



## NMR investigation of the dyes formed under UV irradiation of some photochromic indeno-fused naphthopyrans

Jérôme Berthet<sup>a,b</sup>, Paulo J. Coelho<sup>c,\*</sup>, Luis M. Carvalho<sup>c</sup>,  
Gaston Vermeersch<sup>a,b</sup>, Stephanie Delbaere<sup>a,b,\*\*</sup>

<sup>a</sup> Univ Lille Nord de France, F-59000 Lille, France

<sup>b</sup> UDSL, CNRS UMR8009, Faculté de Pharmacie, F-59000 Lille, France

<sup>c</sup> Centro de Química - Vila Real, Universidade de Trás-os-Montes e Alto Douro, 5001-801 Vila Real, Portugal

### ARTICLE INFO

#### Article history:

Received 20 July 2009

Received in revised form 7 September 2009

Accepted 14 September 2009

Available online 23 September 2009

#### Keywords:

Naphthopyran

Photochromism

NMR analysis

<sup>19</sup>F NMR

### ABSTRACT

New *p*-fluoro-substituted indeno-fused 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyrans were prepared and their photochromic properties studied by UV–vis and NMR spectroscopy. At room temperature UV irradiation of compound **6**, presenting the indene ring fused to the *k*-face of the 3*H*-naphtho[2,1-*b*]pyran gave rise to two diastereoisomeric TT open forms that possess an helical structure with the conjugated 3,3-diaryl-1,3-propdienyl chain out of the plane of the indeno-naphthalen-2(1*H*)-one core, which renders the thermal bleaching very difficult and thus increases the life-time and concentration of these coloured species.

© 2009 Elsevier B.V. All rights reserved.

### 1. Introduction

Naphthopyrans are one of the main classes of photochromic compounds and have been the subject of recent reviews [1]. Under near-UV light irradiation these uncoloured molecules (CF) undergo a pyran-ring opening with formation of the *trans,cis* isomer (TC), usually the major product that upon isomerization of the double bond leads to the *trans,trans* isomer (TT), normally the 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 through a thermal mechanism.

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 frequently shows a fading rate  $10^2$ – $10^3$  times slower. As a result, in the dark, two distinct fading rates are usually observed: one fast bleaching rate due to the process TC → CF and a slower bleaching process involving the TT-isomer [2].

The photochromic properties of naphthopyrans are strongly dependent on structural features. The ability to produce coloured forms, maxima wavelengths of absorption, fading kinetics and resistance to photodegradation can be modulated through the introduction of substituents and/or fusion to different ring systems [3]. Recently we have studied the photochromic properties of two 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyrans, **P1**–**P2**, fused to indene rings in the *i*- and *k*-faces (Scheme 2) [4].

Under UV–vis continuous irradiation these indeno-fused naphthopyrans gave rise to orange/red solutions that bleached in the dark following a bi-exponential kinetic. However, while for compound **P1** the TC was the main photoisomer formed under irradiation (74%), for naphthopyran **P2** the UV–vis irradiation gave rise to a mixture of photoisomers constituted mainly by the TT-isomer (81%). These results seem to indicate a special stability of the TT-isomer of naphthopyran **P2**. To investigate the structure of the photoisomers produced under UV irradiation we prepared naphthopyrans **5** and **6** with fluorine atoms in the *para* position of the phenyl groups. This substitution pattern enables the photoisomerisation process to be probed by <sup>19</sup>F NMR spectroscopy and can improve the spectral resolution at the <sup>1</sup>H NMR by reducing the overlapping of the signals in the aromatic region [5].

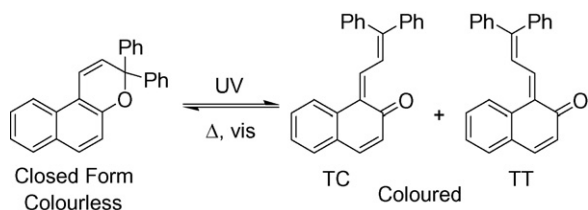
### 2. Experimental

Reaction of 2- and 3-hydroxy-7*H*-fluoren-7-ones **1**–**2** [6] with 1,1-di(*p*-fluorophenyl)prop-2-yn-1-ol in the presence of a catalytic

\* Corresponding author.

\*\* Corresponding author at: UDSL, CNRS UMR8009, Faculté de Pharmacie, F-59000 Lille, France.

E-mail addresses: [pcoelho@utad.pt](mailto:pcoelho@utad.pt) (P.J. Coelho), [stephanie.delbaere@univ-lille2.fr](mailto:stephanie.delbaere@univ-lille2.fr) (S. Delbaere).



**Scheme 1.** Photochromic equilibrium for 3*H*-naphtho[2,1-*b*]pyrans.

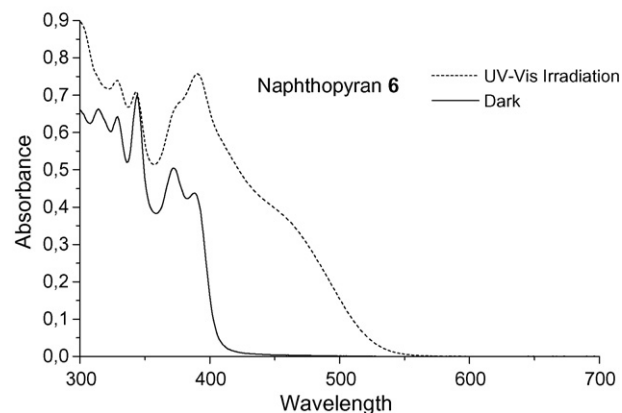
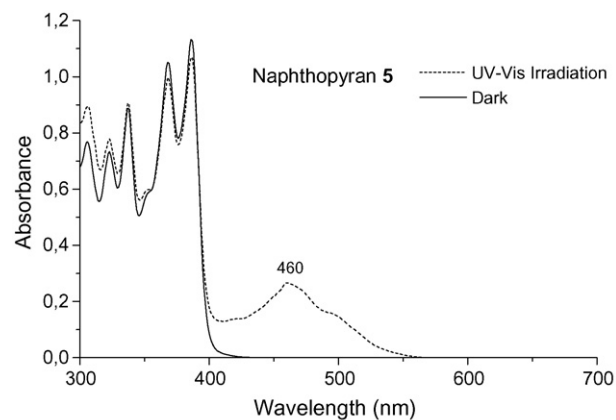
amount of pyridinium *p*-toluenesulphonate (PPTS) and two equivalents of trimethyl orthoformate gave naphthopyrans **3–4** which were then treated with a MeLi solution [7]. After the usual work up the new photochromic indeno-fused naphthopyrans **5–6** were isolated in good yield (Scheme 3). Details of the synthesis and spectroscopic characterization of these compounds, including the assignments of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, can be found in the supplementary data.

### 3. Results and discussion

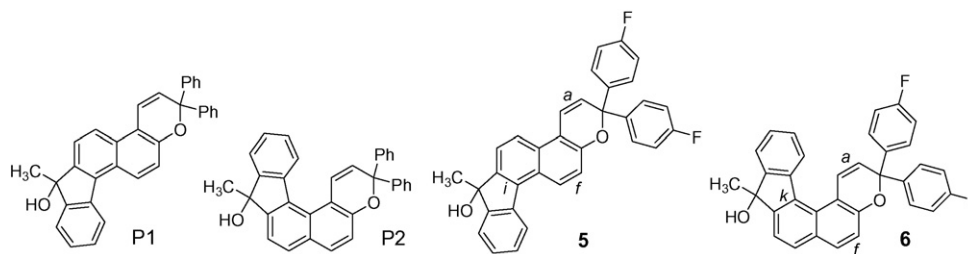
#### 3.1. Photochromic properties

The fluoro-substituted naphthopyrans **5** and **6** show similar photochromic properties to the unsubstituted indeno-fused naphthopyrans **P1** and **P2** previously described [4]. UV-vis continuous irradiation of  $10^{-4}$  M solutions of compounds **5** and **6** gave rise to orange/red solutions, with a maximum wavelength of absorption at 450–460 nm and absorbances at the photostationary equilibrium of 0.22 and 0.31, respectively (Fig. 1).

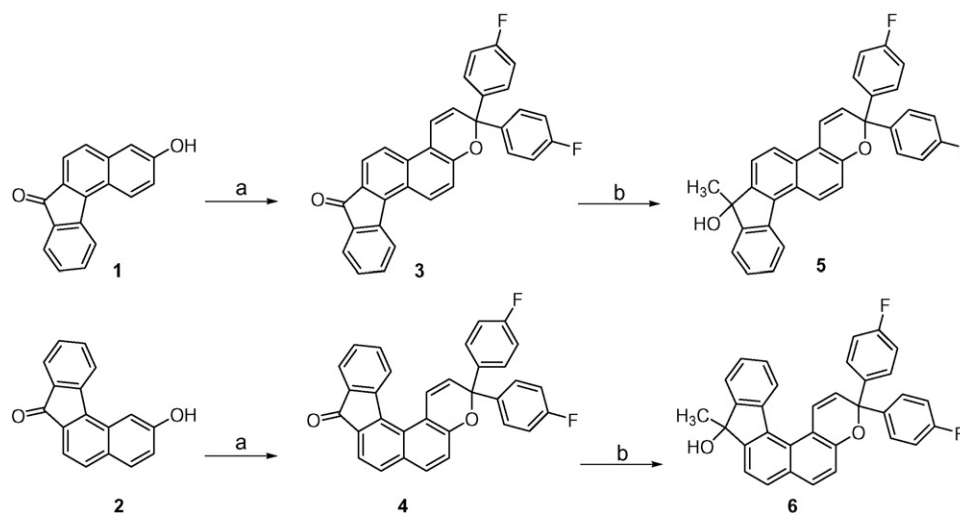
After reaching the photostationary equilibrium the irradiation was stopped and the evolution of the absorbances of the solutions



**Fig. 1.** UV-vis absorption spectra of naphthopyrans **5** and **6** before and after UV irradiation (dark).



**Scheme 2.** Indeno-fused 3*H*-naphtho[2,1-*b*]pyrans.



**Scheme 3.** Reagents and conditions (a) 1,1-di(*p*-fluorophenyl)prop-2-yn-1-ol, PPTS,  $\text{CH}(\text{OMe})_3$ ,  $\text{CHCl}_3$ , reflux and (b) (1) MeLi,  $\text{Et}_2\text{O}$ , reflux (2)  $\text{H}_3\text{O}^+$ .

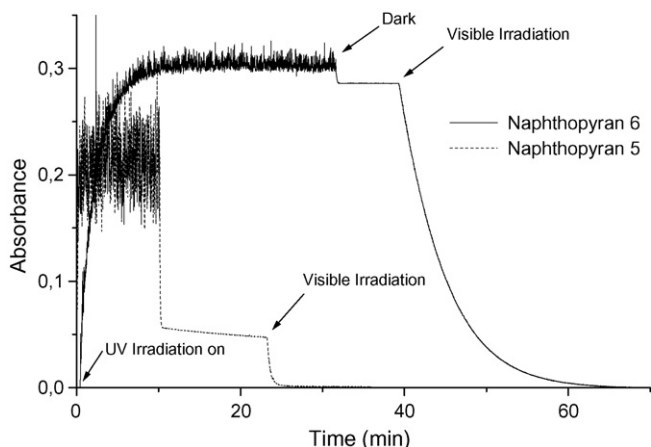


Fig. 2. Colour forming and colour bleaching of naphthopyrans 5 and 6.

of **5** and **6** were followed in the dark, at room temperature. Compound **5** shows the usual naphthopyran bi-exponential behaviour: formation of the fast decay species, presumably the TC-isomer, as the main photoproduct (78%,  $k_{\Delta} = 0.31 \text{ s}^{-1}$ ) along with a small amount of a more stable photoproduct, probably the TT-isomer (22%  $k_{\Delta} = 2.3 \times 10^{-4} \text{ s}^{-1}$ ). As expected naphthopyran **6** shows a different behaviour: UV-vis irradiation led to the formation of a highly stable photoproduct (bleaching kinetic  $k_{\Delta} = 6.6 \times 10^{-7}$ , half-life time: 12 days), as the main product (85%), and a minor amount, 15%, of a much more unstable specie, probably the TC-isomer ( $k_{\Delta} = 0.21 \text{ s}^{-1}$ ). As a result, for the latter compound, when the irradiation is stopped there is only a small decrease of the colouration which remains stable for a long period of time (Fig. 2).

The bleaching of the TC- and TT-coloured forms can also be achieved through a photochemical process. The higher stability of the photoproducts of naphthopyran **6** can also be deduced comparing the photochemical bleaching rates. The total bleaching of a coloured irradiated toluene solution of **6** was achieved by irradiating with visible light for 25 min at room temperature (Fig. 2). The photochemical bleaching was apparently mono-exponential with a constant rate of  $3.1 \times 10^{-3} \text{ s}^{-1}$ . This photochemical process involves two consecutive transformations  $\text{TT} \rightarrow \text{TC} \rightarrow \text{CF}$  the first one being the rate limiting step. For the photoproducts of naphthopyrans **5** the photochemical bleaching was achieved in only 2 min with a higher ring closure rate  $k = 4.1 \times 10^{-2} \text{ s}^{-1}$ .

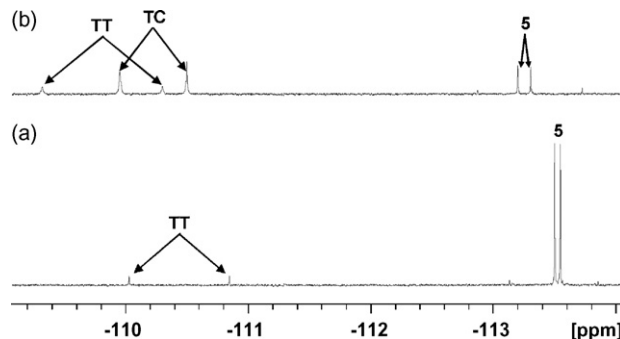


Fig. 3.  $^{19}\text{F}$  spectra of **5** after UV irradiation (a) at room temperature and (b) at 228 K.

### 3.2. NMR analysis of UV irradiated solutions

To clarify the structure of the photoisomers formed upon UV irradiation, NMR studies of the fluoro-substituted naphthopyrans **5** and **6**, in degassed  $5 \times 10^{-3} \text{ M}$  toluene- $d_8$  solutions, were carried out before and after UV irradiation. Experiments were performed at room temperature and at low temperature (228 K) to slow the thermal bleaching of the open forms. The photocoloration was achieved through UV irradiation (005FG09 filter with  $\lambda_{\text{max}} = 360 \text{ nm}$ ).

#### 3.2.1. UV irradiation of naphthopyran **5**

UV irradiation of naphthopyran **5** at room temperature led to the appearance of two low-intensity signals in the  $^{19}\text{F}$ NMR spectrum at  $-110.03$  and  $-110.85 \text{ ppm}$  (Fig. 3a), presenting a thermal stability similar to that observed in UV-vis experiments. Based on the chemical shift values and the thermal stability, the new photoproduct was straightforwardly attributed to TT-isomer [8].

At 228 K, the two previously observed signals characterizing the TT-isomer are again detected at chemical shifts slightly different due to the temperature effect ( $-109.40$  and  $-110.30 \text{ ppm}$ ). In addition, two new resonances at  $-109.95$  and  $-110.50 \text{ ppm}$  were detected and assigned to the second transoid isomer, namely TC (Fig. 3b). The structure of this second photoproduct was proved by the deshielded proton H-2 at 9.10 ppm (Fig. 4b). The monitoring of the time-evolution of concentrations in the dark underlined the reversion of TC into initial naphthopyran **5** ( $^{228}k_{\Delta} = 1.7 \times 10^{-4} \text{ s}^{-1}$ ) whereas TT remained stable (Fig. 5).

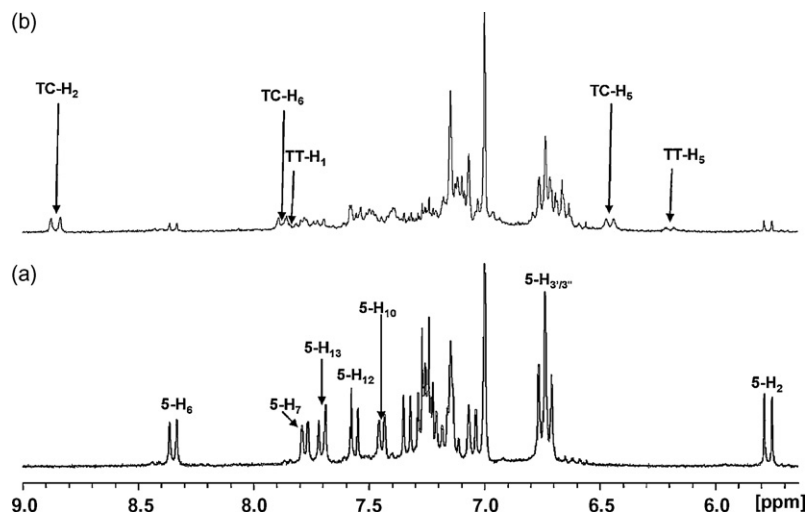


Fig. 4.  $^1\text{H}$  spectra of **5** at 228 K (a) before and (b) after UV irradiation.

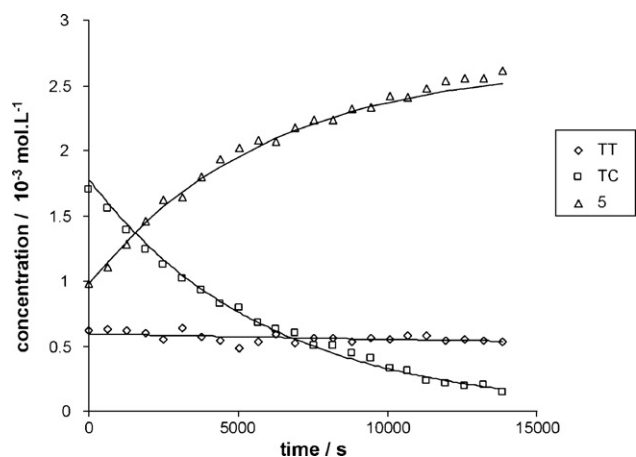


Fig. 5. Thermal evolution of 5 after UV irradiation at 228 K.

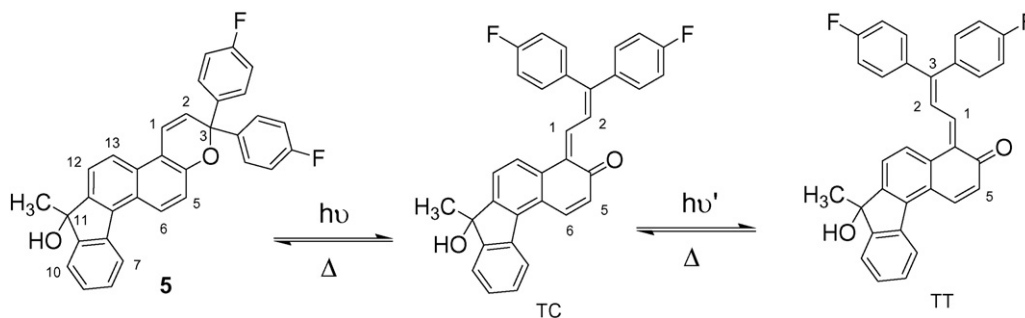
Such behaviour is in complete agreement with the classical photochromic reaction investigated by NMR spectroscopy [9] (Scheme 4).

### 3.2.2. UV irradiation of naphthopyran 6 at room temperature

Irradiation of naphthopyran 6 at room temperature generated four new lines in the  $^{19}\text{F}$  NMR spectrum (Fig. 6a): two signals with a high intensity (48%) at  $-110.90$  and  $-111.11$  ppm (Product A) and two signals being less intense (15%) at  $-110.96$  and  $-111.11$  ppm (Product B). These two photoproducts are highly thermally stable. At this temperature the more unstable TC-isomer is not detected.

In the  $^1\text{H}$  NMR spectrum (Fig. 7a) two doublet signals at 7.54 ppm (Product A) and 7.51 ppm (Product B) with a coupling constant equal to 12.2 Hz are observed. 2D NMR  $^1\text{H}$ - $^{13}\text{C}$  long-distance correlations (HMBC experiment, supplementary material) underlined a scalar coupling between proton at 7.54 ppm and carbon at 189 ppm, characteristic of the C=O function in position 4a. This coupling through three bonds enabled the assignment of the doublet to the proton H-1, and consequently the structure of photoproduct A to the isomer TT<sub>1</sub>. The photoproduct B, presenting similar chemical shifts and similar photochemical and thermal behaviour, is attributed to a second conformer of TT, resulting from the helical structure of the indeno-fused naphthopyran [10].

2D Roesy evidenced dipolar correlations between the methyl group and protons H-10 and H-8 for both compounds. However for compound TT<sub>1</sub> strong correlations between the methyl group and protons H-2 and H-2' were also observed which lead us to propose the conformations drawn in Scheme 5 ( $^1\text{H}$ - $^1\text{H}$  Roesy supplementary material). Finally, one can observe that protons in one of the fluorophenyl group present a shielding in TT<sub>1</sub>. Indeed, the protons H2' and H3' are respectively at 7.28–7.47 and 6.76–6.79 ppm in initial compound 6, whereas they are shifted to 6.25 and 6.45 ppm in TT<sub>1</sub> configuration, as a result of the anisotropic effect of the fluoro-substituted and the aromatic ring of the indene unit. The non-planar structure of these TT species is probably responsible for its unusual stability. The presence of the indeno ring at the *k*-face of the naphthopyran renders the thermal back-isomerization of the double bond to the TC-isomer very difficult thus increasing the amount of the TT-isomer. Since the return to the TC-isomer is much slower the system is biased towards the TT-isomer and thus an accumulation of this isomer is observed.



Scheme 4. Photochromic reaction of 5.

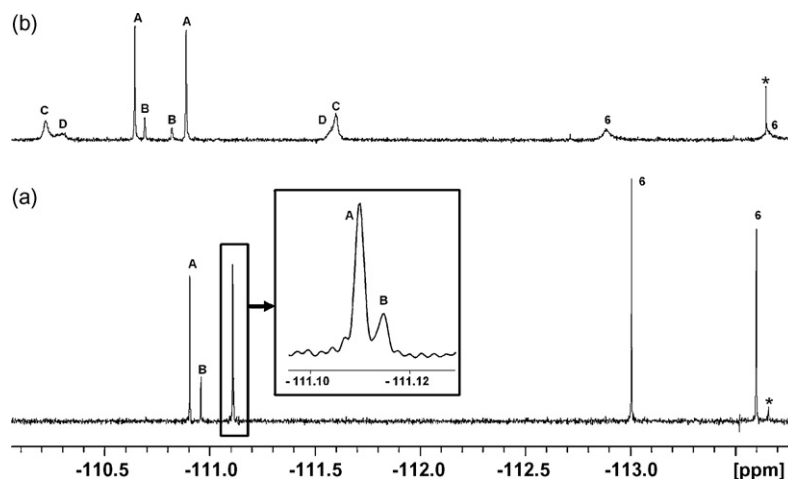


Fig. 6.  $^{19}\text{F}$  NMR spectra of naphthopyran 6 after UV irradiation (a) at room temperature and (b) at 228 K (\*impurity).

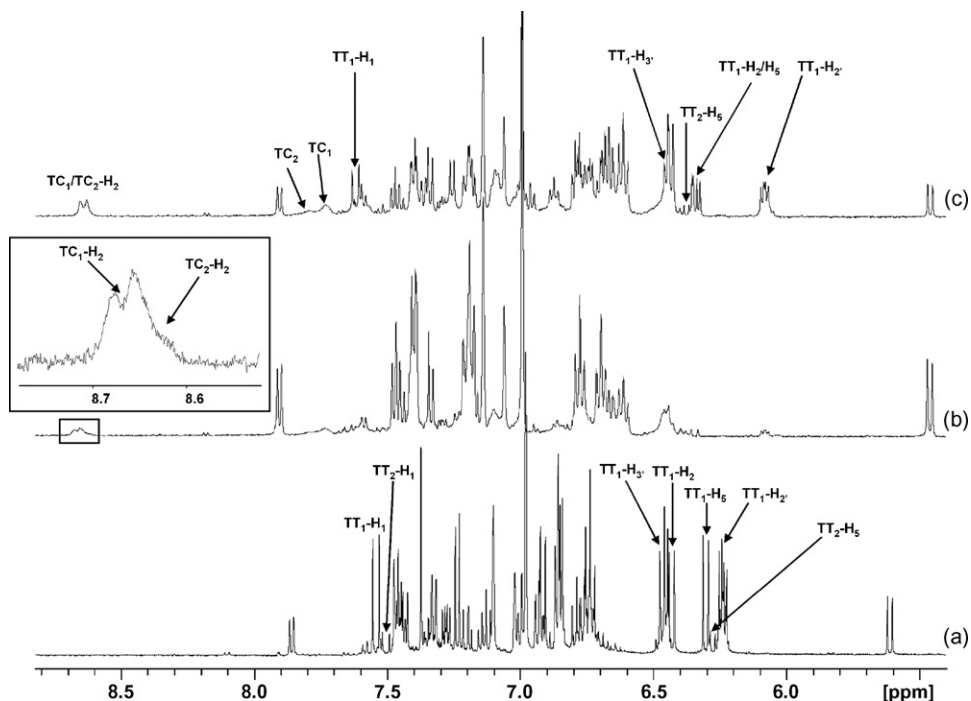
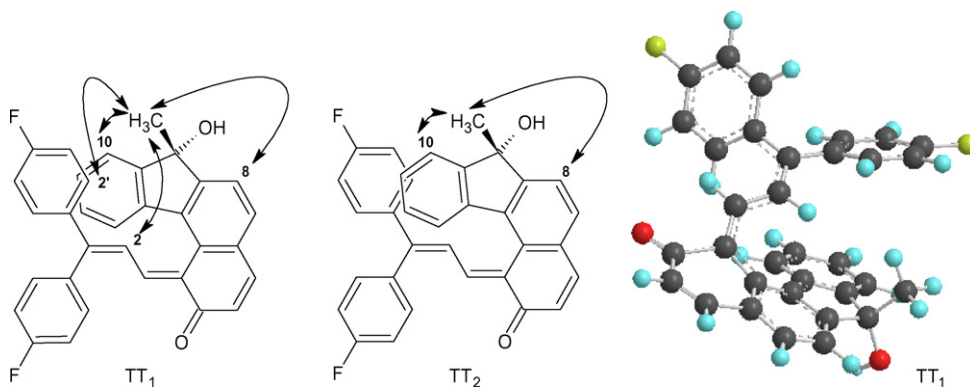


Fig. 7.  $^1\text{H}$  NMR spectra of naphthopyran **6** (a) after UV irradiation at rt, (b) after 1 min of UV irradiation at 228 K, and (c) after 5 min of UV irradiation at 228 K.



Scheme 5. Structure of  $\text{TT}_1$  and  $\text{TT}_2$ .

### 3.2.3. UV irradiation of naphthopyran **6** at low temperature

UV Irradiation of naphthopyran **6** at 228 K generated four supplementary  $^{19}\text{F}$  resonances: two at  $-110.22$  and  $-111.60$  ppm (product C) and two less intense at  $-110.35$  and  $-111.58$  ppm (product D) (Fig. 6b). However, in contrast with the four lines already detected at room temperature, these new signals are broad. Therefore, at this low temperature, the formation of four different photoproducts (**A**, **B**, **C** and **D**) is evidenced. To understand their origin, the photochemical transformation of naphthopyran **6** was monitored by recording  $^{19}\text{F}$  NMR spectra within the UV irradiation. As displayed in Fig. 8, the concentrations of **C** and **D** increased then decreased, whereas the concentrations of **A** and **B** were always increasing. This behaviour suggests the transformation of **6** into **TC**-isomer (products **C** and **D**) then the isomerisation of **TC** into **TT** (products **A** and **B**) (Scheme 6). It should be noticed that a complete transformation of naphthopyran **6** into the photoproducts **A**, **B**, **C** and **D** was observed after 60 min of irradiation. In Fig. 7b, the doublet signal at 8.64 ppm, with a total intensity equal to the sum of **C**+**D** is correlated with two doublets at 7.74 and 7.81 ppm, corresponding to the photoproducts **C** and **D**, respectively. Then, **C** and **D** are attributed to two conformers of the transoid-cis isomer:  $\text{TC}_1$  and  $\text{TC}_2$  in rapid exchange as indicated by the broad shape of their sig-

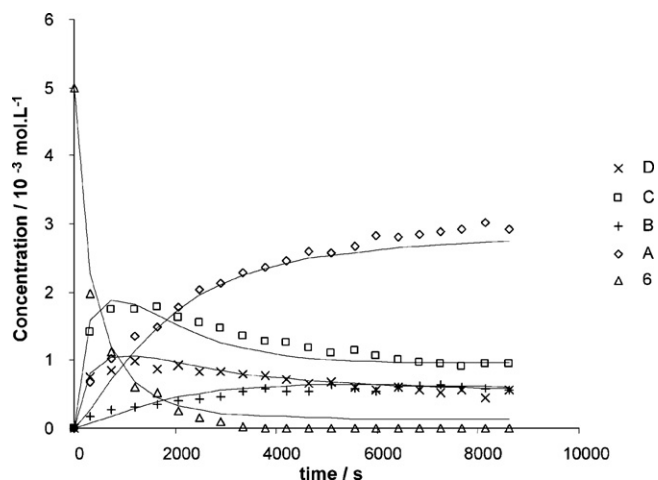
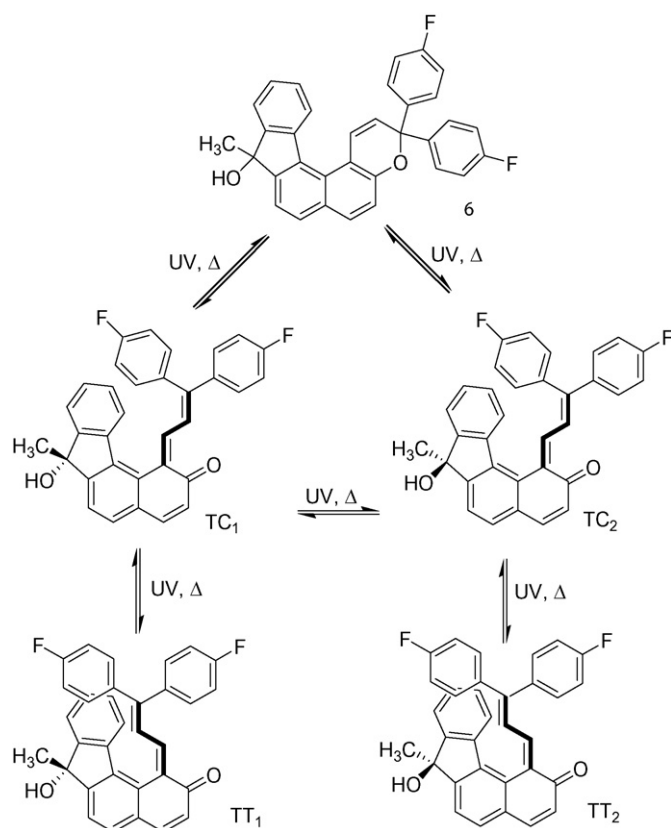


Fig. 8. Time-evolution of photoproducts **A**, **B**, **C** and **D** concentrations upon UV irradiation of **6** at 228 K.



**Scheme 6.** Mechanism for the formation of the coloured species of naphthopyran 6.

nals. The thermal evolution of TC<sub>1</sub> and the thermal evolution of TC<sub>2</sub> could not be measured separately and accurately due to the broadness of signals. Consequently, their peak intensities were integrated together, resulting in an estimated rate constant of thermal relaxation toward the initial compound **6** of  $^{228}k_{\Delta} = 6.4 \times 10^{-5} \text{ s}^{-1}$ .

#### 4. Concluding remarks

The photochromic properties of indeno-fused naphthopyrans are very dependent on the face of ring annellation. While the fusion of the indeno ring to the *i*-face of the 3*H*-naphtho[2,1-*b*]pyran gives rise mainly to the TC-isomer, the annellation in the *k*-face affords mainly the TT-isomer. NMR studies show that UV irradiation of 3,3-di(*p*-fluorophenyl)-3*H*-naphtho[2,1-*b*]pyran **6** gives rise to four isomeric photoproducts: two diastereoisomeric TC-species and two highly stable diastereoisomeric TT-species. The presence of the indeno ring at the *k*-face of this naphthopyran leads to a helical structure of the TT-coloured isomer, with the conjugated 3,3-diaryl-1,3-propdienyl chain out of the plane of the

indeno-naphthalen-2(1*H*)-one, which renders the thermal back-isomerization of the double bond to the TC-isomer very difficult thus increasing the ratio of the TT-isomer.

#### Acknowledgements

To FCT (Portugal's Foundation for Science and Technology) for financial support through the research unit Centro de Química-Vila Real (POCTI-SFA-3-616) and project POCTI/QUI/38771/2001. The 300 and 500 MHz NMR facilities were funded by the Région Nord-Pas de Calais (France), the Ministère de la Jeunesse, de l'Éducation Nationale et de la Recherche (MJENR) and the Fonds Européens de Développement Régional (FEDER).

#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2009.09.013.

#### References

- [1] (a) J.D. Hepworth, B.M. Heron, Photochromic naphthopyrans, in: S.-H. Kim (Ed.), *Functional Dyes*, Elsevier, Amsterdam, 2006, pp. 85–135; (b) B. Van Gemert, Benzo and naphthopyrans (chromenes), in: J.C. Crano, R. Guglielmetti (Eds.), *Organic Photochromic and Thermochromic Compounds. Main Photochromic Families*, vol. 1, Plenum Press, New York, 1998, p. 111.
- [2] (a) D. Venec, S. Delbaere, J.C. Micheau, M. Frigoli, C. Moustrou, A. Samat, G. Vermeersch, *J. Photochem. Photobiol. A: Chem.* 183 (2006) 70–78; (b) S. Delbaere, J.C. Micheau, G. Vermeersch, *J. Org. Chem.* 68 (2003) 8968–8973; (c) P.J. Coelho, L.M. Carvalho, S. Abrantes, M.M. Oliveira, A.M.F. Oliveira-Campos, A. Samat, R. Guglielmetti, *Tetrahedron* 58 (2002) 9505–9511; (d) P.J. Coelho, M.A. Salvador, M.M. Oliveira, L.M. Carvalho, *Tetrahedron* 60 (2004) 2593–2599.
- [3] (a) N. Malic, J.A. Campbell, R.A. Evans, *Macromolecules* 41 (2008) 1206–1214; (b) E.F. Silva, P.P. Coelho, *Lett. Org. Chem.* 5 (2008) 502–506; (c) C.D. Gabbutt, B.M. Heron, A.C. Instone, *Tetrahedron* 62 (2006) 737–745; (d) A. Alberti, Y. Teral, G. Roubaud, R. Faure, M. Campredon, *Dyes Pigments* 81 (2009) 85–90; (e) F. Ortica, L. Bougdid, C. Moustrou, U. Mazzucato, G. Favaro, *J. Photochem. Photobiol. A: Chem.* 200 (2008) 287–293.
- [4] P.J. Coelho, M.A. Salvador, M.M. Oliveira, L.M. Carvalho, *J. Photochem. Photobiol. A: Chem.* 172 (2005) 300–307.
- [5] (a) S. Delbaere, G. Vermeersch, *J. Photochem. Photobiol. C-Photochem. Rev.* 9 (2008) 61–80; (b) S. Delbaere, J.C. Micheau, M. Frigoli, G. Vermeersch, *J. Phys. Org. Chem.* 20 (2007) 929–935; (c) D. Venec, S. Delbaere, J.C. Micheau, M. Frigoli, C. Moustrou, A. Samat, G. Vermeersch, *J. Photochem. Photobiol. A: Chem.* 181 (2006) 174–179; (d) J. Berthet, S. Delbaere, L.M. Carvalho, G. Vermeersch, P.J. Coelho, *Tetrahedron Lett.* 47 (2006) 4903–4905; (e) S. Delbaere, J.C. Micheau, J. Berthet, G. Vermeersch, *Int. J. Photoenergy* 6 (2004) 151–158.
- [6] P.J. Coelho, M.A. Salvador, M.M. Oliveira, L.M. Carvalho, *Synlett* 6 (2004) 1015–1018.
- [7] W.L. Zhao, E.M. Carreira, *Org. Lett.* 5 (2003) 4153–4154.
- [8] X. Sallenave, S. Delbaere, S. Ahmed, G. Vermeersch, J.L. Pozzo, *Tetrahedron Lett.* 46 (2005) 3257–3259.
- [9] S. Delbaere, B. Luccioni-Houze, C. Bochu, Y. Teral, M. Campredon, G. Vermeersch, *J. Chem. Soc., Perkin Trans. 2* (5) (1998) 1153–1157.
- [10] M.M. Oliveira, M.A. Salvador, S. Delbaere, J. Berthet, G. Vermeersch, J.C. Micheau, P.J. Coelho, L.M. Carvalho, *J. Photochem. Photobiol. A: Chem.* 198 (2008) 242–249.