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Thermally reversible photochromic behaviour of new naphthopyrans involving an intramolecular [2+2] cyclization reaction

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ABSTRACT

New 4-(2,2-diphenylethenyl)naphthopyrans were synthesized and their photochromic behaviour in solution were studied under continuous UV light irradiation conditions. Although only one coloured photoproduct was expected to be formed, due to the naphthopyran substitution pattern, NMR analysis on degassed UV irradiated solutions, performed at low temperature, showed the formation of different compounds. Among them, the main product is formed through an intramolecular [2+2] cyclization reaction and show thermally reversible photochromic properties.

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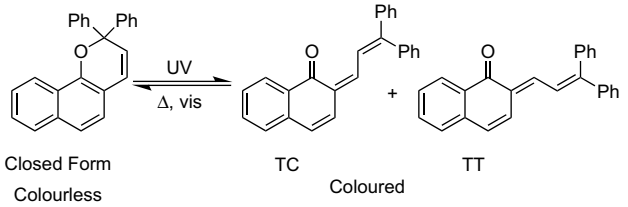
1. Introduction

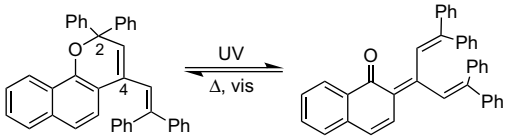
The photochromic properties of naphthopyrans have been extensively studied in the last decade due to the wide range of applications with prominence in the manufacture of ophthalmic plastic lenses and solar protection glasses.[1] Under near-UV light irradiation these uncoloured molecules undergo a pyran-ring opening with formation of the trans,cis isomer (TC, major product) that, upon isomerization of the double bond, leads to the trans,-trans isomer (TT, minor product) (Scheme 1). A photostationary state is usually reached after several minutes of irradiation.

When the light source is removed the system returns to the original colourless state, either via a thermal or a photoinduced process. The two photoisomers, although exhibiting similar absorption spectra, show very different thermal stabilities. While the TC isomer rapidly returns to the uncoloured closed form, the TT isomer is thermally more stable and shows a fading rate 10^2 to 10^3 times slower and is therefore responsible for the persistence of a residual colour for several minutes/hours after the removal of the light source.[2]

In order to tune the photochromic properties of these systems a great number of substitution patterns and/or annelations have been investigated. Although hundreds of substituted naphthopyrans have been synthesized during the last 15 years, there are very few examples of 2*H*-naphtho[1,2-*b*]pyrans substituted in position 4.[3] Such substituent is expected to cause a strong steric hindrance that interferes with the conversion from the *cis*-quinoidal (TC) to the *trans*-quinoidal species (TT). However, the presence of a 4-(2,2-diphenylethenyl) substituent in the 2*H*-naphtho[1,2-*b*]pyran structure could play an interesting role since for such molecule only one photoisomer is expected to be obtained. After the occurrence of the photochemical pyran-ring opening, the photoisomerization of the double bond will not, presumably, produce different



Scheme 1. Photochromic equilibrium for 2*H*-naphtho[1,2-*b*]pyrans.



Scheme 2. Expected photochromic equilibrium for 4-(2,2-diphenylethenyl)-2*H*-naphtho[1,2-*b*]pyran.

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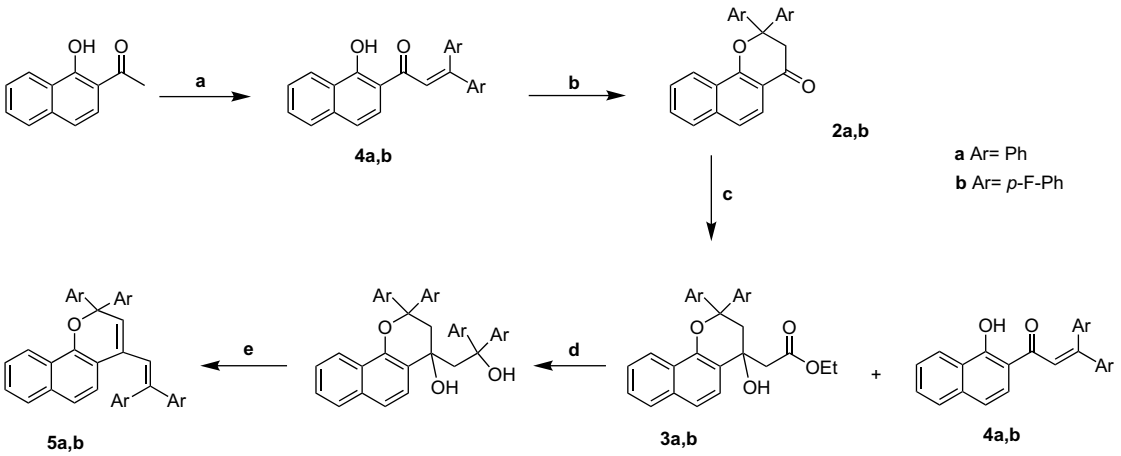
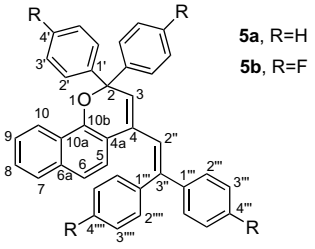


Scheme 3. Synthesis of 4-(2,2-diphenylethenyl)-2*H*-naphtho[1,2-*b*]pyrans **5a**,**b**. Reagents and conditions: (a) ArCOAr **1a**,**b**, *t*-BuOK, toluene, reflux; (b) H_2SO_4, rt; (c) Zn, $BrCH_2COOEt$, I_2, reflux; (d) ArMgBr, THF, reflux; (e) CH_3COOH, reflux.

photoisomers (Scheme 2). Moreover such photoproduct is likely to be relatively unstable due to steric hindrance and rapidly fade to the uncoloured form thus producing a fast bleaching photochromic compound.

In this paper we describe the synthesis and photochromic behaviour, under near-UV irradiation, of two new 4-(2,2-diphenylethenyl)-2*H*-naphtho[1,2-*b*]pyrans **5a** and **5b**. Compound **5b** is the tetrafluoro derivative of **5a** in which the four fluorine atoms are in the *para* position of the phenyl rings. This substitution pattern enables the photoisomerization process to be probed by ^{19}F NMR spectroscopy and to increase the spectral resolution in ^1H NMR by reducing the signals overlapping in the aromatic part.

Table 1
NMR spectral data for naphthopyrans **5a**,**b** in $CDCl_3$



	5a	**5b**	**5a**	**5b**
	^1H (*J* in Hz)		^{13}C	
2	—	—	82.9	82.3
3	5.81, d (1.6)	5.67, d (1.4)	126.9	126.3
4	—	—	131.6	131.9
4a	—	—	116.9	116.4
5	7.50	7.45	122.4	122.0
6	7.39	7.41	120.4	120.8
6a	—		134.6	134.8
7	7.76	7.78, d (7.9)	127.6	127.7
8	7.47	7.49, dd (6.9, 7.9)	126.4	126.7
9	7.51	7.51, dd (6.9, 8.4)	125.6	125.9
10	8.40, d (8.0)	8.33, d (8.33)	122.3	122.1
10a	—	—	124.6	124.6
10b	—	—	147.9	147.6
1′	—		145.2	140.5
2′	7.10	7.06, dd (5.3, 8.8)	126.7	128.4
3′	7.20	6.91, dd (8.8, 8.8)	128.0	115.0
4′	7.20	—	127.2	162.1, d ($^3J_{F-C}$=249 Hz)
2″	6.86, d (1.6)	6.80, d (1.4)	124.8	124.7
3″	—	—	146.2	144.5
1‴	—	—	140.2	135.9
2‴	7.29	7.18, dd (5.4, 8.7)	130.2	131.7
3‴	7.35	7.00, dd (8.7, 8.7)	128.6	115.7
4‴	7.35	—	127.1	162.7, d ($^3J_{F-C}$=250 Hz)
1⁗	—	—	142.4	138.1
2⁗	7.35	7.32, dd (5.4, 8.7)	128.3	129.6
3⁗	7.35	7.05, dd (8.7, 8.7)	127.8	115.3
4⁗	7.35	—	127.6	162.2, d ($^3J_{F-C}$=250 Hz)

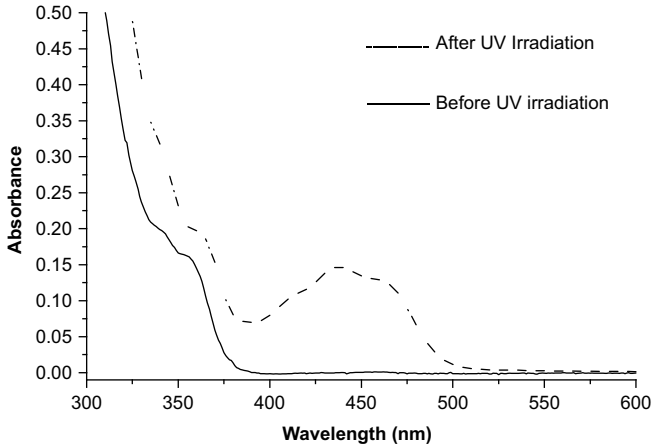


Figure 1. UV–vis absorption spectra of naphthopyran **5a** before and after UV irradiation.

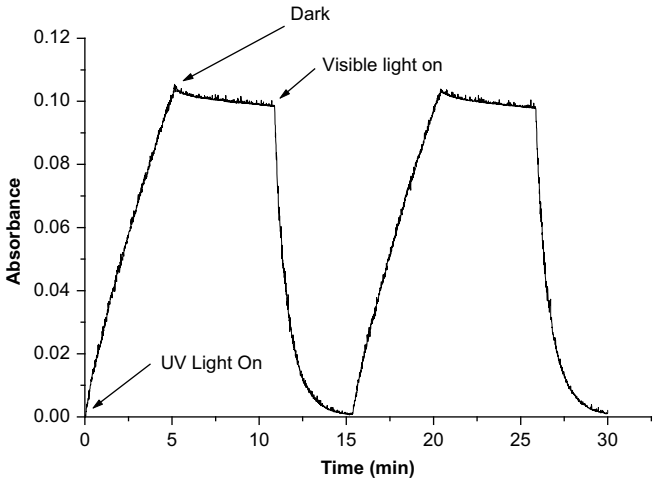


Figure 2. Colour forming and colour bleaching of naphthopyran **5b**.

2. Results and discussion

2.1. Synthesis

Compounds **5a** and **5b** were prepared in three steps from 1-hydroxy-2-acetonaphthone according to Scheme 3. The reaction of 1-hydroxy-2-acetonaphthone with benzophenone in the presence of sodium *tert*-butoxide is known to give a α,β-unsaturated ketone that cyclizes under acidic treatment to give 2,2-diphenylnaphthopyran-4-one **2a**.[4] However a very large excess of benzophenone is used, which renders very difficult the isolation of the product. A typical experiment uses 12 equiv of benzophenone, 9 equiv of base, 20 h of reflux and after treatment with HBr/HOAc and steam distillation of the unreacted starting materials, the naphthopyran-4-one is isolated by column chromatography with 57% yield.[5] We have found an easier methodology using only 3 equiv of the ketone. Thus a mixture of 1-hydroxy-2-acetonaphthone (1 equiv), diarylketone **1a**,**b** (3 equiv) and *t*-BuOK (5 equiv) was heated under reflux for 3 h giving rise to the red coloured α,β-unsaturated ketones **4a**,**b**. Treatment of these compounds with H_2SO_4 for 3 h at room temperature afforded the naphthopyran-4-ones **2a**,**b**, which were easily purified by column chromatography, in 56–61% yield.

The Reformatsky reaction of **2a**,**b** with ethyl bromoacetate/Zn in the presence of iodine gave, after hydrolysis, mainly the naphthopyran-4-ols **3a**,**b** (69–70%) resulting from the addition to the ketone, along with α,β-unsaturated ketones **4a**,**b** formed by isomerization of the starting naphthopyran-4-ones (17–20%). The naphthopyran-4-ols **3a**,**b** were then treated with the Grignard reagent derived from bromobenzene or 1-bromo-4-fluorobenzene, in THF, affording after hydrolysis the corresponding diols that were dissolved in acetic acid and heated under reflux for 20 min affording naphthopyrans **5a**,**b** in 47–58% yield. The complete ^{1}H and ^{13}C assignments for compounds **5a**,**b** are given in Table 1. The spectrum of the tetrafluoro compound **5b** exhibited improved resolution by reducing overlapping of signals, so enabling spectral assignments and measurements of coupling constants to be performed accurately.

2.2. Photochromic behaviour under continuous UV irradiation at 20 °C

In toluene solution (10^{-4} M) naphthopyrans **5a**,**b** are nearly colourless compounds with a very strong absorption in the UV region.

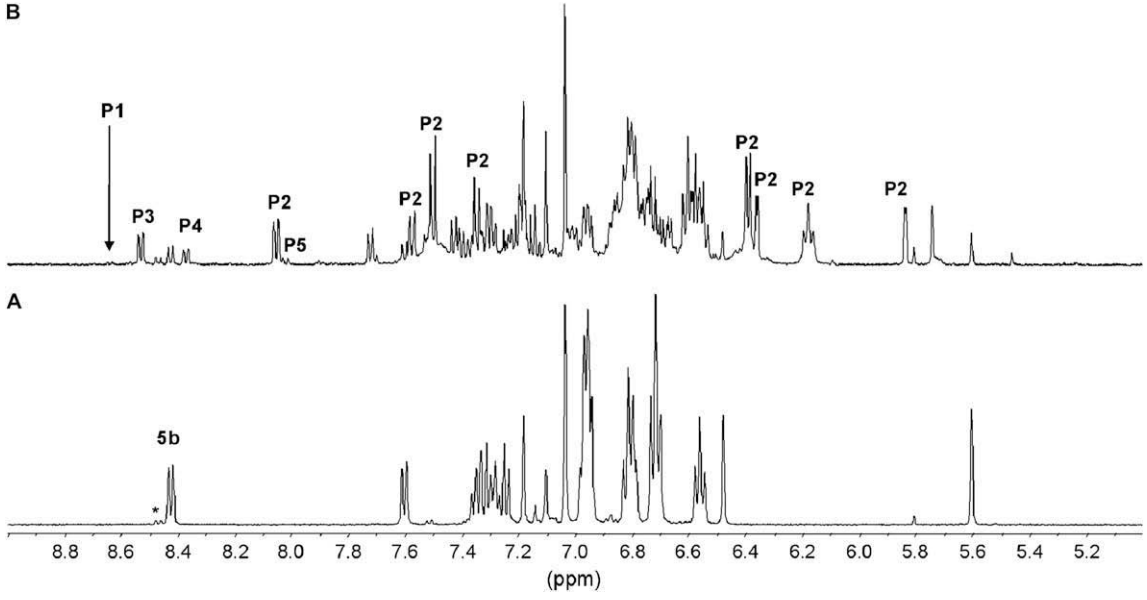


Figure 3. ^{1}H NMR spectra of **5b** (A) before and (B) after 8 min of UV irradiation at 225 K (*, impurities).

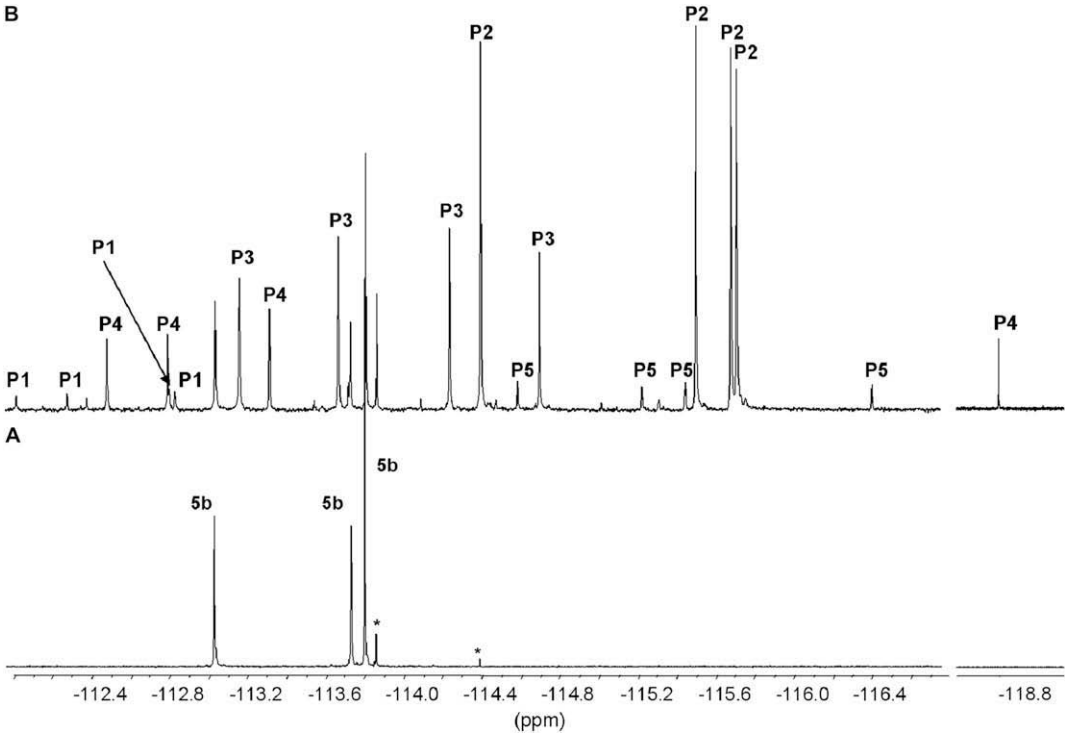


Figure 4. ^{19}F NMR spectra of **5b** (A) before and (B) after 8 min of UV irradiation at 225 K.

Continuous UV light irradiation (150 W ozone free Xe lamp), using a filter Schott 011FG09 ($259<\lambda<388$ nm with $\lambda_{max}=330$ nm and $T=79\%$) of a toluene solution of **5a**, at 20 °C, leads to the development of a pale yellow colouration (Fig. 1) with a maximal absorption at 435 nm.

The absorbance at the maximal absorption wavelength increased with time but the photostationary state was not achieved even after 30 min of irradiation (Fig. 2). When the UV irradiation was turned off, the absorbance decreased very slowly following a monoexponential kinetic underlining the formation of only one relatively stable coloured species. The return to the uncoloured state was achieved under visible irradiation (>420 nm). The photochromic behaviour of these compounds was reproducible.

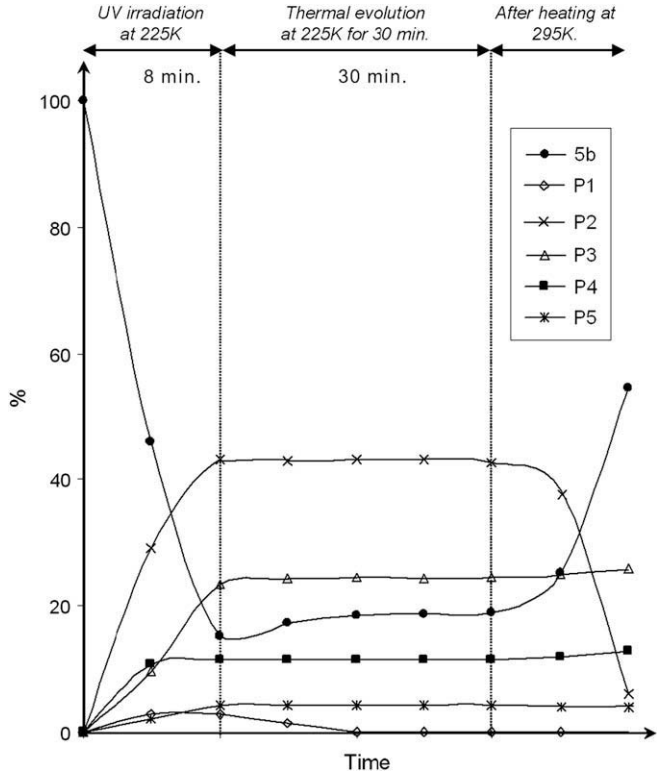


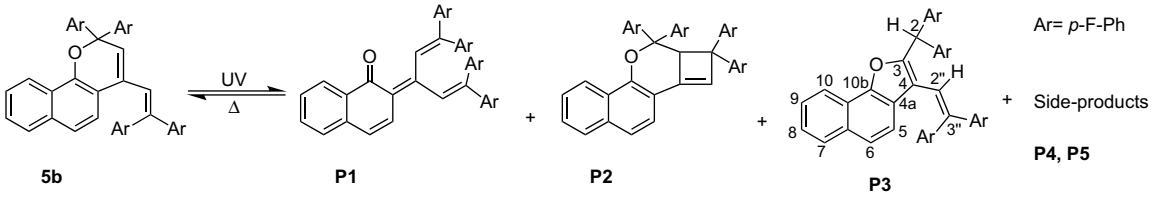
Figure 5. Time-evolution of the different photoproducts of compound **5b**.

2.3. NMR analysis of UV irradiated solutions

To clarify the structure of the photoisomers formed upon UV irradiation, NMR studies of fluoro-substituted naphthopyran **5b**, in degassed toluene solutions, have been carried out before and after UV irradiation.[6] Experiments have been performed at low temperature (225 K) to slow the well-known thermal evolution of open forms.[7] Irradiation with filtered UV-band ($259<\lambda<388$ nm with $\lambda_{max}=330$ nm) led to the appearance of a red colouration that rapidly changed to yellow. This colour change was visible to the naked eye. ^{1}H and ^{19}F NMR spectra (Figs. 3 and 4) of the same sample of **5b** were recorded before irradiation, after 4 and 8 min of UV irradiation, within the thermal evolution at 225 K for 30 min and finally after two periods of heating at room temperature, to accelerate the bleaching.

By measuring the peak-intensities (Fig. 5), five different photoproducts, labelled **P1** to **P5**, were clearly evidenced, but only compounds named **P1** and **P2** presented a reversion to the initial compound while the three other photoproducts remained at constant concentration, and, therefore were attributed to side-products (Scheme 4).

Compound **P1** appears very unstable at 225 K and its concentration is very low, 2% and 3% after 4 and 8 min of irradiation, respectively. It is characterized by a doublet of doublets at 8.64 ppm in ^{1}H NMR and four lines at −112.06, −112.32, −112.84 and −112.87 ppm in ^{19}F NMR. As this structure is not thermally stable and decreases toward **5b**, in parallel with the bleaching from red to yellow colours, it can be reasonably associated with the only possible transoid isomer of photomerocyanine, strongly hindered and



Scheme 4. Photochromic equilibrium for naphthopyran **5b**.

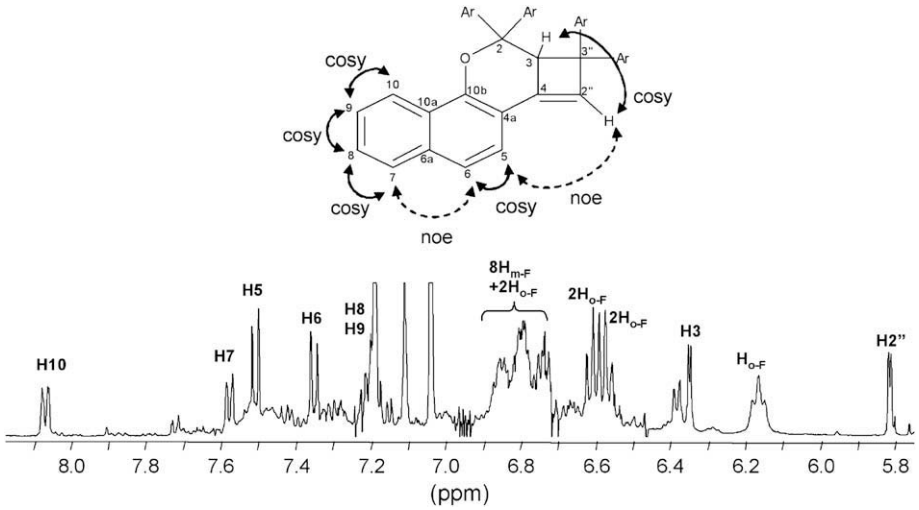


Figure 6. Structure of **P2** with characteristic ^{1}H–^{1}H correlations evidenced from 2D NMR COSY (solid arrows) and NOESY (dotted arrows), and its ^{1}H NMR subtracted spectrum.

therefore very unstable. Moreover, the chemical shifts in ^{19}F NMR are in complete agreement with the area characteristic of the fluoro-phenyl groups attached to sp^2 carbon.[7,8]

The photoproduct **P2** is stable at 225 K, but it undergoes a thermal reversion toward the initial compound **5b** when kept at room temperature. In our experimental conditions, the formation of **P2** appears as the major part of the reactivity of **5b**, as clearly indicated in ^{1}H and ^{19}F NMR spectra (Figs. 3 and 4) and in Figure 5 (29% and 43% after 4 and 8 min of irradiation, respectively). Compound **P2** is evidenced in ^{19}F NMR by four lines at the chemical shifts −114.44, −115.53, −115.10 and −115.75 ppm, therefore in the area characteristic of fluoro-phenyl attached to sp^3 carbon.[7,8] Compound **P2** has been characterized from one (Fig. 6) and two-dimensional (COSY for scalar correlations, NOESY for dipolar correlations, ^{1}H–^{13}C HSQC for direct correlation and HMBC for long-range correlations) NMR experiments (Figs. 7 and 8).

More particularly, scalar couplings have been observed between the two doublet signals at 5.82 and 6.35 ppm, with a coupling constant value of ^{4}J=3.6 Hz, and between the two doublets at 7.35 and 7.50 ppm (^{3}J=8.4 Hz). Besides, a dipolar correlation between the doublet at 5.82 ppm and the doublet at 7.50 ppm enabled us to attribute these signals to proton H2″ and proton H5, respectively. Both tertiary carbon atoms C2″ and C3 have been characterized at 124.7 ppm and 98.9 ppm, respectively (Fig. 7). In the HMBC map, long-range correlations through two, three and four bonds provided further confirmation of the assignment. Particularly relevant were the cross-peaks between H2″–C3 and H3–C2″ (Fig. 8). The set of chemical shifts in ^{1}H and in ^{13}C is close to the data measured with the initial compound, indicating a relatively similar structure. However, the main change concerns the chemical shifts of atoms in position 3. The observed values can be associated to the change in the hybridization of the carbon C3 from sp^2 to sp^3, and the deshielding of H3 can be explained by the electronic environment of the four phenyl groups. The two fluoro-phenyl groups on carbon 2 and the two fluoro-phenyl groups on carbon 3″ are not equivalent because they became diastereotopic due to the C3 stereocenter.

Therefore, the only possible structure able to justify these observations results from an electrocyclic reaction that forms a four-membered ring: the 1,3-diene-type structure **5b** photocyclises toward a cyclobutene derivative through the bond formation between C3 and C3″. Because of the angle strain associated with a four-membered ring, the cyclobutene derivative **P2** can only be produced and stabilized at low temperature and then thermally returns back to the initial compound at room temperature.

Concerning the three remaining photoproducts (**P3**, **P4** and **P5**), they showed no reversion toward the initial naphthopyran; therefore they were attributed to side-products. The photoproduct **P3** (9% and 22% after 4 and 8 min of irradiation, respectively) was identified to a furan derivative, resulting from a ring contraction of the pyranic structure **5b** (Scheme 4). Recently, Gabbutt et al. have reported a similar behaviour with the ring contraction during the 6π-electrocyclisation of naphthopyrans.[9] In **P3**, the carbon atom in position 2 is attributed to a signal at 45.1 ppm and correlated to H2 at 5.75 ppm, in complete agreement with NMR data described in Ref. 9. As for the position 2″, the carbon atom is highly deshielded at 142.7 ppm and is attached to H at 7.12 ppm. The set of data deduced for **P3** is gathered in Table 2. As for **P4** and **P5**, they were not unambiguously identified due to their small concentrations and overlapping signals.

3. Conclusion

Continuous UV light irradiation of a toluene solution of naphthopyran **5b** at low temperature (225 K) led to the formation of different photoproducts: the highly unstable coloured photomerocyanine **P1** that rapidly fades to the uncoloured closed form **5b**, a photochromic cyclobutene derivative **P2** resulting from [2+2] intramolecular cyclization that upon heating to room temperature

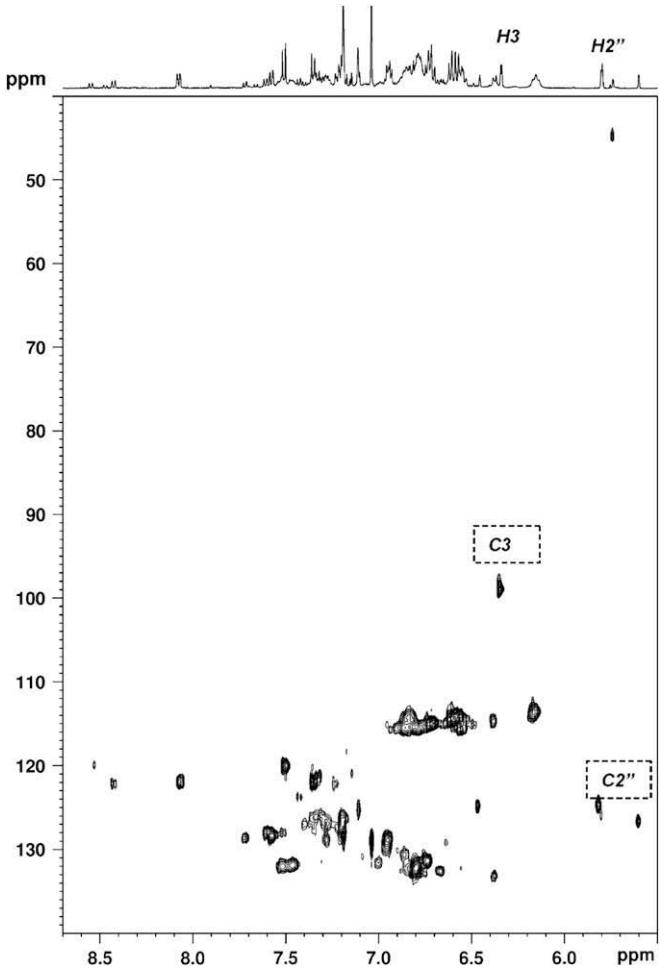


Figure 7. 2D NMR ^{1}H–^{13}C direct correlations (HSQC experiment).

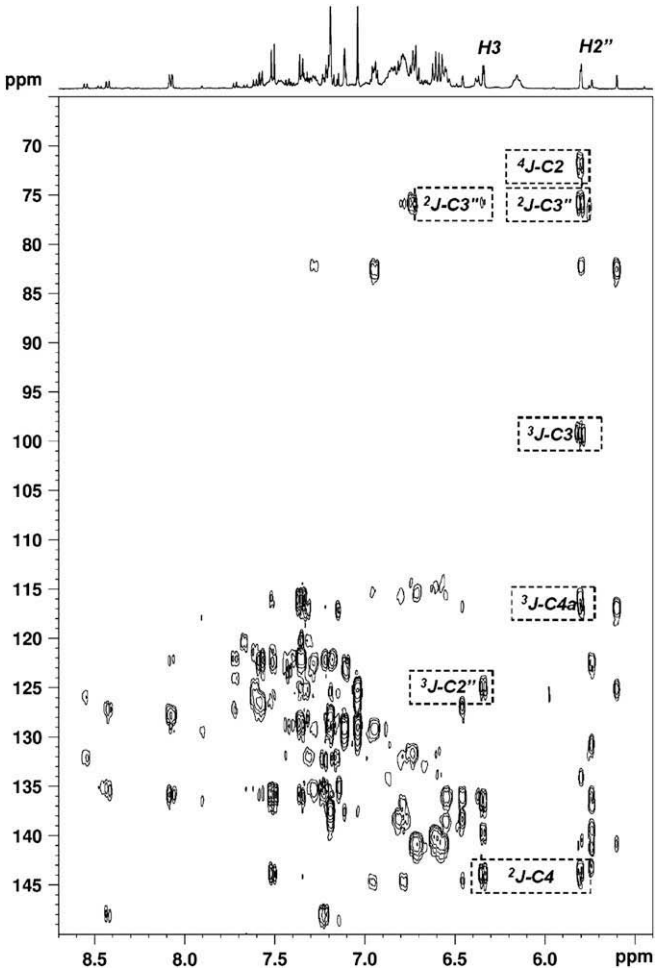


Figure 8. 2D NMR ^{1}H–^{13}C long-range correlations (HMBC experiment).

fades to **5b** and side-products, one of which, **P3**, was identified as a furan derivative.

4. Experimental

4.1. General methods

The reactions were monitored by thin-layer chromatography on aluminium plates precoated with Merck silica gel 60 F_{254} (0.25 mm). Column chromatography (CC) was performed on silica gel 60 (70–230 mesh). The new compounds were determined to be >95% pure by ^{1}H NMR spectroscopy. The ^{1}H and ^{13}C NMR spectra were recorded at 298 K in $CDCl_3$ using a Bruker ARX400 spectrometer (at 400.13 and 100.62 MHz). Chemical shifts (δ) are reported in parts per million and coupling constants (J) in hertz. UV–vis spectra were recorded on a CARY 50 Varian spectrophotometer. IR spectra were obtained on a Perkin–Elmer FTIR 1600 spectrometer using KBr disks (wavenumbers in cm^{-1}). Electronic impact mass spectra were measured with an AutoSpecE spectrometer.

4.2. Spectrokinetic studies under continuous irradiation

UV–vis irradiation experiments were made using a CARY 50 Varian spectrometer coupled to a 150 W Ozone free Xenon lamp (6255 Oriel Instruments), equipped with a filter Schott 011FG09 ($259<\lambda<388$ nm with $\lambda_{max}=330$ nm and $T=79\%$). The light from the UV lamp was filtered using a water filter (61945 Oriel Instruments) and then carried to the spectrophotometer holder at the right angle to the monitoring beam using an optical fiber system (77654 Oriel Instruments); 40 W m^{-2} light flux was used (Goldilux Photometer with UV-A probe). Visible irradiation experiments were performed using a long-pass filter, Schott GG 420 (Oriel 59480). A thermostated (20 °C) 10 mm quartz cell (3.5 mL sample solution, 1.0×10^{-4} M) equipped with magnetic stirring was used. In a preliminary experiment, the UV–vis absorption spectra of the closed and open forms and the λ_{max} of the open form were determined. In a second experiment the absorbance at photostationary equilibrium, A_{eq}, was measured at λ_{max} and then the decrease in the absorbance versus time was monitored.

Table 2
NMR spectral data for photoproducts **P2** and **P3**

	P2		**P3**	
	^{1}H	^{13}C	^{1}H	^{13}C
2	—	71.7	5.75	45.1
3	6.35	98.9	—	?
4	—	143.8	—	122.1
4a	—	116.1	—	122.8
5	7.50	120.0	7.17	118.2
6	7.35	122.0	7.42	123.4
7	7.58	128.4	7.72	128.2
8	7.20	127.8	7.30	125.0
9	7.39	126.0	7.40	126.4
10	8.07	121.9	8.53	119.8
10b	—	163.8	—	151.0
2″	5.82	124.7	7.12	142.6
3″	—	74.6	—	?[a]

[a] Not attributed due to low concentration of the compound.

4.3. NMR studies

For NMR investigations, samples (10^{-3} M in toluene-d_8) were irradiated directly in the NMR tube (5 mm), thermoregulated, using a 1000 W Xe–Hg HP filtered short-arc lamp (Oriel) equipped with filter for UV irradiation (Schott 011FG09, $259<\lambda<388$ nm). After irradiation had been stopped, the sample was transferred into the thermoregulated probe, QNP (^{1}H–^{13}C–^{19}F–^{31}P) or TXI (^{1}H–^{13}C–^{15}N), of a Bruker Avance-500 spectrometer (ν_0 (^{1}H)=500 MHz, ν_0 (^{13}C)=125 MHz, ν_0 (^{19}F)=470 MHz).

4.4. Synthesis of the naphthopyran-4-ones 2a,b

A suspension of diarylketone **1a**,**b** (8.1 mmol), 1-hydroxy-2-acetonaphthone (2.7 mmol, 0.500 g) and *t*-BuOK (13.4 mmol, 1.5 g) in 20 mL of toluene was heated under reflux for 3 h. During the heating the suspension become progressively red. After cooling to room temperature the solution was quenched with H_2O (100 mL), extracted with Et_2O (3×40 mL) and the combined organic layers dried (Na_2SO_4) and concentrated under reduced pressure leaving about 5 mL of solvent. The red residue was treated with H_2SO_4 (4 mL), stirred 3 h at room temperature and then poured into ice. The pale pink mixture was then extracted 3× with EtOAc. The combined organic layers were washed with water, dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by CC (3% EtOAc/petroleum ether then 20% EtOAc and 20% CH_2Cl_2 in petroleum ether) to give pure **2a**,**b** as pale yellow crystals.

*4.4.1. 2,2-Diphenyl-3,4-dihydro-2H-naphtho[1,2-b]pyran-4-one **2a***

White solid. Mp 176–178. Yield 56%. IR: 3058, 3037, 1680. ^{1}H NMR: 8.57 (dd, *J*=7.2, 1 Hz, 1H), 7.76 (m, 2H), 7.64–7.57 (m, 2H), 7.50 (m, 4H), 7.34–7.21 (m, 7H), 3.60 (s, 2H). MS (TOF): *m*/*z* (%): 350 (22), 273 (21), 171 (11), 170 (100), 114 (17), 85 (16), 83 (26).

*4.4.2. 2,2-Di(p-fluorophenyl)-3,4-dihydro-2H-naphtho-[1,2-b]pyran-4-one **2b***

White solid. Mp 187–191. Yield 61%. IR: 3066, 2981, 1672, 1600, 1508, 1380, 1287, 1234, 1150, 1114, 835. ^{1}H NMR: 8.54 (dd, *J*=1.7, 8.5 Hz, 1H), 7.80 (m, 2H), 7.67–7.63 (m, 2H), 7.48 (m, 4H), 7.39 (d, *J*=8.6 Hz, 1H), 7.01–6.97 (m, 4H), 3.57 (s, 2H). ^{13}C NMR: 190.8 (C=O), 163.7 and 160.4 (C–F), 157.3, 138.2 (C), 137.8, 129.7, 128.1, 128.0 (C), 126.6, 125.2, 123.0, 121.4, 121.3, 116.0, 86.5, 48.4. MS (TOF): *m*/*z* (%): 386 (11), 291 (4), 170 (100), 114 (28).

4.5. Reaction of naphthopyran-4-ones 2a,b with ethyl bromoacetate

A solution of **2a**,**b** (0.86 mmol) and ethyl bromoacetate (3.64 mmol, 0.600 g) in 20 mL of ethyl ether/benzene (1:4) was slowly added over 2 h to a mixture of zinc (9.17 mmol, 0.600 g) and iodine (one crystal) and heated with stirring under reflux. After the addition the orange solution was maintained under reflux with stirring for one additional hour and then poured into water. The aqueous phase was extracted 3× with EtOAc and the combined organic layers dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by CC (3–10% EtOAc/petroleum ether).

*4.5.1. From naphthopyran-4-one **2a** two compounds were obtained: alcohol **3a** and ketone **4a***

*4.5.1.1. Ethyl(2,2-diphenyl-4-hydroxy-3,4-dihydro-2H-naphtho[1,2-b]pyran-4-yl)acetate **3a**.* Pale yellow oil. Yield 69%. IR: 3489, 3006, 1729, 1576, 1494, 1397, 1204. ^{1}H NMR: 8.55 (dd, *J*=8.0, 1.6 Hz, 1H), 7.80 (dd, *J*=7.0, 1.4 Hz, 1H), 7.60–7.41 (m, 8H), 7.31–7.17 (m, 6H), 4.14–4.08 (m, 2H), 3.42 (d, *J*=14.5 Hz, AB system, 1H), 3.32 (d, *J*=14.5 Hz, AB system, 1H), 2.85 (d, *J*=16.2 Hz, AB system, 1H), 2.25 (d, *J*=16.2 Hz, AB system, 1H), 1.19 (t, *J*=7.1 Hz, 3H). MS (TOF) *m*/*z* (%): 438 (1), 420 (3), 350 (61), 333 (13), 273 (59), 180 (21), 178 (24), 170 (100), 165 (30), 114 (43).

*4.5.1.2. 2-(1-Oxo-3,3-diphenylprop-2-enyl)-1-naphthol **4a**.* Orange solid. Mp 126–127. Yield 20%. IR: 3047, 3430, 3021, 2960, 1620, 1587, 1314, 1260, 1058, 808. ^{1}H NMR: 14.2 (OH), 8.49 (dd, *J*=1.3, 8.4 Hz, 1H), 7.81 (d, *J*=8.8 Hz, 1H), 7.77 (d, *J*=7.9 Hz, 1H), 7.65 (ddd, *J*=1.3, 6.8, 7.9 Hz, 1H), 7.55 (ddd, *J*=1.2, 6.8, 8.4 Hz, 1H), 7.50–7.28 (m, 10H), 7.28 (s, 1H), 7.25 (d, *J*=78.8 Hz, 1H). ^{13}C NMR: 196.99 (C=O), 163.47, 155.13, 141.43, 139.03, 137.35, 130.13, 129.75, 129.60, 128.78, 128.64, 128.55, 128.28, 127.43, 125.87, 125.35, 125.08, 124.45, 123.12, 118.18, 114.20. MS (TOF) *m*/*z* (%): 350 (21), 273 (30), 170 (100), 114 (7).

*4.5.2. From naphthopyran-4-one **2b** two compounds were obtained: alcohol **3b** and ketone **4b***

*4.5.2.1. Ethyl(2,2-di(4-fluorophenyl)-4-hydroxy-3,4-dihydro-2H-naphtho[1,2-b]pyran-4-yl)acetate **3b**.* Pale yellow oil. Yield 70%. IR: 3486, 3116, 2993, 1729, 1606, 1578, 1509, 1398, 1376, 1229. ^{1}H NMR: 8.47 (d, *J*=7.8 Hz, 1H), 7.80 (dd, *J*=7.0, 1.5 Hz, 1H), 7.60–7.40 (m, 8H), 7.03–6.90 (m, 4H), 4.18–4.06 (m, 2H), 3.31 (s, 2H), 2.88 (d, *J*=16.3 Hz, AB system, 1H), 2.26 (d, *J*=16.3 Hz, AB system, 1H), 1.17 (t, *J*=7.1 Hz, 3H). (M=474). MS (TOF) *m*/*z* (%): 474 (0.2), 456 (0.1), 409 (4), 386 (39), 369 (33), 201 (44), 170 (100), 114 (85).

*4.5.2.2. 2-(1-Oxo-3,3-di(p-fluorophenyl)prop-2-enyl)-1-naphthol **4b**.* Orange solid. Mp 134–135. Yield 17%. IR: 3046, 1610, 1571, 1504, 1411, 1222, 1159, 833, 806. ^{1}H NMR: 14.10 (OH), 8.47 (dd, *J*=1.2, 8.3 Hz, 1H), 7.80–7.74 (m, 2H), 7.66 (dd, *J*=6.8, 7.9 Hz, 1H), 7.54 (dd, *J*=6.8, 8.3 Hz, 1H), 7.40–7.36 (m, 2H), 7.26–7.21 (m, 3H), 7.19 (s, 1H), 7.11 (m, 2H), 7.04 (m, 2H). ^{13}C NMR: 196.56 (C=O), 162.0 and 165.3, 161.3 and 164.6, 163.66, 152.9, 137.4, 137.38, 134.7, 131.6, 130.6, 130.3, 127.43, 126.0, 125.3, 124.8, 124.5, 123.06, 118.32, 115.76, 115.4, 114.0. MS (TOF) *m*/*z* (%): 386 (18), 291 (8), 201 (9), 170 (100), 114 (15). Exact mass: calculated for $C_{25}H_{16}O_2F_2$: 386.1118; found: 386.1126.

4.6. Reaction of naphthopyran-4-ols 3a,b with the Grignard reagent ArMgBr

A solution of arylmagnesium bromide (prepared from bromobenzene (0.78 g, 5 mmol) or 4-bromo-1-fluorobenzene (0.87 g, 5 mmol) and magnesium (0.240 g, 10 mmol) in 20 mL of dry THF) was slowly added to a solution of naphthopyran-4-ol **3a**,**b** (0.40 mmol) in dry THF (15 mL). After heating under reflux for 2 h, the solution was quenched with water, extracted with Et_2O (3×50 mL), dried (Na_2SO_4) and concentrated under reduced pressure. Acetic acid (10 mL) was added to the residue and the solution heated under reflux for 20 min. The red solution thus obtained was quenched with water, extracted with Et_2O (3×50 mL), dried (Na_2SO_4) and concentrated under reduced pressure. The residue was then purified by CC (0–1% EtOAc/petroleum ether) to give pure **5a**,**b** as pale yellow solids. Recrystallization from CH_2Cl_2/petroleum ether gave pure **5a**,**b** compounds as white solids.

*4.6.1. 2,2-Diphenyl-4-(2,2-diphenylethenyl)-2H-naphtho-[1,2-b]pyran **5a***

White solid. Yield 47%. IR: 3052, 3018, 1612, 1490, 1440, 1379, 1263, 1213, 1118, 1074, 973, 754, 696. For NMR data see Table 1. MS (TOF) *m*/*z* (%): 512 (M^+, 43), 435 (M^+−Ph, 100), 345 (31), 333 (27), 167 (19), 165 (16). Exact mass: calculated for $C_{39}H_{28}O$: 512.2140; found: 512.2123.

4.6.2. 2,2-(4-Fluorophenyl)-4-[2,2-di(4-fluorophenyl)-ethenyl]-2H-naphtho[1,2-b]pyran ***5b***

White solid. Yield 58%. IR: 3051, 1602, 1502, 1379, 1225, 1159, 835, 815. For NMR data see Table 1. MS (TOF) *m*/*z* (%): 584 (68), 489 (100), 381 (33), 369 (59), 203 (52), 201 (41). Exact mass: calculated for $C_{39}H_{24}OF_4$: 584.1763; found: 584.1764.

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