Studies under Continuous Irradiation of Photochromic Spiro[fluorenopyran-thioxanthenes]

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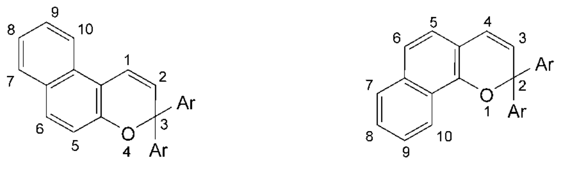
New indeno-fused spiro[benzopyran-thioxanthenes] were synthesized (see **3a** – **d** in *Scheme 3*) and their photochromic properties evaluated under continuous irradiation (*Table 1*). When submitted to irradiation for several minutes with a Xe lamp, the system behaved as one constituted by two open colored forms with different thermal bleaching rates and different susceptibilities to degradation. An increase in irradiation time led to significant degradation and to the apparent predominance of the open colored form with the faster bleaching rate.

1. Introduction. – In recent decades, the synthesis of new molecules with photochromic properties such as naphtho- and benzopyrans (*Fig. 1*), spirooxazines, spiropyrans, *etc.*, has attracted the attention of several academic and industrial research groups [1].

These molecules have the ability to undergo a reversible transformation between two states with different absorption spectra, induced, in at least one direction, by electromagnetic radiation. If the photoactivated state absorbs in the VIS region of the spectrum, a noticeable coloring/bleaching cycle can occur as a consequence of an irradiation/dark cycle. This makes these systems particularly useful for the production of variable-transmission optical materials, such as eyewear that darkens under sunlight [2].

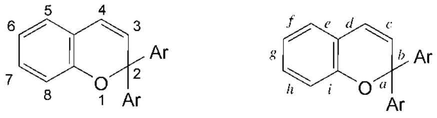
For the majority of naphtho- and benzopyrans, bi-exponential bleaching kinetics is observed corresponding, probably, to the presence of different isomers of the open form of the system. The slower fading rate is attributed to the most stable isomer. According to the results of recent NMR studies performed on the 3,3-bis(4-fluorophenyl)-3*H*-naphtho[2,1-*b*]pyran at low temperature, two *transoid* isomers of the open form are predominantly accumulated under continuous irradiation (*Scheme 1*) [3]. These are described as TC (*transoid-cis*) type and TT (*transoid-trans*) type, and differ in the configuration at the C=C bonds. The thermal back-isomerization occurs from both isomers leading to the observed bi-exponential thermal bleaching rate.

An ideal molecule for use in photochromic lenses should exhibit, in the host material, a broad absorption in the VIS spectrum to develop a neutral color and high colorability for a significant absorption at a minimum concentration, to exhibit an acceptable rate of decay (*ca.* 0.01 – 0.1 s^{-1}), and, finally, to present a good resistance to



3*H*-naphtho[2,1-*b*]pyrans

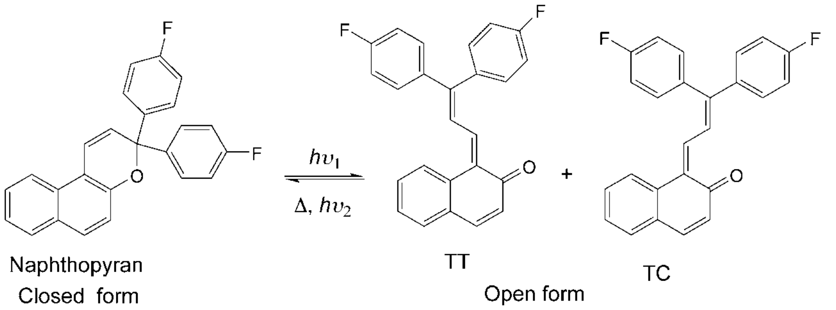
2*H*-naphtho[1,2-*b*]pyrans



2*H*-1-benzopyrans

Fig. 1. *Photochromic benzo- and naphthopyrans*

Scheme 1



photodegradation. A molecule that meets all these requirements has not yet been found.

In the last few years, we have been interested in the development of new benzopyrans derived either from heterocyclic systems (coumarins, xanthones, carbazoles, benzothiophenes, *etc.*) [4] or from fluorenones [5]. These possess diverse photochromic properties. The indeno-fused benzopyrans with a 6,7-fusion[1]) (*Fig. 2*), obtained from hydroxy-9*H*-fluoren-9-ones, have very interesting properties, including an extended absorption in the VIS spectra, showing two bands around 430 and 500–520 nm, and good decoloration rates (0.12–0.16 s^{-1}) [5]. In these compounds, the presence of an sp^3 C-atom in the five-membered ring fused to the benzopyran moiety appears to be a determining factor for observation of photochromic properties.

Recently, we have noticed that in some naphthopyrans, the linkage of the two Ph substituents in the 2-position through an S-bridge to generate a spiro-thioxanthene

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[1]) Locants of 2*H*-1-benzopyran.

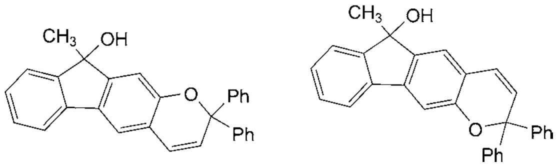
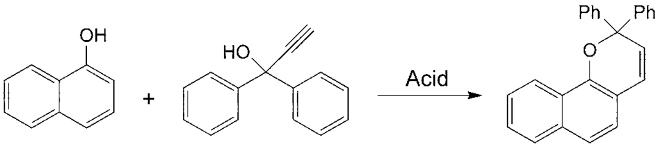


Fig. 2. *Indeno-fused benzopyrans* (= fluorenopyrans)

group, leads to a significant bathochromic shift of the maximum absorption wavelength and to an increase of the thermal fading rate [6]. In this paper, we report the photochromic properties of nonsubstituted indeno-fused 2,2-diphenyl-2*H*-benzopyrans with an S-bridge between the two Ph substituents at the sp^3 C-atom of the benzopyran moiety.

2. Results and Discussion. – 2.1. *Synthesis.* The 2*H*-1-benzopyrans (=2*H*-chromenes) are usually prepared in fair to good yield by reaction of phenols with propynols (*Scheme 2*). This reaction is quite general, and various substituted or fused naphthalen-ols can be used. Several different kinds of aromatic propynols have also been used with success [4–7].

Scheme 2



For the synthesis of the spiro[fluorenopyran-thioxanthenes] **3**, 9*H*-fluorenols **1** and 9-ethynyl-9*H*-thioxanthen-9-ol (**2**) were required. Fluorenols **1** are not commercially available but can be easily prepared from hydroxy-9*H*-fluoren-9-ones by *Wolff–Kishner* reduction (*Scheme 3*). The hydroxy-9*H*-fluoren-9-ones can be synthesized by known methods [5]. The 9-ethynyl-9*H*-thioxanthen-9-ol (**2**) was prepared by reaction of 9*H*-thioxanthen-9-one with lithium acetylide. The purification of **2** proved to be very difficult since extended decomposition was observed upon column chromatography (silica-gel or alumina). However, an almost pure sample of **2** was obtained by silica-gel flash chromatography. Although this technique is limited to a small scale, it did allow us to prepare several grams of sufficiently pure alcohol **2** in approximately 67% yield (*Scheme 3*)[2]). Heating a $CHCl_3$ solution of fluorenols **1a–d** with propynol **2** in the presence of a catalytic amount of pyridinium *p*-toluenesulfonate (PPTS) gave spiro[fluorenopyran-thioxanthenes] **3a–d** in 16–36% yield. From the reaction of fluorenols **1b**, **c** with **2**, only one regioisomer was isolated. The same behavior was observed in the reaction of hydroxy-9*H*-fluoren-9-ones with 1,1-diphenylprop-2-yn-1-ol [5].

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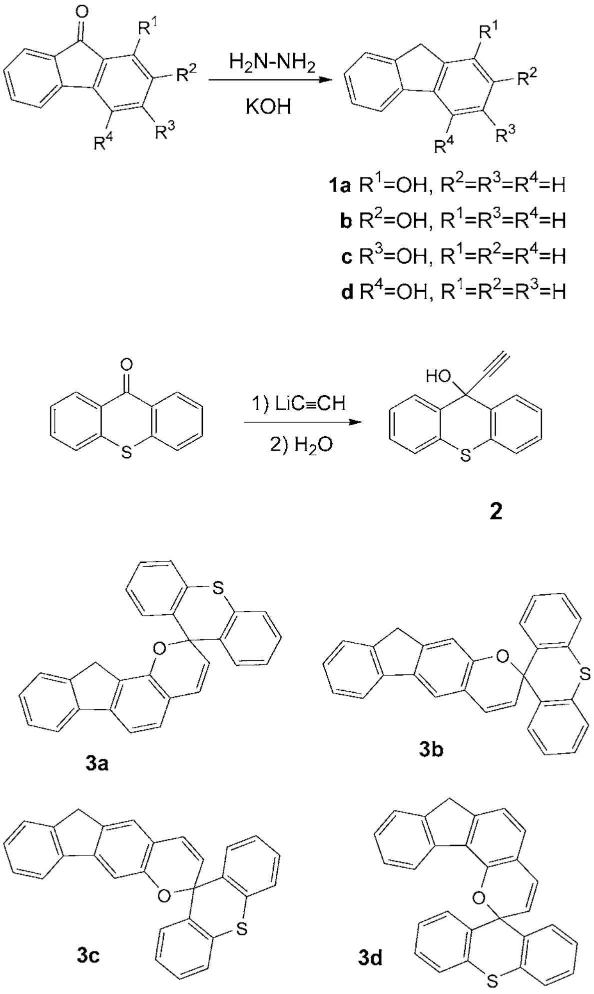
[2]) Alternatively, this compound can be prepared by reaction of lithium (trimethylsilyl)acetylide with 9*H*-thioxanthen-9-one followed by treatment with MeOH/KOH (*cf.* [8]).

Scheme 3



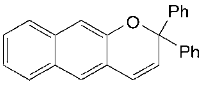
An alternative route to these compounds was attempted through direct reaction of hydroxy-9*H*-fluoren-9-ones with propynol **2**, followed by *Wolff–Kishner* reduction. However, the very low yields observed in the first step indicates that this approach is not tenable. To modulate the photochromic properties of the spiro[fluorenopyran-thioxanthenes] **3a**–**d**, we tried to introduce various substituents at the fluorene CH_2 sp^3 C-atom, through oxidation to nonphotochromic spiro[fluorenopyran-thioxanthene]-ones (air, Bu_4NBr, THF, NaOH(aq)) followed by reaction with *Grignard* reagents. However, although the oxidation step was very successful, the subsequent reaction with MeMgI gave, after hydrolysis, a product that was very unstable and could not be reasonably purified.

2.2. *Photochromic Properties.* Compounds **3a–d** belong to a new series of spiro[benzopyran-thioxanthenes] with an unsubstituted indene moiety fused at different sides of the 2*H*-1-benzopyran ring system, specifically at the *g* and *h* sides (6,7 and 7,8 positions[1])). Evaluation of the spectral and kinetic parameters was performed with 10^{-4} M toluene solutions at 20° under a Xe lamp (150 W) for photolysis. Four main parameters were considered for the characterization of the colored forms: the maximum absorption wavelength in the VIS range (λ_{max}) for the open form, the thermal fading rate (k_Δ), the colorability (A_{eq}), and the fatigue resistance ($t_{1/2}$). Since all the compounds exhibited photodegradation, colorability, the ability of a photochromic material to develop coloration, was defined as the mean absorbance obtained after 5 min of irradiation. A continuous decay was seen in the pseudophotostationary state during the time of irradiation, and the duration of irradiation chosen represents the maximum color development before a significant degradation was observed. The results are reported in *Table 1*.

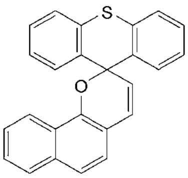
Table 1. *Spectrokinetics Properties under Continuous Irradiation: Maximum Wavelengths of the Colored Form* (λ_{max}), *Colorability* (A_{max} is the absorbance after pseudophotostationary equilibrium at λ_{max}), *Thermal Bleaching Rate* (k_Δ) *of Compounds* **3a–d**, *and of the Two Reference Compounds* **A** *and* **B** *in Toluene Solutions.* **A** = 2,2-diphenyl-2*H*-naphtho[2,3-*b*]pyran , **B** = spiro[2*H*-naphtho[1,2-*b*]pyran-2,9′-[9*H*]thioxanthene][a])

	Fusion side	λ_{max} [nm]	A_{max}	k_Δ [s^{-1}] (Amplitude [%])	$t_{1/2}$ [min]
3b	6,7 (CH_2 at C(7))[b])	547	0.02	0.5 (17), $2 \cdot 10^{-4}$ (83)	108
3c	6,7 (CH_2 at C(6))[b])	473	0.03	0.5 (96), $1 \cdot 10^{-4}$ (4)	24
A	not photochromic at room temperature				
3a	7,8 (CH_2 at C(8))[b])	471	0.10	0.08 (2), $5 \cdot 10^{-3}$ (98)	104
3d	7,8 (CH_2 at C(7))[b])	476	0.09	0.01 (18), $5 \cdot 10^{-3}$ (82)	75
B	7,8[b])	510	0.85	0.011	

[a])



A



B

[b]) Locants of the 2*H*-1-benzopyran part.

Photochromic Behavior. From a general point of view, the observed photochromic properties of **3a–d** are not suitable for sun-lens applications, particularly with respect to the ability for coloring with near-UV radiation and fatigue resistance, since all the compounds showed low colorability (0.02–0.08) and significant degradation ($t_{1/2}$ 24–108 min). This weak photochromism is not surprising, as 2*H*-1-benzopyrans are fatigue-prone and are usually characterized by the absence of significant absorption (activation bands) in the near-UV wavelength range normally used to photoactivate heliochromic compounds (= compounds suitable for sun-lens applications as they are activated with unfiltered sunlight and deactivated, mainly through a thermal process, under diffuse daylight conditions [9]). Compound **3b** is noteworthy because it has the weakest activation bands in the 300–400 nm region and developed the weakest color intensity after irradiation (*Fig. 3*).

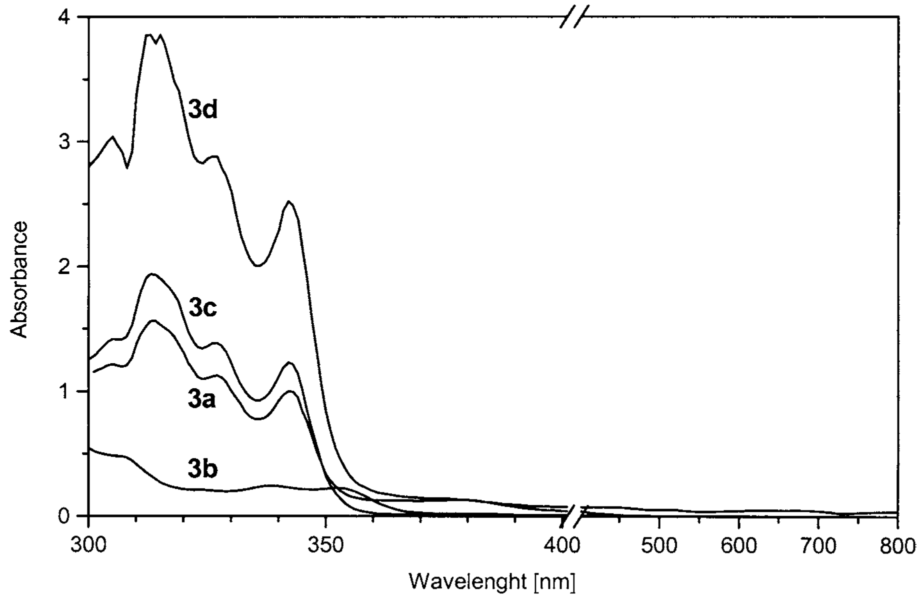


Fig. 3. *UV Absorption spectra of spiro[fluorenopyran-thioxanthenes]* **3a – d** (closed forms)

Under continuous near-UV irradiation, all the compounds described exhibit photochromic behavior in toluene solution at room temperature, with a broad absorption in the VIS range. Considering the 6,7-fusion[1]) (compounds **3b** and **3c**), it is worth noting that the corresponding naphthopyran, *i.e.*, 2*H*-naphtho[2,3-*b*]pyran **A**, is not photochromic at room temperature due to the loss of aromaticity in the attached naphtho component [1]. Both compounds **3b** and **3c**, are photochromic and, therefore, the fusion of the indeno moiety at side *g* of the 2*H*-1-benzopyran structure clearly contributes to the photochromic behavior of 6,7-fused[1]) 2*H*-1-benzopyrans. Considering compounds **3a** and **3d**, the fusion of the indeno moiety at side *h* yielded photochromic compounds with similar behavior. However, the photochromic properties of these compounds are clearly less interesting than those of naphthopyran **B** (higher colorability and faster ring-closure rate).

Maximum Wavelength of Absorption in the VIS Range (λ_{max}). Considering the 6,7-fused 2*H*-1-benzopyrans, two different fusion types may be considered, with a reversed geometry of the fused indeno moiety. The (sp^3) C-atom of the indeno moiety is bound to C(7)[1]) of the 2*H*-1-benzopyran moiety in the case of **3b** and to C(6)[1]) in the case of **3c**. Reversing the fusion geometry leads to a strong bathochromic shift (+ 74 nm) of the maximum absorption wavelength. This can be explained by the extension of the chromophore in compound **3b** as the result of the effective contribution of the indeno benzene ring directly attached at C(6)[1]) in plane with the benzopyran moiety.

In compounds **3a** and **3d**, the geometry of the fused indeno moiety is reversed. With respect to the maximum absorption wavelength, no significant differences were observed in the VIS absorption spectra of the colored forms. This may indicate that the

7,8-fusion[1]) of the indeno moiety results in a similar participation of the indeno benzene ring in the extension of the conjugated π-system.

Thermal Fading Rates (k_Δ). This parameter was evaluated after 5 min of continuous irradiation. Under such circumstances, all compounds **3a**–**d** exhibit bi-exponential bleaching kinetics, although the amplitudes were somewhat different. This means that a similar number of stable photoisomers (at least two) are involved in the ring closure processes. Compounds with the 6,7-fusion[1]) of the indeno moiety exhibit faster decay (first-order rate constants 0.5 s^{-1}) and are thus considered to be less thermally stable than compounds with the 7,8-fusion[1]) (k_Δ between 0.01–0.08 s^{-1}). These last compounds exhibit slower kinetics of ring closure than naphthopyran **B**.

Fatigue Resistance ($t_{1/2}$). As discussed above, all the compounds described exhibited a continuous loss of performance in color development during the irradiation (see, *e.g.*, *Fig. 4*). From the continuous increase of a low residual color with increasing time of irradiation, it is apparent that colored photodegradation products are produced.

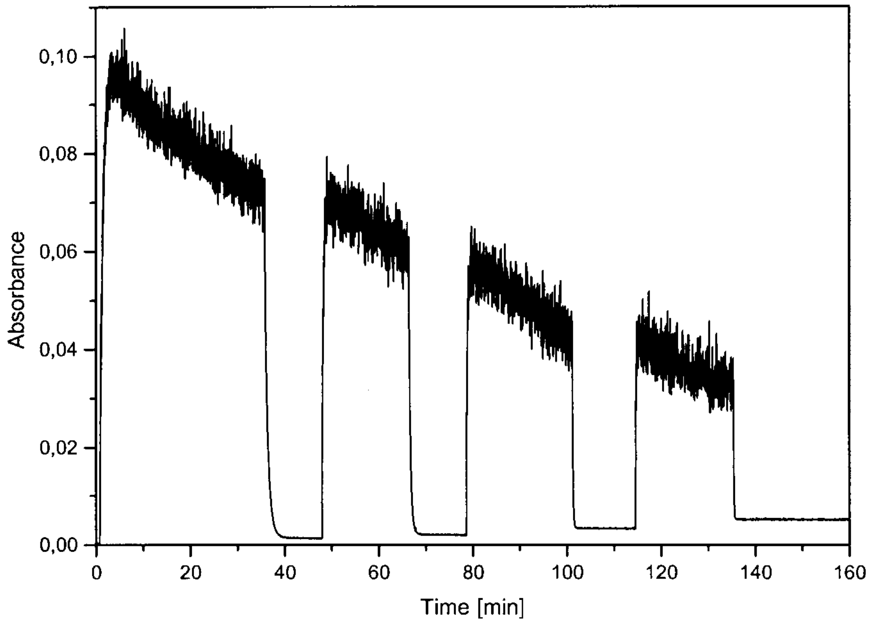


Fig. 4. *Cycles of irradiation/dark for compound* **3c**

A series of experiments with compound **3c** were performed, evaluating the bleaching kinetics under different times of irradiation (and degradation). The results are summarized in *Table 2* and *Fig. 5*. It is noteworthy that the first kinetic constant exhibits a continuous increase with increasing irradiation time. Concomitantly, the amplitude of the faster decay phase becomes predominant in the bleaching process. During the degradation process, the kinetic constant of the slower process exhibits a continuous decrease in its amplitude, and after 75 min of irradiation the bleaching kinetic is essentially mono-exponential. From the kinetics results evaluated with the shortest irradiation times (5 and 15 min), it is apparent that the slowest-decaying

Table 2. *Bleaching Rate Constants for Compound* **3c** *after Different Times of Irradiation*

Time of irradiation [min]	k_Δ [s^{-1}] (Amplitude [%])
5	0.01 (18), $5 \cdot 10^{-3}$ (82)
15	0.01 (84), $5 \cdot 10^{-3}$ (16)
30	0.02 (98), $2 \cdot 10^{-3}$ (2)
60	0.03 (> 99), $1 \cdot 10^{-3}$ (< 1)
75	0.08 (100)

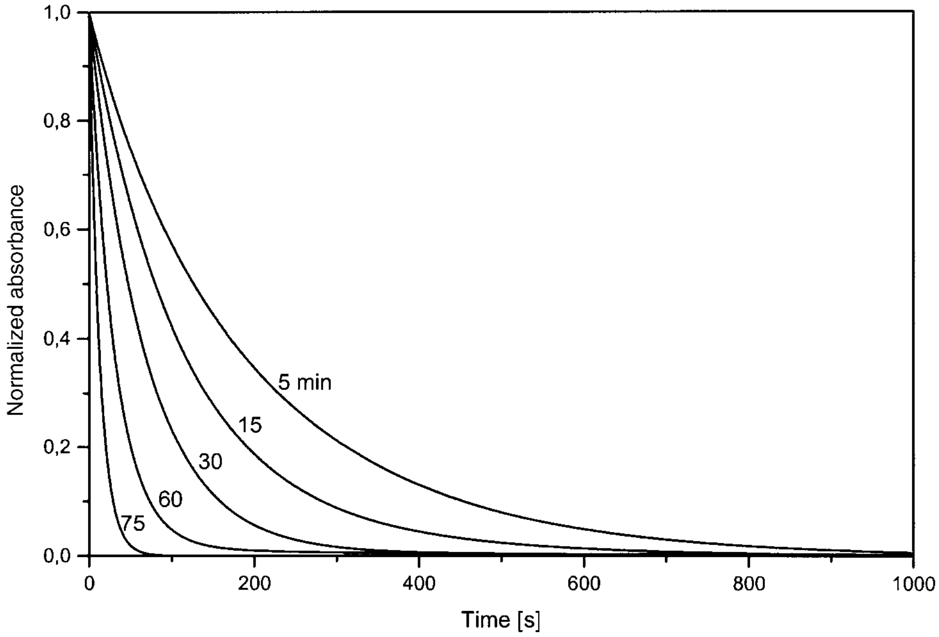


Fig. 5. *Decrease in absorbance of compound* **3c** *after different times of irradiation*

isomer is first produced and probably subsequently converted to the faster decaying isomer.

Considering the bi-exponential kinetic model $A_t = a_0 + a_1e^{(k_1t)} + a_2e^{(-k_2t)}$ (where k_1 is the rate constant for the fast decay and a_0 is the residual absorbance), and assuming that the unstable open forms are the photodegradable species, the system behaves as one consisting of two compounds with different thermal bleaching rates, where the ratio a_1/a_2 increases during the degradation. The most stable isomer, responsible for the slower fading rate, is more prone to photodegradation, probably either because it remains for a longer time in that form or because of its more pronounced absorbance.

However, since these studies were performed with polychromatic irradiation, one cannot be sure whether the closed form or the open forms (or both) are the photodegradable species. The relative importance of these two processes (photocoloration *vs.* photodegradation) will depend also on the irradiation intensity at a definite wavelength. Moreover, the photolysis products can act as catalysts of the thermal reverse reaction, and the experimental result will be the increase in the rate of bleaching with increasing irradiation time [10][11].

3. Conclusions. – The synthesis of nonsubstituted indeno-fused spiro[benzopyran-thioxanthenes] can be achieved by usual methods. These compounds exhibit photochromic activity in dilute toluene solution, with broad absorption bands in the VIS range ($\lambda_{\max}$ 471–547 nm). However, they show low photocoloration efficiencies (colorabilities) and weak resistance to photodegradation. Under short-time (5–15 min) continuous near-UV irradiation, bi-exponential kinetics of thermal bleaching are observed, indicating the presence of at least two colored open forms in the irradiated solution. These species seem to have different susceptibilities to photodegradation, as with increasing irradiation time, a faster mono-exponential-like kinetics is progressively observed, probably due to a decrease in the concentration of the more-stable open-form isomers.

We are grateful to *POCTI*, *FCT* (The Portuguese Foundation for Science and Technology), and *FEDER* for financial support (project POCTI/QUI/38771/2001).

Experimental Part

1. *General.* Column chromatography (CC): silica gel *60* (70–230 mesh). M.p.: *Büchi 535*; uncorrected. FT-IR Spectra: *Perkin-Elmer FTIR 1600*; KBr discs; in cm^{-1}. NMR Spectra: *Varian Unity Plus*; at 300 (^{1}H) and 75.4 Mz (^{13}C); in CDCl$_3$ if not stated otherwise; δ in ppm rel. to Me$_4$Si (=0 ppm); *J* in Hz. MS: *AutoSpecE* spectrometer; in *m/z* (%).

2. *Spectrokinetic Studies under Continuous Irradiation.* For measurements of $\lambda_{\max}$, A_{eq}, and k_δ under continuous irradiation, $1 \cdot 10^{-4}$ M toluene solns. were used. Irradiation experiments were made with a *Varian Cary-50* spectrometer coupled to a 150-W ozone-free Xe lamp (*6255*, *Oriel Instruments*). The light from the UV lamp was filtered with a water filter (*61945*, *Oriel Instruments*) and then carried to the spectrophotometer holder at the right angle to the monitoring beam by using a fiber-optic system (*77654*, *Oriel Instruments*). A light flux of 40 W m^{-2}, measured with a *Goldilux* photometer with a UV-A probe, was used. A thermostated (20°) 10-mm quartz cell containing the sample solution (3.5 ml) and a magnetic stirring bar was used. In a preliminary experiment, the VIS absorption spectrum of the closed form and the $\lambda_{\max}$ of the open form were determined. In a second experiment, the absorbance at photostationary equilibrium, A_{eq}, was measured at $\lambda_{\max}$, and then the decrease in the absorbance with time was monitored. The rate constants were calculated by using a bi-exponential model.

3. *Syntheses. 9*H*-Fluorenols* **1a**–**d**: *General Procedure.* A mixture of the adequate hydroxy-9*H*-fluoren-9-one (0.500 g, 2.55 mmol), KOH (0.714 g, 0.0128 mol), hydrazine hydrate (0.76 ml, 0.023 mmol), and ethylene glycol (3.80 ml, 0.0682 mmol) was heated at 100° for 30 min, then at 160° for 2.5 h, and finally at 160° for 2.5 h. The mixture was treated with sat. NH$_4$Cl soln. and extracted with Et$_2$O (3 × 100 ml). The combined org. layers were dried (Na$_2$SO$_4$) and evaporated: pure **1a**–**d**.

*9*H*-Fluoren-1-ol* (**1a**): Further purification by CC (2.5% AcOEt/hexane) gave a yellow solid (213 mg, 46%). M.p. 112–113°. FT-IR: 3517, 3453, 1585, 1444, 1218. ^{1}H-NMR: 3.85 (*s*, CH$_2$); 6.84 (*dd*, *J* = 7.5, 1.0, 1 H); 7.25 (*t*, *J* = 7.5, H–C(3)); 7.32 (*ddd*, *J* = 7.5, 7.5, 1.5, H–C(7) or H–C(6)); 7.38 (*ddd*, *J* = 7.5, 7.5, 1.5, H–C(7) or H–C(6)); 7.40 (*d*, *J* = 7.5, H–C(2) or H–C(4)); 7.60 (*dd*, *J* = 7.2, 1.0, 1 H); 7.84 (*d*, *J* = 7.2, 1 H); 8.58 (*s*, OH). MS: 182 (100, M^+), 181 (60), 165 (15), 152 (35).

*9*H*-Fluoren-2-ol* (**1b**): White solid (403 mg, 87%). M.p. 229–230°. FT-IR: 3363, 3058, 1616, 1455, 1268. ^{1}H-NMR: 3.84 (*s*, CH$_2$); 6.83 (*dd*, *J* = 7.5, 1.0, H–C(3)); 7.02 (*d*, *J* = 7.5, 1.1, H–C(1)); 7.21 (*t*, *J* = 7.5, H–C(6) or H–C(7)); 7.33 (*t*, *J* = 7.5, H–C(6) or H–C(7)); 7.48 (*d*, *J* = 7.5, 1 H); 7.62 (*d*, *J* = 8.2, 1 H); 7.66 (*d*, *J* = 7.5, 1 H). MS: 182 (100, M^+), 181 (50), 165 (15), 152 (30).

*9*H*-Fluoren-3-ol* (**1c**): Pale yellow solid (390 mg, 84%). M.p. 130–132°. FT-IR: 3305, 3023, 1614, 1486, 1448, 1257. ^{1}H-NMR: 3.84 (*s*, CH$_2$); 4.89 (*s*, OH); 6.80 (*dd*, *J* = 8.1, 2.4, H–C(2)); 7.26 (*d*, *J* = 2.1, H–C(4)); 7.31 (*ddd*, *J* = 7.2, 7.2, 1.5, H–C(6) or H–C(7)); 7.38 (*m*, 2 H); 7.54 (*d*, *J* = 7.5, 1 H); 7.73 (*d*, *J* = 7.5, 1 H). MS: 182 (100, M^+), 181 (65), 165 (13), 152 (35).

*9*H*-Fluoren-4-ol* (**1d**): Yellow solid (391 mg, 84%). M.p. 107–108°. FT-IR: 3303, 1583, 1479, 1448, 1259. ^{1}H-NMR: 3.94 (*s*, CH_2); 5.22 (*s*, OH); 6.75 (*m*, 1 H); 7.17 (*m*, H–C(3) and H–C(2)); 7.30 (*ddd*, *J* = 7.5, 7.5, 1.5, H–C(6) or H–C(7)); 7.40 (*t*, *J* = 7.8, H–C(6) or H–C(7)); 7.54 (*d*, *J* = 7.5, 1 H); 8.13 (*d*, *J* = 7.5, 1 H). MS: 182 (100, M^+), 181 (45), 165 (15), 152 (40).

Spiro[fluorenopyran-thioxanthenes] **3a–d**: *General Procedure.* A suspension of 9*H*-thioxanthen-9-one (2.00 g, 9.43 mmol), and lithium acetylide ethane-1,2-diamine complex (3.00 g, 29.4 mmol) in dry THF (250 ml) was stirred under Ar for 24 h. The suspension was treated with H_2O (200 ml), the aq. phase extracted with Et_2O (3 × 100 ml), and the combined org. phase dried (Na_2SO_4) and evaporated. The obtained crude product was divided into four fractions, and each one was submitted to flash column chromatography (10% AcOEt/hexane; not more than 30 min): almost pure *9-ethynyl-9*H*-thioxanthen-9-ol* (**2**; 1.5 g, 67%).

A soln. of **2** (1.30 mg, 5.50 mmol), 9*H*-fluorenol **1a–d** (0.200 g, 1.10 mmol), pyridinium *p*-toluenesulfonate (50 mg) and $CHCl_3$ (60 ml) was refluxed for 2.5 h under an Ar. Solvent evaporation gave a brown oil, which was purified by CC (0–3% AcOEt/hexane). Recrystallization from Et_2O/pentane gave a crystalline material.

*Spiro[fluoreno[1,2-*b*]pyran-2(11*H*),9′-[9*H*]thioxanthene]* (**3a**): Pale yellow solid (160 mg, 36%). M.p. 249–250°. FT-IR: 3054, 1612, 1454, 1230, 1203. ^{1}H-NMR: 4.04 (*s*, CH_2); 6.13 (*d*, *J* = 9.9, H–C(3)); 6.41(*d*, *J* = 9.9, H–C(4)); 7.07 (*d*, *J* = 7.5, 1 H); 7.28 (*m*, 4 H); 7.40 (*m*, 3 H); 7.49 (*m*, 2 H); 7.60 (*d*, *J* = 7.5, 1 H); 7.80 (*m*, 3 H). ^{13}C-NMR: 33.8 (CH_2); 79.8 (C(2)); 113.0; 117.7; 120.1; 121.1; 121.9; 125.3; 125.8; 126.2; 126.7; 126.8; 126.98; 127.01; 127.6; 128.1; 129.1; 138.8; 141.5; 143.6; 144.5; 149.4. MS: 402 (100, M^+), 221 (70), 196 (12), 152 (25). HR-MS: 402.1075 ($C_{28}H_{18}OS^+$); calc. 402.1078).

*Spiro[fluoreno[2,3-*b*]pyran-2(10*H*),9′-[9*H*]thioxanthene]* (**3b**): Yellow solid (102 mg, 23%). M.p. 229–230°. FT-IR: 3056, 2923, 1662, 1454, 1214. ^{1}H-NMR: 3.94 (*s*, CH_2); 6.12 (*d*, *J* = 10.2, H–C(3)); 6.44 (*d*, *J* = 10.2, H–C(4)); 7.30–7.20 (*m*, 6 H); 7.36 (*dd*, *J* = 7.5, 7.5, H–C(7) or H–C(8)); 7.40 (*s*, H–C(5) or H–C(11)); 7.48 (*m*, 2 H); 7.53 (*d*, *J* = 7.5, 1 H); 7.68 (*d*, *J* = 7.5, 1 H); 7.84 (*m*, 2 H). ^{13}C-NMR: 36.3 (CH_2); 79.8 (C(2)); 106.7; 118.2; 120.1; 121.5; 122.3; 123.1; 125.1; 126.1; 126.7; 126.9; 127.0 (2 C); 127.6; 129.1; 136.0; 128.7; 141.5; 143.6; 144.3; 152.8. MS: 402 (100, M^+), 221 (55), 201 (15), 152 (15). HR-MS: 402.1064 ($C_{28}H_{18}OS^+$; calc. 402.1078).

*Spiro[fluoreno[3,2-*b*]pyran-2(6*H*),9′-[9*H*]thioxanthene]* (**3c**): Yellow solid (71 mg, 16%). M.p. 201–202°. FT-IR: 3054, 1610, 1454, 1428, 1230. ^{1}H-NMR: 3.86 (*s*, CH_2); 6.12 (*d*, *J* = 9.9, H–C(3)); 6.38 (*d*, *J* = 9.9, H–C(4)); 7.16 (*s*, H–C(5) or H–C(11)); 7.30–7.24 (*m*, 6 H); 7.32 (*ddd*, *J* = 7.5, 7.5, 1.2, H–C(8) or H–C(9)); 7.42 (*dd*, *J* = 7.5, 1 H); 7.53–7.46 (*m*, 4 H); 7.55 (*d*, *J* = 7.5, 1 H); 7.79 (*d*, *J* = 7.5, 1 H); 7.89 (*m*, 2 H). ^{13}C-NMR: 36.2 (CH_2); 79.7 (C(2)); 106.6; 118,1; 120.0; 121.4; 122.1; 123.0; 125.0; 126.0; 126.6; 126.8; 126.9; 127.5; 129.0; 135.9; 138.6; 141.4; 143.5; 144.2; 152.7; 170.7. MS: 402 (100, M^+), 221 (55), 196 (15), 152 (12). HR-MS: 402.1079 ($C_{28}H_{18}OS^+$; calc. 402.1078).

*Spiro[fluoreno[4,3-*b*]pyran-2(7*H*),9′-[9*H*]thioxanthene]* (**3d**): Light orange solid (160 mg, 36%). M.p. 243–244°. FT-IR: 3054, 1614, 1455, 1428, 1232, 1205. ^{1}H-NMR: 4.07 (*s*, CH_2). 6.26 (*d*, *J* = 9.9, H–C(3)); 6.48 (*d*, *J* = 9.9, H–C(4)); 7.02 (*d*, *J* = 7.5, H–C(5) or H–C(6)); 7.19 (*d*, *J* = 7.5, H–C(5) or H–C(6)); 7.34 (*m*, 4 H); 7.39 (*m*, 2 H); 7.61 (*m*, 3 H); 8.00 (*m*, 2 H); 8.39 (*m*, 1 H). ^{13}C-NMR: 37.4 (CH_2); 80.0 (C(2)); 117.6; 117.6; 121.2; 121.3; 123.9; 124.5; 125.4; 125.6; 126.2; 126.7; 127.0; 127.1; 127.5; 127.9; 129.1; 138.9; 140.2; 142.8; 146.0; 148.7; 170.6. MS: 402 (25, M^+), 221 (10), 192 (30), 149 (40), 105 (100). HR-MS: 402.1071 ($C_{28}H_{18}OS^+$; calc. 402.1078).

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Received December 8, 2003