

Spectroscopic characterisation and photodegradation studies of photochromic spiro[fluorene-9,3'-[3'H]-naphtho[2,1-b]pyrans]

R. Demadrille^{a,*}, A. Rabourdin^b, M. Campredon^c, G. Giusti^b

^a DRFMC, UMR 5819-SPRAM (CEA-CNRS, Univ. J. Fourier, Grenoble I), Laboratoire de Physique des Métaux Synthétiques, CEA Grenoble, 17 Rue des Martyrs 38054 Grenoble Cedex 9, France

^b Faculté des Sciences de Luminy, Université de la Méditerranée, 163 avenue de Luminy, Case 901-13288 Marseille Cedex 9, France

^c JE-TRACES, Campus de St Jérôme, avenue Escadrille Normandie-Niemen, Case 511, 13397 Marseille Cedex 20, France

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Abstract

Condensation between propargyl alcohol derivatives and appropriate naphthols under acidic catalysis afforded the corresponding spirofluorene-[3'H]-naphtho[2,1-b]pyrans. Here we report on the synthesis of some new substituted compounds in this series. These molecules are photochromic dyes whose properties have been investigated in toluene solution. Thermal bleaching after exposure to polychromatic light has been monitored by UV-Visible spectrophotometry and modelled in order to determine the rate constant of the ring closure process. Photodegradation studies have also been carried out in toluene solution and confirmed that photo-oxidation processes involving both molecular and singlet oxygen are responsible for the loss of optical density when the dyes are irradiated. For the first time, the identification of some new photo-induced by-products was carried out using GC/MS analysis.

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Keywords: Photochromism; Photodegradation; Fluorene; Naphtho[2,1-b]pyrans

1. Introduction

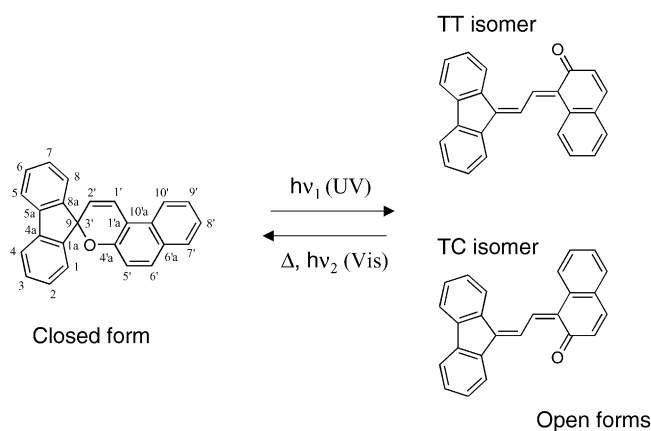
Photochromic compounds can be defined as chemical species that convert under irradiation to other species exhibiting a different absorption spectrum. Although such compounds have been known for decades [1], they are still intensively studied due to their industrial interests. Data storage [2], optical switches [3], non-linear optics [4] and ophthalmology [5] are some of the potential applications for this type of compounds. Among the numerous families of photochromic dyes, 2,2-diphenyl-[2H]-chromenes also known as 3,3-diphenyl-[3H]-naphtho[2,1-b]pyrans are an important class of reversible dyes [6]. The photochromic behaviour of these molecules is based on UV light absorption of the ring-closed molecule (uncoloured) that can undergo isomerisation after the scission of the C–O bond of the pyranic ring. This reaction is reversible and the reverse process is assumed to take place by thermal and/or photochemical pathways. The scientific interest in these photochromic molecules has grown since the 1990s, due to their commercialisation in the field of variable optical materials. For this type of application, photochromic dyes

must have a high level of coloration under polychromatic light exposure, a fast thermal fading when the irradiation is stopped and a strong fatigue resistance. Unfortunately, it is very difficult to elaborate photochromic structures that combine all these properties. For this reason, it is necessary to synthesise new functionalised dyes and to evaluate their photochromic behaviour in order to fully understand the structure–property relationship.

With this goal in mind, we have focused our investigations on spirofluorene-[3'H]-naphtho[2,1-b]pyrans whose structures are very similar to those of the 3,3-diphenyl-[3H]-naphtho[2,1-b]pyrans. The only difference between the two series consists of a linkage between the two benzene rings. In the same way as the 3,3-diphenyl-[3H]-naphtho[2,1-b]pyrans, spirofluorenes reveal photochromic properties and the photo-induced ring opening proceeds in the same manner. The mechanism of the photochromic interconversion of spirofluorene-[3'H]-naphtho[2,1-b]pyrans is detailed in Scheme 1.

Spirofluorene-[3'H]-naphtho[2,1-b]pyrans were first described in 1994 [7–9] but the literature concerning their synthesis or their spectroscopic characterisation is still very scarce [10,11]. In order to extend our knowledge of this class of molecules, the synthesis of new substituted spirofluorene-[3'H]-naphtho[2,1-b]pyrans has been carried

* Corresponding author. Tel.: +33-4-38785712; fax: +33-4-38785113.
E-mail address: demadril@drfmc.ceg.cea.fr (R. Demadrille).



Scheme 1. Photochromic equilibrium between the closed form (uncoloured) and the open forms (coloured).

out and their spectrokinetic parameters have been determined in toluene solution, under continuous irradiation. For the first time, a complete photodegradation study on spirofluorene-[3'*H*]-naphtho[2,1-*b*]pyrans has been performed and the identification of the by-products by gas chromatography coupled mass spectrometry (GC/MS) has been carried out.

1.1. Synthesis

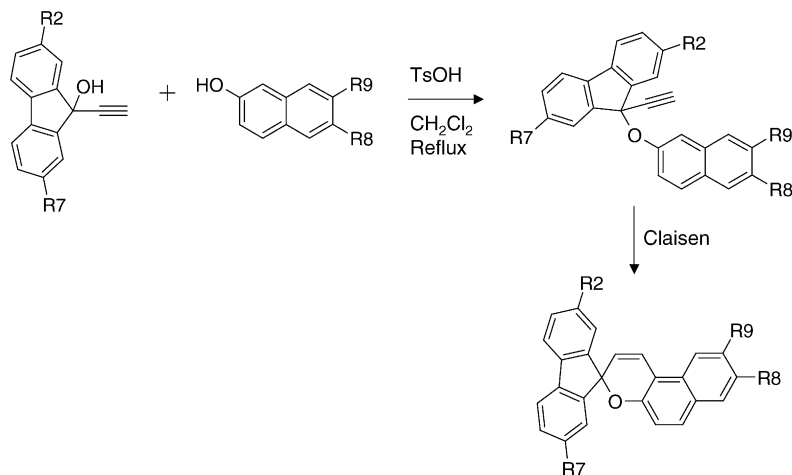
One synthetic approach leading to the formation of 3,3-diphenyl-[3'*H*]-naphtho[2,1-*b*]pyrans or spirofluorene-[3'*H*]-naphtho[2,1-*b*]pyrans consists of the condensation between a propargyl alcohol and a naphthol. The key intermediate of this reaction is alkynyl aryl ether that can undergo a thermally activated cyclisation via a Claisen rearrangement thus leading to a naphthopyran ring (see Scheme 2). This reaction was first described by Iwai and Ide in 1963 [12] and till now [13,14] this approach remains the most convenient way of synthesising this class of molecules. Inspired by this work, the preparation of the

Table 1
Yields of spirofluorene-[3'*H*]-naphtho[2,1-*b*]pyrans

Compounds	R2	R7	R9	R8	Yield (%)
1	H	H	H	H	50
2	H	H	OSO ₂ CF ₃	H	33
3	H	H	H	OSO ₂ CF ₃	24
4	H	H	H	Br	33
5	O _{sec} C ₄ H ₉	H	H	H	56
6	F	H	H	H	50
7	C ₆ H ₅	C ₆ H ₅	H	H	47
8	H	H	OCH ₃	H	30
9	H	H	H	OCH ₃	30

spirofluorene-[3'*H*]-naphtho[2,1-*b*]pyrans was performed using a one-pot method condensation between substituted naphthols and propargyl alcohols under acidic conditions. Such condensation reactions can proceed either via *para*-toluene sulfonic acid (PTSA) catalysis, or with pyridinium *para*-toluene sulfonate salt PPTS [15,16] which provides weaker acidity (this limits the Meyer–Shuster rearrangement reaction during condensation). Significantly, for most of the propargyl alcohols used in this study, we found that PPTS is less efficient than PTSA.

Propargyl alcohols were prepared according to standard procedures [7] by nucleophilic addition of sodium acetylide onto substituted fluoren-9-ones dissolved in dried THF, with good yields (from 55 to 92%). The synthesised propargylic alcohols were condensed onto naphthols to give the photochromic compounds. The results of the condensation reaction are summarised in Table 1. It should be emphasised that the yields of the condensation reaction are rather low



Scheme 2. General synthesis of spirofluorene-[3'*H*]-naphtho[2,1-*b*]pyrans.

(24–33%) but their values increase when the reaction proceeds with unsubstituted naphthol (47–56%).

2. Experimental procedures

2.1. Materials

All the naphthols were purchased from Aldrich except 2-hydroxy-6-methoxy-naphthol and 2-hydroxy-7-methoxy-naphthol which were purchased from Fluka. Trifluoromethane sulfonated naphthols were synthesised according to literature [17] by reaction of trifluoromethane sulfonic anhydride with dihydroxynaphthalenes in pyridine. Compounds 10, 11 and 12 were prepared according to literature procedures [13–15]. 2,7-diphenyl-9-fluorenone was prepared from 2,7-dibromo-9-fluorenone (commercially available from Aldrich) by Suzuki coupling using the standard procedure [13]. Dichloromethane was dried over CaCl_2 . Silica gel was purchased from Merck (Merck 60, 0.063–0.0200 mm). Melting points were measured with Büchi 510 apparatus. All NMR spectra were recorded on Bruker AC 250 spectrometer except for compound 2 recorded on Bruker 500. Acetone- d_6 or chloroform- d (containing TMS as internal standard for the estimation of the chemical shifts) was used as solvent for the NMR experiments depending on the solubility of the molecules.

2.2. General procedure for the condensation reaction

In a two-necked flask fitted with an argon inlet and a condenser, naphthol (1eq.) and propargyl alcohol (1.1eq.) were introduced together with dried dichloromethane. To this mixture was added dropwise a catalytic amount of *para*-toluene sulfonic acid dissolved in the same solvent. The mixture was maintained with vigorous stirring for 2 h at reflux. After this period, the reaction mixture was poured onto an ice/water mixture and the organic layer was further extracted with ether. The organic layers were combined, washed consecutively with saturated brine and water, and finally dried over MgSO_4 . After filtration and concentration under vacuum, the crude product was purified by chromatography on silica gel with pentane and diethyl ether as eluent to afford to the photochromic dye (yields from 30 to 56%).

2.2.1. Spiro[fluorene-9,3'-[3'H]-naphtho[2,1-b]pyran] (1)— $\text{C}_{25}\text{H}_{16}\text{O}$

White powder (yield, 50%), mp 141–142 °C.— ^1H NMR (CDCl_3): δ = 5.56 (H2', d, J = 10.0 Hz), 6.91 (H1', d, J = 10.0 Hz), 7.08 (2H, t, J = 7.3 Hz), 7.25 (4H, tbr, J = 7.3 Hz), 7.37–7.43 (3H, m), 7.50–7.54 (3H, m), 7.64 (H5', d, J = 7.9 Hz), 7.92 (H6', d, J = 7.9 Hz).— ^{13}C NMR (CDCl_3): δ = 85.5 (C3'), 112.9 (C1'a), 118.3 (C5'), 120.1 (C4–C5), 120.2 (C1), 121.1, 123.6, 124.8, 125.2 (C1–C8), 126.7, 128.3 (2C), 128.6, 129.4 (C2–C7), 129.9 (C3–C6), 139.0 (C4a–C5a), 147.4 (C1a–C8a), 152.1 (C4'a) —MS, m/z

(%): 333 (19), 332 (84), 331 (100), 302 (22), 300 (19), 166 (20), 151 (17), 150 (21). GC purity: 98%.

2.2.2. 8'-trifluoromethanesulfonate-spiro[fluorene-9,3'-[3'H]-naphtho[2,1-b]pyran] (2)— $\text{C}_{26}\text{H}_{15}\text{O}_4\text{SF}_3$

White powder (yield, 24%), mp 173–174 °C.— ^1H NMR (CDCl_3): δ = 5.62 (H2', d, J = 10.1 Hz), 7.00 (H1', d, J = 10.1 Hz), 7.12 (2H, tbr, J = 7.4 Hz), 7.25 (2H, d, J = 10.3 Hz), 7.29 (2H, td, J = 6.5 and 2.6 Hz), 7.41 (2H, d, J = 7.4 Hz), 7.51–7.57 (4H, m), 8.00 (1H, d, J = 9.3 Hz).— ^{13}C NMR (CDCl_3): δ = 85.9 (C3'), 113.4, 119.7, 120.1, 120.4, 120.4 (C4–C5), 120.5 (2C), 123.9, 125.3 (C1–C8), 126.1, 128.6 (C2–C7), 129.1, 129.4, 130.27 (C3–C6), 139.2 (C4a–C5a), 145.8, 147.3 (C1a–C8a), 153.2 (C4'a), CF_3 non-observed.—MS, m/z (%): 481 (27), 480 (100), 479 (23), 348 (19), 347 (84), 346 (7), 320 (17) 319 (72), 318 (39), 301 (15), 300 (22), 290 (31), 289 (85), 287 (30), 276 (33), 159 (44), 144 (47). GC purity: 97%.

2.2.3. 9'-trifluoromethanesulfonate-spiro[fluorene-9,3'-[3'H]-naphtho[2,1-b]pyran] (3)— $\text{C}_{26}\text{H}_{15}\text{O}_4\text{SF}_3$

White solid (yield 33%), mp 167–168 °C.— ^1H NMR (CDCl_3): δ = 5.65 (H2', d, J = 10.1 Hz), 7.01 (H1', d, J = 10.1 Hz), 7.23–7.38 (3H, m), 7.33 (2H, t, J = 7.5 Hz), 7.45 (2H, d, J = 7.5 Hz), 7.58 (4H, dbr, J = 7.2 Hz), 7.76 (1H, d, J = 9.0 Hz), 7.83 (1H, d, J = 2.1 Hz).— ^{13}C NMR (CDCl_3): δ = 85.9 (C3'), 113.2, 113.3, 117.1, 119.4, 119.7, 120.2 (C4–C5), 125.2 (C1–C8), 125.7, 128.3, 128.5 (C2–C7), 129.3, 130.2 (C3–C6), 130.3, 131.3, 139.0 (C4a–C5a), 147.2 (C1a–C8a), 148.3, 153.4 (C4'a), CF_3 non-observed.—MS, m/z (%): 481 (16), 480 (56), 348 (37), 347 (100), 346 (14), 319 (35), 318 (25), 300 (15), 290 (20), 289 (59), 287 (19), 159 (22), 144 (27). GC purity: 98%.

2.2.4. 8'-bromo-spiro[fluorene-9,3'-[3'H]-naphtho[2,1-b]pyran] (4)— $\text{C}_{25}\text{H}_{15}\text{OBr}$

White powder (yield 33%), mp 231–232 °C.— ^1H NMR (CDCl_3): δ = 5.62 (H2', d, J = 10.0 Hz), 6.95 (H1', d, J = 10.0 Hz), 7.13 (2H, t, J = 7.5 Hz), 7.27 (1H, d, J = 9.5 Hz), 7.33 (3H, m, J = 7.5 Hz), 7.46 (4H, m), 7.57 (1H, d, J = 7.5 Hz), 7.82 (2H, m).— ^{13}C NMR (CDCl_3): δ = 85.8 (C3'), 113.4 (C1'a), 117.6 (C8'), 119.7 (C5'), 120.0 (C1'), 120.4 (C4–C5), 123.2 (C10'), 125.4 (C1–C8), 125.7 (C2'), 128.6 (C6'a), 128.6 (C2–C7), 128.7 (C9'), 130.1 (C7'), 130.3 (C3–C6), 130.7 (C6'), 130.8 (C10a), 139.2 (C4a–C5a), 147.5 (C1a–C8a), 152.5 (C4'a).—MS, m/z (%): 137 (25), 138 (27), 150 (76), 151 (40), 165 (63), 300 (60), 301 (24), 302 (39), 303 (19), 329 (31), 409 (81), 410 (81), 411 (100), 412 (79), 413 (20). GC purity: 99%.

2.2.5. 2-isobutoxy-spiro[fluorene-9,3'-[3'H]-naphtho[2,1-b]pyran] (5)— $\text{C}_{29}\text{H}_{24}\text{O}_2$

Orange powder (yield 56%), mp 96–97 °C.— ^1H NMR (CDCl_3): δ = 0.81 (6H, d, J = 12.1 Hz), 1.84 (1H, m, J = 12.1, 5.0 Hz), 3.55 (2H, d, J = 1.50 Hz), 5.60 (H2', d, J = 10.0 Hz), 6.87 (H1', d, J = 10.0 Hz), 6.89 (1H,

d, $J = 10.0$ Hz), 6.98 (1H, d, $J = 2.3$ Hz), 7.03 (1H, td, $J = 10.0$, 1 Hz), 7.28 (2H, m), 7.30 (2H, m), 7.46 (1H, d, $J = 10.0$ Hz), 7.54 (1H, d, $J = 7.5$ Hz), 7.57 (1H, d, $J = 7.5$ Hz), 7.62 (1H, d, $J = 8.8$ Hz), 7.71 (1H, d, $J = 8.1$ Hz), 8.06 (1H, d, $J = 8.5$ Hz).— ^{13}C NMR (Acetone d_6): 19.1 (2CH₃), 29.5 (CH), 74.9 (CH₂), 86.4 (C3'), 112.2, 113.5, 116.4, 118.6, 120.0, 120.7, 121.7, 121.9, 124.3, 125.4, 125.6, 127.5, 127.6, 129.2, 130.1 (C3–C6), 130.6, 132.1, 139.7 (C4a–C5a), 147.9 (C1a–C8a), 152.5 (C4'a), 160.7 (C2).—MS, m/z (%): 405 (21), 404 (67), 347 (100), 348 (58), 331 (24), 319 (19), 318 (17), 302 (8), 289 (28), 150 (7). GC purity: 99%.

2.2.6. 2-fluoro-spiro[fluorene-9,3'-[3'H]-naphtho[2,1-b]pyran] (6)—C₂₅H₁₅F

Pale yellow powder (yield 50%), mp 134–135 °C.— ^1H NMR (CDCl₃): $\delta = 5.70$ (H2', d, $J = 10.0$ Hz), 7.06 (1H, d, $J = 8.8$ Hz), 7.11 (1H, td, $J = 8.7$ and 2.3 Hz), 7.23 (1H, t, $J = 7.5$ Hz), 7.26 (1H, dd, $J = 8.4$ and 2.3 Hz), 7.41 (1H, d, $J = 7.6$ Hz), 7.41 (1H, t, $J = 7.6$ Hz), 7.47 (H1', d, $J = 10.0$ Hz), 7.56 (1H, d, $J = 7.4$ Hz), 7.56 (1H, d, $J = 7.8$ Hz), 7.61 (1H, dd, $J = 8.4$ and 4.9 Hz), 7.62 (1H, d, $J = 7.8$ Hz), 7.69 (1H, d, $J = 8.8$ Hz), 7.81 (1H, d, $J = 8.1$ Hz), 8.09 (H10', d, $J = 8.5$ Hz).— ^{13}C NMR (CDCl₃): $\delta = 85.3$ (C3') (d, $J_{\text{CF}} = 1.9$ Hz), 112.9 (C1) (d, $J_{\text{CF}} = 23.3$ Hz), 112.9 (C1'a), 117.0 (C3) (d, $J_{\text{CF}} = 23.0$ Hz), 118.3 (C5'), 119.9 (C5), 120.7 (C1'), 121.2 (C10'), 121.3 (C4) (d, $J_{\text{CF}} = 8.5$ Hz), 123.9 (C8'), 124.3 (C2'), 125.3 (C8), 127.0 (C9'), 128.1 (C7), 128.8 (C7'), 129.6 (C6'a), 129.8 (C6'), 129.9 (C10'a), 130.2 (C6), 135.1 (C4a) (d, $J_{\text{CF}} = 2.6$ Hz), 138.3 (C5a), 147.6 (C8a) (d, $J_{\text{CF}} = 2.0$ Hz), 149.7 (C1a) (d, $J_{\text{CF}} = 7.5$ Hz), 151.9 (C4'a), 163.2 (C2) (d, $J_{\text{CF}} = 247.5$ Hz).—MS, m/z (%): 351 (22), 350 (95), 349 (100), 321 (18), 320 (23), 319 (7), 318 (16), 160 (18), 159 (17), 150 (13). GC purity: 99%.

2.2.7. 2,7-diphenyl-spiro[fluorene-9,3'-[3'H]-naphtho[2,1-b]pyran] (7)—C₃₇H₂₄O

Yellow powder (yield 47%), mp 217–218 °C.— ^1H NMR (CDCl₃): $\delta = 5.65$ (H2', d, $J = 10.1$ Hz), 6.99 (H1', d, $J = 10.1$ Hz), 7.16–7.33 (7H, m), 7.38 (1H, s), 7.42 (1H, s), 7.56–7.62 (4H, m), 7.66 (1H, s), 7.69 (1H, sbr), 7.72 (2H, d, $J = 1.1$ Hz), 8.01 (1H, d, $J = 8.5$ Hz).— ^{13}C NMR (CDCl₃): $\delta = 87.0$ (C3'), 112.5 (C1'a), 118.5 (C5'), 120.2 (C1'), 120.8 (C4–C5), 121.4, 123.9, 124.3 (2C), 124.6, 127.0 (2C), 127.3, 127.4 (4C), 127.6 (2C), 129.0 (4C), 129.3 (2C), 129.9, 129.9, 138.0 (C4a–C5a), 141.0 (2C), 141.9 (2C), 149.1 (C1a–C8a), 152.0 (C4'a).—MS, m/z (%): 486 (8), 485 (39), 484 (100), 483 (50), 408 (8), 407 (24), 377 (7), 376 (10), 328 (13), 242 (26). GC purity: 99%.

2.2.8. 9'-methoxy-spiro[fluorene-9,3'-[3'H]-naphtho[2,1-b]pyran] (8)—C₂₆H₁₈O₂

Light yellow powder (yield 30%), mp 175–176 °C.— ^1H NMR (CDCl₃): $\delta = 3.98$ (3H, s), 5.71 (H2', d, $J = 10.0$ Hz), 6.90 (H1', d, $J = 10.0$ Hz), 7.07 (1H, dd, $J = 0.9$ and

2.4 Hz), 7.24 (2H, dt, $J = 7.5$ and 1.1 Hz), 7.35 (1H, d, $J = 2.4$ Hz), 7.36 (1H, d, $J = 10$ Hz), 7.41 (2H, dt, $J = 7.5$ and 1.1 Hz), 7.56 (2H, dbr, $J = 7.4$ Hz), 7.59 (1H, d, $J = 8.7$ Hz), 7.67 (2H, dbr, $J = 7.5$ Hz), 7.69 (1H, d, $J = 8.9$ Hz).— ^{13}C NMR (CDCl₃): $\delta = 55.4$ (OCH₃), 85.4 (C3'), 100.4 (C10'), 112.3 (C1'a), 115.9, 116.0, 120.1 (C4–C5), 120.4 (C1'), 124.4, 124.9, 125.2 (C1–C8), 128.4 (C2–C7), 129.3, 129.9 (C3–C6), 130.3, 131.2, 140.0 (C4a–C5a), 147.6 (C1a–C8a), 152.8 (C4'a), 158.7 (C9').—MS, m/z (%): 363 (27), 362 (100), 361 (71), 345 (10), 331 (15), 329 (11), 318 (21), 289 (26), 287 (11). GC purity: 97%.

2.2.9. 8'-methoxy-spiro[fluorene-9,3'-[3'H]-naphtho[2,1-b]pyran] (9)—C₂₆H₁₈O₂

Yellow crystals (yield 30%), mp 210–213 °C.— ^1H NMR (CDCl₃): $\delta = 3.93$ (3H, s), 5.71 (H2', d, $J = 10.0$ Hz), 7.02 (1H, d, $J = 8.8$ Hz), 7.11 (1H, d, $J = 2.6$ Hz), 7.25–7.30 (3H, m), 7.40 (2H, tbr, $J = 7.5$ Hz), 7.40 (1H, d, $J = 10.8$ Hz), 7.58–7.62 (3H, m), 7.66 (2H, dbr, $J = 7.5$ Hz), 7.99 (1H, d, $J = 9.2$ Hz).— ^{13}C NMR (CDCl₃): $\delta = 55.6$ (OCH₃), 86.0 (C3'), 107.1 (C7'), 119.0 (C5'), 119.5 (C9'), 120.3 (C4–C5), 120.7 (C1'), 123.0 (C10'), 125.3, 125.4 (C1–C8), 125.5, 128.3, 128.6 (C2–C7), 130.1 (C3–C6), 130.7 (C6'a), 139.3 (C4a–C5a), 147.7 (C1a–C8a), 150.8 (C4'a), 156.4 (C8').—MS, m/z (%): 363 (29), 362 (100), 361 (81), 331 (10), 319 (12), 318 (23), 289 (27), 287 (10), 159 (10), 144 (12). GC purity: 97%.

2.3. Photostationary state experiments

The photochromic compounds were dissolved in anhydrous toluene (10^{-4} M) spectroscopic grade purchased from Aldrich. Irradiation is achieved using an Oriel 150 W high pressure Xenon Lamp equipped with a diaphragm and water filter in order to remove most of the infra-red radiation. Polychromatic light intensity (400 W/m² and 800 W/m² for triflated compounds) was determined using an Oriel Quantum photoradiometer (measurement between 300 and 400 nm). The quartz analysis cell had an optical path length of 1 cm and was enclosed in a thermo-regulated copper block (20 °C) inside the Diode Array Detector (Beckman DU 7500) spectrophotometer. This apparatus is completely described in Ref. [18].

2.4. Degradation experiments

All the degradation experiments were performed in a Sun Test (Atlas) equipped with a Xenon Lamp and a 290 nm filter at the temperature of 25 °C. Light intensity was 80 W/m² measured between 300 and 400 nm. The photochromic solution was irradiated in a quartz reactor with stirring. The GC/MS (6890 HP GC system and 5973 MS detector) apparatus was equipped with a short column (0.2 μm , 12 m \times 0.2 mm). The injector (Merlin) was heated to 255 °C. The best separation was obtained for the following temperature sequence: 5 min at 70 °C (solvent delay), increment to

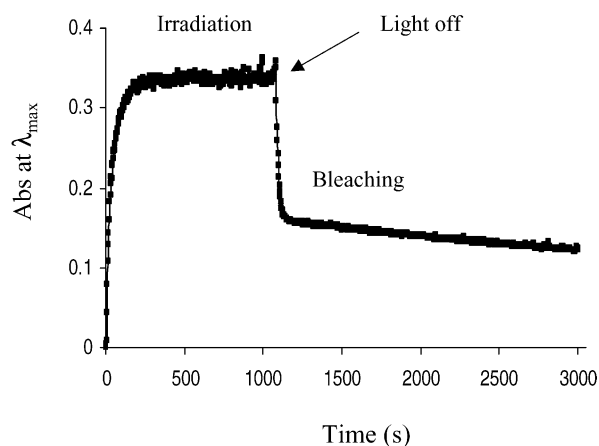


Fig. 1. Photostationary state experiment curve.

310 °C (5 °C/min) and then isotherm at 310 °C for 25 min. The mass spectra were obtained under electronic impact (EI = 70 eV).

For comparative reasons, for **(1)** and **(10)** we have carried out the degradation studies in de-oxygenated solution. The applied procedure can be described as follows. First oxygen was removed by argon bubbling over 30 min. Then the photochromic solutions were irradiated in a quartz reactor filled with argon. The loss of the optical density was measured in regular time intervals.

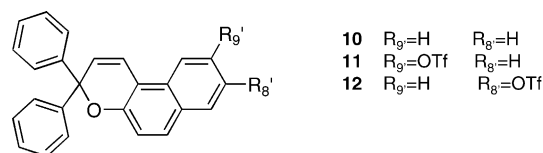
3. Results and discussion

3.1. Spectroscopic studies

It is generally assumed that after absorption of a UV photon by the ring-closed system, heterolytic cleavage of the C–O bond of the pyranic ring occurs and allows its opening and the isomerisation of the dye to give an extended π -conjugated system.

As described in previous studies [11], the absorption spectra of the coloured isomers (λ_{\max}) of spirofluorene-[3'*H*]-naphtho[2,1-*b*]pyrans undergo a bathochromic shift of ca. 20 nm compared to 3,3-diphenyl-[3*H*]-naphtho[2,1-*b*]pyrans. This effect is explained by the higher planarity of the benzene rings in the fluorene system.

After this photochemical reaction, two major transoid isomers of the opened form are produced: TC and TT. As this reaction is in equilibrium between the closed and the opened forms, it is necessary to perform the spectroscopic studies of the dyes at the photostationary state [18]. The photostationary state is obtained under continuous irradiation and can be defined as the stabilisation of the equilibrium between the closed and the opened forms (see Fig. 1). This equilibrium is reached when the variation of the optical density is stabilised. Generally, the analytical wavelength used in order to follow the variation of the optical density corresponds to the highest absorption wavelength of the coloured forms in



Scheme 3. Structures of the studied 3,3-diphenyl-[3*H*]-naphtho[2,1-*b*]pyrans (reference compounds).

the visible part of the spectra and is commonly called λ_{\max} . When the irradiation is cut off, thermal bleaching occurs and it is thus possible to determine the thermal kinetic constants of ring closure k_1 and k_2 , following the decrease in optical density.

The bleaching curve can generally be modelled by a mono- or bi-exponential equation. In this work, we have found that the thermal bleaching curves of spirofluorene-[3'*H*]-naphtho[2,1-*b*]pyrans can be fitted by a bi-exponential equation in all cases, thus confirming the presence of two major isomers of the opened form.

$$A_0(t) = a_1 \exp(-k_1 t) + a_2 \exp(-k_2 t) + \text{offset},$$

where k_1 is the first (fast) thermal bleaching rate constant, a_1 the amplitude of the first kinetic, k_2 the second (slow) thermal bleaching rate constant, a_2 the amplitude of the second kinetic, A_0 the absorbency at the photostationary state, and offset the residual absorbency.

It is important to underline that these results are totally consistent with those obtained during the study of 3,3-diphenyl-[3*H*]-naphtho[2,1-*b*]pyrans. In order to compare, we have also reported in the table, spectrokinetic parameters of three analogues from the 3,3-diphenyl-[3*H*]-naphtho[2,1-*b*]pyrans series (**10**, **11** and **12**) whose structures are detailed in Scheme 3.

All the spectroscopic and kinetic parameters of the synthesised molecules are reported in Table 2. A few years ago, we [19] proved by NMR spectroscopy that for 3,3-diphenyl-[3*H*]-naphtho[2,1-*b*]pyrans, the predominant isomer is a *trans*–*cis* (TC) isomer and that the minor one is the *trans*–*trans* (TT) isomer. This study has also shown that the former can be correlated to the higher kinetic constant

Table 2
Spectroscopic and spectrokinetic parameters

Compounds	λ_{\max} (nm)	A_0	K_1 (s ⁻¹)	a_1 (%)
1	453	0.28	0.055	56
2	464	0.15	0.239	65
3	468	0.16	0.190	61
4	465	0.17	0.117	61
5	456	0.25	0.063	67
6	449	0.40	0.048	39
7	457	0.42	0.056	59
8	449	0.48	0.064	44
9	485	0.68	0.024	65
10	432	0.18	0.061	81
11	445	0.10	0.260	85
12	446	0.08	0.290	86

and the latter can be correlated to the lower kinetic constant. According to this work one could suggest that in the case of the spirofluorene-[3'*H*]-naphtho[2,1-*b*]pyrans, the same transoid species are formed under irradiation. The TC isomer being responsible for k_1 and TT isomer being responsible for k_2 . The fast kinetic constant k_1 is quite homogenous over the series but a significant increase in this constant is observed when electron withdrawing groups are placed in the 8' and 9' positions (compounds **2**, **3** and **4**). In these cases, the increase in the fast kinetic constant leads to a decrease in the concentration of the coloured isomers in the medium and as a consequence, the maximum absorbency (A_0) is lower for these molecules (≤ 0.17). The biggest difference between the two series is found in the second constant k_2 which is very low and does not exceed 2.10^{-4} s^{-1} among the studied spirofluorene-[3'*H*]-naphtho[2,1-*b*]pyrans, showing the very high stability of the second isomer. In general, this slow kinetic constant is 10 times lower than for the equivalent 3,3-diphenyl-[3*H*]-naphtho[2,1-*b*]pyrans. It should also be noted that the distribution between TT and TC isomers for spirofluorene-[3'*H*]-naphtho[2,1-*b*]pyrans is very different from those observed for 3,3-diphenyl-[3'*H*]-naphtho[2,1-*b*]pyrans. In this family the relative abundance of the faster isomer represents more than 80% of the coloured species.

3.2. Photodegradation studies

Till now, the studies dealing with the photodegradation of spirofluorene-[3'*H*]-naphtho[2,1-*b*]pyrans have always been carried out under flash photolysis which does not accurately reproduce the conditions of use of these molecules. For this reason, the decrease in photochromic performance was followed by studying the dyes at the photostationary state after different exposures to light. To compare the photostability of the dyes, the $TA_{0/2}$ value (this corresponds to the time under continuous irradiation which is necessary to reduce the initial absorbency by half) can be defined. After a period of light exposure corresponding approximately to the $TA_{0/2}$, the toluene was removed under a flow of nitrogen and the photo-induced fragments were dissolved in acetonitrile and then analysed by GC/MS. In some cases, the structures of the by-products have been confirmed by the synthesis of authentic material.

As expected, spirofluorene-[3'*H*]-naphtho[2,1-*b*]pyrans are quite unstable under irradiation. The $TA_{0/2}$ values are quite homogenous over the series except for **9** which is dramatically unstable ($TA_{0/2} = 28 \text{ min}$). This particular behaviour can be explained by this compound's very low k_1 constant. On the one hand, this compound presents a very low thermal bleaching kinetic constant that allows an increase in the concentration of coloured species in the solution, which is consistent with the highest absorbency level. On the other hand, it is well known that the photodegradation reactions generally occur on the opened forms of the dyes [21,22]. For all the spirofluorene-[3'*H*]-naphtho[2,1-*b*]pyrans tested in this

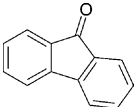
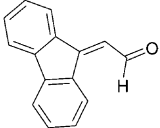
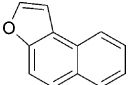
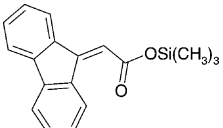
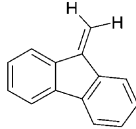
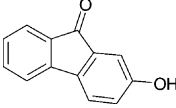
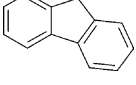
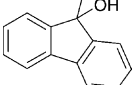
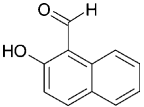
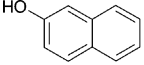
work, we have noted a high photodegradation rate compared to 3,3-diphenyl-[3*H*]-naphtho-[2,1-*b*]pyrans. This behaviour can be explained by the relatively high abundance of the slow isomer whose increased life-time allows its persistence in the solution even when irradiation is cut off and thus favours its degradation. After light exposure, the photo-induced fragments are injected in the GC/MS system. For the sake of clarity, the structures of all the determined by-products are reported in Table 3.

According to previous studies on spiro-indolinonaphthoxazines [20] and 3,3-diphenyl-[3*H*]-naphtho[2,1-*b*]pyrans [21,22] we have found that the by-products formed during the photodegradation of spirofluorene-[3'*H*]-naphtho[2,1-*b*]pyrans clearly result from photo-oxidation processes. Products such as fluorenone **P1**, cinnamaldehyde **P2**, and naphthofuran **P3**, have been determined in high abundance. In accordance with the literature data [23], it is reasonable to assume that **P1** and **P2** are produced when $^1\text{O}_2$ reacts with the diene systems formed in the photochromic interconversion reaction. In this case, it should be noted that singlet oxygen is sensitised by the open form of the photochromic dye [24]. Instead of a usual photophysical energy transfer mechanism one might assume that molecular oxygen can react with the biradical species formed after scission of the C–O bond of the naphthopyran ring [25]. The $^3\text{O}_2$ biradical adduct (shown in Scheme 4) undergoes a ring closure to the adjacent double bond to produce dioxetane intermediate. $^1\text{O}_2$ can then be thermally ejected to regenerate the ring-open form of the dye. Nevertheless, another reaction pathway involving molecular oxygen can be proposed to explain the formation of **P1**, **P2**, and **P3**. The above-mentioned dioxetane intermediate (obtained from cyclisation of the peroxy radical) can undergo a cleavage to give **P1** and **P2**. If cyclisation of the proposed peroxy radical to the more distant carbon of the double bond occurs, a diradical species is formed which can lead to 5-membered peroxide. From this new intermediate, elimination of **P1** followed by water elimination from the second fragment gives **P3**.

In 2000, we first reported [22] the formation of carboxylic acid derivatives during the degradation of 3,3-diphenyl-[3*H*]-naphtho[2,1-*b*]pyrans. Using the same method, i.e. silylating the hydroxyl group with bis(trimethylsilyl)trifluoroacetamide (BSTFA), we confirmed the formation of carboxylic acid **P4**.

In order to propose a mechanism explaining the formation of **P5**, **P2** was synthesised and its degradation was carried out under a range of conditions. The use of Rose Bengal as a photosensitiser enabled us to prove a degradation mechanism involving $^1\text{O}_2$ and to confirm an indirect degradation pathway leading to the fluorenone **P1** (see Scheme 5). When the degradation is performed without sensitiser, we observed the formation of carboxylic acid **P4** and the formation of **P5** is due to a photochemical decarboxylation. Molecular oxygen is also involved in the formation of 2-hydroxy-fluorenone **P6**. The addition of molecular oxygen on fluorenone **P1** under light exposure in the 2-position is already known [26].

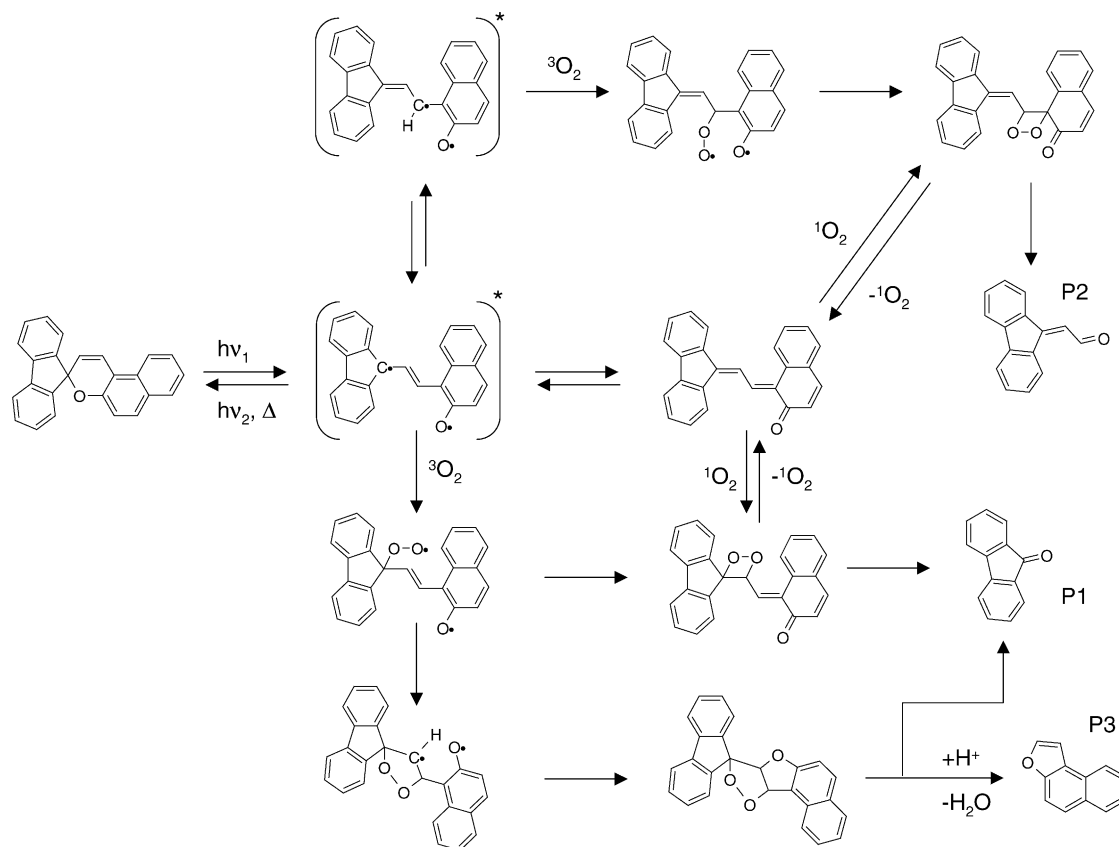
Table 3
Structures of the by-products generated from (1)

Structures	Formulae	Code	GC R.T.	MS most important fragments
	C ₁₃ H ₈ O	P1	10.2	181 (15), M ⁺ = 180 (100), 152 (44), 151 (26), 150 (16), 76 (12)
	C ₁₅ H ₁₀ O	P2	12.9	207 (27), M ⁺ = 206 (100), 205 (94), 180 (16), 178 (90), 177 (40), 176 (69), 151 (34), 76 (18)
	C ₁₂ H ₈ O	P3	8.7	169 (17), M ⁺ = 168 (100), 144 (22), 139 (54), 115 (17)
	C ₁₈ H ₁₈ O ₂ Si	P4	11.7	M ⁺ = 294 (3), 292 (7), 267 (7), 238 (10), 165 (32), 164 (13), 163 (14), 75 (13), 74 (9), 73 (100)
	C ₁₄ H ₁₀	P5	10.1	179 (16), M ⁺ = 178 (100), 177 (13), 176 (24), 152 (14), 151 (10), 150 (8), 76 (8)
	C ₁₃ H ₈ O ₂	P6	11.8	197 (12), M ⁺ = 196 (100), 168 (49), 140 (10), 139 (41)
	C ₁₃ H ₁₀	P7	9.0	167 (16), M ⁺ = 166 (100), 165 (90), 163 (19), 139 (12), 115 (17), 83 (10), 82.5 (11), 69.5 (10)
	C ₁₃ H ₁₀ O	P8	10.7	M ⁺ = 182 (18), 181 (100), 166 (14), 165 (25), 153 (18), 152 (54), 151 (17)
	C ₁₁ H ₈ O ₂	P9	9.2	173 (13), M ⁺ = 172 (100), 171 (66), 144 (51), 143 (12), 116 (16), 115 (81)
	C ₁₀ H ₈ O	P10	8.4	M ⁺ = 144 (100), 116 (14), 115 (63), 89 (7)

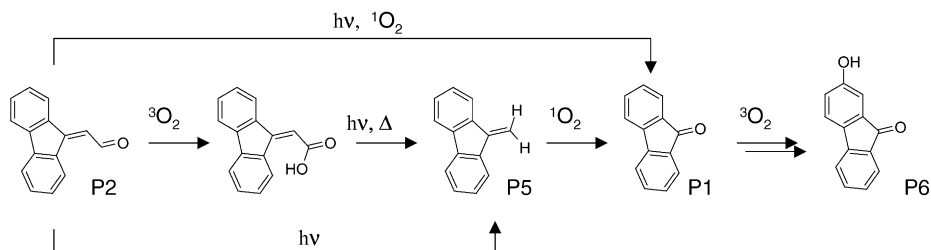
The decomposition of the peroxy radical thus formed, leads to **P6**. In order to explain the by-products resulting from the naphthalene moiety of the dye, we have carried out the same approach by preparing the naphtho[2,1-*b*]furan **P3**. Its degradation under various conditions helped us to support the hypothesis that 1-formylnaphth-2-ol **P9** and naphth-2-ol **P10** are produced via a second degradation pathway from **P3**. Other by-products such as fluorene **P7** and fluoren-9-ol **P8** have also been detected during the degradation experiment but they are suspected to be formed via radical processes, their formation mechanisms are still unknown.

In the case of functionalised spirofluoren-[3'*H*]-naphtho[2,1-*b*]pyrans, the same type of by-products have been de-

tected. The substitution groups seem to have only a minor influence on the general mechanisms of photo-oxidation. However, we can note the appearance of some new by-products in the case of brominated and triflated spirofluorene-[3'*H*]-naphtho[2,1-*b*]pyrans. During the photodegradation of the triflated compounds, hydrolysis of the triflate group is generally observed (formation of 8-hydroxy-spirofluoren-9,3'-[3'*H*]-naphtho[2,1-*b*]pyran during the degradation of (**8**)). This reaction has mostly been observed during the irradiation of (**3**). In the case of 8-bromospirofluoren-9,3'-[3'*H*]-naphtho[2,1-*b*]pyran, it should also be underlined that small amounts of this compound undergo a debromination reaction giving rise to (**1**).



Scheme 4. Speculative degradation mechanisms of spirofluorene-[3'H]-naphtho[2,1-b]pyrans.



Scheme 5. Secondary degradation products from spirofluorene-[3'H]-naphtho[2,1-b]pyrans.

Photodegradation studies reported until now have been performed in the presence of oxygen in order to reproduce the “real conditions” of the use of these dyes. The obtained results clearly indicate that in this case the photo-oxidation processes are responsible for the degradation of the dyes. It would be however interesting to compare the above-described degradation pathway with that occurring in the de-oxygenated solutions.

In these experiments we have limited ourselves to two representative molecules (**1**) and (**10**). The results should however be considered as preliminary.

From the obtained degradation profiles presented in Fig. 2, it is clear that the kinetic rates of bleaching are quite different if the irradiation is carried out with aerated or de-aerated

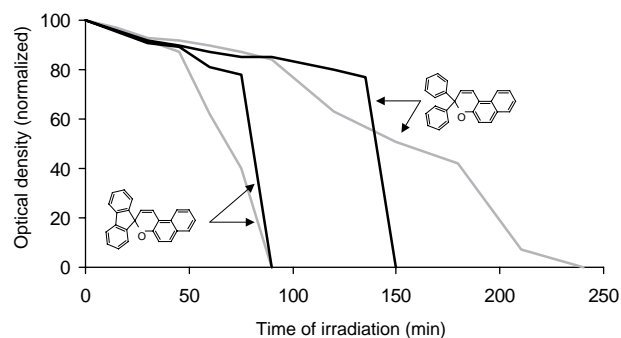


Fig. 2. Loss of the optical density measured in regular time intervals (aerated solution: grey line and de-aerated solution black line) for reference compounds (**1**) and (**10**).

solutions. After a period of relative stability of the dye (75 and 135 min for **(1)** and **(10)**, respectively) the kinetic rate of degradation strongly increases and the total bleaching of the photochromic solution is observed after additional 15 min. These degradation profiles seem to indicate that in the de-aerated solution different type of degradation reactions occurs. In order to understand this phenomenon we have subjected the by-products generated during the degradation of the compound **(1)** in these conditions to GC/MS identification.

In this case, traces of **P1**, **P2** and **P9** (that were the major photo-induced fragments when degradation is carried out with oxygen) have been detected. This indicates that a small amount of oxygen still remains in solution under our conditions despite careful de-aeration. However it should be underlined that secondary degradation products (**P6**, **P8** and carboxylic derivative of **P2**) identified in the first part of this work are not obtained anymore. **P5** becomes now one of the most important by-products and a new reaction pathway (different from that reported in Scheme 5) should be envisioned. One should also note that some fragments originating from the naphthalene moiety of the dye (**P3** and **P10**) seem to undergo the addition of benzyl radical generated during the irradiation of toluene. Further investigations concerning the position in which this addition takes place as well as the determination of the structure of some new by-products are actually in progress.

4. Conclusion

We have reported on the synthesis of new substituted spirofluorene-[3H]-naphtho[2,1-b]pyrans revealing photochromic properties in solution. The spectrokinetic study of these compounds confirms the formation of two isomers of the opened form under irradiation, each with very different kinetic ring closure constants. We have demonstrated that despite their poor kinetic parameters and their high photodegradability, their spectroscopic properties can be matched and significantly enhanced by suitable substitution. Ratios between the different isomers of the opened forms could also be modified in this way using sterically challenging groups. The complete determination of photo-induced fragments, under continuous irradiation, confirms that these molecules are extremely sensitive to photo-oxidation processes and that the degradation pathways are almost identical to those observed for 3,3-diphenyl-[3H]-naphtho-[2,1-b]pyrans. Exploratory degradation experiments in de-aerated solutions have shown that radical processes involving the solvent may be responsible for the degradation when oxygen is removed. Henceforth, this work will help us to develop new strategies for increasing the life-time of these dyes under irradiation (structural modifications or use of antioxidants). Furthermore, some of the new functionalised

molecules bearing bromo or triflate groups could be considered as good precursors for developing more complicated structures using for example palladium cross-coupling reactions.

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