

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/239698329>

# Synthesis and spectrokinetic studies of spiro[thioxanthene-naphthopyrans]

ARTICLE in *TETRAHEDRON* · NOVEMBER 2002

Impact Factor: 2.64 · DOI: 10.1016/S0040-4020(02)01278-4

CITATIONS

35

READS

32

7 AUTHORS, INCLUDING:



**Paulo J Coelho**

Universidade de Trás-os-Montes e Alto Douro

61 PUBLICATIONS 553 CITATIONS

SEE PROFILE



**Luis M. Carvalho**

Universidade de Trás-os-Montes e Alto Douro

45 PUBLICATIONS 587 CITATIONS

SEE PROFILE



**Maria Manuel Oliveira**

Universidade de Trás-os-Montes e Alto Douro

48 PUBLICATIONS 324 CITATIONS

SEE PROFILE

# Synthesis and spectrokinetic studies of spiro[thioxanthene-naphthopyrans]

Paulo J. Coelho,<sup>a,\*</sup> Luis M. Carvalho,<sup>a</sup> Sofia Abrantes,<sup>a</sup> M. Manuel Oliveira,<sup>a</sup>  
Ana M. F. Oliveira-Campos,<sup>b</sup> Andre Samat<sup>c</sup> and Robert Guglielmetti<sup>c</sup>

<sup>a</sup>*Departamento de Química, Universidade de Trás-os-Montes e Alto Douro, 5001-911 Vila Real, Portugal*

<sup>b</sup>*Centro de Química, IBQF, Universidade do Minho, 4710 Braga, Portugal*

<sup>c</sup>*LCMOM, UMR 6114 CNRS, Université de la Méditerranée, 13288 Marseille Cedex 9, France*

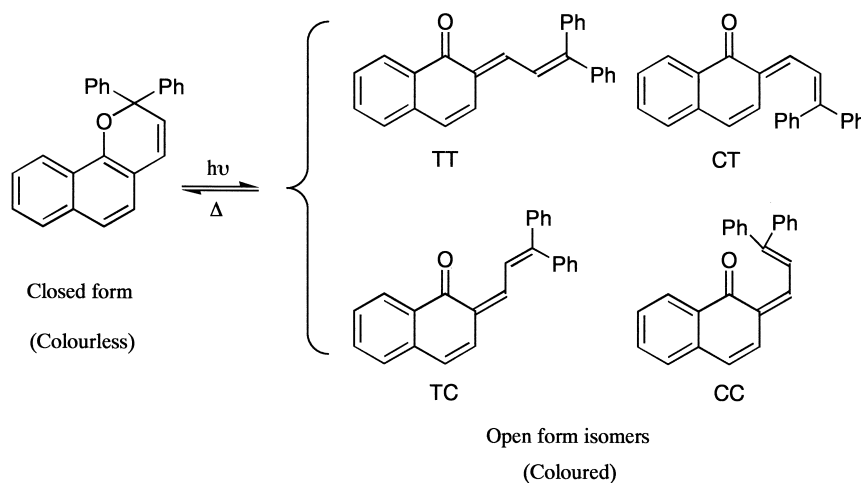
Received 22 April 2002; revised 1 July 2002; accepted 7 October 2002

**Abstract**—Several new spiro[thioxanthene-naphthopyrans] were prepared from substituted naphthols using a one step reaction. The photochromic properties of the new compounds were studied under flash photolysis and continuous irradiation. Compared to reference compounds general significant bathochromic shifts in the absorption spectra of the open forms, faster thermal bleaching kinetics and interesting fatigue resistances were observed. © 2002 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

Naphthopyrans are an important class of photochromic compounds and the classical molecules have the ability to generate a yellow colour on being irradiated with UV light. This photochromic behaviour is based on a photoinduced reversible opening of the pyran ring that converts the colourless form (the ‘closed form’), with non-interacting  $\pi$  systems, into a set of isomers with the pyran ring opened (the ‘open form’) (Scheme 1).<sup>1</sup>

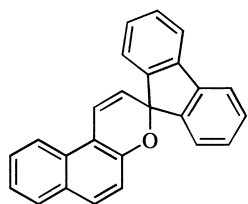
The change in the absorption spectrum is due to an extension of the conjugation in the open form. However, the open form is not completely planar, due to steric hindrance between the two phenyl groups. Linking the two phenyl groups seems a priori an obvious way to improve the conjugation. One approach was to link the two phenyl groups through a covalent C–C bond, thereby producing spiro[fluorene-naphthopyrans].<sup>2–4</sup> The photochromic properties of these compounds include a significant bathochromic shift of the maxima wavelength absorption in the



Scheme 1.

**Keywords:** photochromism; spiro[thioxanthene-naphthopyrans]; naphthopyrans; heterocycles; spectrokinetics.

\* Corresponding author. Tel.: +351-259-350284; fax: +351-259-350480; e-mail: pcoelho@utad.pt

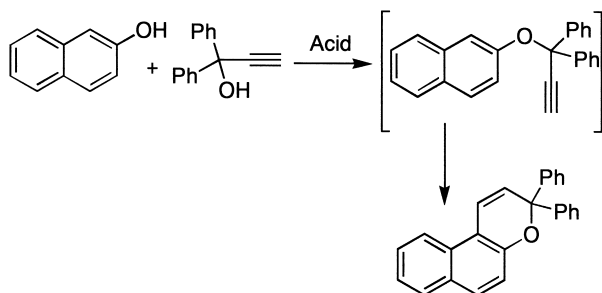


Spiro[fluorene-naphthopyran]

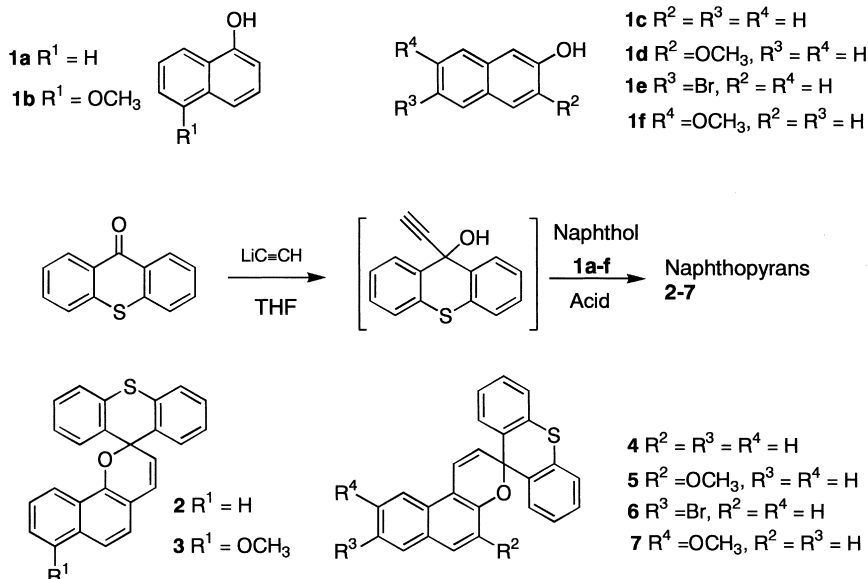
Scheme 2.

open form and, sometimes, an increase in colourability (Scheme 2).

Another possibility was to link the two phenyl groups through a heteroatom bridge. The photochromic behaviour of some spiro[xanthene-naphthopyrans] and spiro[thioxanthene-naphthopyrans]<sup>5</sup> has been known for some time. In the research reported on here, an easy way to prepare several spiro[thioxanthene-naphthopyrans] was developed, making possible the study of their photochromic properties. It should be pointed out that, while in the spiro[fluorene-naphthopyrans] the fluorene nucleus does not obey Hückel's rule for aromaticity (12  $\pi$  electrons), the thioxanthene nucleus constitutes a system with 14  $\pi$  electrons (a Hückel number) and therefore can be expected to be aromatic.



Scheme 3.



Scheme 4.

## 2. Results and discussion

### 2.1. Synthesis

A widely used method for synthesising 2,2-diarylnaphthopyrans involves the thermal condensation of a suitable 1,1-diarylprop-2-yn-1-ol with the naphthol under acid catalysis in an apolar solvent.<sup>6</sup> The propynol used can be either acquired commercially or prepared in the laboratory through the reaction of the appropriate diarylketone with sodium acetylide (Scheme 3).<sup>7</sup>

The preparation of spiro[thioxanthene-naphthopyrans] 2–7 requires the preparation of 9-hydroxy-9-ethynylthioxanthene. This alcohol was obtained through the reaction of thioxanthone with lithium acetylide–ethylenediamine complex in dry THF at room temperature (thioxanthone was found not to react with the corresponding sodium acetylide). We were not successful in isolating this alcohol, as all attempts led to an extensive product degradation. Thus, the reaction with naphthols **1a–f** was performed using the crude reaction mixture, after hydrolysis, using pyridinium *p*-toluenesulfonate (PPTS) as the acid catalyst. Naphthopyrans **2–7** were obtained in low to medium yield (Scheme 4).

### 2.2. Photochromic properties

The photochromic behaviour of the synthesised compounds was observed under flash and continuous irradiation. Both methods are extensively used to quantify the spectrokinetic parameters of organic photochromes, although the information obtained by the two methods can be quite distinct, since the time scales of observation and the light flux intensity applied are completely different. Methods employing continuous irradiation use a longer irradiation time and a lower light flux intensity and operate in experimental conditions quite comparable to those that are found in applications where sunlight activation is intended. They are particularly well suited for the study of slow

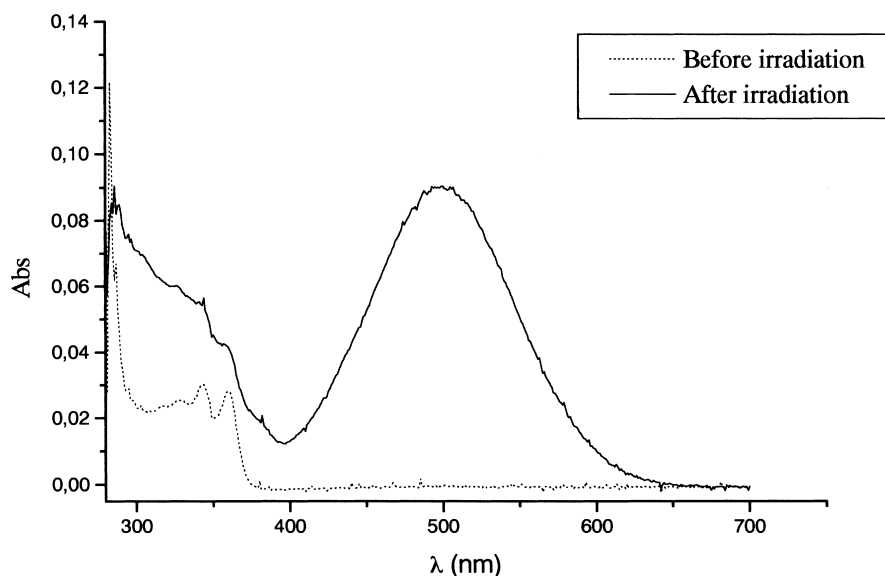


Figure 1. UV/vis absorption spectra of uncoloured (···) and coloured species (—) of naphthopyran **2** in toluene.

photochromic systems such as those used in photochromic lenses.

During continuous irradiation, the open forms are constituted but only the photoisomers with the longest lifetimes accumulate and can be observed. The spectrokinetic analysis is based on assessment of photochemical and thermal equilibrium (photostationary state) reached, or the reaction progress. The kinetics of decolouration is studied in the absence of light (thermal process) or, if desired, under irradiation with a different light (photochemical process). Under continuous irradiation, the usual relevant spectrokinetic parameters are  $A_{eq}$  (the average absorbance attained in the photostationary state) and  $k_{\Delta}$  (the rate constants of thermal bleaching) (Figs. 1 and 2).

The spectrokinetic parameters obtained under continuous irradiation and the usual relevant parameters used to characterise the photochromic behaviour under flash photolysis (namely, the wavelength maxima of the coloured form, colourability and rate constant of thermal bleaching) are summarized in Table 1. In the same table, two reference diphenylnaphthopyrans (Ref 1 and Ref 2) and a spiro[fluorene-3*H*-naphtho[2,1-*b*]pyran] (Ref. 3) are included for comparison.<sup>8</sup>

### 2.2.1. Spectrokinetic studies under flash photolysis.

Under these conditions, all the synthesised compounds exhibit photochromic behaviour, at room temperature in toluene solutions. Compared to the reference naphthopyrans, the effects of linking the phenyl groups through the

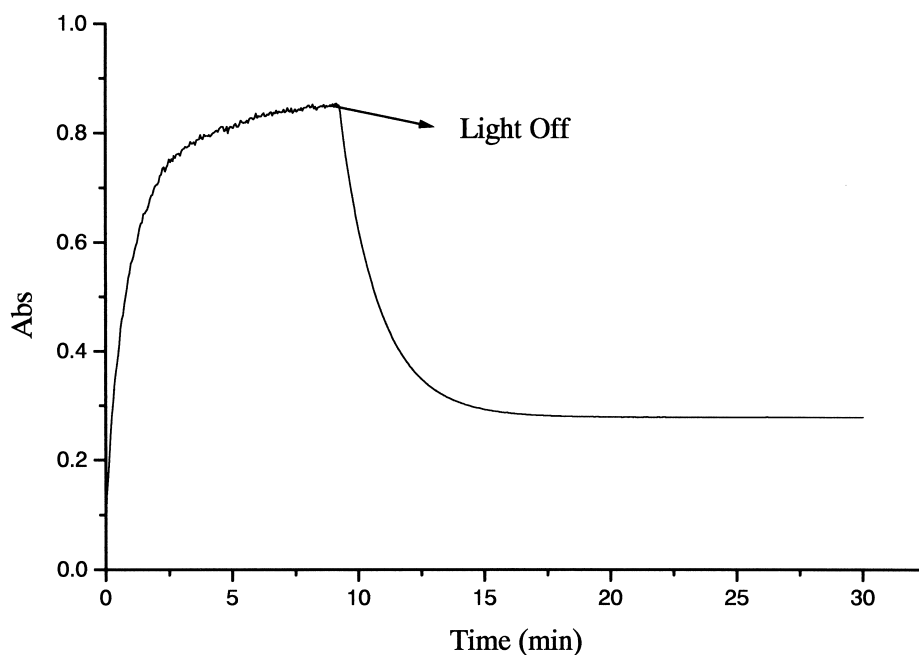
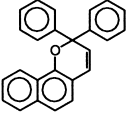
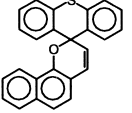
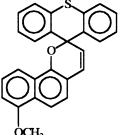
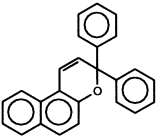
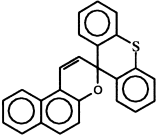
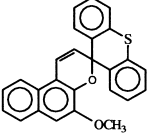
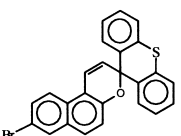
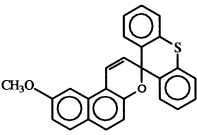
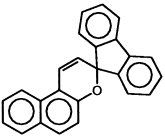


Figure 2. Kinetics of thermal relaxation of compound **2** after UV continuous irradiation.

**Table 1.** Spectrokinetic properties under flash photolysis and continuous irradiation: maxima wavelengths of the coloured form ( $\lambda_1$ ,  $\lambda_2$ ), colourability ( $A_{01}$ ,  $A_{02}$  are the absorbance just after the flash respectively at  $\lambda_1$  and  $\lambda_2$ ), thermal bleaching rate ( $k_{\Delta}$ ) of compounds **2–7**, three reference compounds in toluene solutions: Ref 1=2,2-diphenyl-2H-naphtho[1,2-*b*]pyran, Ref 2=3,3-diphenyl-3H-naphtho[2,1-*b*]pyran, Ref 3=spiro[fluorene-3H-naphtho[2,1-*b*]pyran] and some results concerning photodegradation

Flash photolysis								Continuous irradiation		
Compound	Structure	Annellation	$\lambda_1$ (nm)	$A_{01}$	$\lambda_2$ (nm)	$A_{02}$	$k_{\Delta}$ (s <sup>-1</sup> ) (%)	Photodegradation $t(A_0/2)$ (min)	$A_{eq}$	$k_{\Delta}$ (s <sup>-1</sup> ) (%)
Ref 1 <sup>3,4</sup>		[7,8]	403	1.08	481	1.62	0.002	Very low		
<b>2</b>		[7,8]	510	0.76			0.024 (45), 0.010 (55)	128	0.85	0.011
<b>3</b>		[7,8]	528	0.83			0.031 (42), 0.013 (58)		0.84	0.013
Ref 2 <sup>3,4</sup>		[5,6]	432	0.84			0.090	509	0.21	0.07 (80), 0.003 (20)
<b>4</b>		[5,6]	490	1.00			0.40 (87), 0.064 (13)	429	0.19	0.23
<b>5</b>		[5,6]	483	0.99			0.21 (84), 0.043 (16)		0.22	0.14
<b>6</b>		[5,6]	502	1.10			1.03 (90), 0.12 (10)		0.13	0.46
<b>7</b>		[5,6]	473	0.90			0.30 (93), 0.041 (7)		0.20	0.17
Ref 3 <sup>3,4</sup>		[5,6]	453	1.31			0.08 (62), 0.02 (38)	78	0.23	0.10 (66), 0.0003 (34)

sulphur bridge was always to induce a strong bathochromic shift in the spectra of the open forms. This points to an increased participation of each phenyl nucleus, leading to an extensive  $\pi$ -conjugation in the open forms. A similar effect was already observed in the corresponding spiro[fluorene-naphthopyrans], regardless of the type of annellation or the presence of a fused heterocycle.<sup>3</sup>

As observed with the reference 5,6-annellated naphthopyran (Ref 2) and the corresponding spiro[fluorene-3*H*-naphthopyran] (Ref 3), the absorption spectra of the open forms of compounds **4–7** (spiro[thioxanthene-3*H*-naphthopyrans] with the same type of annellation) exhibit a single absorption band. Compounds **2** and **3** and, in general, the corresponding spiro[fluorene-2*H*-naphthopyrans] behaved similarly, in contrast to the open form of the corresponding reference naphthopyran (Ref 1) which displays two absorption bands.

The colourabilities of all the described compounds, though not of particular interest, are very similar. This may indicate that the sulphur bridge has only a minor influence in the process that leads to the coloured forms.

With regard to the ring closure kinetics, all the described compounds exhibit two phases, with variable amplitudes, in contrast to the kinetics observed for the reference compounds. The slow fading rate is normally attributed to the most stable *transoid* isomer. As usually observed, 2*H*-chromenes with a 7,8-annellation exhibit a slower thermal bleaching rate compared to 5,6 annellated 2*H*-chromenes, due to large non-bonding interactions in the open forms of the latter. Compared to the reference compounds, it can be observed that all the open forms of the new described compounds are less thermally stable (faster kinetics of ring closure). One possible explanation is that the linkage of the phenyl groups through a sulphur bridge promotes some strain in the 'planar' open forms, decreasing their thermal stability. This effect is not observed in spiro[fluorene-2*H*-naphthopyrans] (C–C bridge), particularly with a 7,8-annellation type.<sup>4</sup> The thermal bleaching rates observed with spiro[thioxanthene-naphthopyrans] **2** and **3** makes them promising compounds for applications in organic photochromic lenses.

The effects of the assayed substitutions in the colourability are modest and variable, indicating that the kind of substitution used may not contribute to an enhancement of the quantum yield for photocoloration. When the bleaching kinetics are considered, compound **6** exhibits a faster kinetics of ring closure, indicating that with bromine (a weak electron-withdrawing substituent) at the 8-position, ring closure rates are generally faster. Compounds **5** and **7** indicate that the presence of an electron-donating group such as methoxy, at the 5- and 9- positions (5,6 annellation type), has little effect on the kinetics. The same can be observed with compound **3** (7,8 annellation type) where the methoxy group is located at the 7-position.

**2.2.2. Spectrokinetic studies under continuous irradiation.** All compounds exhibited a relevant residual colour at the end of the measurements (absorbances between 0.1 and 0.3). As a result, under continuous irradiation, the fading

processes seem to have only one kinetic phase (apparently monoexponential bleaching kinetics). In each case, the residual colour can be attributed to a very stable open form (very low second kinetic constant) or to the degradation of the coloured products that mask a possible second kinetic phase, preventing its evaluation. The same phenomenon makes it difficult to attain a photostationary state, as the colour intensity of the solution increases continuously throughout the irradiation.

This indicates that there is a difference between the photoproducts present in the mixture obtained after irradiation in both methods. In part, this is confirmed by the absence of correlation between the slower fading kinetics observed under flash irradiation and the fading kinetics observed under continuous irradiation (except for compounds **2** and **3**).

A good correlation can be observed between the colourabilities obtained in both methods, although the observed colourabilities under continuous irradiation could not be accurately evaluated. Normally under continuous irradiation, the colourabilities are lower. This difference can be explained as  $A_0$  is dependent on the quantum yield of the photochemical colouration and on the absorptivity of the open forms, while  $A_{eq}$  is also inversely proportional to the rate constant of the thermal bleaching reaction.<sup>9</sup> A faster thermal decoloration means a lower  $A_{eq}$ . Compounds **2** and **3** (7,8- annellation type), exhibit slower kinetics of decoloration and the observed  $A_{eq}$  are similar to the colourabilities observed under flash photolysis and almost four times greater than the colourabilities obtained under continuous irradiation for the remaining compounds. With regard to the resistance to photodegradation, the spiro[thioxanthene-naphthopyran] compounds behave in an interesting manner (Table 1): for compound **4**,  $t(A_0/2)=429$  min is comparable to that of 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran (Ref 2, 509 min) and better than spiro[fluorene-3*H*-naphtho[2,1-*b*]pyran] (Ref 3, 78 min); compound **2** exhibits a  $t(A_0/2)=128$  min that is much better than the behaviour of the corresponding naphthopyran (Ref 1).

### 3. Conclusion

The linkage of the two C-sp<sup>3</sup> phenyl groups in diphenyl-naphthopyrans through a sulphur bridge was achieved by a simple and generally-applicable method, producing low to moderate yields. This strategy led to the achievement of novel photochromic spiro[thioxanthene-naphthopyrans] that exhibit a remarkable fatigue resistance and substantial bathochromic shifts in the absorption spectra of the open forms. The observed shifts were greater than those observed for the corresponding spiro[fluorene-2*H*-naphthopyrans], suggesting that the sulphur bridge is an efficient way to increase the participation of each phenyl nucleus in the  $\pi$ -conjugation of the open forms, and which gives at the same time, an aromatic character to that part of the molecule. Compared to the reference naphthopyrans, no modifications seem to occur in the photocoloration efficiencies, as no significant changes were observed in the colourabilities of the novel compounds. Fading kinetics

studies performed under flash photolysis and continuous irradiation indicate that the nature of the photoproducts present in the mixtures obtained after irradiation, was different.

## 4. Experimental

### 4.1. Spectrokinetic measurements

**4.1.1. Flash photolysis.** For the determination of  $\lambda_1$  and  $\lambda_2$ ,  $A_{01}$  and  $A_{02}$ , and  $k_{\Delta}$ ,  $5 \times 10^{-5}$  mol dm $^{-3}$  toluene solutions were used. The flash photolysis apparatus was monitored by a Warner and Swasey rapid spectrometer,<sup>10</sup> allowing to record visible absorption spectra of the coloured forms in the 400–700 nm range (acquisition time 1 ms, repetitivity 1.25 ms). Flashes (duration 50  $\mu$ s) were generated by two xenon tubes with a quartz envelope. The energy of the flashes was 60 J for the whole polychromatic emission spectrum. For measurements, thermostated (25°C) 100 mm cylindrical cells were used. The light from the analysis lamp (50 W, quartz-iodide) was filtered using a Schott GG400 high-pass filter. In a preliminary experiment, the visible absorption spectrum and the  $\lambda_1$  and  $\lambda_2$  of the open form were determined. In a second experiment the initial absorbances  $A_{01}$  and  $A_{02}$  were measured and then the decrease in the absorbance with the time was monitored. The rate constants were calculated using a bi-exponential model.

**4.1.2. Continuous irradiation.** For the determination of absorption spectra of closed form and open form  $1 \times 10^{-5}$  mol dm $^{-3}$  toluene solutions were used. Determinations of  $\lambda_{\max}$  were made with a light flux of 4 W m $^{-2}$ . For measurements of  $A_{\text{eq}}$  and  $k_{\Delta}$  under continuous irradiation,  $1 \times 10^{-4}$  mol dm $^{-3}$  toluene solutions were used. The apparatus was monitored by a CARY 50 Varian spectrometer (2.0 nm spectral band pass) with a Xenon lamp (Ushio type UXL-150SO/Oriel Instruments). For measurements, thermostated (20°C) 10 mm cells were used. The irradiation was carried out in the spectrophotometer holder at the right angle to the monitoring beam, using a fibre-optic system. The relaxation kinetics for both methods was calculated using Origin 5.0 Professional program. The resistance to the fatigue under irradiation was determined on an appropriate Degraphot apparatus in toluene solution.<sup>11</sup>

### 4.2. General remarks

$^1\text{H}$  spectra were recorded in  $\text{CDCl}_3$  on a Varian Unity Plus at 300 MHz.  $^{13}\text{C}$  spectra were recorded in  $\text{CDCl}_3$  on a Varian Unity Plus at 75.4 MHz. IR spectra were recorded on a Perkin–Elmer FTIR 1600 spectrometer, wave numbers in  $\text{cm}^{-1}$ ; Mass spectra were measured on a AutoSpecE spectrometer. Melting points are uncorrected. Column chromatography was performed on silica gel 60 (70–230 mesh).

### 4.3. Preparation of spiro[tioxanthene-naphthopyrans] (2–7): general procedure

A suspension of thioxanthone (2 g, 9.4 mmol), and lithium acetylide (3 g, 29.4 mmol) in dry THF (250 ml) was stirred

under an argon atmosphere for 24 h. The suspension was treated with water (200 ml) and the aqueous phase extracted with ethyl ether (3 $\times$ 100 ml). The organic phase was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and the solvent evaporated leaving the crude 9-hydroxy-9-ethynylthioxanthene as a dark yellow oil. To this oil was added the naphthol **1a–f** (250 mg), PPTS (50 mg) and 60 ml of chloroform. This solution was refluxed for 24 h under an argon atmosphere. Solvent evaporation gave a brown oil which was purified by silica gel column chromatography (ethyl acetate/hexane 0–10%). Recrystallization from  $\text{CHCl}_3/\text{CH}_3\text{OH}$  gave a crystalline material.

**4.3.1. Spiro[2H-naphtho[1,2-*b*]pyran-2,9'-[9H]-thioxanthene] 2.** 18% yield. Mp 160–163°C; IR: 3050, 1652, 1565, 1454, 1265, 1205, 1105;  $^1\text{H}$  NMR: 8.40 (m, 1H), 7.83 (m, 1H), 7.75 (m, 2H), 7.72 (m, 4H), 7.44 (d,  $J=10$  Hz, 1H), 7.30–7.22 (m, 4H), 7.16 (d,  $J=8$  Hz, 1H), 6.45 (d,  $J=10$  Hz, 1H), 6.17 (d,  $J=10$  Hz, 1H);  $^{13}\text{C}$  NMR: 147.73, 138.71, 134.95, 129.15, 127.80, 127.50, 126.98, 126.75, 126.49, 126.09, 125.88, 124.61, 123.72, 121.82, 121.43, 121.39, 120.57, 113.24, 80.35; MS:  $m/z$  (%): 221 (50), 337 (10), 364 ( $\text{M}^+$ , 100). Exact mass for  $\text{C}_{25}\text{H}_{16}\text{OS}$ : 364.092187. Found 364.091103.

**4.3.2. 7-Methoxy-spiro[2H-naphtho[1,2-*b*]pyran-2,9'-[9H]-thioxanthene] 3.** 19% yield. Mp 206–208°C; IR: 3066, 2929, 1648, 1596, 1508, 1400, 1263, 1203, 1074;  $^1\text{H}$  NMR: 7.97 (d,  $J=9$  Hz, 1H), 7.84 (d,  $J=8.7$  Hz, 1H), 7.74 (m, 2H), 7.50 (m, 2H), 7.44 (t,  $J=8.4$  Hz, 1H), 7.30–7.20 (m, 4H), 7.14 (d,  $J=8.4$  Hz, 1H), 6.88 (d,  $J=7.5$  Hz, 1H), 6.44 (d,  $J=9.9$  Hz, 1H), 6.17 (d,  $J=9.9$  Hz, 1H), 4.04 (s,  $\text{CH}_3\text{O}$ , 3H);  $^{13}\text{C}$  NMR: 155.42, 147.62, 138.76, 129.12, 127.46, 126.97, 126.73, 126.04, 125.97, 124.72, 123.79, 121.60, 121.41, 114.69, 114.05, 113.84, 104.63, 104.63, 80.31, 55.53; MS:  $m/z$  (%): 189 (10), 197 (10), 221 (40), 367 (10), 394 ( $\text{M}^+$ , 100). Exact mass for  $\text{C}_{26}\text{H}_{18}\text{O}_2\text{S}$ : 394.102752. Found 394.102658.

**4.3.3. Spiro[3H-naphtho[2,1-*b*]pyran-3,9'-[9H]-thioxanthene] 4.** 58% yield. Mp 153–155°C; IR: 3056, 1633, 1577, 1452, 1203, 1105;  $^1\text{H}$  NMR: 7.94 (d,  $J=10.2$  Hz, 1H), 7.83 (m, 4H), 7.50 (m, 3H), 7.38 (t,  $J=9$  Hz, 1H), 7.36 (d,  $J=9$  Hz, 1H), 7.30–7.20 (m, 4H), 7.05 (d,  $J=10.2$  Hz, 1H), 6.21 (d,  $J=10.2$  Hz, 1H);  $^{13}\text{C}$  NMR: 150.88, 138.34, 130.31, 129.64, 129.41, 129.07, 128.53, 127.59, 126.84, 126.80, 126.67, 126.11, 123.65, 121.85, 121.09, 117.18, 116.61, 111.33, 79.62; MS:  $m/z$  (%): 139 (20), 196 (15), 221 (45), 287 (10), 336 (15), 364 ( $\text{M}^+$ , 100). Exact mass for  $\text{C}_{25}\text{H}_{16}\text{OS}$ : 364.092187. Found 364.091517.

**4.3.4. 5-Methoxy-spiro[3H-naphtho[2,1-*b*]pyran-3,9'-[9H]-thioxanthene] 5.** 9% yield. Mp 162–164°C; IR: 3062, 2958, 1641, 1592, 1509, 1450, 1251, 1118, 1012;  $^1\text{H}$  NMR: 7.90–7.70 (m, 4H), 7.52–7.42 (m, 2H), 7.42–7.32 (m, 2H), 7.30–7.22 (m, 5H), 6.99 (d,  $J=10.2$  Hz, 1H), 6.23 (d,  $J=10.2$  Hz, 1H), 4.09 (s,  $\text{CH}_3\text{O}$ , 3H).  $^{13}\text{C}$  NMR: 147.89, 142.49, 138.51, 129.44, 128.84, 127.58, 127.12, 127.01, 126.66, 125.74, 124.81, 124.48, 124.30, 122.15, 120.96, 116.28, 112.28, 108.02, 79.86, 56.01; MS:  $m/z$  (%): 160 (10), 189 (12), 197 (15), 221 (30), 321 (20), 377 (10), 394 ( $\text{M}^+$ , 100). Exact mass for  $\text{C}_{26}\text{H}_{18}\text{O}_2\text{S}$ : 394.102752. Found 394.103555.



**4.3.5. 8-Bromo-spiro[3H-naphtho[2,1-b]pyran-3,9'-[9H]-thioxanthene] 6.** 18% yield. Mp 246–247°C; IR: 3056, 1641, 1581, 1500, 1459, 1243, 1195, 1074, 1010; <sup>1</sup>H NMR: 7.95 (d, *J*=1.8 Hz, 1H), 7.79 (m, 3H), 7.71 (d, *J*=9 Hz, 1H), 7.53 (dd, *J*=2.1, 9 Hz, 1H), 7.50 (m, 2H), 7.36 (d, *J*=9 Hz, 1H), 7.30–7.23 (m, 4H), 6.98 (d, *J*=9.9 Hz, 1H), 6.22 (d, *J*=9.9 Hz, 1H); <sup>13</sup>C NMR: 151.07, 138.10, 130.57, 130.44, 129.97, 129.31, 129.13, 128.18, 127.72, 126.90, 126.76, 126.08, 122.97, 122.50, 118.34, 117.39, 116.25, 111.62, 79.80; MS: *m/z* (%): 152 (15), 181 (35), 196 (25), 221 (65), 332 (16), 363 (14), 414 (12), 442 (M<sup>+</sup>, 98), 444 (M+2, 100). Exact mass for C<sub>25</sub>H<sub>15</sub>OSBr: 442.002698. Found 442.004410.

**4.3.6. 9-Methoxy-spiro[3H-naphtho[2,1-b]pyran-3,9'-[9H]-thioxanthene] 7.** 61% yield. Mp 149–151°C; IR: 3056, 2929; 1621, 1513, 1459, 1238, 1195, 1033; <sup>1</sup>H NMR: 7.82 (m, 2H), 7.73 (d, *J*=9.6 Hz, 1H), 7.70 (d, *J*=9.6 Hz, 1H), 7.35 (m, 2H), 7.30–7.24 (m, 5H), 7.19 (d, *J*=2 Hz, 1H), 7.03 (dd, *J*=2.1, 9 Hz, 1H), 6.96 (d, *J*=10.2 Hz, 1H), 6.18 (d, *J*=10.2 Hz, 1H), 3.91 (s, CH<sub>3</sub>O, 3H); <sup>13</sup>C NMR: 158.62, 151.61, 138.46, 131.03, 130.13, 130.08, 129.60, 127.55, 126.84, 126.68, 126.00, 124.83, 121.36, 116.75, 115.87, 114.61, 110.60, 100.25, 79.51, 55.18; MS: *m/z* (%): 152 (10), 197 (25), 221 (40), 317 (12), 363 (17), 379 (14), 394 (M<sup>+</sup>, 100). Exact mass for C<sub>26</sub>H<sub>18</sub>O<sub>2</sub>S: 394.102752. Found 394.102485.

#### Acknowledgements

We thank FCT (Portugal's Foundation for Science and Technology) for financial support through project Praxis XXI/P/QUI/10021/1998, Elisa Pinto for NMR spectra monitoring, R. Dubest and J. Aubard (University of Paris

VII, France) for their help in the evaluation of spectrokinetic data by flash photolysis.

#### References

1. Van Gemert, B. *Organic Photochromic and Thermochromic Compounds*, Crano, J. C., Guglielmetti, R. J., Eds.; Kluwer Academic/Plenum: New York, 1999; Vol. 1, pp 111–140 Chapter 3.
2. Aldoshin, S.; Chuev, I.; Filipenko, O.; Pozzo, J. L.; Lokshin, V.; Pepe, G. *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.* **1998**, *54*, 1720–1722.
3. Harié, G. PhD Thesis. Université de la Méditerranée, Marseille, 1996.
4. Pozzo, J. L.; Guglielmetti, R.; Lokshin, V.; Samat, A.; Harié G. Eur. Pat. 0,676,401, 1995.
5. Brown, G. H. In *Photochromism*. Bertelson, R. C., Ed.; Wiley Interscience: New York, 1971; p 55 Chapter 3.
6. Iwai, I.; Ide, J. *Chem. Pharm. Bull.* **1963**, *11*, 1042.
7. Moustrou, C.; Rebière, N.; Samat, A.; Guglielmetti, R.; Yassar, R.; Dubest, R.; Aubard, J. *Helv. Chim. Acta* **1998**, *81*, 1293.
8. Pozzo, J. L.; Lokshin, V.; Samat, A.; Guglielmetti, R.; Dubest, R.; Aubard, J. *J. Photochem. Photobiol. A: Chem.* **1998**, *114*, 185–191.
9. Micheau, J. C. *Organic Photochromic and Thermochromic Compounds*, Crano, J. C., Guglielmetti, R. J., Eds.; Kluwer Academic/Plenum: New York, 1999; Vol. 2, pp 167–209 Chapter 3.
10. Kellmann, A.; Tübel, F.; Dubest, R.; Levoir, P.; Aubard, J.; Pottier, E.; Guglielmetti, R. *J. Photochem. Photobiol. A: Chem.* **1989**, *49*, 63–73.
11. Dubest, R.; Levoir, P.; Meyer, J. J.; Aubard, J.; Baillet, G.; Gusti, G.; Guglielmetti, R. *Rev. Sci. Instrum.* **1993**, *64*, 1803.