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Effect of the chain length on the excited state properties of α-naphthyl,ω-phenyl-polyenes
Photobehaviour of hexatrienes

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Abstract

Three stereoisomers (EEE, EZE and ZEE) of 1-(1′-naphthyl),6-phenyl-hexatriene have been prepared by standard procedures and characterized by spectrophotometry and NMR spectroscopy. The properties of their lowest excited states of singlet and triplet multiplicity have been investigated by fluorimetry, laser flash photolysis and conventional photochemical techniques, and compared with those of the symmetric 1,6-diphenyl-hexatriene and the shorter chain analogues.

Keywords: Naphthyl-phenyl-hexatriene; Photoisomerization; Photophysics; Chain length effect

1. Introduction

During the last years, we have been interested in the effects of the nature of the aryl groups and of the chain length (n) on the excited state behaviour of the first members in the series of asymmetric α,ω-diarylpolyenes ($n = 1$ and 2) where one of the aryl groups was phenyl and the other a larger polycyclic aryl group of low S_1 and T_1 energy [1–4].

This investigation was firstly carried out on the ethene derivatives (the stilbene analogues). It was found that the excited state properties are determined at a large extent by the relative energies of the L_a and L_b states of the polycyclic aryls [1,3]. When one (or both) phenyl group(s) of stilbene is (are) replaced by polycyclic aryls of low S_1 energy (such as naphthyl, phenanthryl, pyrenyl and anthryl groups), the excitation energy is mainly localized in the condensed-ring group. The radiative decay then becomes the prevalent relaxation pathway while the twisting around the double bond is slowed down and is practically not operative in the presence of the larger aryls ("one-way" isomerization, only from *cis* to *trans*) [1–3,5,6]. The same behaviour has been widely described for photoisomerization in the triplet manifold [7].

More recently, we carried out a similar investigation on the corresponding butadiene derivatives [4]. The effect of the polycyclic groups was found in the same direction as that reported for ethenes but at a somewhat reduced extent due to a larger delocalization of the excitation energy in the longer unsaturated chain.

The present work aims to study the effect of a polycyclic group when the length of the olefin chain is further increased ($n = 3$). The model hydrocarbon, *all-trans*-1,6-diphenyl-1,3,5-hexatriene (DPH), the shortest term of the polyene series having certainly the first excited singlet state of ^1A_g character, has been studied in various laboratories [8–11]. The singlet deactivation occurs predominantly by fluorescence from both the ^1A_g and the upper (thermally equilibrated [12]) ^1B_u excited states and is accompanied by scarce photoisomerization and substantial internal conversion (IC). The triplet production is almost negligible in both non-polar and polar solvents [13]. Two main photoisomerization products of *EEE*–DPH were deeply investigated,

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EZE and ZEE. The reasonable mechanism proposed for photoisomerization, on the basis of temperature, solvent and deuterium isotope effects, involves both the two lowest excited singlet states and, possibly, upper excited states [11]. Most twisting of both side and central double bonds occurs prevalently in the singlet manifold [14]. A significant “one photon–two bonds” photoisomerization was observed in the EZE → ZEE direction. A marked increase of the quantum yield in polar solvents has been reported for the EEE → ZEE photoreactions, but rather smaller in the other cases. On the basis of this differential medium effect, it has been suggested that twisting about side and central double bonds leads to zwitterionic (^{1}PEE*) and biradicaloid (^{1}EPE*) perpendicular (P) intermediates, respectively [15].

This paper describes the photobehaviour of a DPH analogue where a phenyl group is replaced by a 1′-naphthyl group. The results obtained are discussed and compared with those of DPH and the shorter chain analogues.

2. Experimental

The l-(1′-naphthyl),6-phenyl-hexatriene (NPH) was prepared by the Wittig reaction between *E*-1-naphtho-3-propenale and *E*-triphenylcinnamylphosphonium-chloride. The aldehyde was prepared by the reaction between 1-naphthaldehyde and triphenylphosphoranylidene–acetaldehyde; the salt was prepared by reaction of *E*-cinnamylchloride with triphenylphosphine. All starting reagents were from Aldrich. The EEE and EZE stereoisomers were separated from the mixture of isomeric photoproducts by column chromatography and HPLC. The ZEE stereoisomer was obtained by irradiation of acetonitrile solution of EEE and separated by preparative HPLC.

NMR identification and assignment of the three isomers in solution was achieved by ^{1}H, ^{1}H-COSY and ^{1}H-NOESY measurements using Bruker DRX Avance 400 spectrometer. A preliminary analysis, based on the relative J_{HH} values of the *trans* and *cis* double bonds in the ^{1}H spectra, was then completed by 2D experiments in order to separate the contribution of overlapped peaks and to reach an unambiguous assignment. The ^{1}H-NOESY spectra were recorded with a mixing time of 800 ms and a relaxation delay of 1 s. For more detailed information, see Supplementary data.

Most photophysical and photochemical measurements were carried out in toluene or in a mixture of methylcyclohexane/3-methylpentane (MCH/3MP, 9/1 (v/v)), some others in benzene, isopentane (IP), acetonitrile (ACN) and carbon sulphide (CS_2). All solvents were of the highest purity degree from Fluka; MCH and 3 MP were purified before use by standard methods. For the NMR experiments, deuterated benzene (C_6D_6) from Cortec and chloroform ($CDCl_3$) from Aldrich were used.

The absorption measurements were carried out by a Perkin-Elmer Lambda 800 spectrophotometer. The fluorescence spectra were measured by a SPEX Fluorolog-2 F112AI spectrofluorimeter. The emission quantum yields (ϕ_F) were determined using 9,10-diphenylanthracene in cyclohexane, as standard ($\phi_F = 0.90$ [16]). The quantum yields reported in the tables are averages of at least three independent experiments with a mean deviation of ca. 5%. The fluorescence lifetimes (τ_F) (mean deviation of three independent experiments, ca. 7%) 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, monitored by HPLC, a 150 W high-pressure xenon lamp coupled with a monochromator and ferrioxalate actinometer were used (mean deviation of ca. 10%). The triplet properties were investigated by laser flash photolysis at 355 nm using the third harmonic of a Continuum (Surelite II) Nd:YAG laser. For chromatographic measurements a Waters apparatus was used equipped with a Simmetry C18 column (4.6 mm × 200 mm) and a UV detector coupled with an integrator (eluent: ACN/water mixtures).

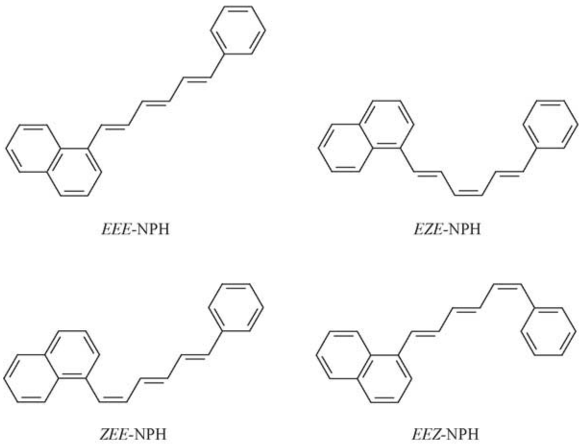
In the sensitized experiments, biacetyl or benzophenone in benzene and 2,3′-dithienylketone in MCH/3MP were used as triplet energy donors.

For the measurements with the various techniques at different temperatures, a cryostat (Oxford Instruments DN 1704) was used to control the temperature in the 200–373 K range. Unless otherwise specified, the measurements were carried out in solutions de-aerated by bubbling nitrogen.

3. Results and discussion

3.1. Photophysical behaviour of NPH

The absorption and emission spectra of the three available stereoisomers of NPH (EEE, EZE and ZEE, Scheme 1) in MCH/3MP, shown in Fig. 1, are very similar in shape, with higher intensity for the *all-trans* isomer. The spectra, red-shifted by about 15 nm with respect to the corresponding



Scheme 1.

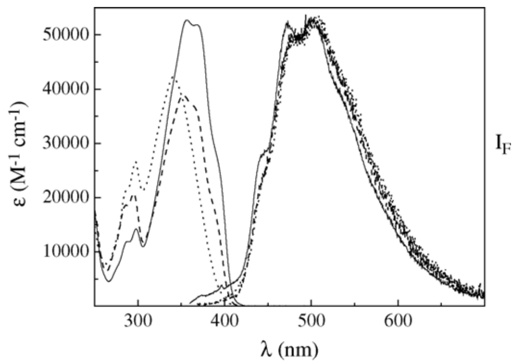


Fig. 1. Absorption and emission spectra of three stereoisomers (EEE, full, EZE, dashed and ZEE, dotted) of NPH in MCH/3MP.

dienes [4], show a main band around 360 nm and a more structured one around 300 nm. The emission spectra, markedly red-shifted, have maxima around 490 nm with a more resolved vibronic structure for EEE.

Table 1 collects the fluorescence properties of the three stereoisomers investigated in different solvents. The Stokes shift is rather large since the emission occurs from the lowest excited singlet state of predominant A_g parentage (the small radiative rate constant, k_F, indicates a forbidden transition), which is separated from the excited state reached by absorption, ^1B_u, by a relevant energy gap. An enhancement in the fluorescence quantum yield of EEE and a decrease in the fluorescence lifetime when the polarizability $[\alpha_s = (n^2 - 1)/(n^2 + 2)]$ of the solvent increases, leads to an increase in k_F, due to intensity borrowing from the closer (upper) state S_2, which is preferentially stabilized by the solvent of higher polarizability, whereas the energy of S_1 remains practically unchanged [12,17]. In any case, k_F is markedly lower than the value calculated by the Strickler–Berg relationship [18] [$k_F^0 = 9.4$, 6.9 and 7.4 ($10^8\ s^{-1}$) for EEE, EZE and ZEE, respectively, in MCH/3 MP]. The strong decrease of the fluorescence quantum yield and lifetime in CS_2 can be explained by the increase in the inter-system crossing due to the solvent-induced spin-orbit coupling.

Dual fluorescence was observed for the EEE and EZE compounds, as reported for *all-trans*-DPH [9,10,12,17,19,20]. In addition to the conventional emission from the lowest excited singlet state of A_g nature, an anti-Kasha emission from the thermally populated S_2 state was recorded in both cases as a blue (weak) shoulder of the spectrum. The observation of such emission, which generally depends on the S_1–S_2 energy gap and the lifetime, was particularly evident in solvents of low polarizability at high temperature. The effect of temperature is shown in Fig. 2.

Table 1
Fluorescence properties (τ_F (ns) and k_F ($10^7\ s^{-1}$)) of three isomers of NPH in different solvents at room temperature

Solvent	EEE isomer			EZE isomer			ZEE isomer		
	ϕ_F	τ_F	k_F	ϕ_F	τ_F	k_F	ϕ_F	τ_F	k_F
IP	0.13	11.3	1.2	0.06	9.2	0.7			
MCH/3MP	0.18	11.0	1.6	0.19	9.3	2.0	0.27	7.9	3.4
Toluene	0.34	9.8	3.5	0.24	9.3	2.6	0.35	7.1	4.9
CS_2	0.02	0.4	5.2	0.012	0.37	3.2			
ACN	0.18	10.2	1.8	0.13	9.6	1.4			

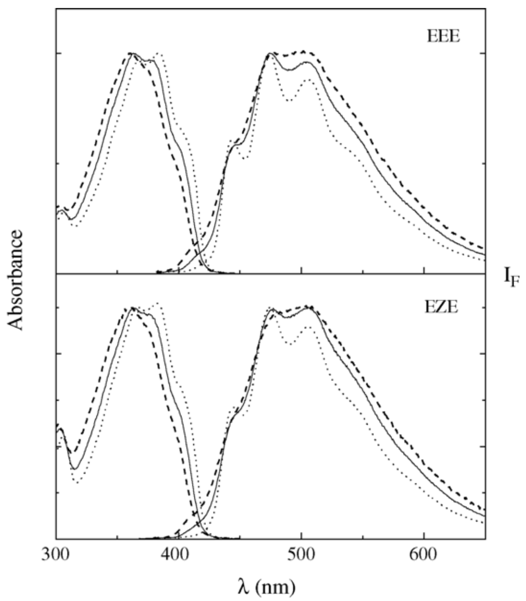


Fig. 2. Fluorescence excitation and emission spectra of the EEE and EZE isomers of NPH in toluene at 373 K (dashed), 293 K (full) and 200 K (dotted).

No clear evidence of ground-state conformational equilibria [21] was obtained for the three isomers from the effect of the excitation (λ_{exc}) and emission (λ_{em}) wavelength on the emission and excitation spectra, respectively. The fluorescence decay was always found to follow a monoexponential trend. This was expected since the equilibrium is largely shifted towards the more stable conformer both in the case of the internal rotation of the 1-naphthyl group [22,23], and of that around the C–C single bonds of the olefin chain [20]. Also for *EEE*-DPH, the *all-s-trans* conformation is generally considered as largely prevalent, even if a combined fluorimetric and statistical (principal component) analysis of the conformational equilibria allowed the emission of the *all-s-trans* to be separated from those of the *s-cis* conformers [20].

The $T_1 \rightarrow T_n$ absorption spectra, obtained from flash photolysis experiments on the three isomers of NPH, sensitized by 2,3′-dithienylketone in de-aerated MCH/3 MP (Fig. 3), showed the same shape with a maximum at 480 nm. A very small triplet yield was measured in benzene ($\phi_T \cong 0.01$ for EEE and 0.02 for EZE and ZEE). In this solvent the transient has a maximum absorption coefficient of 35,000 $M^{-1}\ cm^{-1}$ and decays with a lifetime depending on the olefin concentration (~70 μs at 10^{-6} M and ~30 μs at 3×10^{-5} M).

3.2. *Photochemical behaviour of NPH*

Table 2 collects the photoisomerization quantum yields for *EEE*-NPH in different experimental conditions. Its reactivity

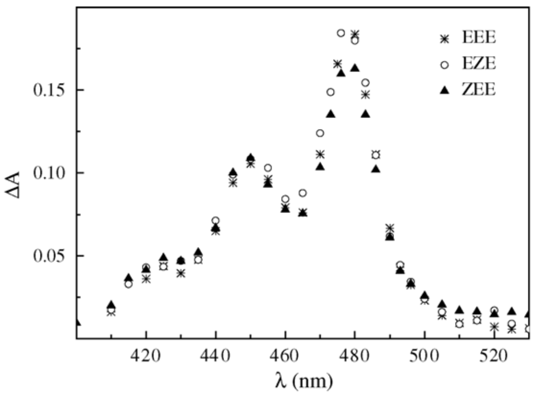


Fig. 3. $T_1 \rightarrow T_n$ absorption spectra of three stereoisomers of NPH sensitized by 2,3′-dithienylketone in MCH/3MP.

Table 2
Direct photoisomerization quantum yields of the EEE stereoisomer in two solvents

Solvent	Concentration (10^{-4} M)	$\phi_{EEE \rightarrow EZE}$	$\phi_{EEE \rightarrow ZEE}$	$\phi_{EEE \rightarrow EEZ}$
ACN	0.43	0.0017[a]	0.019[a]	
ACN	0.43	0.0037[b]	0.0082[b]	
Toluene	1.6	2.2×10^{-4}	5.5×10^{-5}	3.2×10^{-5}
Toluene	9.3	1.0×10^{-3}	3.5×10^{-4}	1.3×10^{-4}
Toluene	19	3.6×10^{-3}	1.3×10^{-3}	4.1×10^{-4}

[a] De-aerated.
[b] Oxygen saturated.

under direct excitation is very low. For the other stereoisomers investigated, the photoisomerization quantum yield is higher than 10% for ZEE, only ($\phi_{EZE \rightarrow EEE} = 0.078$ in ACN and 0.040 in toluene; $\phi_{ZEE \rightarrow EEE} = 0.12$ in toluene).

Excitation of EEE induced the rotation around the central double bond, towards the EZE isomer, and around the side double bond adjacent to the naphthyl group, towards the ZEE isomer. The formation of another, hardly detectable, photoproduct was also observed in toluene. It was tentatively assigned to the EEZ isomer, formed by rotation of the double bond adjacent to the phenyl group, on the basis of its absorption spectrum and reactivity. In fact, a small amount of this photoproduct, separated by HPLC and irradiated at 355 nm, underwent a back photoisomerization to the *all-trans* isomer, as the other two geometrical isomers with one double bond in *cis* configuration (EZE and ZEE, see above). The scarce amount obtained prevented a detailed study of the EEZ stereoisomer, however, the isomerization quantum yield roughly estimated in ACN for ZEE ($\phi_{ZEE \rightarrow EEE} \cong 0.4$) and EEZ ($\phi_{EEZ \rightarrow EEE} \cong 0.2$) showed a photobehaviour similar to that found for the asymmetric butadiene derivatives, where the isomerization of the double bond adjacent to the condensed-ring group was favoured [4].

The triplet-donor (biacetyl) sensitized isomerization yields for the three investigated stereoisomers in benzene are shown in Table 3. They point to substantial triplet reactivity, the efficiencies of the sensitized photoisomerization being quite high for both EZE and ZEE in dilute solutions ($\sim 10^{-4}$ M).

These quantum yields were found to increase with the concentration of the triplet energy acceptor, reaching values higher than 1 in the case of EZE and ZEE. This behaviour is due to the occurrence of a quantum chain process involving an energy transfer from a relatively long-lived triplet state to the ground-state isomers. As in the case of DPH [13], ^{3}*EEE*-NPH* cannot serve as a chain carrier for photoisomerization in the EEE → EZE and EEE → ZEE directions. In fact, a significant increase of the sensitized quantum yields was observed also in the case of EEE. An equilibrium mixture of the *all-trans* triplet, with small contributions of triplets with *cis* double bonds, provides the required chain carrier. Since the equilibrium distribution is dominated by the *all-trans* triplet, the sensitized photoisomerization of EZE and ZEE leads to EEE with high yield. In the case of ZEE, parallel formation of EZE was also observed, due to a “one photon – two bonds” isomerization in the triplet state. The sensitisation of EZE produced EEE only, the amounts of the other isomer being under the detection limit. Only in an experiment on the sensitized EZE photoreaction, where the conversion degree was unusually high (∼50%), a small production of ZEE (∼1%) was observed.

The photoisomerization quantum yields of EEE under direct irradiation were also found to depend on concentration, as shown in Table 2. This behaviour, together with the independence of the fluorescence lifetime of temperature (Table 4), suggests the weak reactivity of EEE to be mainly operative in the triplet manifold. Also for the other isomers (EZE and ZEE), a main triplet mechanism for isomerization in non-polar solvents is proposed on the basis of the non-negligible triplet quantum yields (see Section 3.1)

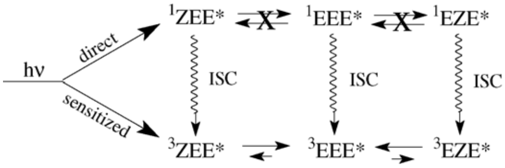
Table 3
Quantum yields of the sensitized photoisomerization of three stereoisomers of NPH as a function of concentration in benzene

EEE			EZE		ZEE		
Concentration (10^{-4} M)	$\phi^{sens}_{EEE \rightarrow EZE}$	$\phi^{sens}_{EEE \rightarrow ZEE}$	Concentration (10^{-4} M)	$\phi^{sens}_{EZE \rightarrow EEE}$	Concentration (10^{-4} M)	$\phi^{sens}_{ZEE \rightarrow EEE}$	$\phi^{sens}_{ZEE \rightarrow EZE}$
4.2	0.053	0.028	1.1	0.84	0.54	0.54	0.020
5.9	0.13	0.11	2.8	1.22	0.62	0.60	0.022
13	0.23	0.14	4.2	1.28	1.1	0.64	0.025
17	0.26	0.15	6.7	1.83	4.7	0.83	0.038
			11.0	3.15	7.5	1.06	0.039

Table 4
Temperature effect on the fluorescence lifetime of three stereoisomers of NPH in toluene

T (K)	τ_F (ns)		
	EEE	EZE	ZEE
373	9.35	8.09	6.17
353	9.17	8.40	6.56
333	9.36	8.67	7.02
313	9.44	8.98	7.37
293	10.2	9.01	7.30
250	10.1	9.36	7.41
200	10.4	10.07	7.28
ΔE (kcal/mol)	>10	6.7	9.6
A (10^{12} s^{-1})		0.1	10
k_{act} (10^6 s^{-1})		1.1	0.80

The derived Arrhenius parameters and kinetic constant at 293 K (k_{act}) for the activated process are also reported.



Scheme 2.

and the high barriers derived for the torsional process in S_1 (see Table 4) by the Arrhenius type equation

$$\ln\left(\frac{1}{\tau_F}-\frac{1}{\tau_F^{\lim}}\right)=\ln A-\frac{\Delta E}{RT}$$

($\tau_F^{\lim}$ is the fluorescence lifetime at low temperature where the activated process is inhibited).

The photoisomerization mechanism in non-polar solvent is schematically described in Scheme 2.

The reactivity of EEE increases of almost two orders of magnitude on going from the non-polar solvent to ACN due to a decrease in the torsional barrier in S_1 and the opening of a singlet mechanism for photoisomerization (Table 2). An interesting effect was found by bubbling oxygen in ACN solutions of EEE. An increase of the EEE → EZE quantum yield was observed, accompanied by a halved EEE → ZEE quantum yield. This behaviour was different from that described for the stereoselective O_2-induced photoisomerization of the *all-trans*-DPH [24], where an exciplex, formed by interaction of oxygen with DPH at a side (1 or 6) carbon atom, was proposed to collapse to a zwitterionic or biradicaloid species where rotation about the single bond at the benzylic position would favour the ZEE formation. The different behaviour observed in the present case is better explained by an O_2-catalyzed intersystem crossing to a more reactive triplet state.

3.3. Comparison with shorter chain analogues

Table 5 collects the photophysical and photochemical parameters of the diphenyl/naphthylphenyl pairs (n = 1, 2 and 3) of *trans* geometry to compare the effects of both the chain length and the naphthyl substitution on the relaxation of their excited states.

The effect of replacing a phenyl group with a polycyclic aryl group on the excited state properties of diarylpolyenes has been investigated in our laboratory, particularly for ethene and butadiene derivatives [1–4]. The peculiar effect was a marked increase in the radiative relaxation to detriment of photoisomerization. In non-polar solvents, the torsional energy barrier for twisting of the isomers in *trans* geometry was high in both the singlet and triplet manifolds of diarylpolyenes bearing condensed-ring groups. Therefore, the geometrical photoisomerization of the *trans* isomers of ethenes and dienes was found to occur with small quantum yields for the naphthyl and phenanthryl derivatives, and to be practically absent in the anthryl and pyrenyl derivatives. As to the naphthalene group, its lower S_1 energy compared with benzene leads to a localization of the excitation energy into the condensed-ring group. This produces an increase in the order of the isomerizable bonds with a consequent increase

Table 5
Photophysical and photochemical parameters of *all-trans*-NPH in MCH/3MP at room temperature compared with those of the symmetric (diphenyl-derivatives) and asymmetric (naphthyl-phenyl-derivatives) analogues with n = 1, 2 and 3

Compound	ϕ_F	τ_F (ns)	k_F (10^8 s^{-1})	k_F^0 (10^8 s^{-1})	ϕ_{ISO}
DPE [1,10,26]	0.04	0.070	5.7	9.7	0.48
DPB [25]	0.42	0.57	7.4	10.0	0.11
DPH	0.65 [8]	13.5 [8]	0.48	13.4	0.048 (→EZE) [15] 0.011 (→ZEE) [15]
NPE [23]	0.60	1.8	3.3	5.2	0.16
NPB [4]	0.98	4.7	2.1	7.9	0.026
NPH	0.18	11	0.16	9.4	2.2×10^4 (→EZE)[a] 5.5×10^{-5} (→ZEE)[a] 3.2×10^{-5} (→EEZ)[a]

[a] In toluene at 1.6×10^{-3} M.

in the torsional energy barrier and a decrease in the isomerization yield.

For the three symmetric, diphenyl-substituted, molecules (diphenylethene, DPE, diphenylbutadiene, DPB and DPH), lengthening of the chain leads to a progressive increase in the yield of the radiative pathway and to a decrease in the reactive one. On passing from stilbene to DPB, the k_F parameter increases, but decreases in DPH owing to the inversion in the order of the two lowest excited singlet states. The olefin chain character (B_u–A_g) of S_1 in diarylpolyenes is known to change from a net B_u character, when $n = 1$, to a net A_g character, when $n = 3$ or greater. The dienes, where the two states are almost degenerate, display an intermediate behaviour: their lowest emitting state has a predominant A_g character in low polarizability solvents, but a state inversion can occur if the polarizability is increased. This olefin character is somewhat perturbed by the interaction with the state localized in the side aryl group (L_a–L_b), the coupling between the allowed B_u and L_a states being expected to decrease in the longer chain homologues.

The participation of the olefin B_u state in the lowest excited states of the naphthyl/phenyl compounds (naphthylphenylethene, NPE, naphthylphenylbutadiene, NPB and NPH) is expected to decrease with respect to the diphenyl analogues, particularly when $n = 1$, where the naphthalenic character probably prevails. The replacement of a phenyl with a naphthyl group causes a shift of the absorption spectrum towards the red, due to a more extended conjugation. The radiative rate constant (k_F^0), calculated by the integral of the absorption intensity using the modified Strickler–Berg relationship, increases with the length of the olefin chain in both series of compounds, but the oscillator strength remains smaller in the naphthyl derivatives with respect to the corresponding diphenyl-derivatives because of the partial localization of the excitation energy on the naphthalene ring. Therefore, the state inversion is favoured for NPB, where the forbidden low-lying S_1 state borrows intensity from the allowed (very close) S_2 state, while the very small k_F value derived for NPH points to a high S_2–S_1 energy gap and to a consequent less efficient S_2–S_1 coupling with respect to DPH. The increased degree of forbidden character of the first electronic transition, as indicated by the decrease in the radiative kinetic parameter, leads to a further enhancement in the non-radiative relaxation with respect to the diphenyl analogue. This behaviour is probably due to a more conjugated system in which the forbidden covalent state is preferentially stabilized with respect to the ionic B_u state.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2005.03.007.

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