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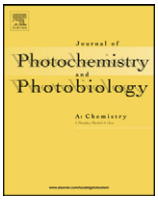

NMR investigation of the dyes formed under UV irradiation of some photochromic indeno-fused naphthopyrans

Jérôme Berthet[a,b], Paulo J. Coelho[c,*], Luis M. Carvalho[c],
Gaston Vermeersch[a,b], Stephanie Delbaere[a,b,**]

[a] Univ Lille Nord de France, F-59000 Lille, France
[b] UDSL, CNRS UMR8009, Faculté de Pharmacie, F-59000 Lille, France
[c] Centro de Química - Vila Real, Universidade de Trás-os-Montes e Alto Douro, 5001-801 Vila Real, Portugal

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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.

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 ^{19}F NMR spectroscopy and can improve the spectral resolution at the ^{1}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

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* Corresponding author.
** Corresponding author at: UDSL, CNRS UMR8009, Faculté de Pharmacie, F-59000 Lille, France.
E-mail addresses: pcoelho@utad.pt (P.J. Coelho), stephanie.delbaere@univ-lille2.fr (S. Delbaere).

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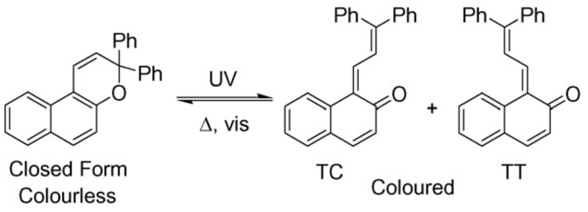


Scheme 1. Photochromic equilibrium for 3*H*-naphtho[2,1-*b*]pyrans.

amount of piridinium *p*-toluenosulphonate (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}H and ^{13}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

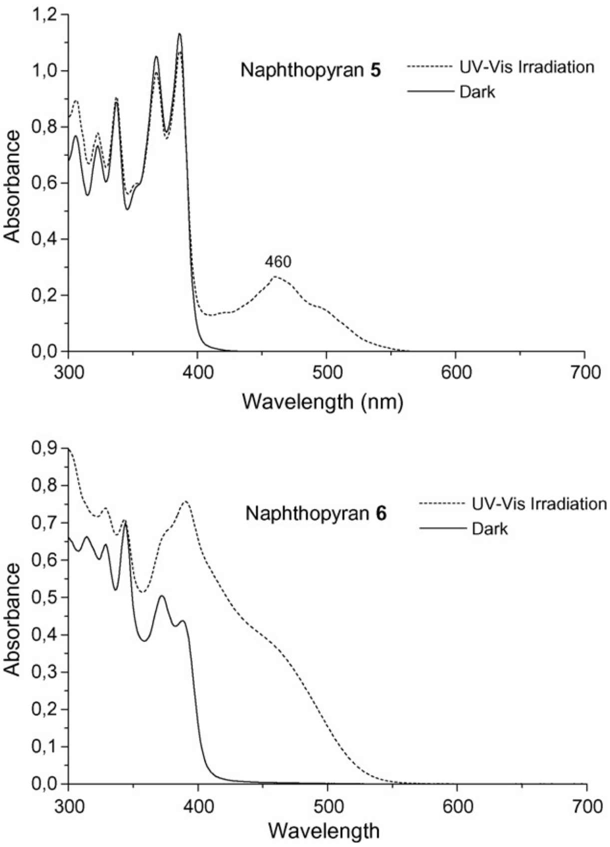
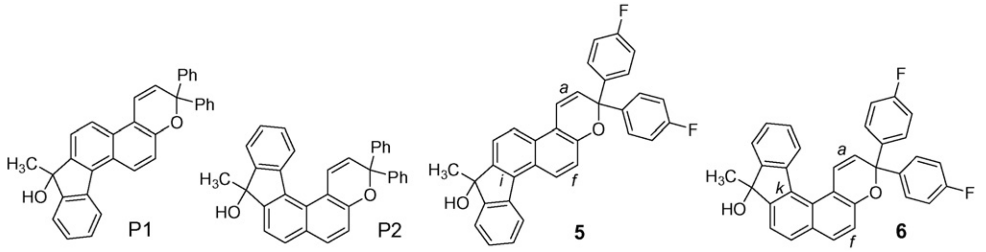
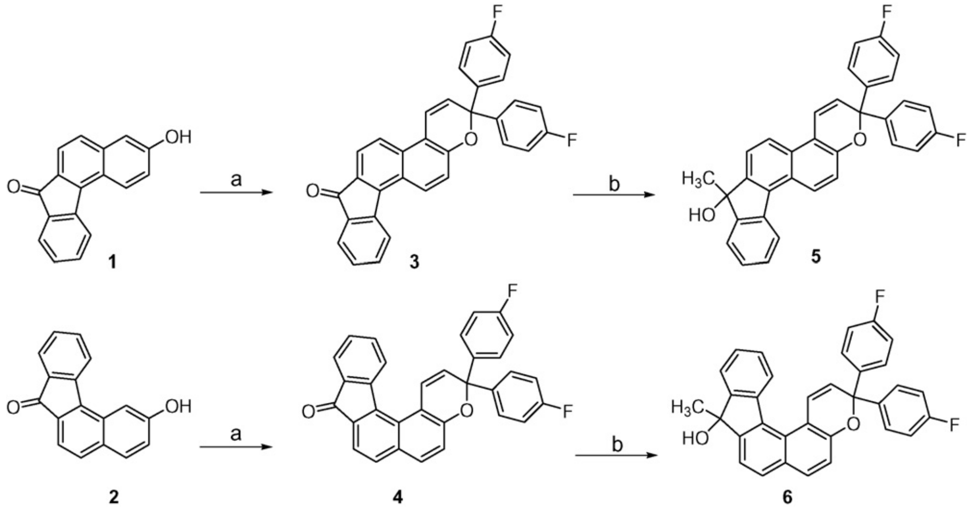


Fig. 1. UV–vis absorption spectra of naphthopyrans 5 and 6 before and after UV irradiation (dark).



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, $CH(OMe)_3$, $CHCl_3$, reflux and (b) (1) MeLi, Et_2O, reflux (2) H_3O^+.