

Photochemical and thermal behaviour of new photochromic indeno-fused naphthopyrans

Paulo J. Coelho*, Maria A. Salvador, M. Manuel Oliveira, Luis M. Carvalho

Centro de Química - Vila Real, Universidade de Trás-os-Montes e Alto Douro, 5001-911 Vila Real, Portugal

Received 11 November 2004; accepted 17 December 2004

Available online 26 January 2005

Abstract

Three new indeno-fused naphthopyrans were prepared and their photochromic behaviour was investigated. UV–vis continuous irradiation of indeno-fused 3*H*-naphtho[2,1-*b*]pyrans generates two photoisomers in variable relative amounts with very different thermal stabilities. While one isomer exhibits a fast thermal bleaching the other is thermally very stable and returns to the uncoloured form mainly through a photochemical process promoted by visible light irradiation.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Photochromism; Photokinetics; Heterocycles; Naphthopyrans; Thermal bleaching

1. Introduction

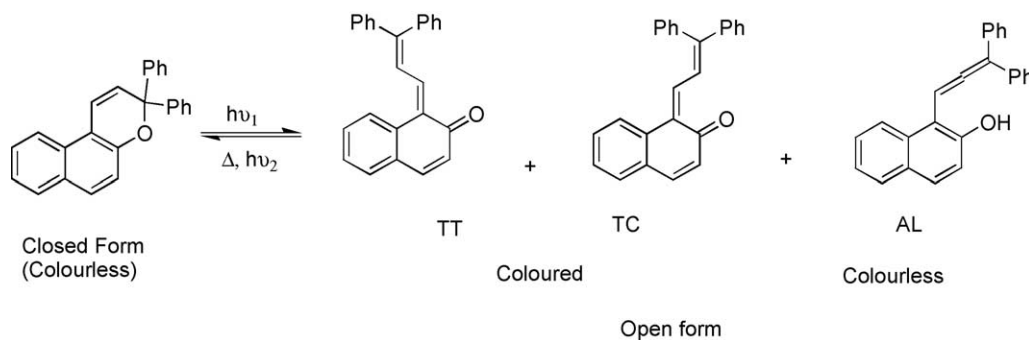
Naphthopyrans are one of the main classes of photochromic compounds. UV light irradiation of these compounds, in solution or in polymeric matrices, produces a mixture of coloured isomers (open forms) with similar absorption spectra, although with different thermal stabilities. When the irradiation ceases the system returns to its original colourless closed form (CF) via a thermal or a photoinduced process [1]. Recent NMR studies on 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran showed that UV continuous irradiation, at low temperature, leads mainly to the production of three species: two coloured stereoisomers, transoid-*cis* (TC) and transoid-*trans* (TT), and an uncoloured allenynaphthol (AL) (Scheme 1) [2,3].

While the allenynaphthol (AL) is not thermally stable (it was only detected at low temperature in some solvents), the two stereoisomers can be studied at room temperature [4]. The TT-isomer is usually more stable than TC. 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. In the dark the return to the uncoloured state occurs mainly through a thermal mechanism at room temperature. However, some photochromic molecules yield thermally very stable photoproducts. For such systems, back reactions can be photochemically promoted usually with visible light. The main photochemical process is the conversion of the TT- to the TC-isomer that subsequently returns thermally to the closed form [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 [1,5–7]. UV irradiation of 2,2-diphenyl-2*H*-naphtho[1,2-*b*]pyran solutions generates very stable open forms (slow bleaching rates) with a maximum wavelength of absorption at 469 nm. The fusion of an indene group to the 5,6 positions (*f*-face) of this naphthopyran is a well known strategy to improve the photochromic properties because it effectively extends the conjugation of the π -electron system and introduces important non-bonding interactions in the open forms (Fig. 1). The net result is the production of coloured products with an observable bathochromic

* Corresponding author. Tel.: +351 259350284; fax: +351 259350480.
E-mail address: pcoelho@utad.pt (P.J. Coelho).



Scheme 1.

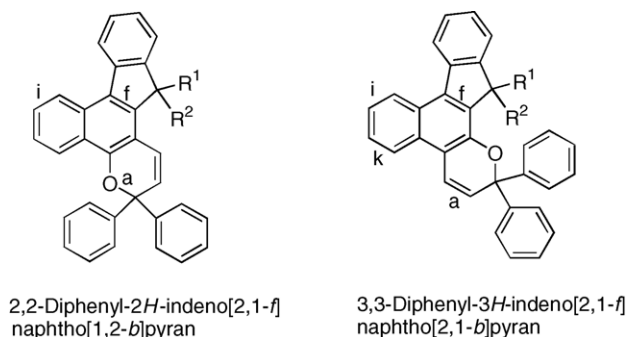


Fig. 1. Indeno-fused naphthopyrans.

shift in the visible spectra and faster bleaching kinetics due to the increased instability of the open forms. These indeno-fused naphthopyrans provide a wide range of colours, high molar absorptivities in the near-UV and interesting decolouration kinetics [8–14]. The annelation of an indene ring on the *f*-face of 3,3-diphenyl-2*H*-naphtho[2,1-*b*]pyran does not produce the same effects since it does not give rise to a significant decrease in the thermal stabilities of the open forms [15,16].

Due to their excellent photochromic properties 2,2-diphenyl-2*H*-indeno[2,1-*f*]naphtho[1,2-*b*]pyrans have been extensively studied. However, there is no report on the photochromic behaviour of naphthopyrans fused to indene rings in other faces. In this paper we report the synthesis and spectrokinetic properties, in solution, of three indeno-fused naphthopyrans with an indene ring fused in new positions: two 3,3-diphenyl-2*H*-naphtho[2,1-*b*]pyrans fused to indene rings in the *i*- and *k*-faces, and a 2,2-diphenyl-2*H*-naphtho[1,2-*b*]pyran fused to an indene ring in the *i*-face.

2. Results and discussion

2.1. Synthesis

The new compounds were prepared in two steps from hydroxy-7*H*-fluoren-7-ones **1–3**, which can be synthesised from dimethoxynaphthaldehydes [17]. Thus condensation of 2-, 3- and 4-hydroxy-7*H*-fluoren-7-ones **1–3** with 1,1-

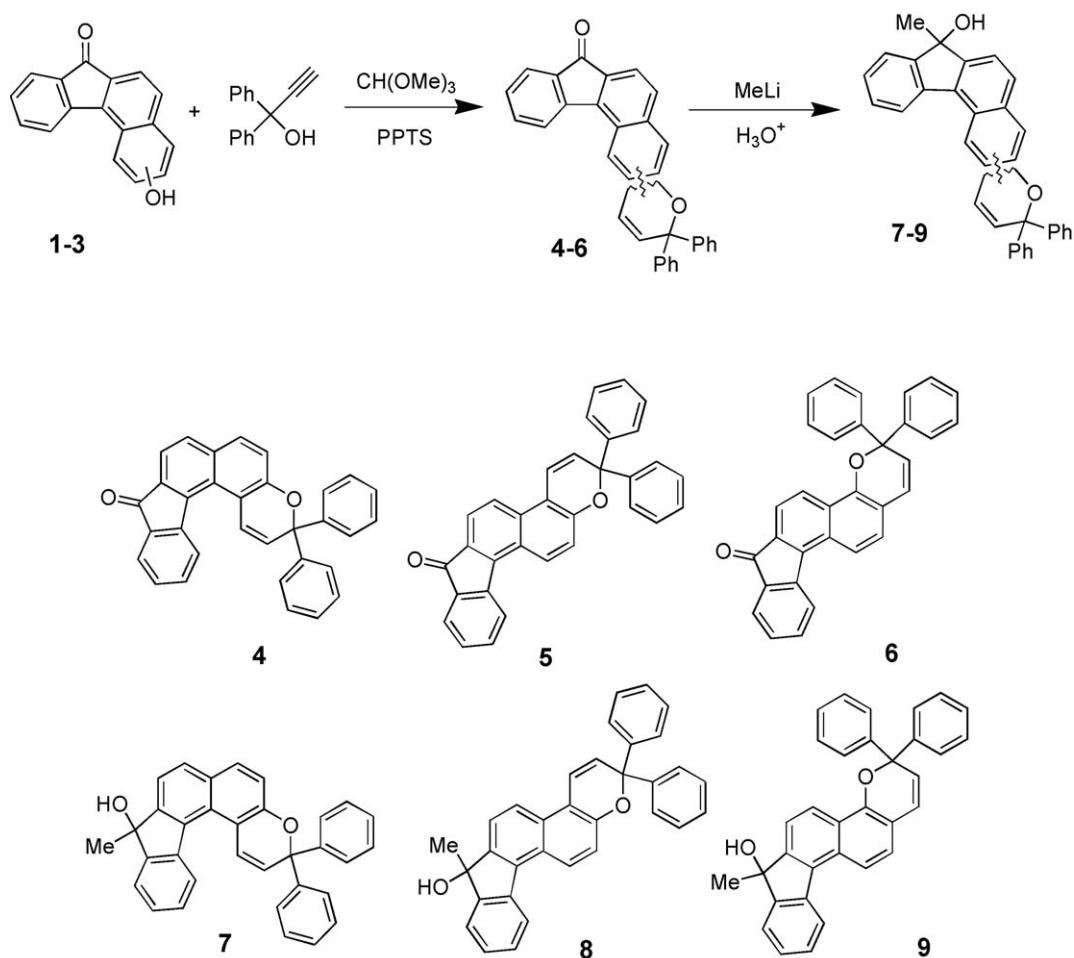
diphenylprop-2-yn-1-ol in the presence of pyridinium *p*-toluenesulphonate (PPTS) gave in low yields (25–30%) naphthopyrans **4–6**. This multi-step reaction is acid catalysed and liberates one molecule of water. The yields of this reaction were considerably increased (56–70%) when two equivalents of trimethyl orthoformate, a dehydrating agent, were added to the reaction mixture [18]. Treatment of naphthopyrans **4–6** with a MeLi solution gave after hydrolysis the new photochromic indeno-fused naphthopyrans **7–9** in good yield (70–86%) (Scheme 2).

2.2. Photochromic properties

Photochromic behaviour in naphthopyrans normally involves $\pi \rightarrow \pi^*$ transitions. Compounds **4–6** are not photochromic at room temperature, probably because the presence of the carbonyl group changes the nature of the lowest excited state making the transition $n \rightarrow \pi^*$ the main UV absorption process and thus hindering the ring overture [19]. The photochromic behaviour of compounds **7–9** was studied in 10^{-4} M toluene solutions under continuous near-UV-vis irradiation. Three spectrokinetic parameters normally quoted when describing the properties of photochromic compounds were evaluated: maximum wavelength of absorption of the open form (λ_{\max}), thermal bleaching rates (k_{Δ}) and colourability, estimated under the experimental conditions by the absorbance of the solution after reaching a photostationary equilibrium (A_{eq}). The bleaching kinetics was studied under thermal and photochemical conditions. The data are summarised in Table 1 where we included two reference compounds for comparison purposes.

2.2.1. Compounds 7–8

Under UV-vis continuous irradiation (150 W ozone free Xe lamp, light flux of 40 W m^{-2} , quartz cell 1 cm light path, toluene solutions 10^{-4} M, 20 °C) the new indeno-fused naphthopyrans **7–8** gave rise to orange/red solutions, with a maximum wavelength of absorption at 460 nm and absorbances at the photostationary equilibrium of 0.40 and 0.27, respectively. Compared to 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran (Ref 1), an expected bathochromic shift of the maximum wavelength of absorption (+28 nm) due to the extended



π -electron system conjugation and a colourability increase was observed. After reaching a photostationary equilibrium the irradiation was stopped and the evolution of the absorbance of the solutions was followed in the dark, at room

temperature. Solutions of both compounds exhibited similar bleaching behaviours. In the beginning the absorption decreased very rapidly reaching a significant absorbance level that lasts for long time (Figs. 2 and 3).

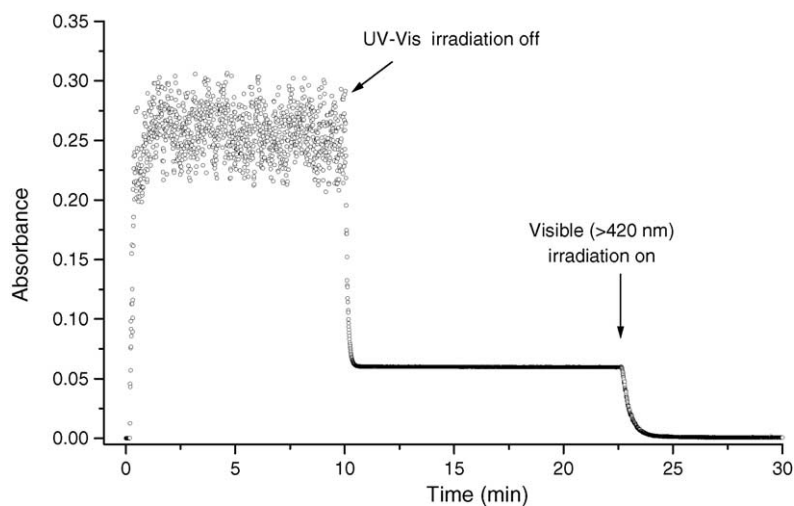
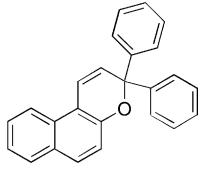
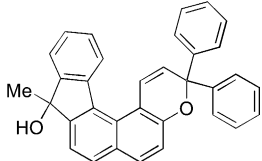
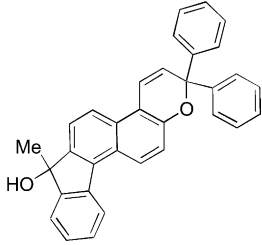
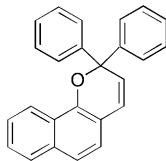
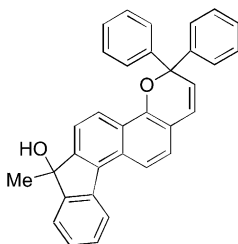


Fig. 2. Colouration/decolouration cycle, at 20 °C, in the dark and under visible irradiation for compound 8.

Table 1

Maxima wavelengths of the coloured forms (λ_{\max} , nm), colourability (A_{eq}), thermal fading rate constants (k_{Δ} , s^{-1}) of compounds **7–9** and two reference compounds in toluene solutions under continuous irradiation (1×10^{-4} M at 20°C)

Compound	λ_{\max}	A_{eq}	k_{Δ}
Ref 1 	432	0.21	7×10^{-2} (80) 3×10^{-3} (20)
7 	460	0.40	0.14 (19) 3×10^{-6} (81)
8 	460	0.27	0.20 (74) 1×10^{-5} (26)
Ref 2 	469	0.72	6×10^{-4} (98) 3×10^{-4} (2)
9 	491	0.59	1×10^{-2} (71) 6×10^{-5} (29)

Ref 1, 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran; **Ref 2**, 2,2-diphenyl-2*H*-naphtho[1,2-*b*]pyran.

Using a multiexponential model, two rate constants were calculated, one very fast ($0.14\text{--}0.20 \text{ s}^{-1}$) responsible for the initial absorbance decay and one very slow (3×10^{-6} to $1 \times 10^{-5} \text{ s}^{-1}$) responsible for the persistence of a residual colour for very long time. This is the usual behaviour of the solutions of photochromic naphthopyrans where UV irradiation originates a short-lived species as the major component (TC-isomer) and a long-lived species as the minor component (TT-isomer) [20]. Compared to the reference naphthopyran (**Ref 1**), these compounds exhibit a faster first kinetic and a slower second kinetic. This suggests that the fusion of the indene ring in the *i*- or *k*-faces of the 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran had different effects on the stability of the main photoisomers (TT and TC) present in solution: the stability of the TC-isomer decreased (faster first bleaching kinetic) whereas the

stability of the TT-isomer increased (slower second bleaching kinetic).

For compound **8** the amplitudes of the two kinetics are very similar to the reference compound (74% for the first kinetics and 26% for the second). However, for compound **7** we observed an inversion in the amplitude values (19% for the first kinetic and 81% for the second). This means that the relative amounts of the two isomers in the irradiated solutions of compounds **7** and **8** are probably quite different. While for compound **8** the UV–vis irradiation leads mostly to the TC-isomer, the TT-isomer seems to be the main product of the UV irradiated solutions of compound **7**. The predominance of the TT-isomer of compound **7** is quite surprising because a planar structure for this photoisomer would introduce strong non-bonding interactions between the fused indene ring and the opened pyran ring. This may

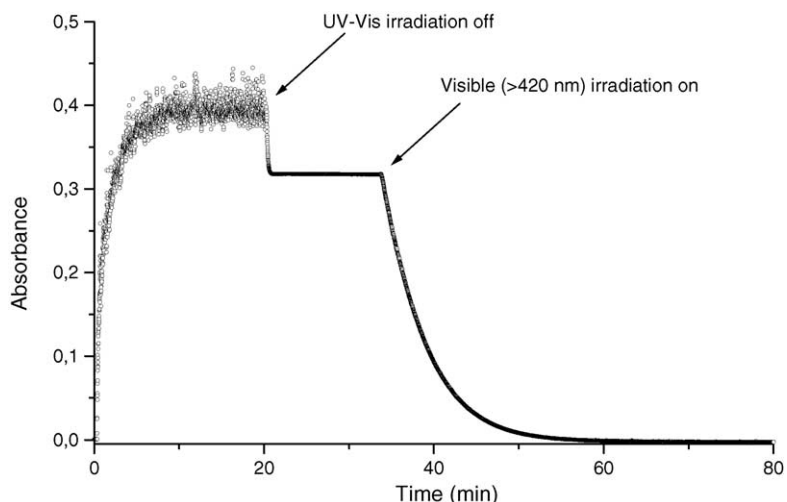


Fig. 3. Colouration/decolouration cycle, at 20 °C, in the dark and under visible irradiation for compound **7**.

indicate that this coloured isomer should have a non-planar structure.

For these compounds the TT-isomer seems to be particularly stable with thermal bleaching half-times ($t_{1/2}$) of 1–3 days contrary to the TC-isomer that shows $t_{1/2}$ of 3–5 s. The reason for this difference can be rationalised in terms of the extent of structural changes in reversion to the original closed form. TT-isomer reverts to the closed form through a two-step process (TT → TC and TC → CF) where the TC-isomer plays the role of intermediate. The first step is a double bond isomerization, which is normally very slow at room temperature but easily achieved through visible light irradiation [21].

After the thermal decay, visible light irradiation of solutions of compounds **7** and **8** led, as expected, to a decrease in

the absorbance (Figs. 2 and 3). For compound **8** the bleaching kinetic observed upon >420 nm visible light irradiation, using a long-pass Schott GG 420 filter, was monoexponential and a 0.025 s^{-1} rate was calculated (Fig. 2). This rate is eight times slower than the rate for the thermal TC → CF conversion suggesting that under these conditions the TT → TC step is the rate-limiting one. This was confirmed in another experiment where the visible irradiation was used only for 2 min. When the visible irradiation was turned off the decrease in absorbance ceased and a new plateau was observed, indicating that it remained a significant amount of the TT-isomer in the solution. A new visible light irradiation for more 6–7 min led the system to its uncoloured state.

In another experiment with a solution of compound **8**, after reaching the photostationary state, the UV irradiation

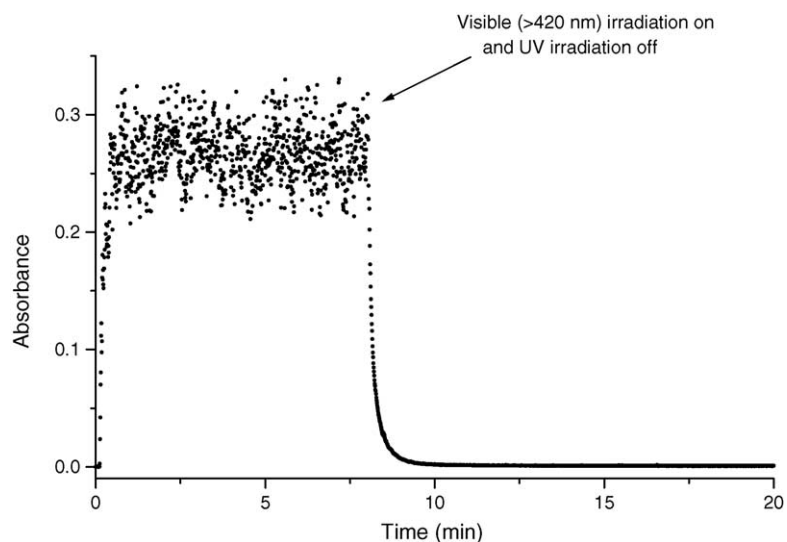


Fig. 4. Colouration/decolouration cycle, at 20 °C, under visible irradiation for compound **8**.

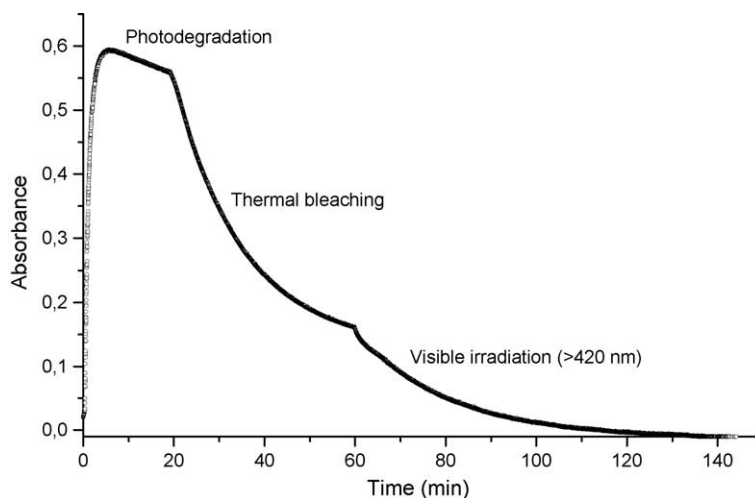


Fig. 5. Colouration/decolouration cycle, at 20 °C, in the dark and under visible irradiation for compound **9**.

was stopped using a long-pass Schott GG 420 filter (Fig. 4). At this point, besides CF, the solution included a mixture of TC- and TT-isomers, in an estimated 4:1 ratio (assuming similar absorption coefficients for both photoisomers). Under conditions of thermal and photochemical (>420 nm) bleaching, processes involving both TT- and TC-isomers occur simultaneously and the system returned completely to the uncoloured state. The analysis of the bleaching kinetics revealed two fast kinetic constants, 0.21 s^{-1} (66%) and 0.11 s^{-1} (34%). The first kinetic constant value is almost the same as for the thermal process alone, suggesting that the TC \rightarrow CF process is a thermal one. The second kinetic constant is lower pointing to a slower bleaching process, under the conditions used, probably retarded by a slow photochemical process TT \rightarrow TC before the return to the uncoloured (CF) form.

2.2.2. Compound **9**

Compound **9** belongs to the 2,2-diphenyl-2*H*-naphtho [1,2-*b*]pyran (Ref **2**) series. The open forms of these compounds are generally more stable and present slower thermal fading rates than the corresponding derivatives with a 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyrans skeleton. As expected, compound **9** exhibits slower fading rates than compounds **7–8** (Table 1, Fig. 5). The fusion of an indene ring at the *i*-face of the Ref **2** had a similar effect to the observed for compounds **7–8**: a bathochromic shift in the maximum wavelength of absorption (+22 nm), a decrease in the stability of the TC-isomer (higher fading rate) and an increase in the stability of the TT-isomer (slower fading rate). A decrease in colourability was observed, probably associated to the increase in the principal fading rate. Visible irradiation of the coloured solution led to an acceleration of the bleaching kinetic. However, the return to the uncoloured state remained very slow ($8 \times 10^{-4} \text{ s}^{-1}$). This compound exhibited a significant photodegradation and, under UV–vis irradiation a photostationary state was never attained.

3. Experimental

3.1. Materials

Hydroxyfluorenones **1–3** were prepared according to reference [17]. All reagents were obtained from Aldrich and were used as supplied. The new compounds, prepared according to Scheme 2, were determined to be >95% pure by ^1H NMR spectroscopy. The melting points of photochromic naphthopyrans **7–9** were not measured because thermochromism was observed at high temperatures. Column chromatography (CC) was performed on silica gel 60 (70–230 mesh). THF was pre-dried under sodium/benzophenone and distilled before use.

3.2. Instrumentation

All compounds were characterised by IR, NMR and MS. ^1H spectra were recorded in CDCl_3 on a Varian Unity Plus at 300 MHz. ^{13}C spectra were recorded in CDCl_3 on a Varian Unity Plus at 75.4 MHz. IR spectra were obtained on a Perkin-Elmer FTIR 1600 spectrometer using KBr disks (wave numbers in cm^{-1}). Electronic impact mass spectra were measured on an AutoSpecE spectrometer.

For measurements of λ_{max} , A_{eq} and k_{Δ} under continuous UV–vis irradiation, $1 \times 10^{-4} \text{ M}$ toluene solutions were used. Irradiation experiments were made using a CARY 50 Varian spectrometer coupled to a 150 W Ozone free Xenon lamp (6255 Oriel Instruments). The light from the UV–vis 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 a fiber-optic system (77654 Oriel Instruments). A light flux of 40 W m^{-2} , measured with a Goldilux Photometer with a UV-A probe was used. Visible irradiation experiments were performed using a long-pass filter, Schott GG 420 (Oriel 59480). A thermostated (20 °C) 10 mm quartz cell, containing the sample solution (3.5 ml),

equipped with magnetic stirring was used. In a preliminary experiment, the visible absorption spectrum of the closed form 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 with time was monitored. The thermal bleaching rate constants, k_{Δ} , were calculated fitting the absorbance curve obtained in the dark, at 20 °C, to a multi exponential model.

3.3. Synthetic procedures

Synthesis of naphthopyrans 4–6: A mixture of the pertinent hydroxy-7*H*-benzo[*c*]fluoren-7-one **1–3** (200 mg, 0.81 mmol), 1,1-diphenylprop-2-yn-1-ol (312 mg, 1.5 mmol), of piridinium *p*-toluenesulphonate (10 mg), trimethoxymethane (265 mg, 2.5 mmol) in 1,2-dichloroethane (20 ml) was refluxed for 2 h under an argon atmosphere. Solvent evaporation gave a brown oil, which was purified by silica gel column chromatography (3% ethyl acetate/hexane). Recrystallization from diethyl ether/pentane gave a crystalline material.

3.3.1. 3*H*-9-oxo-3,3-diphenylindeno[3,2-*e*]naphtho[2,1-*b*]pyran **4**

Red solid. mp 208–210 °C. Yield 70%. IR: 1708, 1658, 1598, 1446, 1276. ¹H NMR (acetone-*d*₆): 7.93 (d, *J* = 8.9 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 7.7 Hz, 1H), 7.69 (d, *J* = 8.7 Hz, 4H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.59 (d, *J* = 7.5 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 8.9 Hz, 1H), 7.42–7.26 (m, 8H), 6.43 (d, *J* = 9.50 Hz, 1H). ¹³C NMR: 194.32, 152.99, 145.90, 144.24, 141.77, 137.00, 134.77, 134.16, 133.50, 132.40, 132.35, 130.02, 129.99, 128.10, 127.72, 126.88, 125.70, 125.05, 123.86, 123.05, 120.62, 117.92, 115.14, 82.44. MS: *m/z* (%): 436 (100), 359 (70), 165 (15). Exact mass for C₃₂H₂₀O₂: 436.1463. Found 436.1459.

3.3.2. 4*H*-9-oxo-4,4-diphenylindeno[2,3-*g*]naphtho[2,1-*b*]pyran **5**

Red solid. mp 208–210 °C. Yield 56%. IR: 1702, 1602, 1461, 1396, 1253. ¹H NMR: 8.38 (d, *J* = 9.2 Hz, 1H), 7.96 (d, *J* = 7.6 Hz, 1H), 7.92 (d, *J* = 8.5 Hz, 1H), 7.74 (d, *J* = 8.5 Hz, 1H), 7.68 (d, *J* = 7.2 Hz, 1H), 7.50 (m, 5H), 7.35 (m, 5H), 7.30 (m, 4H), 6.34 (d, *J* = 10.0 Hz, 1H). ¹³C NMR: 194.04, 167.74, 152.53, 144.37, 143.47, 134.83, 134.71, 134.18, 132.44, 130.86, 128.78, 128.52, 128.20, 127.77, 126.96, 126.67, 123.84, 123.24, 122.58, 120.59, 120.12, 119.32, 115.24, 82.95. MS: *m/z* (%): 436 (100), 359 (75), 165 (10). Exact mass for C₃₂H₂₀O₂: 436.1463. Found 436.1458.

3.3.3. 5*H*-9-oxo-5,5-diphenylindeno[2,3-*g*]naphtho[1,2-*b*]pyran **6**

Red solid. mp 215–217 °C. Yield 60%. IR: 1702, 1567, 1396, 1236. ¹H NMR: 8.35 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.7 Hz, 1H), 7.95 (d, *J* = 7.6 Hz, 1H), 7.73 (d, *J* = 8.4 Hz,

1H), 7.65 (m, 1H), 7.48 (d, *J* = 7.1, 4H), 7.34–7.24 (m, 9H), 6.75 (d, *J* = 9.7 Hz, 1H), 6.30 (d, *J* = 9.7 Hz, 1H). ¹³C NMR: 194.36, 148.46, 144.93, 144.59, 142.50, 134.35, 132.00, 129.67, 129.21, 129.15, 128.62, 128.28, 127.72, 126.81, 126.38, 125.95, 123.91, 123.67, 123.29, 119.49, 117.72, 117.57, 83.58. MS: *m/z* (%): 436 (100), 359 (45), 191 (15). Exact mass for C₃₂H₂₀O₂: 436.1463. Found 436.1459.

Synthesis of indeno-fused naphthopyrans 7–9: A solution of MeLi in hexanes (1.6 M, 0.50 ml) was slowly added to a solution of naphthopyrans **4–6** (100 mg, 0.215 mmol) in THF (10 ml) at 0 °C. After stirring at room temperature for 30 min, the solution was quenched with NH₄Cl (aq. sat.), extracted with Et₂O (3 × 40 ml), and the combined organic layers dried (Na₂SO₄) and concentrated under reduced pressure. The residue was purified by CC (3% ethyl acetate/petroleum ether) to give pure naphthopyrans **7–9** as oils. Recrystallization from diethyl ether/pentane afforded crystalline materials.

3.3.4. 3*H*-3,3-diphenyl-9-hydroxy-9-methylindeno[3,2-*e*]naphtho[2,1-*b*]pyran **7**

Light yellow solid. Yield 86%. IR: 3272, 1488, 1446, 1155. ¹H NMR: 7.80 (d, *J* = 7.8 Hz, 1H), 7.73 (d, *J* = 8.8 Hz, 1H), 7.67 (m, 2H), 7.57 (d, *J* = 7.5 Hz, 1H), 7.53 (m, 3H), 7.40–7.30 (m, 6H), 7.30–7.20 (m, 6H), 6.13 (d, *J* = 9.5 Hz, 1H), 1.80 (s, 3H), 1.54 (s, OH). ¹³C NMR: 152.64, 151.76, 150.90, 145.02, 144.22, 140.16, 132.47, 131.92, 131.16, 129.48, 128.15, 128.04, 128.01, 127.68, 127.53, 127.18, 126.84, 126.78, 126.52, 124.81, 122.65, 122.44, 118.56, 118.12, 115.08, 82.29, 79.79, 26.22. MS: *m/z* (%): 452 (100), 437 (30), 375 (35), 359 (33), 180 (25), 165 (20). Exact mass for C₃₃H₂₄O₂: 452.1776. Found 452.1750.

3.3.5. 4*H*-4,4-diphenyl-9-hydroxy-9-methylindeno[2,3-*g*]naphtho[2,1-*b*]pyran **8**

Light yellow solid. Yield 70%. IR: 3149, 1629, 1562, 1260. ¹H NMR: 8.49 (d, *J* = 9.2 Hz, 1H), 8.11 (d, *J* = 7.7 Hz, 1H), 7.99 (d, *J* = 8.6 Hz, 1H), 7.69 (d, *J* = 8.6 Hz, 4H), 7.63 (m, 1H), 7.54 (m, 4H), 7.45–7.26 (m, 7H), 6.35 (d, *J* = 10 Hz, 1H), 1.77 (s, 3H). ¹³C NMR: 151.05, 150.39, 146.17, 144.70, 144.65, 139.63, 133.96, 131.14, 128.96, 128.37, 128.29, 128.12, 127.58, 127.34, 127.02, 125.96, 125.76, 125.17, 123.09, 123.04, 122.19, 121.45, 119.88, 119.13, 115.21, 82.48, 79.11, 25.79. MS: *m/z* (%): 452 (100), 437 (35), 375 (55), 359 (15), 180 (20), 165 (15). Exact mass for C₃₃H₂₄O₂: 452.1776. Found 452.1757.

3.3.6. 5*H*-5,5-diphenyl-9-hydroxy-9-methylindeno[2,3-*g*]naphtho[1,2-*b*]pyran **9**

Light orange solid. Yield 75%. IR: 3428, 1643, 1594, 1265. ¹H NMR: 8.46 (d, *J* = 8.3 Hz, 1H), 8.15 (m, 1H), 7.72 (d, *J* = 8.5 Hz, 1H), 7.70–7.40 (m, 5H), 7.30–7.00 (m, 10H), 6.80 (d, *J* = 9.7 Hz, 1H), 6.25 (d, *J* = 9.6 Hz, 1H), 1.80 (s, 3H). MS: *m/z* (%): 452 (100), 437 (20), 375 (25), 180 (15), 165 (15). Exact mass for C₃₃H₂₄O₂: 452.1776. Found 452.1758.

4. Conclusion

The fusion of an indene ring to the *i*- and *k*-faces of 3,3-diphenyl-2*H*-naphtho[2,1-*b*]pyrans and to the *i*-face of 2,2-diphenyl-2*H*-naphtho[1,2-*b*]pyran has a major effect on the photochromic behaviour. In general, a global bathochromic shift of the maximum wavelength of absorption of the open forms and a global acceleration of the bleaching process was observed. For all the solutions the persistence of a significant residual colour for long time under thermal bleaching conditions (dark, room temperature) was also observed. Compound **9** exhibited very slow bleaching kinetics even under visible irradiation and presents significant photodegradation under UV–vis irradiation, which prevents to attain a photostationary state. Under UV–vis irradiation, toluene solutions of indeno-fused naphthopyrans **7** and **8** led to mixtures of TT- and TC-isomers in significantly different relative amounts. For the indeno-fused naphthopyran **8** the TC-isomer was the main photoproduct, while the irradiation of toluene solution of naphthopyran **7** led to the predominance of the long-lived TT-isomer. The influence of the indene fused ring on the stability of both photoisomers obtained under continuous irradiation was different; while the TC-isomer decreased its thermal stability, the TT-isomer became more stable. At 20 °C the conversion of the TT-isomer to an uncoloured form was achieved rapidly through irradiation with visible light of the coloured solution.

Acknowledgements

To FCT (Portugal's Foundation for Science and Technology) and FEDER for financial support through project POCTI/QUI/38771/2001.

References

- [1] B. Van Gemert, in: J.C. Crano, R. Guglielmetti (Eds.), Organic Photochromic and Thermochemical Compounds, vol. 1, Kluwer Academic/Plenum Publishers, New York, 1999, Chapter 3, pp. 111–140.
- [2] S. Delbaere, J. Micheau, G. Vermeersch, J. Org. Chem. 68 (2003) 8968–8973.
- [3] S. Delbaere, G. Vermeersch, J. Photochem. Photobiol. A: Chem. 159 (2003) 227–232.
- [4] F. Ortica, P. Smimmo, G. Favaro, U. Mazzucato, S. Delbaere, D. Venec, G. Vermeersch, M. Frigoli, C. Moustrou, A. Samat, Photochem. Photobiol. Sci. 9 (2004) 878–885.
- [5] A. Kumar, B. Van Gemert, D.B. Knowles, Mol. Cryst. Liq. Cryst. 344 (2000) 217–222.
- [6] 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.
- [7] C. Moustrou, N. Rebière, A. Samat, R. Guglielmetti, R. Yassar, R. Dubest, J. Aubard, Helv. Chim. Acta 81 (1998) 1293–1302.
- [8] P.J. Coelho, M.A. Salvador, M.M. Oliveira, L.M. Carvalho, Tetrahedron 60 (2004) 2593–2599.
- [9] B. Van Gemert, U.S. Patent 5,645,767 (1997).
- [10] M. Melzig, C. Mann, U. Weigand, U.S. Patent 6,146,554 (2000).
- [11] C.M. Nelson, A. Chopra, O.G. Petrovskaia, D.B. Knowles, B. Van Gemert, A. Kumar, U.S. Patent 6,296,785 (2001).
- [12] C. Mann, U. Weigand, M. Melzig, U.S. Patent 6,333,625 (2001).
- [13] C. Mann, M. Melzig, U. Weigand, U.S. Patent 6,373,615 (2002).
- [14] O.G. Petrovskaia, A. Kumar, U.S. Patent 0071247 A1 (2003).
- [15] L. Jibing, B. Van Gemert, U.S. Patent 5,869,658 (1999).
- [16] C. Mann, M. Melzig, U. Weigand, U.S. Patent 6,315,928 (2001).
- [17] P.J. Coelho, M.A. Salvador, M.M. Oliveira, L.M. Carvalho, Synlett 6 (2004) 115–118.
- [18] W. Zhao, E. Carreira, Org. Lett. 12 (2003) 4153–4154.
- [19] J.D. Coyle, H.A.J. Carless, Chem. Soc. Rev. 1 (1972) 465.
- [20] S. Delbaere, B. Luccioni-Houze, C. Bochu, Y. Teral, M. Campredon, G. Vermeersch, J. Chem. Soc., Perkin Trans. 2 (1998) 1153–1157.
- [21] N. Takakazu, N. Nishi, H. Sakuragi, Sci. Prog. 2 (2001) 137–156.