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The intramolecular capture of thermally generated merocyanine dyes derived from naphthopyrans: Photochromism of 5-(diarylhydroxymethyl)-2*H*-naphtho[1,2-*b*]pyrans

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ABSTRACT

A series of 2*H*-naphtho[1,2-*b*]pyrans bearing a diarylmethanol unit at C-5 have been synthesised by the addition of an excess of an aryllithium reagent to alkyl 2*H*-naphtho[1,2-*b*]pyran-5-carboxylate precursors. These naphthopyrans show photochromism when exposed to ultraviolet irradiation and also generate intense colours at low pH through triarylmethine cation generation. However, photochromism of the triarylmethine cation derived from the naphthopyran unit could not be detected. An irreversible cascade process initiated by the thermally-induced ring-opening of the diarylmethanol substituted 2*H*-naphtho[1,2-*b*]pyrans in the presence of an acid catalyst afforded novel benzopentalenonaphthalenone dyes.

1. Introduction

There has been a resurgence of interest in the design, synthesis and properties of dye systems over the last decade or so. Of particular note is the interest in probe and sensor systems [1], dyes/sensitizers for dye sensitised solar cells [2] and organic conducting and emitting systems [3]. A healthy interest has also been maintained in established functional dye systems, such as those used in photodynamic therapy [4], bio-labelling [5] and photochromism [6,7]. The control of various phenomena through the cycling sequence of a photochromic unit [8] and the properties of hybrid photochromic systems [9] have recently been reviewed.

Our interest has focussed upon cationic dyes whose colour can be modulated by the variation of pH and also through the switching of a photochromic naphthopyran unit [10]. In this study the cationic centre was generated at the terminus of a thienyl group on the 3*H*-naphtho[2,1-*b*]pyran **1** and through variation of pH and irradiation switching between one colourless and three coloured states was accomplished. We now report our full observations [11] on the 2*H*-naphtho[1,2-*b*]pyran system, wherein the cationic centre is generated at C-5 adjacent to the naphthalene unit in close proximity to the photomerocyanine moiety Scheme 1.

2. Experimental

2.1. Equipment

Unless otherwise stated, reagents were used as supplied. NMR spectra were recorded on a Bruker Avance 400 MHz instrument (^{1}H NMR 400 MHz, ^{13}C NMR 100 MHz) for sample solutions in $CDCl_3$ with tetramethylsilane as an internal reference. FT-IR spectra were recorded on a Perkin Elmer Spectrum One spectrophotometer system equipped with a golden gate ATR attachment (neat sample). UV–visible spectra were recorded for spectroscopic grade CH_2Cl_2 solutions of the samples (4 min activation with UV irradiation, 10 mm pathlength quartz fluorescence cuvette, PTFE capped, *ca.* 1×10^{-4}–10^{-6} mol dm^{-3}) using a Cary 50 Probe spectrophotometer equipped with a single cell Peltier temperature controlled (20 °C) stirred cell attachment with activating irradiation provided by an Oriel 150 Watt xenon arc lamp source (Newport 66906), xenon ozone free arc lamp (Newport 6255), distilled water liquid filter (Newport 6177), multiple filter holder (Newport 62020), UG11 filter (Newport FSO-UG11), fibre optic coupler (Newport 77799) and liquid light guide (Newport 77557). All compounds with the exception of **4c** were homogeneous by TLC (Merck TLC Aluminium sheets, silica gel 60 F_{254}) using a range of eluent systems of differing polarity. Mass spectra were recorded at the National EPSRC Mass Spectrometry Service Centre, Swansea. Ethyl 9-methoxy-2,

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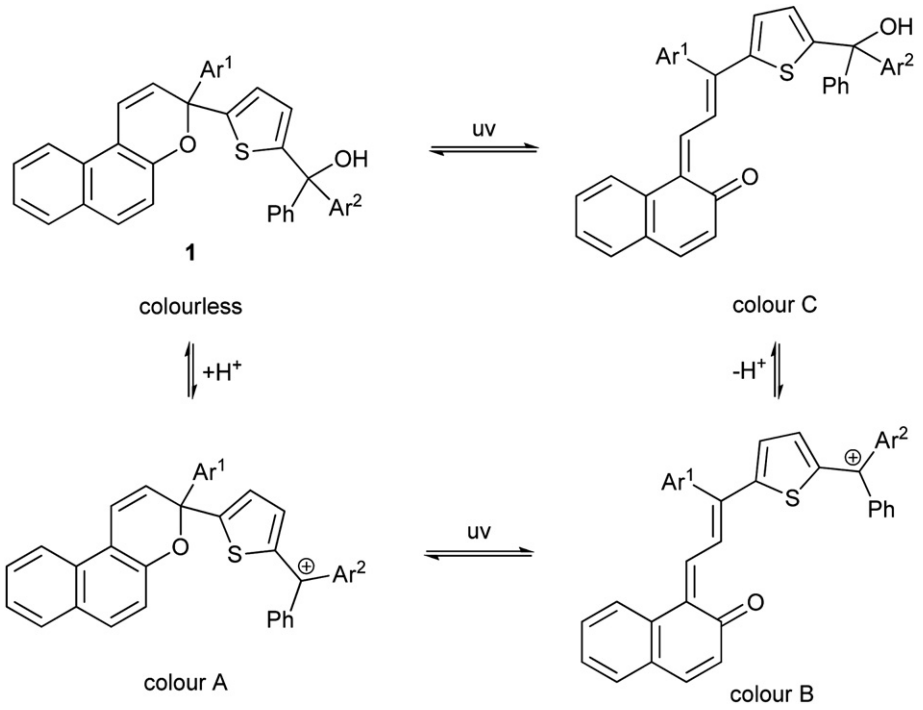


Scheme 1. Colour modulation of naphthopyran **1** through changes in pH and irradiation.

2-bis(4-methoxyphenyl)-2*H*-naphtho[1,2-*b*]pyran-5-carboxylate **2a** was obtained according to the literature procedure in 72% yield and was identical in all respects to authentic material [12]; λ_{max} after irradiation = 514, 432 nm (CH_2Cl_2), δ_H ($CDCl_3$) 1.42 (3H, t, J = 7.1 Hz, $CH_2\underline{CH_3}$), 3.76 (6H, s, OMe), 3.94 (3H, s, 9-OMe), 4.38 (2H, q, J = 7.1 Hz, $\underline{CH_2}CH_3$), 6.15 (1H, d, J = 10.0 Hz, 3-H), 6.81 (4H, m, Ar–H), 7.14 (1H, dd, J = 8.9, 2.6 Hz, 8-H), 7.41 (4H, m, Ar–H), 7.56 (1H, d, J = 2.6 Hz, 10-H), 7.67 (1H, d, J = 8.9 Hz, 7-H), 7.69 (1H, d, J = 10.0 Hz, 4-H), 8.02 (1H, s, 6-H); δ_H (CD_3CO_2D) 1.26 (3H, t, J = 7.1 Hz, $CH_2\underline{CH_3}$), 3.59 (6H, s, OMe), 3.80 (3H, s, 9-OMe), 4.24 (2H, q, J = 7.1 Hz, $\underline{CH_2}CH_3$), 6.13 (1H, d, J = 10.0 Hz, 3-H), 6.71 (4H, m, Ar–H), 7.01 (1H, dd, J = 8.9, 2.6 Hz, 8-H), 7.31 (4H, m, Ar–H), 7.51 (1H, d, J = 2.6 Hz, 10-H), 7.52 (1H, d, J = 10.0 Hz, 4-H), 7.59 (1H, d, J = 8.9 Hz, 7-H), 7.90 (1H, s, 6-H).

2.2. Preparation of ethyl 2,2-bis(4-dimethylaminophenyl)-9-methoxy-2H-naphtho[1,2-b]pyran-5-carboxylate **2b**

A suspension of ethyl 4-hydroxy-6-methoxynaphthalene-2-carboxylate 3.0 g (12.2 mmol), 1,1-bis(4-dimethylaminophenyl) prop-2-yn-1-ol 3.60 g (12.2 mmol) and Sasol Pural MG-30 (magnesium aluminium hydroxy carbonate, 30% Mg content on silica) (10 g) in toluene (120 mL) were heated under reflux until TLC examination of the mixture indicated that no propynol remained. The cooled solution was filtered and the spent MG-30 catalyst was washed with toluene (2 × 30 mL). Removal of the combined toluene washings and reaction solvent gave a dark brown gum that was eluted from silica with 2% ethyl acetate in toluene to afford the title compound **2b** as colourless microcrystals (3.85 g), 60.5%, mp = 185–186 °C, ν_{max} 1694.1, 1607.0, 1513.1, 1435.8, 1350.4, 1287.8, 1194.6, 1167.2, 997.0, 809.9 cm^{-1}, λ_{max} after irradiation = 614, 472 nm (CH_2Cl_2), δ_H 1.41 (3H, t, J = 7.1 Hz, $CH_2\underline{CH_3}$), 2.90 (12H, s, NMe_2), 3.93 (3H, s, OMe), 4.37 (2H, q, J = 7.1 Hz, $\underline{CH_2}CH_3$), 6.15 (1H, d, J = 10.1 Hz, 3-H), 6.34 (4H, m, Ar–H), 7.09 (1H, dd, J = 8.9, 2.5 Hz, 8-H), 7.34 (4H, m, Ar–H), 7.58 (1H, d, J = 2.5 Hz, 10-H), 7.62 (1H, d, J = 10.1 Hz, 4-H), 7.66 (1H, d, J = 8.9 Hz, 7-H), 7.98 (1H, s, 6-H), δ_C 14.68, 40.74, 55.81, 61.02, 63.76, 82.83, 100.91, 112.08, 115.85, 119.73, 121.51, 122.61, 124.47, 128.33, 128.52, 129.39, 130.70, 133.44, 148.17, 149.99, 159.58, 167.56. Found $[M + H]^+$ = 523.2591, $C_{33}H_{34}N_2O_4$ requires $[M + H]^+$ = 523.2587.

2.3. Preparation of ethyl 2-(4-dimethylaminophenyl)-9-methoxy-2-(4-methoxyphenyl)-2H-naphtho[1,2-b]pyran-5-carboxylate **2c**

A suspension of ethyl 4-hydroxy-6-methoxynaphthalene-2-carboxylate 3.0 g (12.2 mmol), 1-(4-dimethylaminophenyl)-1-(4-methoxyphenyl)prop-2-yn-1-ol 3.42 g (12.2 mmol) and acidic alumina (6 g) in toluene (120 mL) were heated under reflux until TLC examination of the mixture indicated that no propynol remained. The cooled solution was filtered and the spent acidic alumina catalyst was washed with toluene (2 × 30 mL). Removal of the combined toluene washings and reaction solvent gave a purple gum that was eluted from silica with 5% ethyl acetate in toluene to afford the title compound as a pale blue microcrystalline solid (4.72 g) 76%, mp = 140–142 °C, ν_{max} 1696.0, 1607.4, 1508.4, 1287.1, 1209.6, 1190.7, 1172.7, 1032.0, 995.4, 812.9 cm^{-1}, λ_{max} after irradiation 570, 476 (sh) nm (CH_2Cl_2), δ_H 1.42 (3H, t, J = 7.1 Hz, $CH_2\underline{CH_3}$), 2.91 (6H, s, NMe_2), 3.76 (3H, s, OMe), 3.94 (3H, s, OMe), 4.80 (2H, q, J = 7.1 Hz, $\underline{CH_2}CH_3$), 6.15 (1H, d, J = 10.1 Hz, 3-H), 6.63 (2H, m, Ar–H), 6.82 (2H, m, Ar–H), 7.10 (1H, dd, J = 8.9, 2.5 Hz, 8-H), 7.33 (2H, m, Ar–H), 7.42 (2H, m, Ar–H), 7.57 (1H, d, J = 2.5 Hz, 10-H), 7.64 (1H, d, J = 10.1 Hz, 4-H), 7.67 (1H, d, J = 8.9 Hz, 7-H), 8.00 (1H, s, 6-H); δ_C 14.59, 40.60, 55.39, 55.72, 60.97, 82.52, 100.78, 111.98, 113.52, 115.76, 119.70, 121.81, 122.48, 124.58, 128.24, 128.39, 128.48, 128.94, 130.67, 132.90, 137.78, 147.90, 149.99, 158.97, 159.57, 167.40. Found $[M + H]^+$ = 510.2264 $C_{32}H_{31}NO_5$ requires $[M + H]^+$ = 510.2275.

2.4. General method for the preparation of the 5-[1,1-bis (4-methoxyphenyl)-1-hydroxymethyl] substituted naphthopyrans

n-Butyllithium 10.1 mL (16.1 mmol, 1.6 M in hexanes) was added via syringe to a cold (~ −70 °C) stirred solution of 4-bromoanisole

3.01 g (16.1 mmol) in anhydrous THF (60 mL) under nitrogen. After 2 h the naphthopyran (4 mmol) was added in a single portion and the solution was allowed to stir and warm to rt overnight. The reaction mixture was quenched with water (30 mL) and the layers separated. The aqueous phase was extracted with EtOAc (2 × 30 mL) and the combined organic layers were washed with water (50 mL), dried (anhyd. Na_2SO_4) and evaporated to afford the crude product as an off-white powder which was purified by column chromatography. The following compounds were obtained in this manner.

2.4.1. 9-Methoxy-5-[1,1-bis(4-methoxyphenyl)-1-hydroxymethyl]-2,2-bis(4-methoxyphenyl)-2H-naphtho[1,2-b]pyran **3a**

9-Methoxy-5-[1,1-bis(4-methoxyphenyl)-1-hydroxymethyl]-2,2-bis(4-methoxyphenyl)-2*H*-naphtho[1,2-*b*]pyran **3a** as colourless microcrystals (2.13 g) 79% after elution from silica with 40% EtOAc in hexane and recrystallisation from acetone and methanol, mp = 181–182 °C, ν_{max} 3446.8, 1607.1, 1504.9, 1297.7, 1246.7, 1171.9, 1032.3, 944.4, 824.9, 585.9 cm^{-1}, λ_{max} after irradiation = 514, 429 nm (CH_2Cl_2) then upon addition of acid λ_{max} = 498 nm, $\varepsilon_{max} = 7.87 \times 10^4$ mol^{-1} dm^3 cm^{-1}, λ_{max} = 648 nm, $\varepsilon_{max} = 1.26 \times 10^4$ mol^{-1} dm^3 cm^{-1} (CH_2Cl_2 + 2 μL $MeSO_3H$), δ_H 2.96 (1H, s, OH), 3.76 (6H, s, OMe), 3.82 (6H, s, OMe), 3.92 (3H, s, OMe), 5.78 (1H, d, J = 10.1 Hz, 3-H), 6.68 (1H, s, 6-H), 6.82 (8H, m, Ar–H), 6.89 (1H, d, J = 10.1 Hz, 4-H), 7.03 (1H, dd, J = 9.2, 2.4 Hz, 8-H), 7.14 (4H, m, Ar–H), 7.32 (4H, m, Ar–H), 7.39 (1H, d, J = 9.2 Hz, 7-H), 7.56 (1H, d, J = 2.4 Hz, 10-H), δ_C 55.47, 55.51, 55.76, 81.80, 82.36, 100.86, 113.44, 113.55, 116.52, 119.02, 121.86, 124.10, 126.20, 126.84, 128.28, 128.57, 129.24, 130.04, 137.53, 138.29, 139.52, 148.58, 158.35, 158.80, 159.07. Found $[M + Na]^+ = 689.2503C_{43}H_{38}O_7$ requires $[M + Na]^+ = 689.2510$.

2.4.2. 2,2-Bis(4-dimethylaminophenyl)-9-methoxy-5-[1,1-bis(4-methoxyphenyl)-1-hydroxymethyl]-2H-naphtho[1,2-b]pyran **3b**

2,2-Bis(4-dimethylaminophenyl)-9-methoxy-5-[1,1-bis(4-methoxyphenyl)-1-hydroxymethyl]-2*H*-naphtho[1,2-*b*]pyran **3b** as pale green microcrystals (1.64 g), 59% after elution from silica with 10% ethyl acetate in toluene and recrystallisation from CH_2Cl_2 and hexane, mp = 136–138 °C, ν_{max} 3489.9, 1604.5, 1506.4, 1348.7, 1245.0, 1169.4, 1030.9, 996.5, 816.2, 547.2 cm^{-1}, λ_{max} after irradiation = 615, 495 nm (CH_2Cl_2) then upon addition of acid λ_{max} = 476 nm, $\varepsilon_{max} = 5.11 \times 10^4$ mol^{-1} dm^3 cm^{-1}, λ_{max} = 568 nm, $\varepsilon_{max} = 1.72 \times 10^4$ mol^{-1} dm^3 cm^{-1} (CH_2Cl_2 + 2 μL $MeSO_3H$), δ_H 2.96 (6H, s, NMe_2), 2.99 (6H, s, NMe_2), 3.77 (3H, s, OMe), 3.78 (3H, s, OMe), 3.92 (3H, s, OMe), 5.69 (1H, s, OH), 5.87 (1H, d, J = 10.1 Hz, 3-H), 6.12 (1H, d, J = 10.1 Hz, 4-H), 6.63 (2H, m, Ar–H), 6.74 (2H, m, Ar–H), 6.81 (4H, m, Ar–H), 7.09 (1H, dd, J = 8.9, 2.5 Hz, 8-H), 7.10 (1H, s, 6-H), 7.23 (2H, m, Ar–H), 7.29 (2H, m, Ar–H), 7.37 (4H, m, Ar–H), 7.44 (1H, d, J = 2.5 Hz, 10-H), 7.63 (1H, d, J = 8.9 Hz, 7-H), δ_C 40.44, 55.23, 55.26, 55.37, 77.53, 91.80, 99.87, 111.86, 112.08, 113.14, 113.26, 114.26, 119.00, 121.36, 123.02, 125.09, 128.81, 129.15, 129.23, 129.41, 130.46, 131.17, 136.21, 138.27, 143.15, 144.76, 149.02, 157.25, 158.71, 158.87. Found $[M + H]^+ = 693.3320C_{45}H_{44}N_2O_5$ requires $[M + H]^+ = 693.3323$.

2.4.3. 2-(4-Dimethylaminophenyl)-9-methoxy-2-(4-methoxyphenyl)-5-[1,1-bis(4-methoxyphenyl)-1-hydroxymethyl]-2H-naphtho[1,2-b]pyran **3c**

2-(4-Dimethylaminophenyl)-9-methoxy-2-(4-methoxyphenyl)-5-[1,1-bis(4-methoxyphenyl)-1-hydroxymethyl]-2*H*-naphtho[1,2-*b*]pyran **3c** as colourless microcrystals (1.82 g) 67% after elution from silica with 25% EtOAc in hexane and recrystallisation from Et_2O and hexane, m.p. 189–190 °C, ν_{max} 3517.5, 1607.2, 1506.1, 1243.8, 1173.1, 1019.7, 823.8 cm^{-1}, λ_{max} = after 30 s of irradiation 547, 462(sh) nm (CH_2Cl_2) then upon addition of acid λ_{max} = 478 nm, $\varepsilon_{max} = 6.30 \times 10^4$ mol^{-1} dm^3 cm^{-1} λ_{max} = 582 nm, $\varepsilon_{max} = 1.90 \times 10^4$ mol^{-1} dm^3 cm^{-1} (CH_2Cl_2 + 2 μL $MeSO_3H$), δ_H 2.90, (1H, s, OH), 2.92 (6H, s, NMe_2), 3.76 (3H, s, OMe), 3.82 (6H, s, OMe), 3.92 (3H, s, OMe), 5.78 (1H, d, J = 10.0 Hz, 3-H), 6.62 (2H, m, Ar–H), 6.67 (1H, s, 6-H), 6.82 (7H, m, Ar–H, 4-H), 7.01 (1H, dd, J = 8.9, 2.4 Hz, 8-H), 7.13 (4H, m, Ar–H), 7.27 (2H, m, Ar–H),7.34 (2H, m, Ar–H), 7.36 (1H, d, J = 8.9 Hz, 7-H), 7.57 (1H, d, J = 2.4 Hz, 10-H), δ_C 40.35, 40.47, 55.25, 55.30, 55.37, 55.52, 81.77, 82.11, 91.84, 99.79, 100.64, 111.74, 113.16, 113.27, 113.57, 113.91, 114.37, 116.22, 118.74, 119.07, 121.46, 122.85, 123.47, 125.08, 126.01, 126.99, 128.01, 128.09, 128.33, 128.72, 128.99, 129.24, 129.44, 129.73, 130.47, 131.07, 131.36, 135.95, 138.03, 138.12, 139.35, 143.14, 144.67, 148.53, 149.72, 150.60, 157.30, 158.03, 158.51, 158.69, 158.90, 159.46. Found $[M + H]^+ = 680.3002C_{44}H_{41}NO_6$ requires $[M + H]^+ = 680.3007$.

2.5. General method for the intramolecular capture of the merocyanine form of a naphthopyran

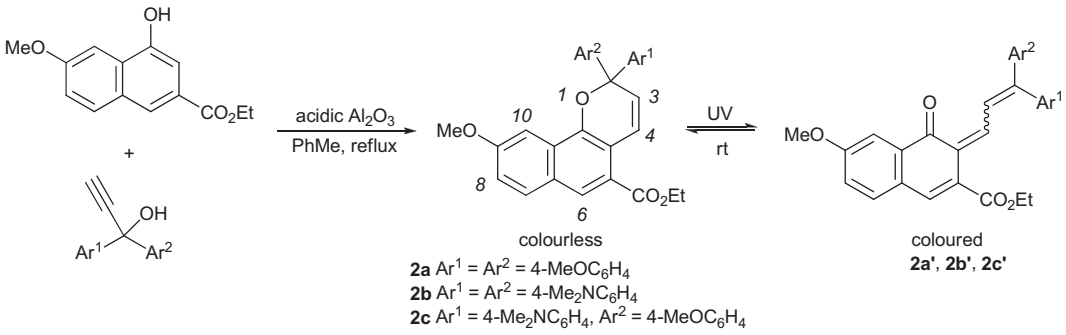
A solution of the 5-[1,1-bis(4-methoxyphenyl)-1-hydroxymethyl]-2*H*-naphtho[1,2-*b*]pyran (0.75 mmol) in toluene (30 mL) containing a catalytic amount of 4-TsOH 20 mg (0.1 mmol) was heated until TLC examination of the reaction mixture indicated that no naphthopyran remained (see individual examples for temperature and time). The cooled solution was diluted with EtOAc (20 mL) and the mixture washed with water (2 × 30 mL). Removal of the dried (Na_2SO_4) solvent gave a deep purple solid that was eluted from silica. The following compounds were obtained in this fashion.

2.5.1. 3,7-Dimethoxy-11,11,12-tris(4-methoxyphenyl)-11H-benzo[5,6]pentaleno[1,2-b]naphthalene-5-one **4a**

3,7-Dimethoxy-11,11,12-tris(4-methoxyphenyl)-11*H*-benzo[5,6]pentaleno[1,2-*b*]naphthalene-5-one **4a** from heating **3a** at 60 °C for 20 h, as deep purple microcrystals 0.37 g (76%) after elution from silica with 5% ethyl acetate in toluene and recrystallisation from acetone and methanol, mp = 252–255 °C, ν_{max} 3002.7, 2949.2, 2831.4, 1583.4, 1505.3, 1491.4, 1244.1, 1222.9, 1175.1, 1030.5, 824.8, 787.2, 551.9 cm^{-1}, λ_{max} = 586 nm, $\varepsilon_{max} = 1.06 \times 10^4$ mol^{-1} dm^3 cm^{-1}, λ_{max} = 376 nm, $\varepsilon_{max} = 1.59 \times 10^4$ mol^{-1} dm^3 cm^{-1} (CH_2Cl_2), δ_H 3.75 (6H, s, OMe), 3.78 (3H, s, OMe), 3.92 (3H, s, OMe), 3.95 (3H, s, OMe), 6.42 (1H, s, 10-H), 6.71 (6H, m, Ar–H), 6.75 (1H, dd, J = 8.2, 2.6 Hz, 2-H), 6.95 (3H, m, Ar–H), 7.11 (1H, d, J = 8.4, 2.8 Hz, 8-H), 7.19 (5H, m, Ar–H), 7.80 (1H, d, J = 2.8 Hz, 6-H), 8.51 (1H, d, J = 2.6 Hz, 4-H), δ_C 55.66, 56.13, 56.35, 58.66, 110.15, 113.72, 113.94, 115.54, 116.33, 120.66, 122.28, 122.80, 126.58, 130.17, 130.21, 130.56, 131.93, 131.99, 132.16, 133.21, 136.52, 140.85, 144.10, 150.53, 156.95, 158.65, 159.50, 159.91, 160.34, 160.46, 184.16. Found $[M + H]^+ = 647.2419C_{43}H_{34}O_6$ requires $[M + H]^+ = 647.2428$.

2.5.2. 3-Dimethylamino-12-(4-dimethylaminophenyl)-7-methoxy-11,11-bis(4-methoxyphenyl)-11H-benzo[5,6]pentaleno[1,2-b]naphthalene-5-one **4b**

3-Dimethylamino-12-(4-dimethylaminophenyl)-7-methoxy-11,11-bis(4-methoxyphenyl)-11*H*-benzo[5,6]pentaleno[1,2-*b*]naphthalene-5-one **4b**, from heating **3b** at 100 °C for 48 h, as deep purple microcrystals 0.29 g (58%) after elution from silica with 10% ethyl acetate, 10% hexane in toluene and recrystallisation from acetone and methanol, mp = 266–269 °C, ν_{max} 2901.7, 2833.8, 1600.2, 1586.6, 1504.9, 1489.4, 1243.8, 1430.8, 1284.1, 1243.8, 1178.1, 1033.1, 832.9, 817.1, 801.2 cm^{-1}, λ_{max} = 545 nm, $\varepsilon_{max} = 1.61 \times 10^4$ mol^{-1} dm^3 cm^{-1}, λ_{max} = 370 nm, $\varepsilon_{max} = 1.04 \times 10^4$ mol^{-1} dm^3 cm^{-1} (CH_2Cl_2), δ_H 2.95 (6H, s, NMe_2), 3.12 (6H, s, NMe_2), 3.75 (6H, s, OMe), 3.92 (3H, s, OMe), 6.41 (1H, s, 10-H), 6.45 (1H, dd, J = 8.5, 2.5 Hz, 2-H), 6.49 (2H, m, Ar–H), 6.70 (4H, m, Ar–H), 7.01 (2H, m, Ar–H), 7.05 (1H, d, J = 8.5 Hz, 1-H), 7.08 (1H, dd, J = 8.5, 2.5 Hz, 8-H), 7.21 (1H, d, J = 8.5 Hz, 9-H), 7.25 (4H, m, Ar–H), 7.82 (1H, d, J = 2.5 Hz, 6-H), 8.53 (1H, d, J = 2.5 Hz, 4-H), δ_C 40.24, 41.01, 55.21, 55.69, 58.44, 109.32, 111.42, 111.61, 113.17, 115.28, 118.64, 121.59, 121.99, 123.19,



Scheme 2. Preparation and Photochromic Response of naphthopyrans **2**.

129.54, 129.79, 129.88, 130.11, 131.92, 132.38, 132.97, 136.52, 138.16, 143.33, 147.46, 150.23, 150.81, 157.49, 158.04, 158.69, 162.82, 183.11. Found $[M + H]^+ = 673.3054 C_{45}H_{40}N_2O_4$ requires $[M + H]^+ = 673.3061$.

2.5.3. 3-Dimethylamino-7-methoxy-11,11,12-tris(4-methoxyphenyl)-11H-benzo[5,6]pentaleno[1,2-b]naphthalene-5-one ***4c***

Elution from silica with 5% EtOAc in PhMe of the crude reaction mixture from 5-[1,1-bis(4-methoxyphenyl)-1-hydroxymethyl]-2*H*-naphtho[1,2-*b*]pyran **3c** after heating at 60 °C for 30 h, gave two fractions: Fraction 1, 3-dimethylamino-7-methoxy-11,11,12-tris (4-methoxyphenyl)-11*H*-benzo[5,6]pentaleno[1,2-*b*]naphthalene-5-one **4c** as a deep purple powder 150 mg (30%)[1] after recrystallisation from acetone and methanol, ν_{max} 2933.9, 2832.5, 1599.5, 1573.6, 1504.5, 1488.5, 1433.1, 1286.8, 1242.7, 1172.9, 1087.1, 1027.2, 805.3, 789.2, 643.9, 628.8, 523.2 cm^{-1}, green solution, $\lambda_{max} = 390$ nm, $\varepsilon_{max} = 1.2 \times 10^4$ mol^{-1} dm^3 cm^{-1}, $\lambda_{max} = 426$ nm, $\varepsilon_{max} = 9.3 \times 10^3$ mol^{-1} dm^3 cm^{-1} and $\lambda_{max} = 571$ nm, $\varepsilon_{max} = 7.8 \times 10^3$ mol^{-1} dm^3 cm^{-1} (CH_2Cl_2), δ_H 3.14 (6H, s, NMe_2), 3.78 (6H, s, OMe), 3.81 (3H, s, OMe), 3.95 (3H, s, OMe), 6.44 (1H, s, 10-H), 6.48 (1H, dd, J = 8.3, 2.3, Hz, 2-H), 6.72 (5H, m, Ar–H), 6.95 (1H, d, J = 8.3 Hz, 1-H), 6.99 (2H, m, Ar–H), 7.12 (1H, dd, J = 8.5, 2.7 Hz, 8-H) 7.24 (6H, m, Ar–H), 7.84 (1H, d, J = 2.7 Hz, 6-H), 8.53 (1H, d, J = 2.3 Hz, 4-H), δ_C 41.41, 55.62, 56.10, 58.62, 109.91, 112.23, 113.61, 113.80, 115.81, 119.70, 122.10, 123.18, 126.94, 130.05, 130.53, 131.03, 132.23, 133.27, 136.76, 138.79, 142.51, 149.02, 151.22, 157.38, 158.52, 159.25, 159.80, 183.78; and Fraction 2, 12-(4-dimethylaminophenyl)-3,7-dimethoxy-11,11,bis(4-methoxyphenyl)-11*H*-benzo[5,6]pentaleno [1,2-*b*]naphthalene-5-one **4d** as deep purple microcrystals 100 mg (20%) after recrystallisation from acetone and methanol, mp = 278–280 °C, ν_{max} 3003.6, 2931.9, 2833.5, 1582.8, 1554.9, 1505.0, 1490.5, 1427.1, 1243.6, 1175.7, 1025.7, 815.8, 524.3 cm^{-1}, blue solution, $\lambda_{max} = 369$ nm, $\varepsilon_{max} = 1.0 \times 10^4$ mol^{-1} dm^3 cm^{-1} and $\lambda_{max} = 642$ nm (broad with shoulder at 499 nm), $\varepsilon_{max} = 1.2 \times 10^4$ mol^{-1} dm^3 cm^{-1} (CH_2Cl_2), δ_H 2.95 (6H, s, NMe_2), 3.75 (6H, s, OMe), 3.92 (3H, s, OMe), 3.95 (3H, s, OMe), 6.41 (1H, s, 10-H), 6.50 (2H, m, Ar–H), 6.71 (4H, m, Ar–H), 6.76 (1H, dd, J = 8.2, 2.6 Hz, 2-H), 6.99 (2H, m, Ar–H), 7.09 (1H, dd, J = 8.4, 2.8, Hz, 8-H), 7.10 (1H, d, J = 8.2 Hz, 1-H), 7.20 (1H, d, J = 8.4 Hz, 9-H), 7.24 (4H, m, Ar–H), 7.80 (1H, d, J = 2.8 Hz, 6-H), 8.53 (1H, d, J = 2.6 Hz, 4-H), δ_C 40.25, 55.24, 55.71, 55.93, 58.46, 109.55, 111.51, 113.27, 114.92, 115.68, 119.60, 121.77, 122.76, 126.11, 129.69, 129.86, 130.09, 130.67, 131.83, 132.13, 132.90, 136.29, 141.60, 143.49, 148.86, 150.20, 150.29, 157.03, 158.16, 158.93, 159.90, 183.53. Found $[M + H]^+ = 660.2740 C_{44}H_{37}NO_5$ requires $[M + H]^+ = 660.2744$.

3. Discussion

Alkyl 2,2-diaryl-2*H*-naphtho[1,2-*b*]pyran-5-carboxylates **2a**–**c** were readily prepared in good yield using the established acid-catalysed route from a 1,1-diarylprop-2-yn-1-ol and an alkyl 4-hydroxynaphthalene-2-carboxylate (Scheme 2) [12,13]. The ^1H NMR spectra of **2a**–**c** were characterised by a doublet at *ca.* δ 6.1 with 10 Hz coupling which is assigned to 3-H and which is coupled to 4-H (*ca.* δ 7.6). A low field singlet was also noted at *ca.* δ 8.0 (6-H) due to the *peri* disposition of this proton and the adjacent electron withdrawing ester function.

The photochromic response of these naphthopyrans **2** in CH_2Cl_2 solution upon UV irradiation (4 min) to a steady state was characterised by the generation of two overlapping absorption bands which were typical for the generation of photomerocyanines **2′**. The long wavelength absorption maxima followed the expected trend in accord with terminal aryl ring donor strength [7] with that of **2b** appearing at 614 nm ($Ar^1 = Ar^2 = 4\text{-}Me_2NC_6H_4$), **2c** at 570 nm ($Ar^1 = 4\text{-}Me_2NC_6H_4$, $Ar^2 = 4\text{-}MeOC_6H_4$) and **2a** at 514 nm associated with the least electron donating aryl group ($Ar^1 = Ar^2 = 4\text{-}MeOC_6H_4$) (Fig. 1). The persistence of the photomerocyanine was also in agreement with the increasing electron donating character of the *geminal* aryl unit with the photomerocyanine derived from **2b** fading most rapidly and that derived from **2a** relatively slowly; **2c** exhibited an intermediate lifetime.

The addition of an excess of 4-methoxyphenyllithium to **2a**–**c** at low temperature gave the diarylmethanols **3a**–**c** in good yield (59–79%) (Scheme 3). The ^1H NMR spectra of these compounds displayed a readily identifiable doublet at δ 5.8 (J = 10 Hz) for the

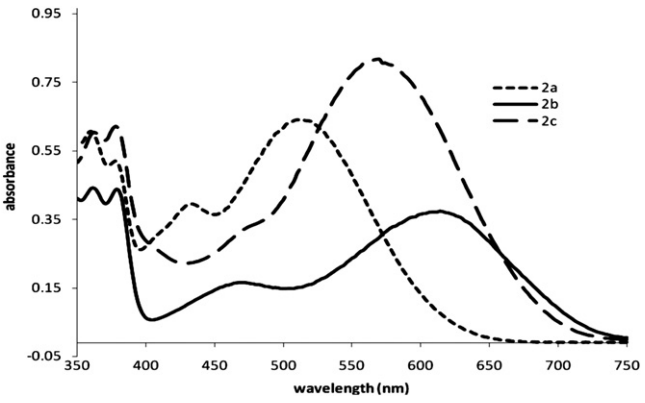


Fig. 1. Absorption spectra for irradiated naphthopyrans **2a**–**c**.

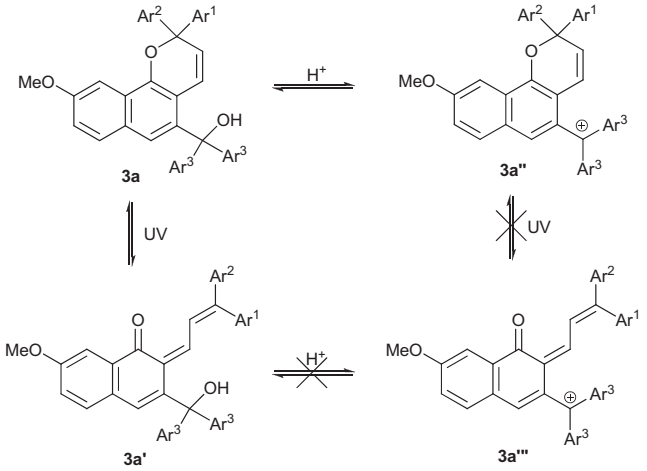
[1] It was not possible to isolate analytically pure material by column chromatography due to the poor resolution between **4c** and **4d** in a variety of solvent systems. The sample of **4c** isolated contains ~3% of the isomer **4d** by ^1H NMR spectroscopy. All spectroscopic analyses were undertaken on the mixture.

pyran ring proton, 3-H [7]. 6-H now resonates much further upfield in the range δ 6.6–7.1 relative to that of 6-H ($\sim\delta$ 8.0) in **2** as a consequence of conversion of the ester function into a diarylmethanol unit. The presence of the hydroxyl unit was confirmed by IR spectroscopy which displayed a broad stretching band at *ca.* 3480 cm^{-1}. The successful addition of 4-methoxyphenyllithium to **2a**–**c** was further confirmed by the absence of an ester CO signal in the ^{13}C NMR spectra of **3a**–**c** which appeared at $\sim\delta$ 167 in the precursors.

The electrocyclic ring-opening of the diarylmethanol substituted naphthopyran **3a** to afford merocyanine **3a′** (Scheme 4) in CH_2Cl_2 solution (*ca.* 1×10^{-5} mol dm^{-3}) through irradiation with ultraviolet light (275–375 nm) for 4 min resulted in the generation of a red solution with λ_{max} 514 nm which faded gradually to colourless upon cessation of irradiation (Fig. 2). Treatment of the colourless solution of **3a** in CH_2Cl_2 with $MeSO_3H$ (98%, 2 μL injected directly into 10 mm pathlength cuvette) resulted in the development of an intense violet colour derived from the cationic dye **3a″** which displayed two new bands in the absorption spectrum that could only be measured after dilution to *ca.* 1×10^{-6} mol dm^{-3}. These new bands had λ_{max} = 498 nm, $\varepsilon_{max} = 7.87 \times 10^4$ mol^{-1} dm^3 cm^{-1} and λ_{max} = 648 nm, $\varepsilon_{max} = 1.26 \times 10^4$ mol^{-1} dm^3 cm^{-1} and may be considered typical for unsymmetrically substituted triarylmethine cationic dyes [10,14]. In marked contrast to the behaviour of **1**, UV irradiation of this acidified solution of **3a** resulted in no appreciable change in the absorption spectrum (Fig. 2).

In comparison with the thienyl substituted naphthopyran **1** where different shades could be reversibly generated by either irradiation or treatment with acid or a combination of both stimuli [10] the present compound **3a** is insensitive to irradiation after protonation. This behaviour suggests that the absorption spectrum results from either a combination of pyran ring-opening and cation generation upon protonation to afford **3a‴** or that once the cation **3a″** is formed its resonance stabilisation with disruption of the naphthalene π-electron density, inhibits the electrocyclic ring-opening of the pyran unit which would also lead to **3a‴** (Scheme 4).

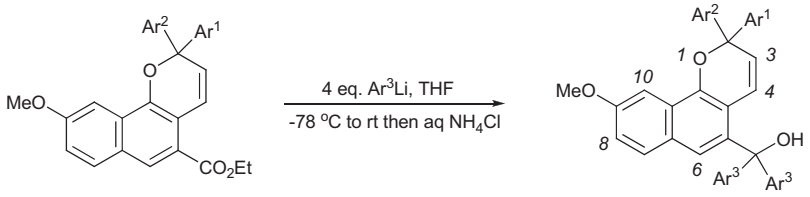
In order to establish which of the foregoing phenomena may operate, the ^1H NMR spectra of **2a** and **3a** in CD_3CO_2D solution were examined. The ^1H NMR spectrum of a colourless solution of **2a** in CD_3CO_2D was remarkably similar to the spectrum recorded in $CDCl_3$ with only minor solvent induced shifts noted. No low field doublets associated with a merocyanine unit and exhibiting *trans*-coupling [15] which could be attributed to the acid-induced ring-opening of the pyran ring were apparent. The ^1H NMR spectrum of **3a** in CD_3CO_2D (deep purple solution) was more complex and indicated a mixture of two pyran containing species in an approximate 2:1 ratio after standing for 10 h at room temperature with signals at δ 5.68 (J = 9.9 Hz) and δ 5.71 (J = 10.1 Hz), each of which is indicative of 3-H in a pyran ring [7,15]. It is likely that these signals are due to 3-H in **3a** and 3-H in the cationic species **3a″**



Scheme 4. Proposed relationship between merocyanine and cationic species derived from **3a**.

(Scheme 4). The 2:1 ratio of **3a**:**3a″** was also reflected in the NMR signals assigned to the MeO groups in the δ 3.5–4.1 region. In $CDCl_3$ solution **3a** exhibits three signals accounting for two sets of equivalent MeO groups and the 9-MeO group. However, in CD_3CO_2D solution there are 6 signals, presumably the three original signals (shifted slightly due to the change in solvent) and three further signals associated with the MeO groups in **3a″**. The ^1H NMR spectrum of **3a** in $CDCl_3$ to which had been added 1 μL of $MeSO_3H$ was complex and further examination of the ^1H NMR spectra of this compound in a variety of media both with and without added acid is ongoing. Finally, the UV–visible absorption spectrum of an irradiated CH_2Cl_2 solution of **3a** was recorded after the addition of $MeSO_3H$ (98%, 2 μL). This spectrum was essentially identical to those obtained for the addition of acid and the addition of acid followed by irradiation further suggesting that species **3a‴** is not present under these conditions.

Ultra-violet irradiation of a solution (*ca.* 1×10^{-5} mol dm^{-3}) of **3b** led to the development of photomerocyanine **3b′** with a weak blue colour, λ_{max} 615 nm, which faded very rapidly, a feature that was not wholly unexpected since it has been established that a combination of strong electron donating groups at 2-C of a naphtho[1,2-*b*]pyran combined with a bulky substituent at the 5-position results in only transient photocolouration [7]. Subsequent treatment of this solution with 2 μL of $MeSO_3H$ similarly resulted in the generation of two new absorption bands with λ_{max} = 476 nm, $\varepsilon_{max} = 5.11 \times 10^4$ mol^{-1} dm^3 cm^{-1}, λ_{max} = 568 nm, $\varepsilon_{max} = 1.72 \times 10^4$ mol^{-1} dm^3 cm^{-1} (after dilution to *ca.* 1×10^{-6} mol dm^{-3}); further examination under UV irradiation resulted in no discernable photochromism (Fig. 3), a feature comparable with observations noted for **3a**.



2a $Ar^1 = Ar^2 = 4\text{-}MeOC_6H_4$
2b $Ar^1 = Ar^2 = 4\text{-}Me_2NC_6H_4$
2c $Ar^1 = 4\text{-}Me_2NC_6H_4$, $Ar^2 = 4\text{-}MeOC_6H_4$

3a $Ar^1 = Ar^2 = Ar^3 = 4\text{-}MeOC_6H_4$
3b $Ar^1 = Ar^2 = 4\text{-}Me_2NC_6H_4$, $Ar^3 = 4\text{-}MeOC_6H_4$
3c $Ar^1 = 4\text{-}Me_2NC_6H_4$, $Ar^2 = Ar^3 = 4\text{-}MeOC_6H_4$

Scheme 3. Preparation of Substituted Naphthopyrans **3**.

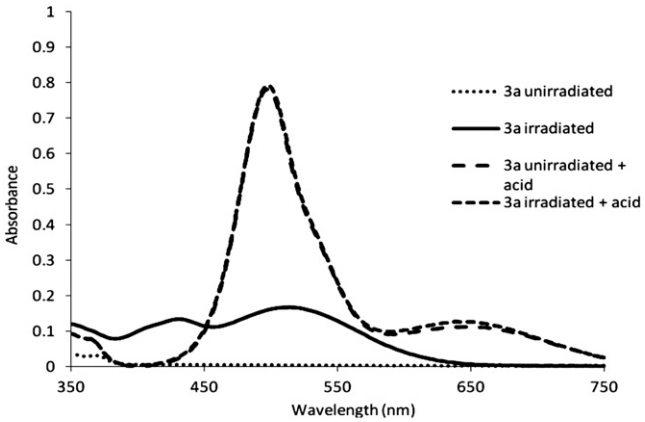


Fig. 2. Absorption spectra of **3a** before and after treatment with acid.

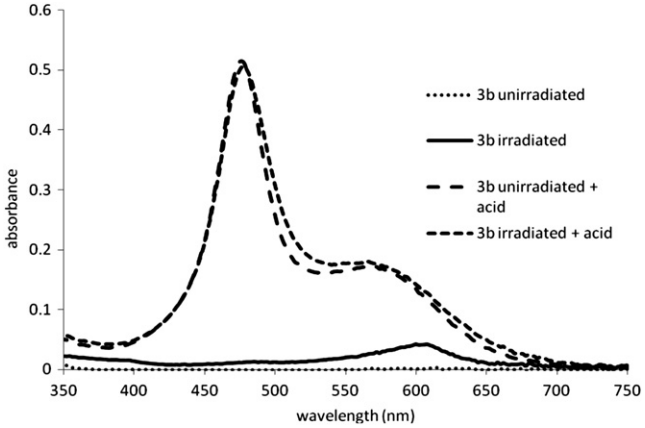


Fig. 3. Absorption spectra of **3b** before and after treatment with acid.

Finally, examination of the photochromic properties of a solution of **3c** (CH_2Cl_2, *ca.* 1×10^{-5} mol dm^{-3}) in a similar manner to that of **3a** and **b** resulted in a quite unusual observation. Irradiation of **3c** for the standard 4 min period resulted in no apparent photochromic response. Re-examination of a fresh sample of the stock solution with a simple TLC inspection lamp (Spectroline, 8 Watt, 365 nm) resulted in the instantaneous development of a red-violet shade attributed to the formation of photomerocyanine **3c**′. A solution of **3c** was next examined in the spectrophotometer under continuous irradiation using the 150 Watt xenon lamp irradiation system in which the irradiation beam is delivered perpendicularly to the recording beam. Spectra of **3c** were collected at regular intervals (10 s) over 4 min. From a selection of the spectra (Fig. 4) it is evident that **3c**′ is generated rapidly with a maximum absorption at 547 nm noted after *ca.* 30 s of irradiation. After this time continued irradiation presumably results in the degradation of the photomerocyanine with an attendant decrease in the 547 nm absorption and the shoulder at 462 nm ultimately resulting in a near colourless solution. The cause of this unexpected facile photodegradation of **3c** is presently under investigation. However, our preliminary observations upon repeating the irradiation sequence on a more concentrated solution of **3c** in $CDCl_3$ resulted in the formation of a complex (^{1}H NMR) reaction product.

For comparative purposes a solution of **3c** was also examined upon treatment with acid in an identical manner to that reported for **3a**, **b**. Protonation of **3c** afforded the predictable intense absorption bands with $\lambda_{max} = 478$ nm, $\varepsilon_{max} = 6.30 \times 10^4$ mol^{-1} dm^3 cm^{-1}, $\lambda_{max} = 582$ nm, $\varepsilon_{max} = 1.90 \times 10^4$ mol^{-1} dm^3 cm^{-1} (after dilution to *ca.* 1×10^{-6} mol dm^{-3}) (Fig. 5). Once again subsequent irradiation (8 Watt) of this acidified solution resulted in no discernible colour change.

We have recently communicated that on heating a toluene solutions of **3a** and **b** containing a catalytic amount of 4-TsOH, the initial colour gradually intensified and **3a** and **b** had been irreversibly converted into the intensely violet benzopentalenonaphthalenones **4a** and **b** respectively in good yield (Scheme 5); the pentacyclic structure **4a** was confirmed by X-ray crystallography [11].

It was of interest to explore the behaviour of the unsymmetrically substituted naphthopyran **3c** towards a similar acid-catalysed thermal rearrangement since the opportunity exists for the formation of a mixture of isomers. Thus heating **3c** with 4-TsOH in PhMe resulted in a complex reaction product from which two new isomeric benzopentalenonaphthalenones **4c** and **4d** were isolated by column chromatography. The structural characterisation of these two new isomers was accomplished by comparison of key signals in their ^{1}H NMR spectra with those of **4a** and **b**. In compound **4a** 2-H, *ortho* to a methoxy group resonates at δ 6.75 and

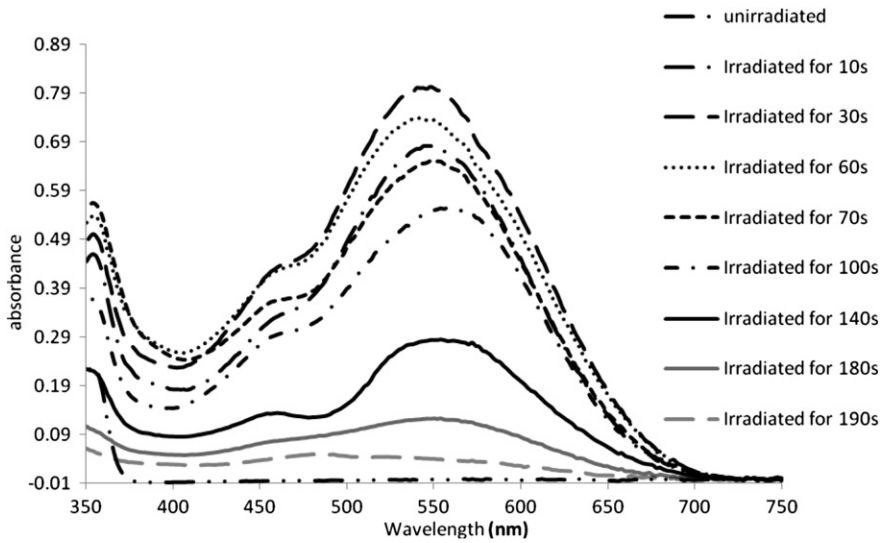


Fig. 4. Absorption spectra of **3c** during UV irradiation.

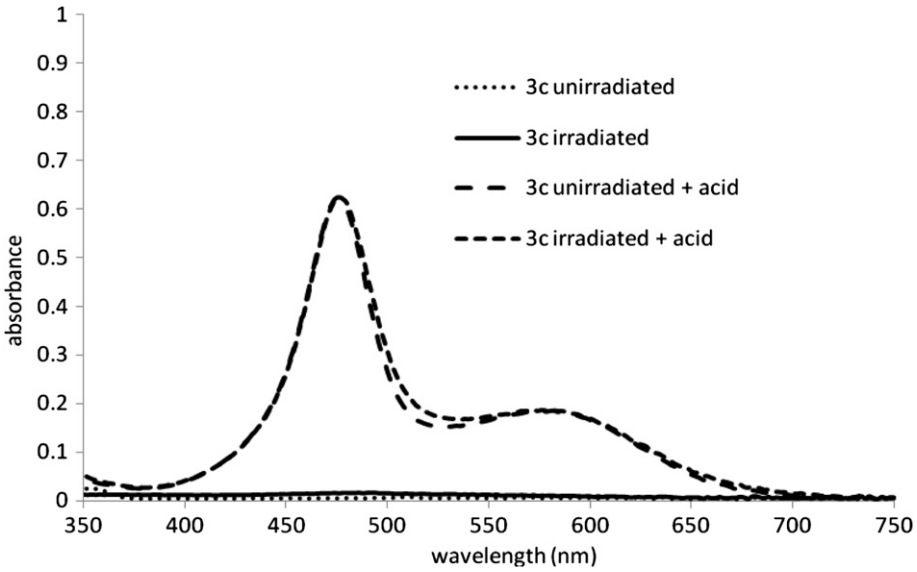
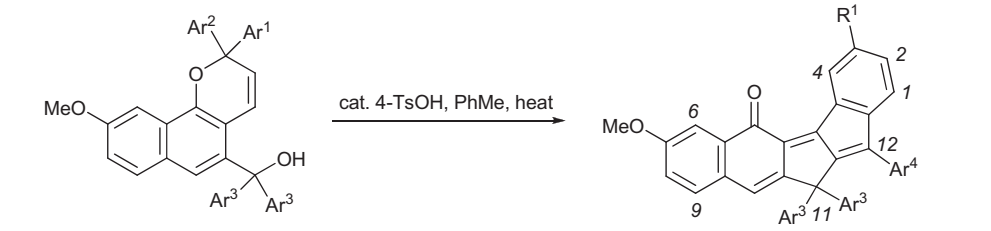


Fig. 5. Absorption spectra of **3c** before and after treatment with acid.



3a $Ar^1 = Ar^2 = Ar^3 = 4\text{-}MeOC_6H_4$
3b $Ar^1 = Ar^2 = 4\text{-}Me_2NC_6H_4$, $Ar^3 = 4\text{-}MeOC_6H_4$
3c $Ar^1 = 4\text{-}Me_2NC_6H_4$, $Ar^2 = Ar^3 = 4\text{-}MeOC_6H_4$

4a $Ar^3 = Ar^4 = 4\text{-}MeOC_6H_4$, $R^1 = OMe$
4b $Ar^3 = 4\text{-}MeOC_6H_4$, $Ar^4 = 4\text{-}Me_2NC_6H_4$, $R^1 = NMe_2$
4c $Ar^3 = Ar^4 = 4\text{-}MeOC_6H_4$, $R^1 = NMe_2$
4d $Ar^3 = 4\text{-}MeOC_6H_4$, $Ar^4 = 4\text{-}Me_2NC_6H_4$, $R^1 = OMe$

Scheme 5. Acid-catalysed thermal rearrangement of naphthopyrans **3**.

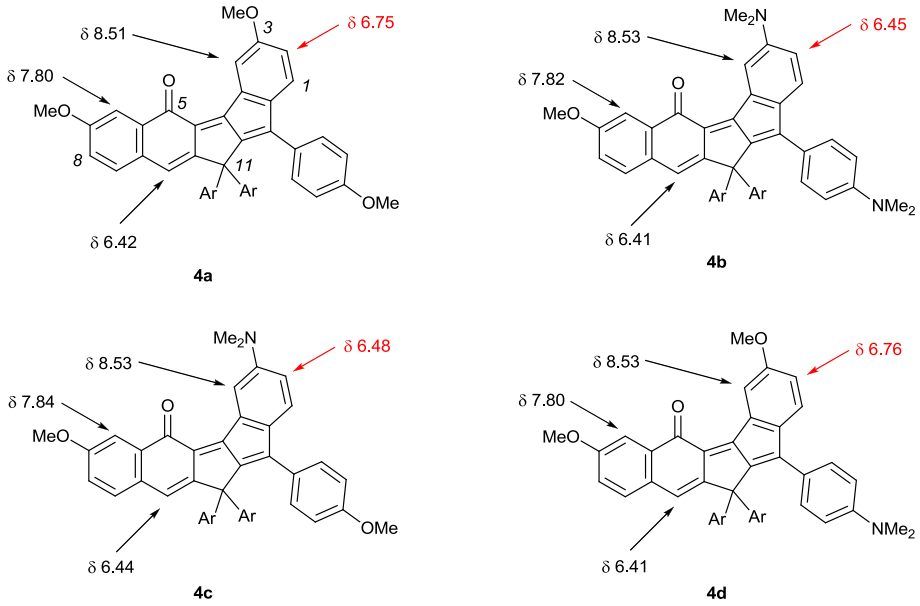
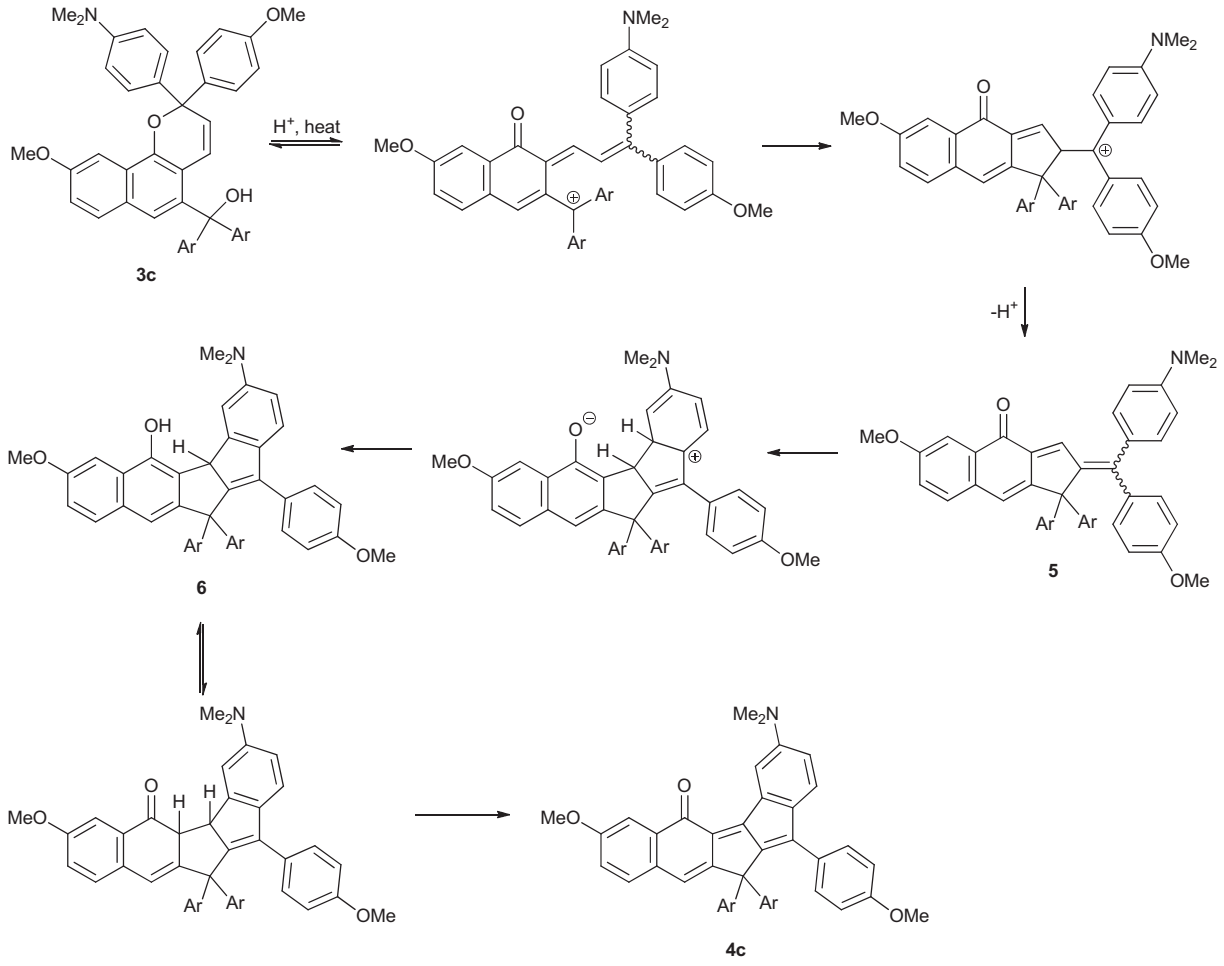


Fig. 6. ^1H NMR chemical shifts of selected protons in **4a**–**d**.



Scheme 6. Proposed mechanism for the formation of **4c**.

in **4b** 2-H, *ortho* to an NMe_2 group resonates further upfield at δ 6.45. Thus **4c** in which 2-H resonates at δ 6.48 was assigned to the 3-dimethylamino isomer and **4d** in which 2-H resonates at δ 6.76 was assigned to the 3-methoxy compound (Fig. 6). The insensitivity of the chemical shift of 4-H, which resonated at δ 8.5, to the electronic nature of the adjacent OMe/NMe_2 group was noticeable; presumably the chemical shift of 4-H is dominated by the proximal CO group at C-5. Isomers **4c** and **d** each displayed a low field signal

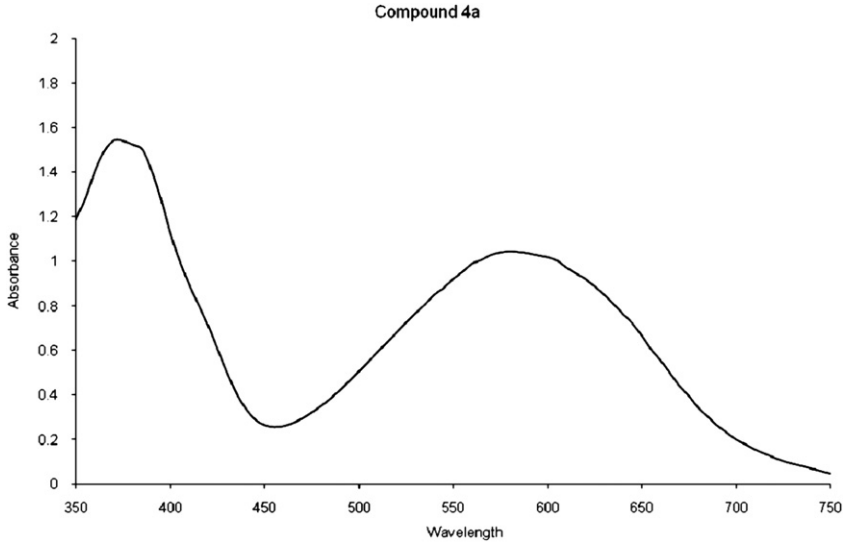


Fig. 7. Uv-visible absorption spectrum of **4a** (*ca.* 1×10^{-4} mol dm^{-3}) in CH_2Cl_2.

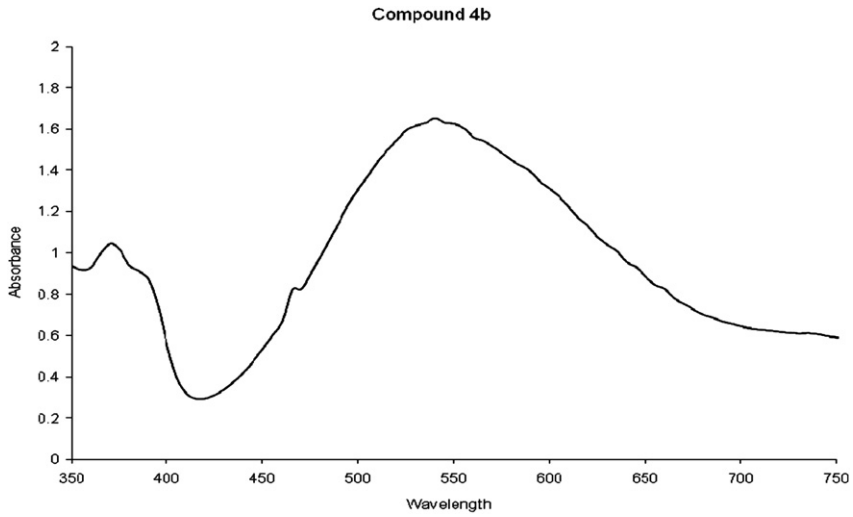


Fig. 8. Uv-visible absorption spectrum of **4b** (*ca.* 1×10^{-4} mol dm^{-3}) in CH_2Cl_2.

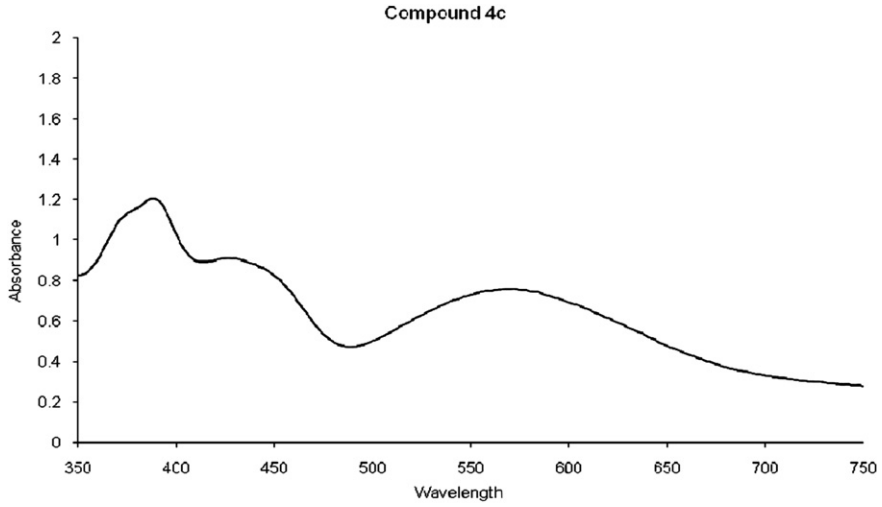


Fig. 9. Uv-visible absorption spectrum of **4c** (*ca.* 1×10^{-4} mol dm^{-3}) in CH_2Cl_2.

at $\sim\delta$ 183.6 assigned to the CO group which was confirmed by infrared spectroscopy which revealed a CO stretching band at *ca.* 1590 cm^{-1} indicative of the extended conjugation.

The formation of the isomers **4c** and **d** may be rationalised by initial intramolecular trapping of the bis(4-methoxyphenyl) stabilised cation to afford a mixture of isomeric dienones **5**. At this juncture the formation of either **4c** or **4d** is determined since only the aryl group which is in a *cis*-relationship with the enone moiety can undergo intramolecular cyclisation in the presence of 4-TsOH to afford the naphthol **6**. Enol–keto tautomerism of **6** followed by aerial oxidation generations the stabilising extended conjugated π system of the product (Scheme 6).

The planar, highly conjugated pentalenones **4a** and **4b** exhibited two significant absorption bands in CH_2Cl_2 solution with **4a** (turquoise) $\lambda_{max} = 586$ nm, $\varepsilon_{max} = 1.1 \times 10^4$ mol^{-1} dm^3 cm^{-1} and $\lambda_{max} = 376$ nm, $\varepsilon_{max} = 1.6 \times 10^4$ mol^{-1} dm^3 cm^{-1} (Fig. 7) and **4b** (violet) $\lambda_{max} = 545$ nm, $\varepsilon_{max} = 1.6 \times 10^4$ mol^{-1} dm^3 cm^{-1} and $\lambda_{max} = 370$ nm, $\varepsilon_{max} = 1.0 \times 10^4$ mol^{-1} dm^3 cm^{-1} (Fig. 8).

However, more complex solution spectra (CH_2Cl_2), displaying three broad bands were observed for the pentelenones **4c** and **d** derived from the unsymmetrically substituted precursor **3c**, with **4c** (green) $\lambda_{max} = 390$ nm, $\varepsilon_{max} = 1.2 \times 10^4$ mol^{-1} dm^3 cm^{-1}, $\lambda_{max} = 426$ nm, $\varepsilon_{max} = 9.3 \times 10^3$ mol^{-1} dm^3 cm^{-1} and $\lambda_{max} = 571$ nm, $\varepsilon_{max} = 7.8 \times 10^3$ mol^{-1} dm^3 cm^{-1} (Fig. 9) and **4d** (blue) $\lambda_{max} = 369$ nm, $\varepsilon_{max} = 1.0 \times 10^4$ mol^{-1} dm^3 cm^{-1} and $\lambda_{max} = 642$ nm

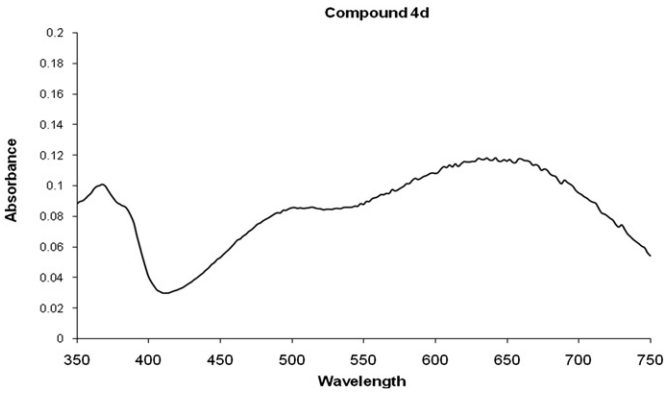


Fig. 10. Uv-visible absorption spectrum of **4d** (*ca.* 1×10^{-5} mol dm^{-3}) in CH_2Cl_2.

(broad with shoulder at 499 nm), $\varepsilon_{max} = 1.2 \times 10^4$ mol^{-1} dm^3 cm^{-1} (Fig. 10).

4. Conclusions

Readily accessible alkyl 2*H*-naphtho[1,2-*b*]pyran-5-carboxylates **2** afford diarylmethanol substituted naphthopyrans **3** upon reaction with excess organolithium reagents. These naphthopyrans exhibit photochromism through the reversible electrocyclic ring-opening of the pyran unit. The addition of methanesulfonic acid to solutions of **3** leads to the formation of intensely coloured cationic dyes **3″**; ^{1}H NMR studies of which indicate that the pyran ring remains intact. However these cationic dye solutions no longer exhibit photochromism.

The thermally generated merocyanine derived from the ring-opening of the naphthopyran unit of **3c** has been trapped with a proximal cationic centre to afford a mixture of isomeric benzopentalenonaphthalenones **4c**, **d** which have been distinguished using key ^{1}H NMR chemical shifts. Further examination of the syntheses of these unusual polycyclic dye systems is ongoing.

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