Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Photochemistry and Photobiology A: Chemistry 171 (2005) 173–180
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Synthesis and spectrokinetic studies of a new family of thiophenic [2*H*]-chromens

Alain Maggiani, Frédéric Garzino, Pierre Brun*

Laboratoire de Synthèse Organique Sélective UMR-CNRS 6114, Faculté des Sciences de Luminy, Université de la Méditerranée, 163 Avenue de Luminy, Case 901, 13288 Marseille Cedex 09, France

Received 12 July 2004; received in revised form 28 September 2004; accepted 6 October 2004
Available online 13 November 2004

Abstract

A series of methyl 8,9-dimethoxy-2,2-diaryl-6-(2′-thienyl)-2*H*-naphtho[1,2-b]pyran-5-carboxylates were obtained from 1-hydroxy-3-methoxycarbonyl-4-(2′-thienyl)-6,7-dimethoxynaphthalene. The photochromic properties of this new family of 2*H*-naphtho[1,2-b]pyrans were studied under continuous irradiation and compared to those of reference's compounds. All the studied molecules appeared to have a better colourability and in some cases interesting ring closure kinetic constant (k_Δ).

Keywords: Thiophene; [2*H*]-chromens; Photochromism; Absorbance; Thermal ring-closure rate constant

1. Introduction

Photochromic compounds are very interesting substances owing to their ability to undergo a photoinduced change of colour and have been extensively studied since 1950 [1]. Many applications were found; the principal one, actually used on an industrial scale, being in the field of light sensitive sunglasses [2]. However, new applications are under development in the field of molecular electronics [3], optical memories [4–7] and biological photo switches [8,9].

Among the different families of photochromic compounds, benzo and naphthopyrans were particularly studied and the influence of the nature of the substituents, their position and the annellation type was investigated in order to establish structure–photochromic behaviour relationships [10–12].

It was thus shown that 3*H*-naphtho[2,1-b]pyran I had a faster thermal ring-closure rate constant (k_Δ) and a lower colourability (A_{eq}: absorbance at the λ_{max} of the open form under continuous irradiation) than the corresponding 2*H*-naphtho [1,2-b]pyran II [13] (Scheme 1).

It was also reported that thiophen groups seems to be very promising in the 3*H* series [14]. As only few information are available in the 2*H* series [15] we synthesized and studied the photochromic properties of a series of 2*H*-naphtho[1,2-b]pyrans substituted respectively in the 5- and 6-positions by a methyl carboxylate group and by a thiophen group and bearing different substituents in the 2-position.

Our choice for the position of the thiophen group was based on previous results in which it was shown that the introduction of an electron rich substituent, like a phenyl group, in the 6-position led to a bathochromic shift of the A_{eq} [11,14].

2. Experimental

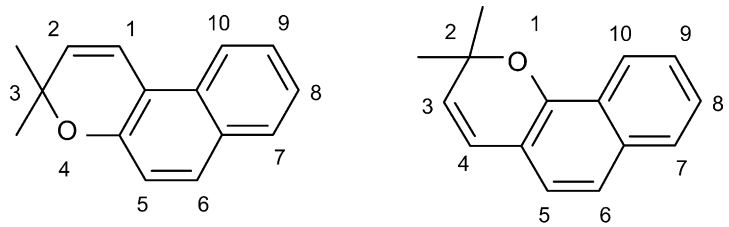
2.1. Materials

2.1.1. Trans-1-(2′-thienyl)-2,3-dimethoxycarbonyl-4-hydroxy-6,7-dimethoxy-1,2-dihydronaphthalene (2)

To a mixture of 2,3-dihydrofuran in methylene chloride (0.04 mol L^{-1}) $SnCl_4$ (10 eq.) was added, under Ar. The reaction was stirred at room temperature until total conversion was observed by TLC. The mixture was then neutralized

* Corresponding author. Tel.: +33 4 91 82 92 70; fax: +33 4 91 82 94 15.
E-mail address: brun@chimlum.univ-mrs.fr (P. Brun).

1010-6030/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2004.10.002



3*H*-Naphtho[2,1-b]pyran

I

2*H*-Naphtho[1,2-b]pyran

II

Scheme 1. Nomenclature of naphthopyranes.

by addition of a $NaHCO_3$ saturated solution. Then the same quantity of water was added and the aqueous layer was extracted with ether. The organic layer was successively washed by a saturated solution of $NaHCO_3$ (×2) and then by water (×2). The organic layer dried on $MgSO_4$ was concentrated under reduced pressure. The crude product was purified on silicagel (hexane/ether) (95%).

^{1}H NMR: 3.60 (s, 3H); 3.72 (s, 3H); 3.84 (s, 3H); 3.88 (s, 3H); 4.00 (s, 1H); 4.77 (s, 1H); 6.56 (d, 1H, J = 3.0); 6.67 (s, 1H); 6.75 (dd, 1H, J = 5.1); 7.03 (dd, 1H, J = 1.0); 7.35 (s, 1H); 12.70 (s, 1H). ^{13}C NMR: 34.7; 45.5; 51.9; 52.4; 55.9; 60.8; 61.0; 93.1; 104.2; 123.6; 123.7; 124.7; 126.1; 126.3; 145.1; 145.9; 150.5; 153.0; 165.7; 172.6 (2C). Anal. calc. for $C_{20}H_{20}O_7S$ (402.43): C 59.40, H 4.98; found: C 59.48, H 5.13.

*2.1.2. Trans-1-(2′-thienyl)-2-methoxycarbonyl-4-oxo-6,7-dimethoxy-1,2-dihydro-3H-naphthalene (**3**)*

To a solution of the tetralone (8.9 mmol) in DMF (10 mL) NaCl (8.9 mmol) and water (0.3 mL) were added. The mixture was stirred and heated at 150 °C during 1.5 h. After cooling at room temperature, the mixture was diluted with ether (20 mL) and then the organic layer was washed with water (15 mL ×10). The organic layer dried on $MgSO_4$ was concentrated under reduced pressure. Compound **3** was purified by chromatography (hexane/ether) (88%).

^{1}H NMR: 2.74 (dd, 1H, J = 16.5; 4.8); 2.87 (dd, 1H, J = 4.9); 3.35 (q, 1H, J = 5.5); 3.57 (s, 3H); 3.79 (s, 3H); 3.89 (s, 3H); 4.87 (d, 1H, J = 5.4); 6.55 (s, 1H); 6.60 (d, 1H, J = 3.6); 6.86 (dd, 1H, J = 5.4); 7.18 (dd, 1H, J = 0.9); 7.50 (s, 1H). ^{13}C NMR: 36.9; 42.3; 48.9; 52.5; 56.2 (2C); 108.4; 111.2; 125.2; 126.7; 127.0; 137.5; 145.4; 148.9; 154.2; 172.9; 193.9. Anal. calc. for $C_{18}H_{18}O_5S$ (346.41): C 62.41, H 5.24; found: C 62.50, H 5.27.

*2.1.3. 1-(2′-Thienyl)-2-methoxycarbonyl-4-acetyloxy-6,7-dimethoxy-1,2-dihydronaphthalene (**4**)*

To a mixture of the decarbomethoxylated tetralone (1 mmol) and isopropenyl acetate (14 mL) TsOH (14 mg) and acetic anhydride (1.4 mL) were successively added. The mixture was stirred under reflux during 60 h. After cooling at room temperature, the mixture was diluted with water (20 mL) and extracted with ether (3 × 15 mL). The organic layer was washed with a saturated $NaHCO_3$ solution and then with water. The organic layer dried on $MgSO_4$ was concentrated under reduced pressure. The crude **4** was purified by chromatography (hexane/ether) (77%).

^{1}H NMR: 2.25 (s, 3H); 3.61 (s, 3H); 3.74 (s, 3H); 3.81 (s, 3H); 3.63 (m, 1H); 4.79 (d, 1H, J = 4.8); 5.55 (d, 1H, J = 5.8); 6.60 (s, 1H); 6.66 (s, 1H); 6.81 (m, 2H); 7.08 (dd, 1H, J = 3.8; 2.3). ^{13}C NMR: 20.9; 40.4; 47.8; 52.3; 55.9; 56.0; 105.2; 108.3; 112.0; 121.3; 124.1; 125.5; 126.7; 130.0; 145.6; 146.3; 148.0; 149.5; 168,6; 172.4. Anal. calc. for $C_{20}H_{20}O_6S$ (388.44): C 61.84, H 5.19; found: C 61.98, H 5.35.

*2.1.4. 1-Acetyloxy-3-methoxycarbonyl-4-(2′-thienyl)-6,7-dimethoxynaphthalene (**5**)*

To a mixture of the enol acetate (3.1 mmol) and toluene (70 mL) DDQ (9.3 mmol) was added. The mixture was stirred under reflux for 2 h. After cooling at room temperature, the mixture was diluted with ether. The organic layer is washed with a $NaHCO_3$ saturated solution. The organic layer dried on $MgSO_4$ was concentrated under reduced pressure. The crude **5** was purified by chromatography (hexane/ether) (83%). Melting point 180–181 °C.

^{1}H NMR: 2.40 (s, 3H); 3.61 (s, 3H); 3.70 (s, 3H); 3.92 (s, 3H); 6.95 (dd, 1H, J = 3.3; 1.1); 7.02 (s, 1H); 7.04 (s, 1H); 7.09 (dd, 1H, J = 5.1); 7.42 (dd, 1H); 7.55 (s, 1H). ^{13}C NMR: 21.2; 52.2; 55.8; 56.1; 99.6; 106.8; 116.9; 124.4; 126.4; 126.9; 128.1; 131.1; 133.2 (2C); 139.1; 145.7; 150.6; 151.5; 167.0; 168.2. Anal. calc. for $C_{20}H_{18}O_6S$ (386.43): C 62.17, H 4.70; found: C 62.23, H 4.75.

*2.1.5. 1-Hydroxy-3-methoxycarbonyl-4-(2′-thienyl)-6,7-dimethoxynaphthalene (**6**)*

The naphthyl acetate (2.6 mmol) was solubilized with 40 mL of a MeOH/water (4:1) mixture. K_2CO_3 (7.8 mmol) was added and the mixture was stirred under reflux overnight. After cooling at room temperature, the MeOH was evaporated under reduced pressure. The product is solubilized with CH_2Cl_2. The organic layer is washed with water and then dried with $MgSO_4$. The solvent was evaporated under reduced pressure and the crude product purified on silicagel (hexane/ether) (90%). Melting point: 147 °C.

^{1}H NMR: 3.55 (s, 3H); 3.70 (s, 3H); 3.95 (s, 3H); 4.60 (s, 1H); 6.92 (dd, 1H, J = 3.3; 0.9); 6.99 (s, 1H); 7.06 (dd, 1H, J = 4.8); 7.17 (s, 1H); 7.37 (dd, 1H); 7.46 (s, 1H). ^{13}C NMR: 52.4; 55.8; 56.2; 101.0; 106.5; 107.4; 121.9; 124.2; 126.2; 126.9; 128.1; 128.6; 131.1; 140.1; 150.5; 150.6; 151.4; 168.7. Anal. calc. for $C_{18}H_{16}O_5S$ (344.39): C 62.78, H 4.4.68; found: C 62.74, H 4.70.

*2.1.6. General procedure for the synthesis of 2H-chromene (**8a**–**h**)*

The naphthol **6** (1 mmol) was solubilized with a minimal amount of methylene chloride. To this mixture the propargylic alcohol (1.2 mmol) solubilized in CH_2Cl_2 (minimal amount) was added. A catalytic amount of *p*TsOH was added and the mixture was stirred at room temperature, under Ar, until no evolution of the reaction was observed by TLC. The mixture was washed with a $NaHCO_3$ saturated solution and then the organic layer was dried on $MgSO_4$ and finally concentrated under reduced pressure. The product was purified on silicagel (hexane/ether from 1:0 to 7:3).

*2.1.7. Methyl 8,9-dimethoxy-2,2-methyl-6-(2′-thienyl)-2H-naphtho[1,2-b]pyrane-5-carboxylate (opened form) (13%) (**8a**)*

^{1}H NMR: 1.18 (s, 6H); 3.54 (s, 3H); 3.72 (s, 3H); 3.96 (s, 3H); 6.11 (d, 1H, J = 10.0); 6.67 (d, 1H, J = 10.0); 6.96 (m, 1H); 7.01 (s, 1H); 7.03 (m, 1H); 7.54 (s, 1H). ^{13}C NMR: 40.7; 52.7; 115.7; 116.4; 128.1; 128.4; 128.6; 129.3; 131.0; 131.7; 135.3; 136.6; 139.1; 139.4; 143.9; 167.4; 169.7; 170.0; 183.2. Anal. calc. for $C_{23}H_{22}O_5S$ (410.49): C 67.30, H 5.40; found: C 67.42, H 5.67.

*2.1.8. Methyl 8,9-dimethoxy-2,2-diphenyl-6-(2′-thienyl)-2H-naphtho[1,2-b]pyrane-5-carboxylate (64%) (**8b**) (melting point: 200 °C)*

^{1}H NMR: 3.54 (s, 3H); 3,72 (s, 3H); 3.96 (s, 3H); 6.10 (d, 1H, J = 10.0); 6.67 (d, 1H, J = 10.0); 6.96 (dd, 1H, J = 3.5; 1.5); 7.01 (s, 1H); 7.04 (t, 1H); 7.19–7.34 (m, 6H); 7.35 (dd, 1H, J = 6.5; 1.5); (dd, 4H, J = 7.7; 1.7); 7.54 (s,1H). ^{13}C-NMR: 52.2; 55.7; 56.1; 83.4; 100.6; 105.7; 111.1; 120.2; 120.5; 120.9; 126.5; 126.8; 126.9; 127,6; 127.7; 128.2; 128.6; 128.9; 129.9; 138.2; 144.8; 150.2; 150.6; 168.8. Anal. calc. for $C_{33}H_{26}O_5S$ (534.64): C 74.14, H 4.90; found: C 74.27, H 4.93.

*2.1.9. Methyl 2-ferrocenyl-8,9-dimethoxy-2-phenyl-6-(2′-thienyl)-2H-naphtho[1,2-b]pyrane-5-carboxylate (72%) (**8c**) (melting point: decomposition)*

^{1}H NMR: 3.54 (s, 3H); 3.75 (s, 3H); 4,02 (s, 1H); 4.03 (s, 5H); 4.17 (m, 2H); 4.27 (m, 1H); 6.19 (dd, 1H, J = 10.0); 6.57 (d, 1H, J = 10.0); 6.98 (dd, 1H, J = 3.2; 1.2); 7.02–7.06 (m, 2H); 7.16–7.20 (m, 3H); 7.35–7.44 (m, 3H); 7.63 (s, 1H). ^{13}C NMR: 52.1; 55.7; 56.2; 66.1; 66.6; 68.1; 69.1; 81.0; 89.2; 95.1; 100.4; 105.8; 111.0; 119.4; 120.2; 121.1; 125.6; 126.6; 126.8; 127.2; 127.5; 128.0; 128.6; 129.9; 138.9; 145.3; 147.7; 150.2; 150.5; 169.0. Anal. calc. for $C_{37}H_{31}FeO_5S$ (643.57): C 69.05, H 4.86; found: C 69.17, H 4.91.

*2.1.10. Methyl 2,9′-fluorene-8,9-dimethoxy-6-(2′-thienyl)-2H-naphtho[1,2-b]pyrane-5-carboxylate (67%) (**8d**) (melting point: decomposition)*

^{1}H NMR: 3.60 (s, 3H); 3.71 (s, 3H); 5.50 (d, 1H, J = 9.7); 6.74 (d, 1H, J = 9.7); 7.03–7.10 (m, 2H); 7.14–7.24 (m, 3H); 7.27–7.41 (m, 4H); 7.52–7.55 (d, 2H, J = 7.5); 7.60–7.66 (m, 2H). ^{13}C NMR: 55.1; 54.6; 51.1; 85.2; 99.8; 104.4; 109.1; 119.0; 119.2; 119.4; 120.1; 120.5; 123.2; 124.0; 124.4; 125.9; 127.4; 127.6; 128.7; 128.9; 137.8; 137.9; 146.7; 147.8; 148.9; 149.5; 168.1. Anal. calc. for $C_{33}H_{24}O_5S$ (532.62): C 74.42, H 4.54; found: C 74.69, H 4.58.

*2.1.11. Methyl 8,9-dimethoxy-2-(4′-methoxyphenyl)-2-phenyl-6-(2′-thienyl)-2H-naphtho[1,2-b]pyrane-5-carboxylate (82%) (**8e**) (melting point 129 °C)*

^{1}H NMR: 3.52 (s, 3H); 3.68 (s, 3H); 3.93 (s, 3H); 6.06 (d, 1H, J = 9.7); 6.64 (d, 1H, J = 9.7); 6.76 (d, 2H, J = 8.7); 6.95 (dd, 1H, J = 3.5; 1.2); 7.00 (s, 1H); 7.02 (m, 1H); 7.16–7.42 (m, 8H); 7.52 (s, 1H). ^{13}C NMR: 51.0; 54.2; 54.7; 55.0; 82.2; 99.5; 104.6; 110.3; 112.5; 119.4; 119.6; 120.2; 125.5; 125.8 (2C); 126.5; 126.8; 127.2; 127.4; 127.9; 128.8; 135.8; 137.8; 144.0; 146.2; 149.1; 149.5; 158.0; 168.0. Anal. calc. for $C_{34}H_{28}O_6S$ (564.66): C 72.32, H 5.00; found: C 72.52, H 5.17.

*2.1.12. Methyl 8,9-dimethoxy-2,2-bis-(4′-methoxyphenyl)-6-(2′-thienyl)-2H-naphtho[1,2-b]pyrane-5-carboxylate (51%) (**8f**) (melting point 202 °C)*

^{1}H NMR: 3.55 (s, 3H); 3.72 (s, 9H); 3.95 (s, 3H); 6.03 (d, 1H, J = 10.0); 6.62 (d, 1H, J = 10.0); 6.78 (d, 2H, J = 8.7); 6.95 (m, 1H); 7.00 (s, 1H); 7.03 (m, 1H); 7.29–7.36 (m, 3H); 7.50 (s, 1H). ^{13}C-NMR: 52.1; 55.3; 55.7; 56.1; 83.0; 100.6; 105.7; 111.3; 113.5; 120.5; 121.2; 126.5; 126.8; 128.1; 128.3; 128.6; 129.8; 137.1; 138.9; 141.9; 148.8; 150.1; 150.5; 159.0; 169.1; 171.5. Anal. calc. for $C_{35}H_{30}O_7S$ (594.69): C 70.69, H 5.08; found: C 70.93, H 5.04.

*2.1.13. Methyl 2,2-bis-(4′-chlorophenyl)-8,9-dimethoxy-6-(2′-thienyl)-2H-naphtho[1,2-b]pyrane-5-carboxylate (48%) (**8g**) (melting point 247 °C)*

^{1}H NMR: 3.53 (s, 3H); 3.72 (s, 3H); 3.95 (s, 3H); 5.99 (d, 1H, J = 10.0); 6.70 (d, 1H, J = 10.0); 6.96 (m, 1H); 7.01 (s, 1H); 7.04 (m, 1H); 7.23 (d, 4H, J = 8.5); 7.34 (m, 5H); 7.45 (s, 1H). ^{13}C NMR: 51.1; 54.7; 55.0; 81.5; 99.2; 104.8; 110.2; 119.3; 120.7; 120.9; 125.5; 125.6 (3C); 125.8; 127.4; 127.5; 127.6; 127.8; 129.0; 132.9; 137.6; 141.7; 145.7; 149.3; 149.7; 167.8. Anal. calc. for $C_{33}H_{24}Cl_2O_5S$ (603.53): C 65.68, H 4.01; found: C 65.90, H 4.07.

*2.1.14. Methyl 2,2-bis-(4′-fluorophenyl)-8,9-dimethoxy-6-(2′-thienyl)-2H-naphtho[1,2-b]pyrane-5-carboxylate (66%) (**8h**) (melting point 260 °C)*

^{1}H NMR: 3.54 (s, 3H); 3.72 (s, 3H); 3.95 (s, 3H); 6.01 (d, 1H, J = 10.0); 6.68 (d, 1H, J = 10.0); 6.92-7.06 (m, 6H); 7.19 (s, 1H); 7.33–7.40 (m, 5H); 7.46 (s, 1H). ^{13}C NMR: 52.1; 55.7; 56.1; 82.6; 100.3; 105.8; 111.2; 115.0; 115.4; 120.4; 121.3; 121.8; 126.6; 126.9; 127.1; 128.6; 128.7; 128.9; 130.0; 138.7; 140.3; 140.4; 146.9; 150.3; 150.7; 160.3; 164.2; 168.9. Anal. calc. for $C_{33}H_{24}F_2O_5S$ (570.62): C 69.46, H 4.24; found: C 69.58, H 4.29.

*2.1.15. 8,9-dimethoxy-2,2-diphenyl-2H-naphtho[1,2-b]pyrane (19%) (**10**)*

^{1}H NMR: 3.76 (s, 3H); 3.95 (s, 3H); 6.05 (d, 1H, J = 9.7); 6.63 (d, 1H, J = 9.7); 6.95 (t, 2H); 7.11 (d, 1H, J = 8.5); 7.19–7.28 (m, 8H); 7.43 (dd, 2H, J = 8.0; 1.5); 7.50 (s, 1H). ^{13}C NMR: 54.8; 55.0; 99.6; 105.4; 113.4; 117.9; 118.7; 121.9; 123.0; 125.6; 125.9; 126.4; 127.1; 129.7; 129.9; 131.0; 131.2; 144.2; 148.3; 148.9; 166.8. Anal. calc. for $C_{27}H_{22}O_3$ (394.47): C 82.21, H 5.62; found: C 82.33, H 5.87.

2.2. Apparatus and analytical methods

Melting points were measured with an Electrothermal-IA-9100 apparatus in capillary tubes. ^{1}H and ^{13}C NMR Spectra: were realized with a Bruker-AC-250 spectrometer; at 250 and 62.2 MHz, respectively, and in $CDCl_3$ as solvent. The chemical shifts δ was in ppm and the coupling constant J in Hz.

A Cary 50 spectrophotometer was used for recording the absorption spectra and measuring the thermal ring-closure rate constant by following time-evolution under and after continuous irradiation with an Oriel Xe lamp (150 W) using an optical fibre and a thermostated cell. The all emission spectra of the Xe lamp was used (no chromatic filter) in order to mimic day light

Photodegradation experiments were realized using a SUN TEST SPC system using a xenon lamp (1500 W).

3. Results

3.1. Synthesis

By taking advantage of a rearrangement reaction we described previously, the required 2*H*-naphtho[1,2-b]pyrans were prepared from 2,5-diaryl-2,3-dihydrofuran which could be easily obtained by intermolecular $Mn(OAc)_3$-mediated radical addition of a β-ketoester to a functionalised olefin (Scheme 2). The reaction carried out in acetic acid at 70 °C led to *trans*-2,3-dihydrofuran **1** as a sole product in good yield (58%) [16].

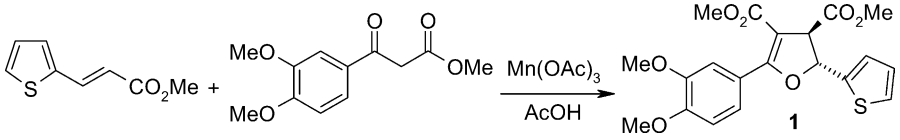
A Lewis acid induced rearrangement of the 2,3-dihydrofuran (Scheme 3) led to the naphthol framework. Several Lewis acids could be used to perform this reaction but previous studies have shown that $SnCl_4$ was the most efficient reagent for this kind of thiophenylated substrates. Tetralone **2** (in its enol form) was thus obtained in excellent yield (95%).

Compound **3** was obtained by selective decarbomethoxylation of **2** and among the different strategies tested, only the straightforward one described by Krapcho (NaCl, DMF, H_2O) gave good results (1.5 h, 88% yield).

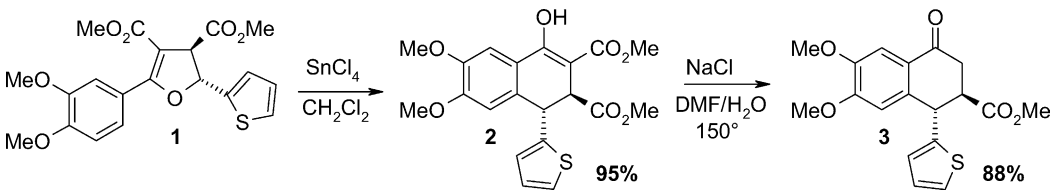
Aromatization of the intermediary tetralone **3** was performed as depicted in Scheme 4. Formation of the enol acetate **4** (Ac_2O/isopropenyl acetate, 77%) followed by dehydrogenation with DDQ for 2 h afforded the naphthyl acetate **5** in high yield (83%). The subsequent cleavage of the acetate with K_2CO_3 in a MeOH/water mixture led to the expected naphthol **6**.

The α-naphthol obtained **6** is a versatile building-block for the subsequent synthesis of chromens (**8a–h**), which were obtained by reaction of **6** with various propargylic alcohols **7** (Scheme 5).

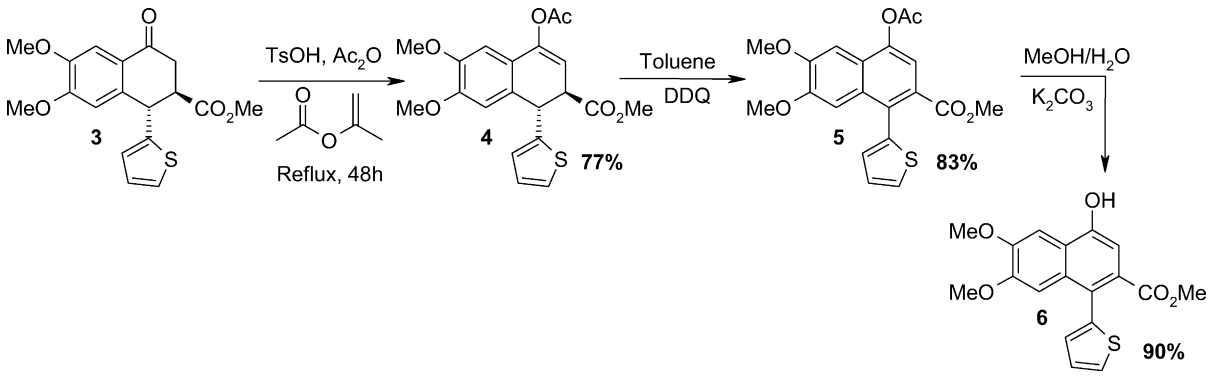
Some studies have previously shown that when the propargylic alcohol is substituted by an aromatic ring bearing an electron donor group in the *para* position, then the corresponding chromens have a better ring closure kinetic constant. This is why we have chosen in our study only propargylic alcohol substituted in the *para* position. No changes are observed with *meta* substitutions whereas *ortho* substi-



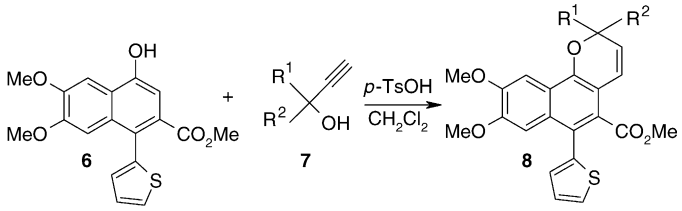
Scheme 2. Synthesis of the dihydrofuran **1**.



Scheme 3. Synthesis of the tetralone.



Scheme 4. Synthesis of the naphthol **6**.



8a :R^1=Me, **R^2**=Me	**13%**
8b :R^1=Ph, **R^2**=Ph	**64%**
8c :R^1=Ph, **R^2**=Fc	**72%**
8d :R^1, **R^2**=Fluorene	**67%**
8e :R^1=*p*-MeOC$_6$H$_4$, **R^2**=Ph	**82%**
8f :R^1=*p*-MeOC$_6$H$_4$, **R^2**=*p*-MeOC$_6$H$_4$	**51%**
8g :R^1=*p*-ClC$_6$H$_4$, **R^2**=*p*-ClC$_6$H$_4$	**48%**
8h :R^1=*p*-FC$_6$H$_4$, **R^2**=*p*-FC$_6$H$_4$	**66%**

Scheme 5. Synthesis of the 8,9-dimethoxy-2,2-diaryl-6-(2′-thienyl)-2*H*-naphtho[1,2-b]pyran-5-carboxylates series.

tutions give a better absorbance but reduce the ring closure kinetic constant. As mentioned previously, α-naphthols give generally chromens, which present a great absorbance (colourability) and a small thermal ring-closure rate constant.

Propargylic alcohols were synthesized by reacting sodium acetylide on the corresponding substituted ketones (65–92%).

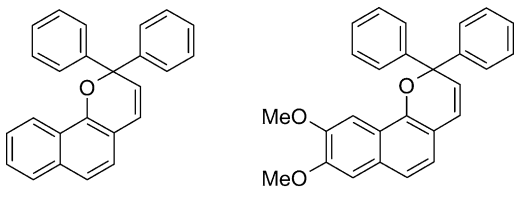
In order to know the influence of the various substituents, we synthesized two products (**9** and **10**) that we considered as reference's molecules (Scheme 6).

Compound **9** was synthesized starting from the commercial α-naphtol (19%) and **10** from catechol [17].

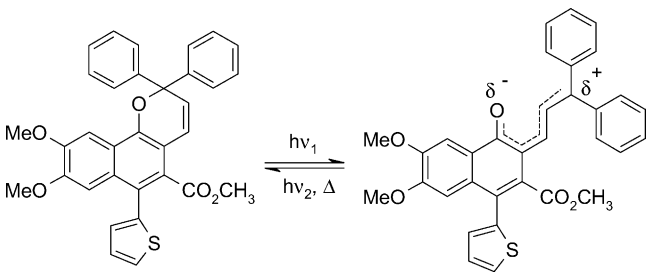
Bromination of catechol and methylation in acetone with K_2CO_3 and methyl iodide gave 1,2-dibromo-4,5-dimethoxybenzene (63%). This compound reacted with BuLi and furan gave an oxabicyclic derivative [18]. The 1,4-dihydro-6,7-dimethoxy-1,4-epoxynaphthalene thus obtained with a yield of 48% was quantitatively opened in acidic conditions into **10** [19].

3.2. Photochromic properties

Photochromic phenomenon can be described by Scheme 7. Under irradiation, chromens are opened by cleavage of the Csp2-oxygen bond and several isomeric open forms are generated. Theses open forms are generally coloured ones while the starting chromens are colourless or pale yellow. The back closure of the open forms (often



Scheme 6. Reference compounds.



Scheme 7. Photochromic equilibrium for the chromen series.

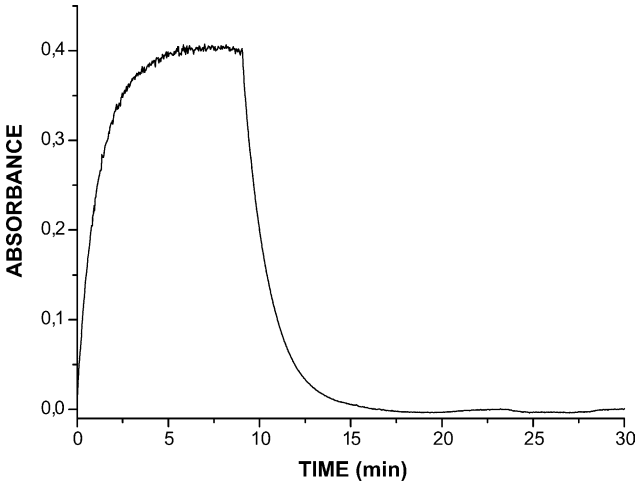


Fig. 1. Colouration/decolouration graph for **8c** compound at 500 nm.

referred as the photomerocyanine forms) is generally a thermal process but may also be induced by irradiation in the visible range.

The samples for the spectrokinetic studies were prepared in toluene and acetonitrile (5×10^{-4} mol L^{-1}) and then irradiated at 23 °C for 10 min (until photostationary state was obtained) under UV and visible light with a Xe lamp (4 W/m^2).

The irradiation was then stopped and the ring closure process was monitored by recording the decrease of the absorbance of the open form.

The results are reported in Table 1.

Figs. 1 and 2 are the colouration-decolouration graphs obtained for **8c** and Fig. 3 shows the spectrums obtained for the same compound. They are given as example.

4. Discussion

We have reported in the Table 1 the absorption spectra of the closed forms of the compounds studied. All the compounds are colourless in their closed form and they absorb only in the UV range before irradiation. It must be noted that, depending on the solvent, several k_Δ can be measured (compounds **8b–d** in CH_3CN and **8d** and **8f** in MeOH). This is the result of multi-exponential decay curves which indicate that more than one open form is involved in the back-closure process.

Table 1
Spectrokinetic behaviour of the [2*H*]-chromens under continuous irradiation

	R^1	R^2	λ_{max} "closed" form (nm)[a]	MeCN			Toluene		
				λ_{max} (nm)[b]	k_Δ (s^{-1})[c]	A_{eq}[d]	λ_{max} (nm)[b]	k_Δ (s^{-1})[c]	A_{eq}[d]
8a	Me	Me	288, 324			No photochromic system			
8b	Ph	Ph	202, 206, 216, 274, 278, 282, 288, 328	422	8.2×10^{-3}, 6.5×10^{-5}	1.37	420	5.2×10^{-3}	1.63
8c	Ph	Fc	206, 214, 222, 226, 232, 268, 276, 286	425, 588	25×10^{-3}, 4.2×10^{-4}, 2.7×10^{-4}	0.16, 0.12	430, 635	11.7×10^{-3}, 11.7×10^{-3}	0.40, 0.23
8d		Fluorene	202, 212, 224, 230, 236, 270, 276, 280, 288, 344	452	12.7×10^{-3}, 1.2×10^{-3}, 2×10^{-3}	0.92, 1.10	452	9.2×10^{-3}, 2×10^{-3}	1.10
8e	*p*-$MeOC_6H_4$	Ph	210, 230, 270, 280, 330	440	23.3×10^{-3}	0.80	440	11.5×10^{-3}	1.11
8f	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	215, 225, 270, 280, 290, 325	450	76.3×10^{-3}, 9.5×10^{-5}	0.44, 0.65	450	41×10^{-3}, 9.5×10^{-5}	0.65
8g	*p*-ClC_6H_4	*p*-ClC_6H_4	230, 280, 284, 325	426	8.8×10^{-3}	1.20	425	7.3×10^{-3}	1.36
8h	*p*-FC_6H_4	*p*-FC_6H_4	210, 274, 290, 329	420	13×10^{-3}	1.12	425	9.7×10^{-3}	1.45
9				471	2×10^{-3}	0.5	471	5×10^{-4}	0.7
10			225, 260, 270, 280, 320	408	0.7×10^{-3}	0.65	410	1.7×10^{-5}	0.8

[a] Absorption wavelength of the closed form in toluene.
[b] λ_{max} of the open form.
[c] Kinetic constants of the ring closure.
[d] Absorbance at the photostationnary state.

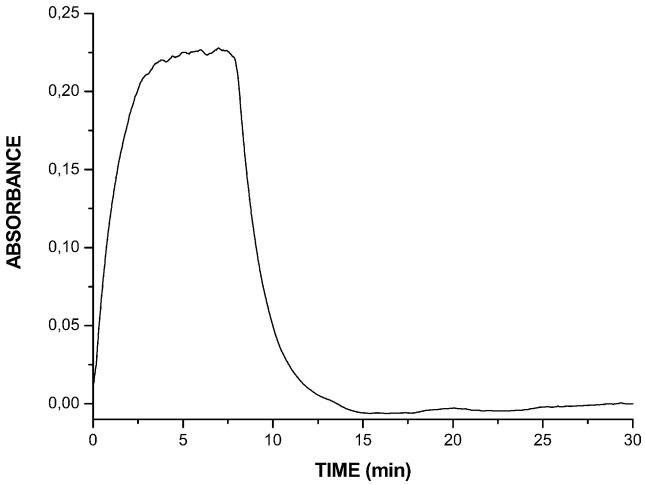


Fig. 2. Colouration/decolouration graph for **8c** compound at 635 nm.

It can be seen from Table 1 that the nature of the solvent has no effect on the λ_{max} of the open form. Indeed, when toluene is replaced by the more polar acetonitrile only very little differences can be observed. This result suggests that the open forms are best described by neutral form, with localised double bonds, than zwitterionic forms. In order to verify this result we also tried to perform the same experiments in more polar solvents like methanol or ethanol. Unfortunately, our compounds were insoluble in these solvents.

Compound **8a** does not present any photochromic properties. In fact, it was already known in other chromen series that when the substituents in the 2-position are methyl groups such a non photochromic behaviour is observed.

The effect of the dimethoxy substitution on positions 8 and 9 can be seen when the λ_{max} of the two reference compounds **9** and **10** are compared: the presence of the methoxy

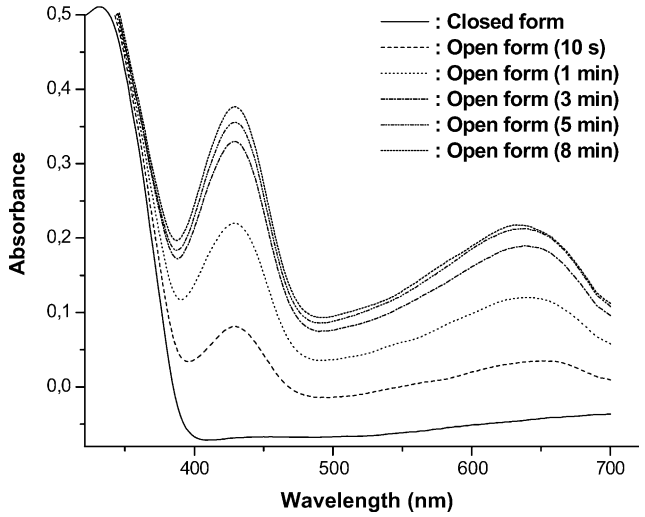


Fig. 3. Spectrums of **8c** compound under continuous irradiation.

groups induces a hypsochromic shift. It can be noted that in the **8a**–**h** series the λ_{max} is always lower than the one observed for **9**. However, the λ_{max} depends on the nature of the substituent and increases with the electro donating ability of the substituent (compare **8h**, **8g**, **8b** and **8e** and **8f**). The highest value is found when 2,2′ is a fluorine group. This bathochromic effect can be explained by the fact that electron donating substituants increase the energy of the HOMO of the polyene and thus increase the λ_{max} by decreasing the energy difference between the HOMO and the LUMO. It must be noted that when a ferrocenyl group is present in the 2-position a second absorption band can be observed at a higher λ_{max} as previously described in other similar series. This could be explained by the presence of π-electron conjugated chains in the open form including either a phenyl or a ferrocenyl group as substituent [20].

As it is the case for reference compounds **9** and **10** the k_Δ have always a higher value in acetonitrile than in toluene.

The effect of the substituents in the 5-, 6-, 8- and 9-positions can be seen by comparing **8b** and **9**. The k_Δ is accelerated by a factor 4 in CH_3CN and a factor 10 in toluene.

When **8b** is compared with **10**, where only the influence of the thiophen and the methoxy carbonyl groups is implied, the effect is not so marked and the k_Δ differs only by a factor of 10 in acetonitrile and 10^2 in toluene. The same trend is observed for all the compounds studied with an accelerating factor of 4 to 10^3 in acetonitrile and 10 to 10^3 in toluene. In all the cases the presence of the thiophen has a marked effect on the k_Δ which is notably accelerated.

Concerning the colourability (A_{eq}) the comparison of **9** and **10** shows that the 8,9-substitution by methoxy group does not have a significant effect.

This is not anymore the case for 5-carbomethoxy and 6-thiophen substituted compounds. The A_{eq} is increased in all cases except for compound **8f** which bears two electro donating groups in the 2-position and for the ferrocenyl substituted compound **8c**.

For **8b**, **8d**, **8e**, **8g** and **8h** the A_{eq} are twice as important as in the reference compounds **9** and **10**, the best result being observed for **8b**.

In summary in this series the substitution by a methoxy carbonyl group and a thiophen in the 5- and 6-positions leads to an important increase of the colourability and the thermal ring-closure rate constant.

As compared with the results obtained in the 3*H*-naphtho[2,1-b]pyrans it must be noted that the colourability increases in the same range of magnitude in the **8a**–**h** series. The main difference lies on the k_Δ values: similar or small increase is observed in the 3*H*-naphtho[2,1-b]pyrans series while an important increase (10^2–10^3) is characteristic of the 2*H*-naphtho[1,2-b] series.

Some preliminary experiments have been realized to compare the photodegradation behaviour of the compounds of that series with the one of the reference compound **10**. For this preliminary study, compound **8b** was chosen as a model

compound for the new series of [2*H*]naphtho[1,2-b]pyrans. It appeared that the photo resistance of **8b** is much better than the one of **10**. When compound **10** in acetonitrile (5×10^{-4} mol L^{-1}) is irradiated in a SUN TEST (SPC model) system with a xenon lamp (1500 W) the absorbance of the open form of **10** decreased rapidly and reached an $A_{eq}/2$ value after 44 min whereas under the same conditions the absorbance for compound **8a** remained unaffected even after one hour of irradiation. More detailed studies will be carried out in order to quantify the photodegradation process for all the compounds of the series.

5. Conclusions

The synthesis of a new family of 2*H*-naphtho[1,2-b]pyrans is described. The synthesis is based on the Lewis acid induced rearrangement of a dihydrofuran. This synthetic approach could be extended to the synthesis of other chromens families.

For the naphthol the yield is good and is low to good for the final photochromic compounds, depending on the nature of the propargylic alcohol.

The studies of the photochromic properties show that all the synthesized compounds have a better absorbance than the one observed for the reference's compounds. Among the compounds studied product (**8f**) must be noticed and could be a good model for further studies as it presents a good compromise between A_{eq} and k_{Δ}.

References

[1] H. Dürr, H. Bouas-Laurent (Eds.), Photochromism: Molecules and Systems, Elsevier, Amsterdam, 1990.
[2] G. McArdle (Ed.), Applied Photochromic Polymers Systems, Blackie, London, 1992.
[3] J.A. Delaire, K. Nakatami, Chem. Rev. 100 (2000) 1817.
[4] M. Irié, Chem. Rev. 10 (2000) 1685.
[5] G. Berkovic, V. Krongauz, V. Weiss, Chem. Rev. 100 (2000) 1741.
[6] S. Kawata, Y. Kawata, Chem. Rev. 100 (2000) 1777.
[7] B.L. Feringa, W.F. Jager, B. deLange, Tetrahedron 49 (1993) 8267.
[8] I. Willner, S. Rubin, Angew. Chem. Int. Ed. Engl. 35 (1996) 367.
[9] O. Pieroni, A. Fissi, G. Popova, Progr. Polymer Sci. 23 (1998) 81.
[10] J. Kolc, R.S. Becker, Photochem. Photobiol. 12 (1970) 383.
[11] B. Van Gemert, US Patent 5,645,767 (1997).
[12] J.C. Crano, R. Guglielmetti (Eds.), Organic Photochromic and Thermochromic Compounds, Kluwer Academic publishers/Plenum Press, New York, 1999.
[13] M. Frigoli, V. Pimienta, C. Moustrou, A. Samat, R. Guglielmetti, J. Aubard, F. Maurel, J.-C. Michaud, Photochem. Photobiol. Sci. (2003) 888.
[14] M. Frigoli, Ph.D. thesis, Université de la Méditerranée, Marseille, 2000.
[15] P.J. Coelho, M.A. Salvador, M.M. Oliveira, L.M. Carvalho, Tetrahedron 60 (2004) 2593.
[16] F. Garzino, A. Méou, P. Brun, Tetrahedron Lett. 41 (2000) 9803.
[17] M. Kohn, J. Am. Chem. Soc. 73 (1951) 480.
[18] R.G.F. Giles, A.B. Hughes, M.V. Sargent, J. Chem. Soc. Perkins Trans. 1 (1991) 1581.
[19] A. Maggiani, A. Tubul, P. Brun, Tetrahedron Lett. 39 (1998) 4485.
[20] S. Anguille, P. Brun, R. Guglielmetti, Y.P. Stokach, A.A. Ignatin, V.A. Barachevsky, M.V. Alfimov, J. Chem. Soc., Perkin Trans. 2 (2001) 639.