3TH. The problem of s-trans−s-cis rotamerism around the single bonds of the polyene skeleton was unraveled using statistical methods applied to the fluorescence spectra of diphenyl-hexatriene (DPhH)[21] and DPhB.[22−25] By fluorometric measurements as a function of λ_{exc} at two temperatures, it was possible to resolve the experimental spectra into two components, one consisting of a combination of emission of s-trans from the two lowest ^1B_u* and ^1A_g* excited states, and a second one, red-shifted, assigned to s-cis of the diene, or to a mixture of s-cis conformers (in the case of the triene).

A preliminary investigation of our thienyl derivatives indicated that, with the exception of D3TH, the shape of the emission and excitation spectra of DTPs was practically independent of the excitation and monitoring wavelength (λ_{exc} and λ_{em}), respectively, and the excitation spectra satisfactorily reproduced the absorption spectra. This result led us to conclude that an unique absorbing and emitting species is generally present and then to exclude the intervention of conformational equilibria in the solutions of these DTPs. In fact, a slight dependence of the fluorescence spectra on λ_{exc}, particularly for the longer chain compounds ($n = 3, 4$) in the series of the 2-thienyl derivatives, was observed at higher temperatures (up to 354 K). However, the presence of the less stable conformers was generally too small to be easily detected, even by exciting at the red edge of the absorption spectrum. Therefore, we have postponed (with the mentioned exception) the delicate investigation on the rotamerism of DTPs to later work.
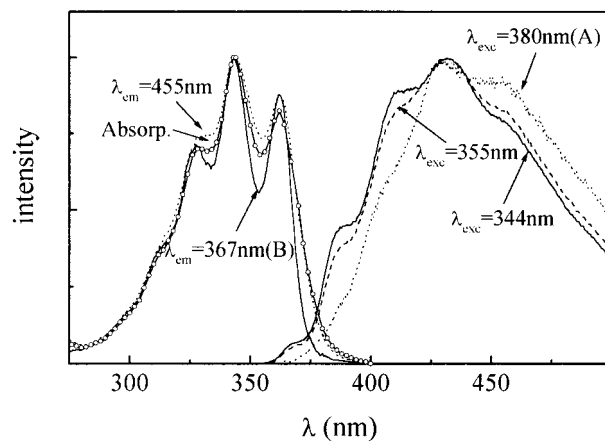
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Figure 7. Normalized absorption, excitation and emission spectra of di(3-thienyl)hexatriene in MCH/3MP at room temperature.
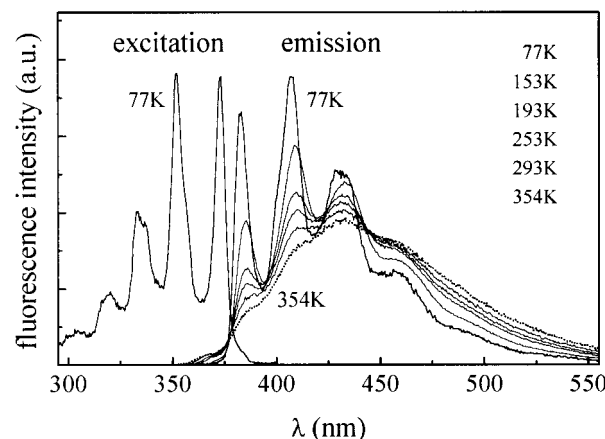

Figure 8. Excitation spectrum of di(3-thienyl)hexatriene in MCH/3MP at 77 K and normalized (at unity area) emission spectra at different temperatures.

It has to be noted that, as stressed in the paper on DPhH,[21] the decrease in the yield of the radiative pathway when temperature is increased cannot be ascribed to the competition of the reactive decay only, since a contribution of the temperature effect on the conformational equilibrium could be also operative. However, the presence of more than one species generally is so small in these compounds that it cannot significantly affect their photochemical and photophysical behavior.

Only for D3TH were the changes in the excitation and emission spectra with λ_{exc} and λ_{em} clearly evident; these findings, and the observation that the excitation spectrum did not reproduce the absorption one, pointed to an equilibrium of at least two different species in solution. Selective excitation at the extreme tail of the absorption spectrum of this compound ($\lambda_{exc} = 380$ nm) gave the emission spectrum A in Figure 7, which represents the quasi-pure spectrum of the bathochromic species, as confirmed by the fact that its shape did not change in that λ_{exc} range. On the other hand, the excitation spectrum obtained at $\lambda_{em} = 367$ nm, where the bathochromic rotamer no longer emits, corresponds to the quasi-pure excitation spectrum of the hypsochromic B rotamer. Similar changes in the spectra with λ_{exc} and λ_{em} were found in the polar solvent BuCN. Also, the temperature effect on the fluorescence spectrum did indicate the presence of conformational equilibria for this compound. In fact, at high temperatures, an increase in the weight of the bathochromic species A was observed (see Figure 8) while at low temperatures its weight decreased and became negligible

all-trans-α.ω-Dithienylpolyenes

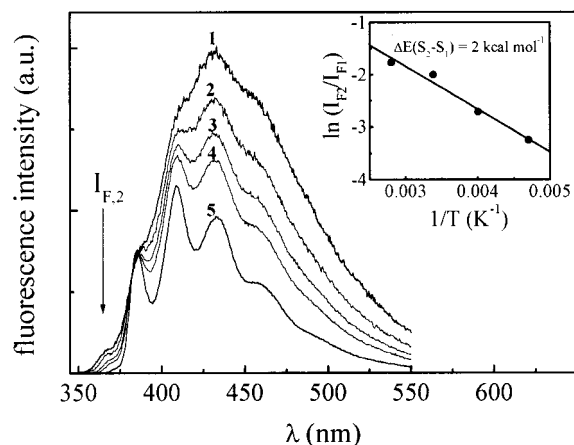*J. Am. Chem. Soc., Vol. 121, No. 5, 1999* 1071

Figure 9. Emission spectra of di(3-thienyl)hexatriene in MCH/3MP at 354 (1), 293 (2), 253 (3), 193 (4), and 153 (5) K. Inset: Arrhenius-type plot (see ref 10b).
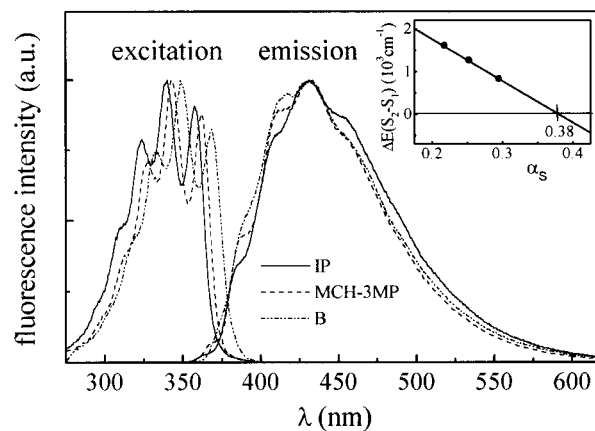

Figure 10. Normalized excitation and emission spectra of di(3-thienyl)-hexatriene in solvents of different polarizabilities at room temperature. Inset: $\Delta E(S_2-S_1)$ plot as a function of solvent polarizability.

in the structured emission and excitation spectra (independent from λ_{exc} and λ_{em}) recorded in a rigid matrix of MCH/3MP at 77 K, which were assigned to the more stable B rotamer (see Figure 8).

Emission from an Upper Excited State in D3TH. As previously found for *trans*-2-styrylanthracene (2-StAn)[10b] and *all-trans*-DPhH,[10a,20,26] an anomalous emission was also observed in the spectrum of D3TH appearing as a shoulder at 365 nm whose intensity changed with temperature but not with λ_{exc}. It was assigned to a second emissive component from the B rotamer on the basis of the following observations: (i) it is not present in the spectrum of the quasi-pure A rotamer obtained at $\lambda_{exc} > 375$ nm (see Figure 7); (ii) the corresponding excitation spectrum recorded at $\lambda_{em} = 365$ nm is the same as that recorded at $\lambda_{em} = 386$ nm, where the quasi-pure B spectrum was obtained (the A rotamer contributes very little to the emission at this wavelength); (iii) the intensity ratio between the first two shoulders of the fluorescence spectrum (at 365 and 386 nm) remains practically constant on changing λ_{exc}, thus indicating that the two emissive components originate from the same excited species and that the A rotamer does not affect significantly the second vibronic component at 386 nm.

The decrease in the intensity ratio of the two components on decreasing temperature, up to the disappearance of the first component at 133 K (Figure 9), indicates that the latter pertains to an emission from an upper excited-state S_2 thermally populated from S_1 during its lifetime.[10,20,26] The energy difference between the two states was obtained from the linear relationships between $\ln(I_{F,2})$ or $\ln(I_{F,2}/I_{F,1})$ and $1/T$ (see inset in Figure 9), as reported for 2-StAn.[10b] Some uncertainty in the $\Delta E (S_2-S_1)$ value thus obtained can be due to the low $I_{F,2}$ value as well as to some contribution from the A rotamer, particularly at the higher temperatures investigated. The energy gap could also be estimated by the difference in the $\bar{v}_{00}$ of the two components (27 400 and 25 980 cm^{-1} for $S_2 \rightarrow S_0$ and $S_1 \rightarrow S_0$, respectively) or from the spectral shifts of the $\bar{v}_{00}$ vibronic components in rigid matrixes at 77 K. The tail of the excitation spectrum in a glass matrix shows the 0−0 vibronic component of the weak $S_0 \rightarrow S_1$ transition, which matches the same component in the emission spectrum. This component was observable at low temperature only since the better spectral resolution reduces the overlap with the stronger $S_0 \rightarrow S_2$ absorption. The different methods above led to an average value $\Delta E(S_2-S_1) = 3 \pm 1$ kcal mol^{-1}, which allowed the ratio $k_{F2}/$

$k_{F1} \cong 30$ to be obtained by the equation

$$I_{F,2}/I_{F,1} = (k_{F,2}/k_{F,1})[S_2]/[S_1] \qquad (14)$$

This value is in agreement with the adopted model and with the A_g nature of S_1. The different nature of the two lowest excited states of singlet multiplicity is also reflected by the effect of the solvent polarizability [evaluated from the refraction index (n_r) as $\alpha_S = (n_r^2 - 1)/(n_r^2 + 2)$] on the absorption and emission spectra (Figure 10).[27,28] When α_S increased (e.g., passing from isopentane to benzene), a red-shift of the $S_0 \rightarrow S_2$ and $S_2 \rightarrow S_0$ transitions was observed while the energy of the $S_1 \rightarrow S_0$ transition was practically insensitive. The $\Delta E(S_2-S_1)$ value shows a linear trend with α_S (inset of Figure 10). Interestingly, such a correlation allows for a determination of the solvent and/or the temperature at which the inversion in the nature of the lowest excited state occurs (corresponding, in the present case, to $\alpha_S > 0.38$). This peculiar emission from an upper excited state was found for D3TH only. It was not observed for D2TH, probably because of a larger S_2-S_1 energy gap owing to a less distorted geometry.

Mechanism of Photoisomerization. Table 5 collects the experimental and derived photophysical and photochemical parameters for *all-trans*-D2TPs in two solvents of different polarity. The quantum yields for the photosensitized isomerization of one double bond are also reported. The net decrease in reactivity when the number of double bonds increases and the parallel decrease in fluorescence indicate that IC becomes more important for the deactivation of S_1. The higher torsional barrier of the butadiene with respect to the ethene derivative is in line with these findings. The IC quantum yield can be derived by the equation

$$\phi_{IC} \cong 1 - (\phi_F + \phi_T + 2^1\phi_{iso}) \qquad (15)$$

or, in case of a very small energy barrier to rotation in T_1 (which induces internal rotation of all molecules that intersystem cross, as substantiated by the isomerization quantum yield sensitized by triplet donors, ϕ_{sens}, which reaches a value of ∼0.5), by the equation

$$\phi_{IC} \cong 1 - (\phi_F + 2\phi_{iso}) \qquad (16)$$

where the coefficient 2 accounts for the almost 50:50 partitioning

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Table 5. Photophysical and Photochemical Parameters of Di(2-thienyl)polyenes at Room Temperature in MCH/3MP and BuCN

compd	solvent	ϕ_F	ϕ_T	ϕ_{iso}	ϕ_{sens}	$^3\phi_{iso}$	$^1\phi_{iso}$	$^1\phi_{iso}{}^a$	ϕ_{IC}
D2TE	MCH/3MP	0.05	0.27	0.41	0.48^c	0.13	0.28	0.36	0.12
	BuCN	0.009	0.02	0.43^b		0.0096	0.42		0.13
D2TB	MCH/3MP	0.29	0.69	0.068	0.10^c	0.069		0.008	≤ 0.02
	BuCN	0.049	0.07	0.25	0.065^b	0.005	0.245		0.39
D2TH	MCH/3MP	0.077	0.11^c	$\leq 0.004^d$					~ 0.81
	BuCN	0.089	0.14	0.004^d					0.76
D2TO	MCH/3MP	0.0031	0.01^c	$\leq 0.0006^d$					~ 0.99
	BuCN	0.0041	≤ 0.005	0.0006^d					~ 0.99

^{a} Calculated by $k_{act}\tau_F/2$ at 293 K. ^{b} In AcCN. ^{c} In benzene. ^{d} Disappearance quantum yield.

factor from the perp configuration (as assumed for arylethenes[4,29] and DPhPs[30]) and $^1\phi_{iso}$ is the contribution of the singlet mechanism to isomerization. The strong increase in ϕ_{IC} with n, shown in the last column, could be due to a progressive decrease of $\Delta E(S_1-S_0)$, as already shown by the spectral data, which should drastically increase the $S_1 \to S_0$ IC. The parallel decrease in reactivity indicates a substantial torsional barrier in S_1 when $n \geq 2$, as found for DPhPs.[20,31] An increase of more than 1 order of magnitude in τ_F (from 0.36 to 4.7 μs) and a parallel decrease in ϕ_{sens} (from 0.48 to 0.10) were observed on going from $n = 1$ to $n = 2$, thus confirming that the torsional barrier also increases in the T_1 state of the butadiene derivative, as already found in S_1.

The solvent effect is evident for the first two members of the series of D2TPs: the more polar solvent leads to a decrease in the torsional barriers through a stabilization of the twisted configuration of zwitterionic nature.[32] However, having the two solvents practically the same polarizability ($\alpha_S = 0.252$ and 0.234 for MCH/3MP and BuCN, respectively), they are not expected to change the ordering of the two lowest excited singlet states.

It was interesting to evaluate the weight of the singlet and triplet contributions to photoisomerization. In fact, the overall yield ϕ_{iso} can be considered as the sum of the two contributions, $^1\phi_{iso}$ and $^3\phi_{iso}$. The weight of the triplet mechanism was estimated by the relationship

$$^3\phi_{iso} = \phi_T\phi_{sens} \qquad (17)$$

For D2TE, ϕ_{iso} is high in a nonpolar solvent: its value accounts for most of the quanta absorbed. The isomerization proceeds through both mechanisms with a prevalent singlet contribution, in agreement with previous results.[33] In BuCN, ϕ_{iso} remains practically unchanged, but the weight of the triplet contribution becomes negligible ($\phi_{iso} \approx {}^1\phi_{iso}$). The $^1k_{act}$ is here much higher (~ 40 times) than k_{ISC}, thus drastically reducing the ϕ_T value. The polar solvent preferentially stabilizes the twisted form compared to the planar geometry reducing the torsional barrier in S_1, thus opening an efficient singlet path to isomerization.

The D2TB gives rise to a unique detectable photoproduct, the trans,cis isomer, with a small yield in nonpolar solvent. A triplet mechanism is operative in MCH/3MP at room temperature. In the polar solvent, the reaction yield increases markedly: the reduction of the energy barrier leads to a largely

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Table 6. Rate Constants (10^7 s^{-1}) of the Deactivation Processes of the Lowest Excited Singlet State of Di(2-thienyl)polyenes in MCH/3MP at 293 K

compd	k_F^0	k_F	k_{ISC}	$^1k_{act}$	k_{IC}
D2TE	60	31	170	460	75
D2TB	87	8.9	21	0.47	≤ 0.6
D2TH	98	1.0	3.3	0.053	11
D2TO	98	0.3	≤ 0.5	0.050	99

predominant singlet mechanism, whereby the triplet yield is drastically reduced, as observed for the ethene counterpart. Prolonged irradiation leads to formation of a second photoproduct, probably the cis,cis isomer produced by the trans,cis one through a consecutive reaction. For this butadiene derivative, some measurements were also carried out above room temperature. While ϕ_{sens} did not increase with temperature, the direct (overall) isomerization yield increased markedly in both nonpolar and polar solvents (from 0.068 and 0.25 at 293 K to 0.18 and 0.44 at 354 K, in MCH/3MP and BuCN, respectively). Using eqs 12 and 17 and assuming that k_{ISC} is independent of temperature, the contribution of the two reaction paths in MCH/3MP at high temperature was obtained. The rate constant $^1k_{act}$ at 354 K was calculated by the relationship

$$^1k_{act} = (2^1\phi_{iso}/\tau_F) \qquad (18)$$

which again assumes the same partitioning factor of the perp geometry toward the trans and cis configurations, as assumed for DPhPs.[30] The same value of $^1k_{act}$ (1.0×10^8 s^{-1}) was obtained by eq 18 and from the Arrhenius parameters (eq 8) at 354 K. Finally, the values $^1\phi_{iso} = 0.13$ and $3\phi_{iso} = 0.054$ were obtained, which give evidence for a prevalence of the singlet mechanism at high temperatures.

In BuCN, by assuming the same frequency factor as found in MCH/3MP ($^1A_{act} = 2.5 \times 10^{14}$ s^{-1}), the following values were obtained: $^1k_{act} = 9.6 \times 10^8$ s^{-1} at 293 K and $\Delta E_{act} = 7.3$ kcal mol^{-1}. These results gave a further indication of the effect of the solvent polarity in reducing the energy barrier to rotation, as previously found for DPhB, whose ΔE_{act} value goes from 5.3 kcal mol^{-1} in nonpolar solvents[19] to 4.0 kcal mol^{-1} in ethanol.[34] It was not possible to perform a detailed study on the photoreactivity of the compounds with $n = 3$ and 4 due to the small values of their disappearance quantum yields ($<10^{-3}$). Table 5 also reports the isomerization yields derived from the $^1k_{act}$ values obtained, in turn, by the Arrhenius parameters of D2TE and D2TB, using eq 18 at 293 K and again assuming a partitioning factor from ^{1}perp of 0.5. Table 6 shows the rate constants for the radiative and nonradiative deactivation of S_1 for *all-trans*-D2TPs in the nonpolar solvent at room temperature. For comparison, the radiative rate constant (k_F^0) is reported, as obtained by the approximate natural lifetime (τ_F^0), calculated from the integral of the absorption intensity using the modified

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Strickler–Berg relationship[35]

$$k_F^0 = 1/\tau_F^\circ = 2.88 \times 10^{-9} \times \bar{\nu}_{00} n_r^2 \int \epsilon(\nu) \, d\nu \quad (19)$$

where n_r is the refractive index of the solvent and $\bar{\nu}_{00}$ is the 00 component of the $^1A_g \rightarrow {}^1B_u^*$ transition, which is considered the main factor responsible for the absorption. Table 6 shows how the increase in the extent of planarity and conjugation of these molecules with the increase of n can affect their excited-state properties and in particular the k_F^0 value. The latter increases with n and differs more and more from the k_F value experimentally obtained. This further confirms the different nature of the excited states implied in the absorption (^1B_u) and emission (^1A_g) processes in DTPs with $n \geq 2$. Also, k_{ISC} decreases when n increases, going from 1.7×10^9 s^{-1} in DTE to $< 5 \times 10^6$ s^{-1} in DTO; a small value has also been reported for DPhO.[36] In conclusion, the enhancing effect of the sulfur atom on ISC, clearly present in DTE, is practically extinguished with $n = 4$, showing that the degree to which thiophene rings affect the excited-state properties decreases with increasing polyene chain length.[8]

Similarly to k_F and k_{ISC}, $^1k_{act}$ also decreases drastically (almost 4 orders of magnitude), from 4.6×10^9 s^{-1} for DTE to 5×10^5 s^{-1} for DTO at 293 K. This huge decrease in $^1k_{act}$ can be due to an increased torsional barrier, unexpected by theoretical predictions[6] when S_1 has an A_g nature and/or to a larger solvent–solute friction parameter, which should lead to a decrease of the preexponential Arrhenius parameter.[19]

The rate parameter of the $S_1 \rightarrow S_0$ IC shows an expected trend when n increases. In fact, it increases (except for D2TE) in agreement with what is expected on the basis of the smaller energy gap between the two states in the longer polyenes. However, one should consider, in addition to the smaller energy gap, the effective modes of vibronic coupling. By analogy with the behavior of polyenes, theoretically interpreted by Orlandi et al.,[6] the active Franck–Condon modes could be, in addition to the C=C stretching vibration, the out-of-plane twisting, which could become an effective accepting mode in the IC process in nonplanar configurations. The C=C stretching acts as the promoting as well as accepting mode and is the dominant mode in the nonradiative decay of polyenes with "planar" S_1 configuration. On the other hand, the C=CHT twisting mode can act as an accepting mode in the presence of a strongly distorted configuration (out of plane) as in the case of DTE. The participation of this further active mode in the vibronic coupling is probably responsible for the substantial k_{IC} value for $n = 1$. Only for D2TO is the energy gap such to make the IC process by far the fastest even in the presence of a unique active mode of vibronic coupling, the stretching one, because of the planarization of the equilibrum geometry of S_1. The high k_{IC} value for $n = 1$ and 4 is thus probably related to the nonplanar equilibrium geometry of S_1 in the first case and to the small energy gap in the longer chain compound.

Solvent Effect on the Photophysical Properties of *all-trans*-D2TB. The solvent properties, polarity and polarizability, can affect the relative energy levels of the $^1A_g^*$ and $^1B_u^*$ states of the trans configuration and/or those of the twisted ^{1}perp* form. This can, in turn, affect the fluorescent properties but also the shape of the potential energy surfaces of S_1 and T_1, thus affecting the dynamics of the geometrical isomerization. In particular, in the case of D2TB, a trend of k_F with temperature was found

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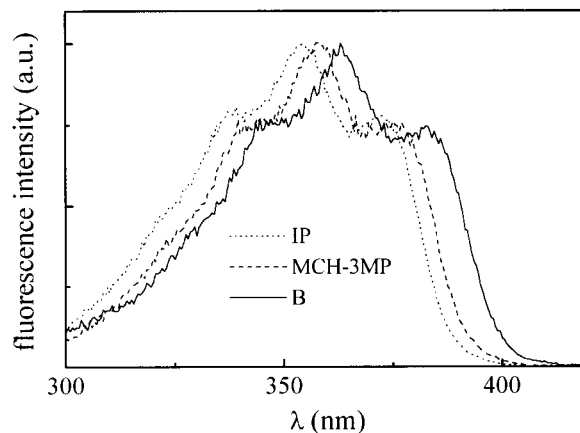

Figure 11. Normalized excitation fluorescence spectra of di(2-thienyl)-butadiene in solvents of different polarizabilities at room temperature.

(Table 4). As testified by the k_F value at room temperature, the lowest excited singlet state, of A_g symmetry, could be strongly vibronically coupled with the quasi-isoenergetic S_2 state of B_u character. When the temperature changed to 77 K, k_F increased more than 5 times, reaching in the rigid matrix a value similar to that of D2TE, whose S_1 state has a quasi-pure B_u character. To clarify the reason of the anomalous dependence of k_F on temperature, a detailed study of the solvent effect on the spectral shape and photophysical properties of D2TB was performed.

Figure 11 shows the fluorescence excitation spectra, which reproduce the corresponding absorption spectra, in solvents of different polarizability at room temperature. A substantial red-shift was observed on increasing α_S. In Table 7, the absorption and emission spectral maximums and the photophysical parameters in various solvents are reported together with the k_F^0 values. When α_S increases, ϕ_F and τ_F display an opposite behavior: the yield increases while the lifetime tends to decrease in nonpolar solvents. On the contrary, in BuCN both parameters decrease markedly.

These results clearly indicate the different role of polarity and polarizability on the excited-state properties of D2TB. The polarity reduces the energy barrier for rotation in the lowest excited states of both multiplicities, as found in other diarylethenes,[37] stabilizing the twisted ^{1,3}perp* configuration more than the "planar" ^{1,3}trans* ones, without altering the order of the S_1 and S_2 states.[30,32] This explains the decrease in the fluorescence yield and lifetime in BuCN. On the other hand, a more polarizable solvent stabilizes the $^1B_u^*$ state, where the electronic density is partially localized,[3,6] while the covalent $^1A_g^*$ state is not affected by changes in α_S thus modifying the state order and the mixing by vibronic coupling. The spectral data of Table 7 show that the $^1A_g \rightarrow {}^1B_u^*$ transition, which is responsible for the absorption spectrum, does strongly depend on the medium polarizability. Its energy decreases with increasing the α_S value, while the fluorescence transition is practically independent of α_S. This is because the emission has a small transition dipole, which points to a $^1A_g^*$ nature of the S_1 state. The proximity of the S_1 and S_2 states produces a large mixing leading to a rather high k_F value for the forbidden $^1A_g^* \rightarrow {}^1A_g$ transition.[28]

The k_F^0 values of Table 7, calculated by the integral of the absorption intensity (eq 20), were found to be independent of α_S. These findings indicate that the oscillator strength of the allowed $^1A_g \rightarrow {}^1B_u^*$ transition does not change with the solvent

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Table 7. Spectral and Photophysical Properties of the Di(2-thienyl)butadiene in Different Solvents at 293 K[a]

solvent	D (298 K)	α_S	η (cP, 293 K)	k_F^0 (10^7 s^{-1})	ϕ_F	τ_F (ns)	k_F (10^7 s^{-1})	absorption λ (nm)[b]	emission λ (nm)[b]
IP	1.828	0.2174	0.225	88	0.21	4.5	4.67	322.0[sh], 339.0, *354.5*, 363.0	*426.0*, 453.8[sh]
Do	2.002	0.2487	1.508		0.32	3.16	10.1	323.0[sh], 342.0, *359.0*, 378.0	*429.8*, 453.7[sh]
MCH/3MP	2.007	0.2522	0.6909	87	0.29	3.27	8.87	322.5[sh], 343.0, *357.2*, 377.0	*428.0*, 458.0[sh]
B	2.274	0.2947	0.6487	84	0.29	1.33	21.8	328.5[sh], 346.0, *363.0*, 382.5	397.0[sh], *427.0*, 457.6[sh]
BuCN	24.83	0.2337	0.5837		0.049	0.51	9.6	326.0[sh], 342.0, *358.0*, 377.0	*432.0*
MCH/3MP (233K)	2.053	0.2690	1.5203		0.40	3.22	12.4	328.0[sh], 345.0, *360.8*, 381.0	400.0[sh], *425.9*, 456.7[sh]

[a] The solvent characteristics at room temperature (dielectric constant, D, polarizability, α_S, and viscosity, η) are also reported. [b] The main maximum is in italics.
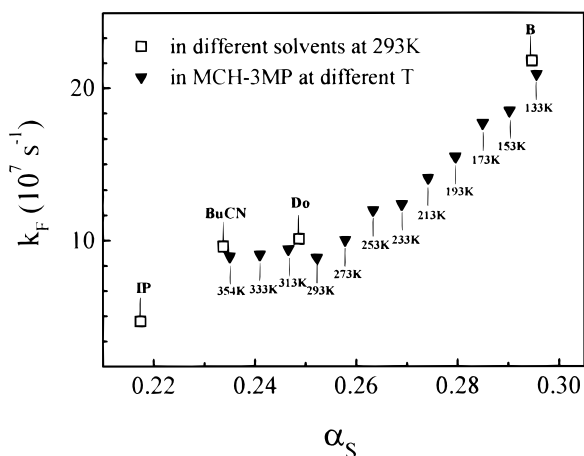
Figure 12. Plot of k_F as a function of α_S for di(2-thienyl)butadiene.

polarizability; namely, it does not depend on the mixing between S_1 and S_2, in agreement with previous results of theoretical calculations.[27b,28] Only in CS_2 at room temperature, the energy of the $S_1 \rightarrow S_0$ transition also decreases (its fluorescence maximum changes from 426 to 441 nm on going from MCH/3MP to CS_2, respectively) as does that for the absorption maximum, thus indicating a B_u nature of the lowest excited singlet states in these experimental conditions. This gives a satisfactory interpretation of the increase of k_F with α_S confirming that (i) fluorescence originates from a $^1A_g^*$ state that contains (at room temperature and in low-polarizability solvents, such as isopentane) a high degree of $^1B_u^*$ character; (ii) the increase in α_S leads to a smaller S_1-S_2 energy gap, thus increasing their mixing and then k_F. Figure 12 shows the trend of the radiative rate constant with α_S for various solvents at room temperature and for MCH/3MP at different temperatures. In fact, an increase in temperature leads to a small decrease in α_S due to the lowering in density and refraction index. As said above, these findings confirm the results of previous calculations which indicated that only the mixing of an allowed state, as $^1B_u^*$, into a lowest forbidden state, as $^1A_g^*$, has a noticeable effect on the natural lifetime, τ_F^0.[28]

The k_F values in Tables 4 and 7 show a nonlinear trend with α_S, in agreement with the dependence of k_F on the S_1-S_2 energy gap [$k_F \propto \Delta E(S_1-S_2)^2$], as found for DPhH.[27,38] This explains the temperature effect on k_F in MCH/3MP. In the other DTPs investigated, k_F was found not to depend on the solvent polarizability, probably because of a reduced state mixing produced by a larger S_1-S_2 energy gap.

The solvent viscosity does not change the ordering of states in the singlet manifold but can affect the spectral shapes and the photophysical parameters of such flexible molecules if the spectra are given by an overlap of electronic transitions

belonging to sets of different geometries near to the equilibrium one.[14,15] In Table 7, some fluorescence parameters of D2TP in MCH/3MP and in Do at room temperature are reported. These solvents have the same polarizability and different viscosity. The absorption spectrum in Do is ~2 nm bathochromically shifted with respect to that in MCH/3MP. This is consistent with the presence of a set of distorted geometries of the ground state in fluid media, which are forced to quasi-planar forms in more viscous solvents. Matching the viscosity of the two solvents by cooling the MCH/3MP to 233 K, the absorption spectrum in the latter solvent inverts its position, becoming now bathochromic by ~2 nm with respect to that in Do at 293 K. This is in agreement with the higher α_S of MCH/3MP at 233 K, which leads to a greater stabilization of the S_1 state of B_u character. The viscosity seems not to have substantial effects on k_F, which remains unchanged (within the experimental error). Only in a rigid matrix at low temperature was a marked increase of k_F (from 2.2×10^8 s^{-1} at 133 K to 5.1×10^8 s^{-1} at 77 K) observed, which can be due not only to the polarizability increase but also to a quasi-planar emitting geometry induced by the high viscosity of the matrix.

Conclusions

The results obtained with the present work gave interesting information on the effect of the thienyl side groups on the excited-state properties of DTPs. In particular, the influence of the chain length and of the chain position with respect to the sulfur atom on the mixing and ordering of the lowest excited singlet states of B_u and A_g character has been elucidated. The inversion of states occurs with $n \geq 2$ in MCH/3MP at room temperature, when S_1 acquires an A_g character and k_F starts decreasing. The increase of k_{IC} from $n = 2$ to $n = 4$ and its high value with $n = 1$ has been shown to be due to the changes in the S_1-S_0 energy gap and in the active modes of vibronic coupling (the role of the out-of-plane torsional modes decreases in the longer chain compounds and only the C=C stretching mode remains operative in the planarized compounds with $n = 4$, where the small value of $\Delta E (S_1-S_0)$ prevails in determining the high k_{IC}).[6]

There are several analogies between the behavior of DTPs and that of the corresponding DPhPs but also some important differences, particularly concerning the triplet yield which is favored by the presence of the sulfur heteroatom (mainly in the 3-thienyl compounds) which increases the spin–orbit coupling, particularly in the nonpolar solvent. This effect becomes less important for longer chain compounds.

The chain length is also important for the photoreactivity of these compounds. The kinetic rate constant of the activated torsional process drastically decreases when n increases, so that isomerization is the most important relaxation channel when $n = 1$ but becomes negligible in both S_1 and T_1 for $n = 3$ and 4, at least in nonpolar solvents.

The role of the polarity and polarizability of the solvents on

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the torsional barriers has been clearly substantiated: the polarity reduces the torsional barrier to trans → cis isomerization, thus confirming for these compounds the polar nature of the ^{1}perp* configuration, while the polarizability can change the order of the lowest singlet excited states of different nature, as observed for D2TB and D3TH.

This research allowed the emission from an upper singlet state of D3TB and the role of conformers in solutions of D3TH to be spectrally characterized. The latter deserves further attention in a later work.

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