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Short communication

Synthesis and photochromic properties of spiro[naphthopyran-7′*H*-benzocyclohepta-5′,8′-dienes]

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ABSTRACT

A series of spironaphthopyrans has been synthesised by the acid-catalysed condensation between either a substituted 1-naphthol or 2-naphthol and the propargylic alcohol derived from the addition of lithium trimethylsilylacetylide to a 7*H*-benzocycloheptan-7-one with subsequent *in situ* silyl group removal. The photochromism of the novel spironaphthopyrans was characterised by a bathochromically shifted λ_{max} coupled with a relatively quick initial fade of the photogenerated species relative to the comparable diphenyl substituted model compounds. After initial fading a relatively intense residual colour persisted for the spironaphthopyrans.

1. Introduction

Labile spirocyclic systems have featured prominently in stimuli responsive colorant chemistry over the years (Fig. 1) [1]. The spiroindolinobenzopyrans **1** came to the fore in the mid 70's and were noted for their photo- and thermochromic properties and continue to be of interest today as a model responsive system for exploring a range of optical phenomena [2]. Spiroindolizines **2** [3], spiroindolinonaphthoxazines **3** [4] and spiroindolinonaphthopyrans **4** [5] have all been investigated for their photochromic properties with the most commercially successful series being the spiroindolinonaphthoxazines **3**, which have generated appreciable commercial interest in the ophthalmic photochromic lens industry [6]. The fluorescence of the rhodamines e.g. **5** is well-known and has been harnessed in a variety of sensor and labelling applications [7]. The closely related fluoran (spiro[isobenzofuran-1(3*H*),9′-(9*H*) xanthen]-3-one) system is a key unit in commercial, reversible thermochromic inks and which is still attracting interest today with linked colour former – developer systems such as **6** [8]. The photochromism of a series of spirofluorene-**7** [9] and spirothioxanthene – naphthopyrans **8** has been discussed [10]. Given the interest in such a diversity of spirocyclic compounds we elected to examine the synthesis and photochromism of a new series of spironaphthopyrans derived from the condensation between a naphthol and a 7-ethynyl-7*H*-benzocyclohepta-5.8-dien-7-ol; the results of this preliminary study are described in this short paper.

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 either tetramethylsilane as an internal reference or referenced to the residual protonated solvent signal. 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 freshly prepared spectroscopic grade toluene solutions of the samples, previously unexposed to daylight, with a 4 min activation with UV irradiation (UV exposure time determined to give a maximum absorption value), absorption decay data collected over either 15 or 30 min at 18 s intervals, 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 W xenon arc lamp source (Newport 66906), xenon ozone free arc lamp (Newport 6255), distilled water liquid filter (Newport 6177),

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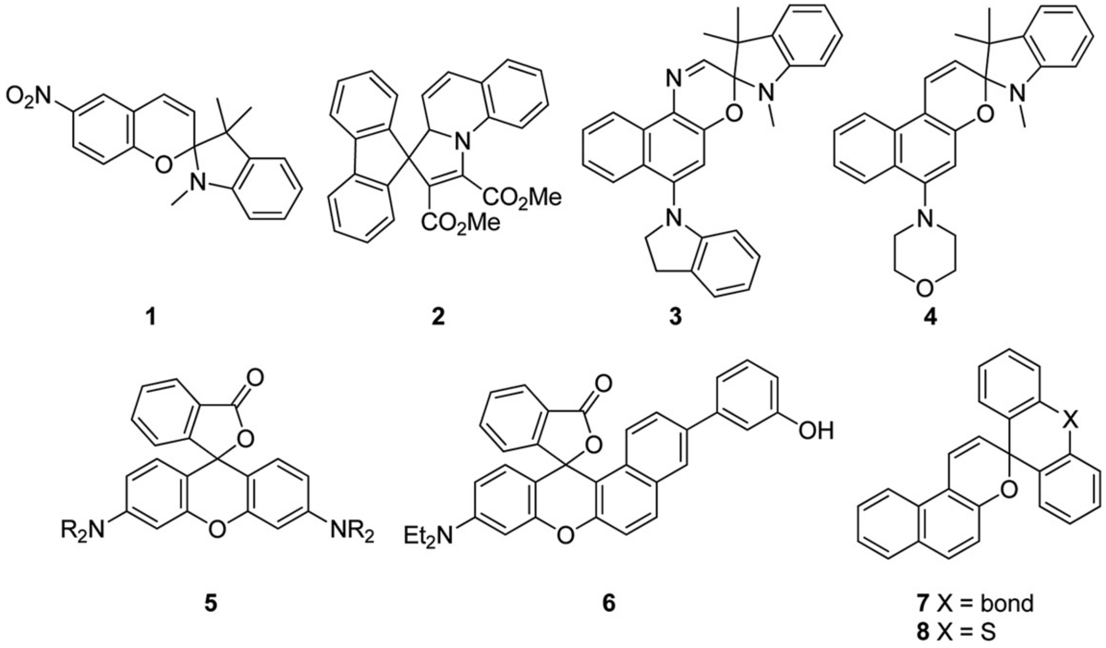


Fig. 1. Some examples of spirocyclic colorants.

multiple filter holder (Newport 62020), UG11 filter (Newport FSO-UG11), fibre optic coupler (Newport 77799) and liquid light guide (Newport 77557). Flash column chromatography was performed on chromatography grade silica gel (Fluorochem, 40–63 micron particle size distribution). All the compound yields are unoptimised. All new compounds 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 using a Thermo Scientific LTQ Orbitrap XL Fourier transform mass spectrometer. The naphthols employed were either commercially available (Alfa-Aesar, Aldrich) or were prepared according to published protocols. 1,1-Diphenylprop-2-yn-1-ol was obtained by the well-established protocol of the addition of lithium trimethylsilylacetylide to benzophenone with subsequent *in situ* base promoted desilylation [11]; physical data for this propynol was in accord with that previously reported [12]. Ethyl 4-hydroxy-1-phenylnaphthalene-2-carboxylate [13] and methyl 4-hydroxy-1-methylnaphthalene-2-carboxylate [14] were prepared according to literature procedures.

2.2. Preparation of 6,8-diphenyl-7H-benzocycloheptan-7-one **9**

A solution of potassium hydroxide (1.06 g, 19 mmol) in ethanol (30 mL) was added dropwise over 5 min to a warm stirred solution of *o*-phthalaldehyde (10 g, 74.6 mmol) and 1,3-diphenylacetone (15.7 g, 74.6 mmol) in ethanol (100 mL). A colour change from pale gold to red and finally to orange was then observed upon the addition. The reaction mixture was then heated under reflux for 1.5 h. After cooling to 5 °C the resulting pale yellow precipitate was collected by vacuum filtration and washed with cold ethanol. The resulting solid was then recrystallised from ethyl acetate and hexane, to afford the title compound as pale yellow microcrystals (15.1 g, 65%), mp = 117–119 °C (lit. mp = 119 °C [15]).

2.3. Preparation of 6,8-diphenyl-7-ethynyl-7H-benzocyclohepta-5.8-dien-7-ol **10**

n-Butyllithium (1.6 M in hexanes) (2 mol equiv.) was added portionwise over 5 min, *via* syringe to a cold (−15 °C) stirred solution of trimethylsilylacetylene (2 mol equiv.) in anhydrous THF (200 mL) under nitrogen. On completion of the addition the solution was stirred at −15 °C for 30 min 6,8-Diphenyl-7*H*-benzocycloheptan-7-one (10.67 g, 34.6 mmol) was then added in a single portion and the reaction mixture was stirred whilst warming to room temperature until TLC examination showed no further ketone remained (ca. 3 h). The reaction mixture was then cooled to −15 °C and a methanolic KOH [(2 mol equiv.) in methanol (100 mL)] was added. The reaction mixture was stirred at −15 °C until TLC confirmed that no further change in composition occurred (ca. 30 min). The reaction mixture was then poured into water (500 mL), extracted with ethyl acetate (3 × 50 mL), washed with water (2 × 100 mL) and dried (anhyd. $MgSO_4$). The solvent was removed under reduced pressure and the residue was crystallised from hexane to yield the title compound [16] as an off-white powder (9.11 g, 79%), mp 128–132 °C, ν_{max} 3500, 3264, 3022, 1615, 1598, 1490, 1443, 1241, 1032, 753, 696 cm^{-1}, δ_H 2.13 (1H, s, acetylene-H), 2.17 (1H, s, OH), 6.81 (2H, s, 5-H, 9-H), 7.28–7.50 (14H, overlapping m, Ar–H). Found $[M + Na]^+ = 357.1253$, $C_{25}H_{18}O$ requires $[M + Na]^+ = 357.1250$.

2.4. General method for the preparation of naphthopyrans

A stirred solution of the naphthol (1 equiv.) and the prop-2-yn-1-ol (1 equiv.), trimethyl orthoformate (2 equiv.) with a catalytic amount of pyridinium *para*-toluenesulfonate (0.05 equiv.) in 1,2-dichloroethane (40 mL) was heated under reflux until TLC examination confirmed no further conversion had occurred (ca. 8 h). The cooled mixture was diluted with CH_2Cl_2 (30 mL), washed with water (100 mL), dried (anhyd. $MgSO_4$) and the solvent removed under reduced pressure. The residue was then either crystallised from ethyl acetate and hexane or eluted from silica to afford the naphthopyran. The following compounds were obtained in this manner:

2.4.1. 6′,8′-Diphenyl-spiro[3H-naphtho[2,1-b]pyran-3,7′-7′H-benzocyclohepta-5′,8′-diene] **12a**

From 2-naphthol **11a** and propynol **10** as a pale pink solid after elution from silica with 20% EtOAc in hexane (0.51 g, 37%), mp 202–204 °C, ν_{max} 3050, 1634, 1587, 1488, 1441, 1243, 1171, 1093, 880, 812, 754, 697 cm^{-1}, δ_H 5.60 (1H, d, J = 10.0 Hz, 2-H), 6.14 (1H, d, J = 9.0 Hz, 5-H), 6.765 (2H, s, 5′-H, 9′-H), 6.77 (1H, d, J = 10.0 Hz, 1-H), 7.19 (6H, m, Ar–H), 7.27 (5H, m, Ar–H), 7.32 (1H, d, J = 9.0 Hz, 6-H), 7.38 (2H, m, Ar–H), 7.41 (1H, m, Ar–H), 7.51 (2H, m, Ar–H), 7.62 (1H, d, J = 8.0 Hz, 7-H), 7.81 (1H, d, J = 8.5 Hz, 10-H). Found $[M + H]^+ = 461.1903$, $C_{35}H_{24}O$ requires $[M + H]^+ = 461.1900$.

2.4.2. 6′,8′-Diphenyl-8-methoxy-spiro[3H-naphtho[2,1-b]pyran-3,7′-7′H-benzocyclohepta-5′,8′-diene] ***12b***

From 6-methoxy-2-naphthol **11b** and propynol **10** as a pale pink solid after elution from silica with 10% EtOAc in hexane (0.26 g, 24%), mp 162–164 °C, ν_{max} 3048, 1617, 1592, 1489, 1373, 1242, 1204, 1192, 1166, 1099, 1028, 852, 748, 696, 678 cm^{-1}, δ_H 3.85 (3H, s, 8-OMe), 5.60 (1H, d, J = 9.9 Hz, 2-H), 6.12 (1H, J = 9.0 Hz, 5-H), 6.73 (1H, d, J = 9.9 Hz, 1-H), 6.77 (2H, s, 5′-H, 9′-H), 6.95 (1H, d, J = 2.5 Hz, 7-H), 7.09 (1H, dd, J = 9.0, 2.5 Hz, 9-H), 7.20 (6H, m, Ar–H), 7.28 (5H, m, Ar–H), 7.37 (2H, m, Ar–H), 7.50 (2H, m, Ar–H), 7.71 (1H, d, J = 9.0 Hz, 10-H). Found $[M + H]^+ = 491.2009$, $C_{36}H_{26}O_2$ requires $[M + H]^+ = 491.2006$.

2.4.3. 6′,8′-Diphenyl-9-methoxy-spiro[3H-naphtho[2,1-b]pyran-3,7′-7′H-benzocyclohepta-5′,8′-diene] ***12c***

From 7-methoxy-2-naphthol **11c** and propynol **10** as a pale pink solid after recrystallisation from EtOAc and hexane (0.36 g, 30%), mp 198–201 °C, ν_{max} 3061, 3938, 1621, 1591, 1469, 1447, 1364, 1241, 1160, 1095, 1056, 1009, 819, 763, 732, 695 cm^{-1}, δ_H 3.86 (3H, 9-OMe), 5.70 (1H, d, J = 10.0 Hz, 2-H), 6.01 (1H, d, J = 8.8 Hz, 5-H), 6.71 (1H, d, J = 10.0 Hz, 1-H), 6.76 (2H, s, 5′-H, 9′-H), 6.94 (1H, dd, J = 8.8, 2.2 Hz, 8-H), 7.05 (1H, d, J = 2.2 Hz, 10-H), 7.19–7.28 (11H, m, Ar–H), 7.36 (2H, m, Ar–H), 7.51 (3H, m, Ar–H, 7-H). Found $[M + H]^+ = 491.2012$, $C_{36}H_{26}O_2$ requires $[M + H]^+ = 491.2006$.

2.4.4. 5-Ethoxycarbonyl-6,6′,8′-triphenyl-spiro[2H-naphtho[1,2-b]pyran-2,7′-7′H-benzocyclohepta-5′,8′-diene] ***14a***

From ethyl 1-hydroxy-4-phenylnaphthalene-3-carboxylate **13a** and propynol **10** as off-white microcrystals after elution from silica with 30% EtOAc in hexane (0.52 g, 36%), mp 112–114 °C, ν_{max} 2952, 1713, 1606, 1505, 1461, 1442, 1432, 1372, 1295, 1225, 1165, 1108, 1037, 1025, 998, 897, 749, 677 cm^{-1}, δ_H 0.88 (3H, t, J = 7.2 Hz, $CH_2C\underline{H}_3$), 3.94 (2H, q, J = 7.2 Hz, $C\underline{H}_2CH_3$), 5.55 (1H, d, J = 10.3 Hz, 3-H), 6.35 (1H, d, J = 10.2 Hz, 4-H), 6.50 (1H, d, J = 8.4 Hz, 10-H), 6.91 (3H, s, 5′-H, 9′-H and m, Ar–H), 7.13–7.24 (7H, m, Ar–H), 7.28–7.41 (10H, m, Ar–H), 7.42 (2H, m, Ar–H), 7.52 (2H, m, Ar–H). Found $[M + H]^+ = 609.2437$, $C_{44}H_{32}O_3$ requires $[M + H]^+ = 609.2424$.

2.4.5. 6′,8′-Diphenyl-5-methoxycarbonyl-6-methyl-spiro[2H-naphtho[1,2-b]pyran-2,7′-7′H-benzocyclohepta-5′,8′-diene] ***14b***

From methyl 1-hydroxy-4-methylnaphthalene-3-carboxylate **13b** and propynol **10** as a pale orange microcrystals after elution from silica with 25% EtOAc in hexane (0.39 g, 31%), mp 176–178 °C, ν_{max} 3017, 1715, 1432, 1362, 1292, 1250, 1223, 1204, 1115, 1050, 890, 765, 750, 707, 689, 642 cm^{-1}, δ_H 2.52 (3H, s, 6-Me), 3.92 (3H, s, OMe), 5.53 (1H, d, J = 10.0 Hz, 3-H), 6.22 (1H, d, J = 10.0 Hz, 4-H), 6.45 (1H, d, J = 8.4 Hz, 10-H), 6.92 (2H, s, 5′-H, 9′-H), 6.96 (1H, m, Ar–H), 7.20–7.29 (8H, m, Ar–H), 7.35 (1H, m, Ar–H), 7.45 (2H, m, Ar–H), 7.57 (2H, m, Ar–H), 7.82 (1H, d, J = 8.4 Hz, 7-H). Found $[M + H]^+ = 533.2123$, $C_{38}H_{28}O_3$ requires $[M + H]^+ = 533.2111$.

2.4.6. 3,3-Diphenyl-3H-naphtho[2,1-b]pyran ***16a***

From 2-naphthol **11a** and propynol **15** as colourless microcrystals after elution from silica with 10% EtOAc in hexane (3.1 g 67%), mp 158–160 °C (lit. mp 158–159 °C [17]), ν_{max} 3062, 1635, 1588, 1489, 1445, 1241, 1215, 1093, 1083, 1008, 945, 803, 751, 744, 696, 678 cm^{-1}, δ_H 6.26 (1H, d, J = 9.9 Hz, 2-H), 7.19 (1H, d, J = 8.8 Hz, 5-H), 7.23–7.33 (8H, Ar–H, 1-H), 7.43–7.50 (5H, m, Ar–H), 7.65 (1H, d, J = 8.8 Hz, 6-H), 7.70 (1H, d, J = 8.2 Hz, 7-H), 7.94 (1H, d, J = 8.2 Hz, 10-H). Found $[M + H]^+ = 335.1434$, $C_{25}H_{18}O$ requires $[M + H]^+ = 335.1430$.

2.4.7. 3,3-Diphenyl-8-methoxy-3H-naphtho[2,1-b]pyran ***16b***

From 6-methoxy-2-naphthol **11b** and propynol **15** as pale beige microcrystals after recrystallisation from EtOAc and hexane (0.71 g, 40.6%), mp 179–181 °C (lit. mp 173–175 °C [18]), ν_{max} 2937, 1620, 1590, 1471, 1446, 1363, 1328, 1246, 1195, 1160, 1095, 1055, 1009, 818, 764, 731, 696, 676 cm^{-1}, δ_H 3.86 (3H, s, 8-OMe), 6.26 (1H, d, J = 9.9 Hz, 2-H), 7.02 (1H, d, J = 2.4 Hz, 7-H), 7.12 (1H, dd, J = 8.8, 2.4 Hz, 9-H), 7.19 (1H, d, J = 8.7 Hz, 5-H), 7.22–7.33 (7H, m, Ar–H, 1-H), 7.47 (4H, m, Ar–H), 7.53 (1H, d, J = 8.7 Hz, 6-H), 7.84 (1H, d, J = 8.8 Hz, 10-H). Found $[M + H]^+ = 365.1539$, $C_{26}H_{20}O_2$ requires $[M + H]^+ = 365.1536$.

2.4.8. 3,3-Diphenyl-9-methoxy-3H-naphtho[2,1-b]pyran ***16c*** *[18,19]*

From 7-methoxy-2-naphthol **11c** and propynol **15** as off-white microneedles after recrystallisation from EtOAc and hexane (0.45 g, 25.6%), mp 176–179 °C, ν_{max} 3058, 1634, 1618, 1592, 1509, 1444, 1244, 1220, 1019, 968, 914, 828, 754, 698, 670 cm^{-1}, δ_H 3.91 (3H, s, 9-OMe), 6.24 (1H, d, J = 9.9 Hz, 2-H), 6.96 (1H, dd, J = 8.7, 2.1 Hz, 8-H), 7.05 (1H, d, J = 8.7 Hz, 5-H), 7.21–7.33 (8H, m, Ar–H, 1-H), 7.48 (4H, m, Ar–H), 7.57 (2H, app. t, Ar–H). Found $[M]^+ = 364.1460$, $C_{26}H_{20}O_2$ requires $[M]^+ = 364.1458$.

2.4.9. Ethyl 2,2,6-triphenyl-2H-naphtho[1,2-b]pyran-5-carboxylate ***17a***

From ethyl 1-hydroxy-4-phenylnaphthalene-3-carboxylate **13a** and propynol **15** as off-white microcrystals after elution from silica with 20% EtOAc in hexane (0.58 g, 24.0%), mp 174–177 °C, ν_{max} 2921, 1718, 1446, 1366, 1228, 1165, 1114, 1041, 938, 762, 698, 672, 606 cm^{-1}, δ_H 0.91 (3H, t, J = 7.2 Hz, $CH_2C\underline{H}_3$), 4.02 (2H, q, J = 7.2 Hz, $C\underline{H}_2CH_3$), 6.25 (1H, d, J = 9.9 Hz, 3-H), 6.85 (1H, d, J = 9.9 Hz, 4-H), 7.28–7.63 (18H, m, Ar–H), 8.44 (1H, dd, J = 8.7, 1.5 Hz, 10-H). Found $[M + H]^+ = 483.1947$, $C_{34}H_{26}O_3$ requires $[M + H]^+ = 483.1955$. Spectroscopic data comparable to that reported previously [20].

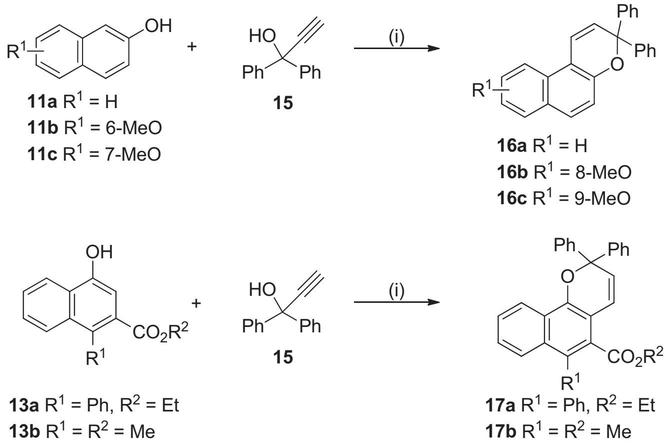
2.4.10. Methyl 2,2-diphenyl-6-methyl-2H-naphtho[1,2-b]pyran-5-carboxylate ***17b*** *[21]*

From methyl 1-hydroxy-4-methylnaphthalene-3-carboxylate **13b** and propynol **15** as a pale yellow powder after recrystallisation from EtOAc and hexane (1.36 g, 58.6%), mp 175–178 °C, ν_{max} 2952, 1725, 1489, 1445, 1432, 1365, 1288, 1251, 1220, 1114, 1043, 985, 956, 761, 696, 658 cm^{-1}, δ_H 2.56 (3H, s, Me), 4.01 (3H, s, OMe), 6.22 (1H, d, J = 9.9 Hz, 3-H), 6.70 (1H, d, J = 9.9 Hz, 4-H), 7.26 (6H, m, Ar–H), 7.60 (6H, m, Ar–H), 7.94 (1H, m, 7-H), 8.43 (1H, dd, J = 8.8, 1.6 Hz, 10-H). Found $[M + NH_4]^+ = 424.1907$, $C_{28}H_{22}O_3$ requires $[M + NH_4]^+ = 424.1907$.

3. Discussion

The base-catalysed condensation between *o*-phthalaldehyde and 1,3-diphenylacetone proceeded smoothly to afford 6,8-diphenyl-7*H*-benzocycloheptan-7-one **9** as pale yellow crystals in 65% yield after recrystallisation from ethyl acetate/hexane. Addition of lithium trimethylsilylacetylide to **9** with *in situ* hydroxide-mediated removal of the trimethylsilyl group gave, after aqueous work-up, the propynol **10** in 79% yield (Scheme 1). The formation of **10** was readily confirmed by ^1H NMR spectroscopy which displayed a singlet at δ 2.13 and at δ 2.17 (D_2O exchangeable) assigned to the acetylene and hydroxyl protons, respectively. The condensation of a naphthol with a propynol to afford a propargylic ether with subsequent rearrangement and isomerisation is the classical approach to naphthopyrans [11,19,22]. Many variations in conditions have been reported to offer enhanced yields in the foregoing condensation and include the use of various acidic catalysts including acidic alumina [23], substituted acetic acids [24], sulfonic acids [18] and pyridinium *p*-toluenesulfonate (PPTS) [20]; the application of solvent free conditions has also been advocated [25]. In the present work PPTS in conjunction with trimethyl orthoformate as a dehydrating agent was employed.

Thus heating 2-naphthol **11a** and the propynol **10** under reflux for 6 h in 1,2-DCE containing PPTS and $(MeO)_3CH$ gave, after aqueous work up and elution of the crude product from chromatography silica, the pure spironaphthopyran **12a** in a moderate 37% yield. The remaining naphthopyrans were obtained by a similar protocol in 24–67% yield (Scheme 2). The ^1H NMR spectrum of **12a** displayed a singlet at δ 6.77 for the equivalent benzocycloheptadiene alkene protons (5′-H and 9′-H) together with some interesting chemical shifts for the pyran ring protons with 2-H appearing as a doublet at δ 5.6 and 1-H as a doublet at δ 6.7 with a mutual coupling constant of 10 Hz. Whilst the magnitude of $J_{1,2}$ is typical at ca. 10 Hz [11,26] the signal for 2-H and for 1-H have been shifted upfield by ca. 0.7 ppm and 0.6 ppm, respectively from the chemical shift of the comparable protons in the simple diphenyl substituted naphthopyran **16a**. Furthermore, 5-H in **12a**, which appears as a doublet with $J = 9.0$ Hz and resonates at δ 6.14 is also shifted upfield relative to that in **16a** (ca. δ 7.2) (Table 1). It is clear that such upfield chemical shifts must arise through the unique interaction between the C-3 spiro linked diphenylbenzocycloheptane residue and these protons. A similar upfield shift was noted for the pyran ring protons of the spironaphtho[1,2-*b*]pyrans **14** with 3-H resonating at ca. δ 5.5 and 4-H at ca. δ 6.3 relative to 3-H (δ 6.2) and 4-H (δ 6.8) in the model 2,2-diphenyl-2*H*-naphtho[1,2-*b*]pyrans **17**.

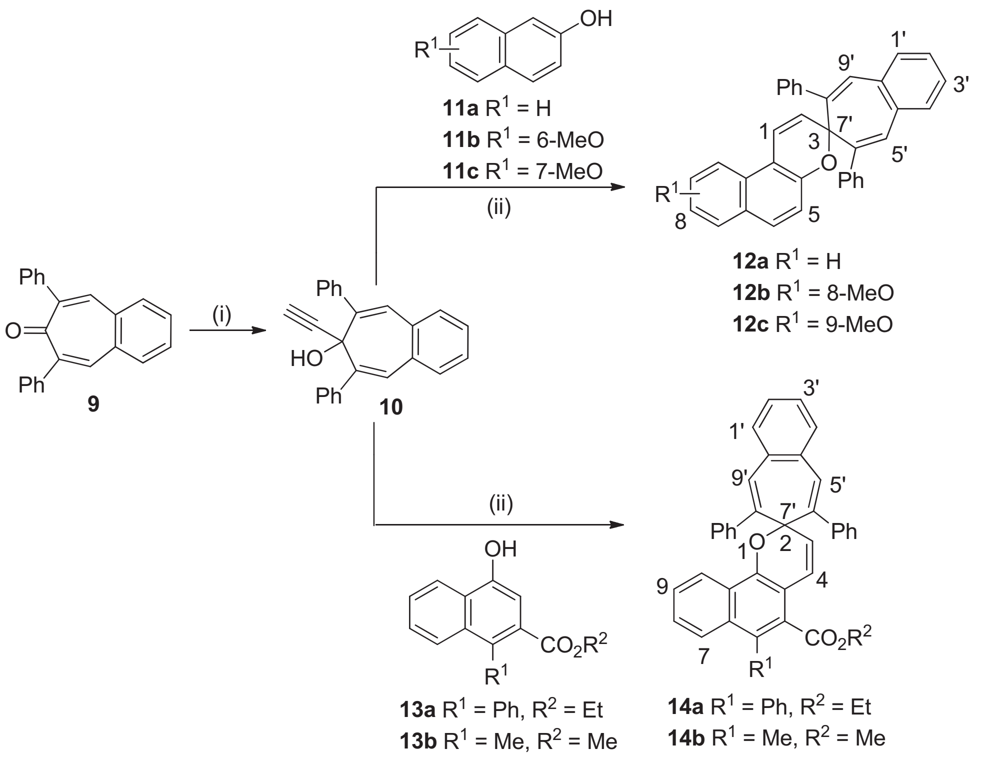


Reagents and conditions: (i) PPTS, $(MeO)_3CH$, 1,2-DCE, reflux

Scheme 2. Formation of diphenyl substituted naphthopyrans.

Preliminary energy minimized modelling (Molecular Mechanics 3, Chem 3D Ultra, version 12) of **12a** (Fig. 2) revealed that 5-H is located within the shielding zone of one of the pendant phenyl rings resulting in an upfield shift. Furthermore, due to the puckered nature of the seven-membered ring it appears that 2-H, and to a lesser extent 1-H, experience a shielding effect from the benzene ring of the benzotropone unit and thus experience a significant upfield shift. Attempts to obtain suitable crystals for X-ray analysis are ongoing.

The photochromic response, wavelength of maximum absorption of the photoinduced dye (λ_{max}) and the time taken for the



Reagents and conditions: (i) lithium trimethylsilylacetylide, THF, 0 °C - rt then KOH, MeOH, 0 °C - rt;
(ii) PPTS, $(MeO)_3CH$, 1,2-DCE, reflux

Scheme 1. Formation of spironaphthopyrans.

Table 1
Selected ^{1}H NMR data (CDCl$_3$) for spironaphtho[2,1-*b*]pyrans **12** and model 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyrans **16.**

	$\delta_{2\text{-H}}$	$\delta_{1\text{-H}}$	$J_{1,2}$ (Hz)	$\delta_{5\text{-H}}$
12a	5.60	6.77	10.0	6.14
16a	6.26	7.22–7.33[a]	9.9	7.19
12b	5.60	6.73	9.9	6.12
16b	6.26	7.22–7.33[a]	9.9	7.19
12c	5.70	6.71	10.0	6.01
16c	6.24	7.21–7.33[a]	9.9	7.05

[a] 1-H is obscured by other aromatic signals.

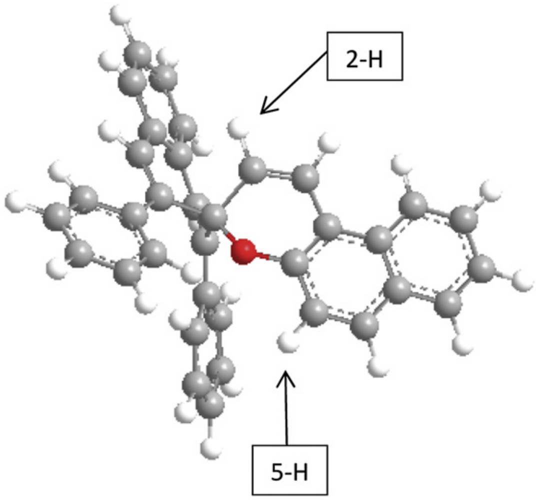


Fig. 2. Molecular Mechanics 3 (MM3) representation of spironaphthopyran **12a**.

photoinduced colour to fade to half of its original intensity under steady state irradiation immediately after cessation of the irradiation (half-life, $t_{½}$), of colourless freshly prepared toluene solutions of the spironaphthopyrans **12** and **14** were compared with those of the simple diphenyl substituted analogues **16** and **17** (Table 2). From these data it is evident that the replacement of the diphenyl unit with the spirocycle induces a bathochromic shift of ~33 nm in λ_{max} of the naphtho[2,1-*b*]pyran isomers **12a** – **c** with an associated decrease in the half-life of the photogenerated colour (Fig. 3). Whilst as expected, the 2*H*-naphtho[1,2-*b*]pyrans **14** and **17** afforded longer wavelength absorbing photomerocyanines relative to their 3*H*-naphtho[1,2-*b*]pyran analogues [11]; a significantly smaller bathochromic shift of ~12 nm was noted upon replacement of the diphenyl moiety with the spirocycle in the naphtho[1,2-*b*]pyran isomers **14a**,**b** with a decrease in the persistence of the photoinduced colour (Fig. 4). A significant and limiting feature of all of these new spirocyclic compounds is their residual solution colour, i.e. after cessation of irradiation the intense colour fades relatively quickly but never fades completely under ambient laboratory lighting to that of the initial colourless, freshly prepared solutions. This latter feature is easily demonstrated by examining the selected fading spectra (Fig. 5) for **14a**; these spectra show intense colour generation [spectrum **14a** (1) recorded immediately after cessation of activating radiation] with gradual decrease of the

Table 2
Photochromic response of toluene solutions of naphthopyrans.

	λ_{max} (nm)	$t_{½}$ (s)
12a	464	24
16a	428	40
12b	497	81
16b	468	136
12c	457	22
16c	424	46
14a	496	107
17a	482	202
14b	482	62
17b	472	104

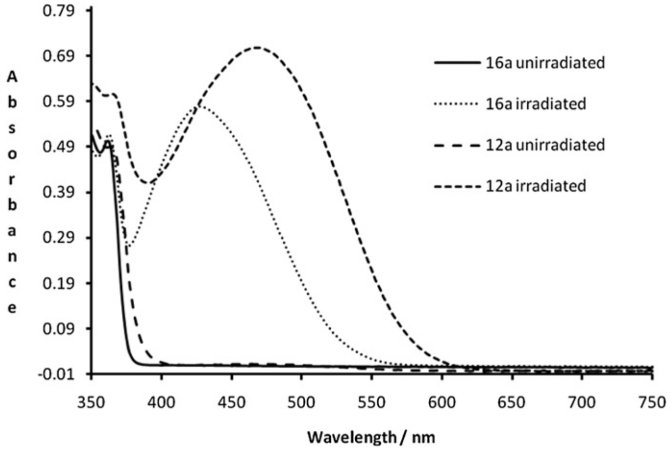


Fig. 3. Absorption spectra of spironaphthopyran **12a** and reference compound **16a**.

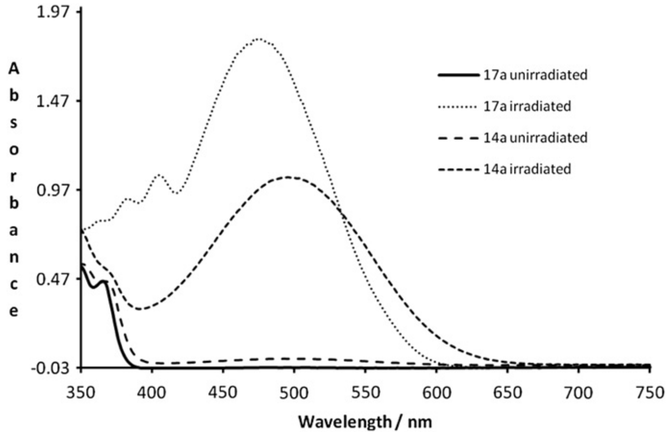


Fig. 4. Absorption spectra of spironaphthopyran **14a** and reference compound **17a**.

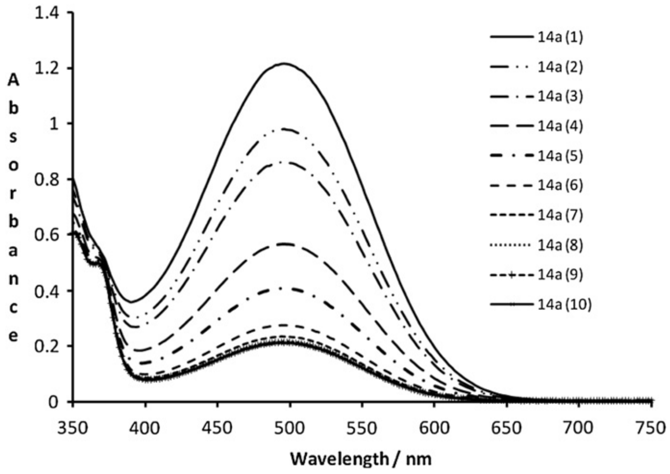
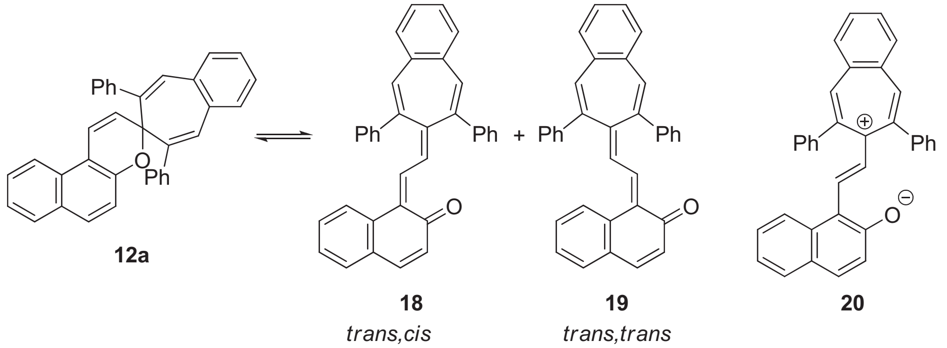


Fig. 5. Selected absorption spectra of 14a recorded after cessation of irradiation.



Scheme 3. Photomerocyanines derived from the ring-opening of the spironaphthopyran **12a**.

photogenerated colour [spectrum **14a** (2) through to spectrum **14a** (9)] until the final spectrum [**14a** (10) recorded 30 min after cessation of activating radiation] which retains an appreciable absorption at 496 nm (Fig. 5).

The lifetime of the isomeric photomerocyanines derived from the irradiation of a naphthopyran has been discussed with photobleaching of the persistent isomer to the parent naphthopyran reported [27]. Additionally, the structures of photomerocyanines have been examined by NMR spectroscopy which revealed that the most persistent isomer was that possessing a *trans,trans* geometry [26–28] which is equivalent to **19** in this study, which arises from photochemical isomerisation of **18** (*trans,cis*) (Scheme 3). A further complication in this work may arise from a contribution from the zwitterionic species **20** which may be favoured since the benzotropylium species is stabilised through aromaticity. Further investigation of the structure and spectroscopic features including photobleaching and degradation of this series of compounds is ongoing.

4. Conclusions

A series of novel spironaphthopyrans, spiro[naphthopyran-7′*H*-benzocyclohepta-5′,8′-dienes], derived from the reaction between either a 1- or 2-naphthol and 6,8-diphenyl-7-ethynyl-7*H*-benzocyclohepta-5.8-dien-7-ol are reported. The photochromic response of these new spironaphthopyrans is characterised by a bathochromically shifted λ_{max} accompanied by more rapid fading than their corresponding diphenyl substituted analogues. Unfortunately, complete thermal fading to the pre-irradiated colourless state is not observed with moderately intensely coloured solutions remaining; a feature which limits the application of these interesting compounds.

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