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CONTROL OF THE FADING PROPERTIES OF PHOTOCHROMIC 3,3-DIARYL-3*H*-NAPHTHO[2,1-*b*]PYRANS

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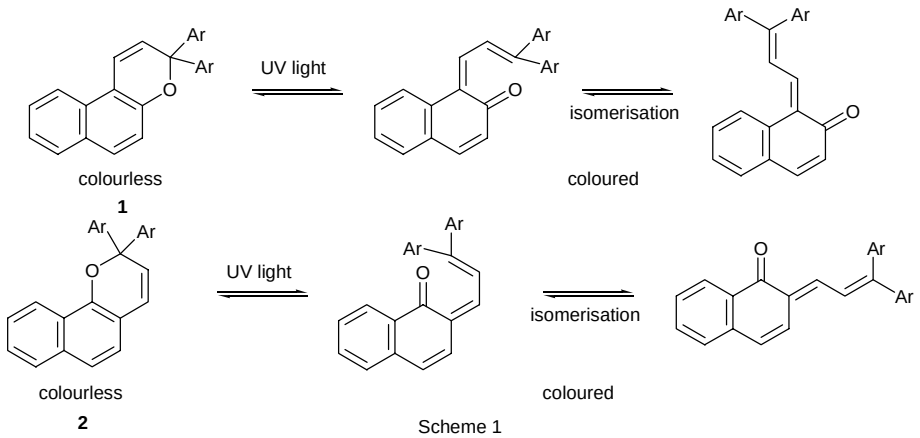
Abstract — The synthesis and spectroscopic properties of some novel photochromic 3*H*-naphtho[2,1-*b*]pyrans are reported. Varying the size of an *ortho*-substituent on one of the geminal aryl rings allows the rate of fade of the photogenerated color to be controlled.

INTRODUCTION

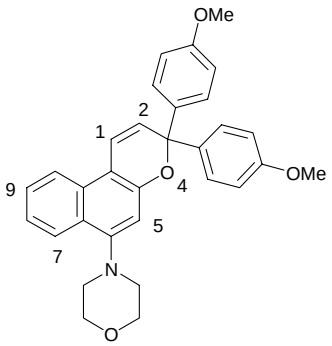
The facile electrocyclic ring opening and closing of the 2*H*-pyran system, particularly of the angular naphthopyran isomers (**1**) and (**2**) (Scheme 1) where the process is accompanied by a reversible change from colorless (pyran) to colored (merocyanine), on irradiation with UV light has attracted significant commercial interest.[1] This light induced reversible color change phenomenon is known as photochromism[2] and the photochromism of the isomeric diaryl substituted naphthopyrans (**1**) and (**2**) has been reviewed.[3]



Scheme 1

The photochromic properties of the 3*H*-naphtho[2,1-*b*]pyran isomer (**1**) are typified by the photo-generation of vibrant yellow to purple colors that unfortunately fade relatively rapidly on removal of the

source of irradiation. This rapid fade of the photo-generated color gives the overall impression to an observer of weak color generation and is an undesirable property of this naphthopyran isomer.[3] The intensification of the photo-generated color of the 3*H*-naphtho[2,1-*b*]pyran system has been accomplished through the incorporation of an amino or methoxy group at the 6-position *e.g.* **3**,[4] or alternatively by introduction of a group into at least one of the *ortho* positions of one of the aryl groups attached to 3-C *e.g.* **4**.[5] In the former compounds (**3**) the intensification of color, termed hyperchromism, has been rationalised by the presence of an additional resonance form that stabilises the ring-opened form (merocyanine dye). In the latter (**4**) the *ortho* substituent hinders the ring closure to the colorless pyran form resulting in a photostationary state in which there is an appreciable concentration of the merocyanine valence tautomer. This leads to intensification of the developed color.



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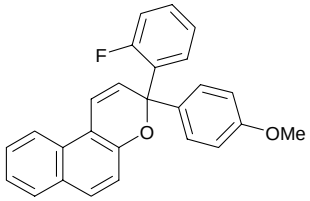

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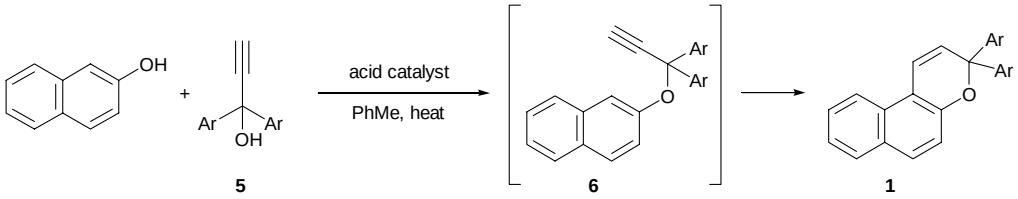
We have explored the influence of both the size and type of some '*ortho*' substituents on the photochromic properties of some 3,3-diaryl-3*H*-naphtho[2,1-*b*]pyrans (**1**).

DISCUSSION

Perhaps the most versatile and efficient route to the 3,3-diaryl-3*H*-naphtho[2,1-*b*]pyrans (**1**) relies upon the one pot, acid-catalysed etherification of a 2-naphthol with a 1,1-diarylprop-2-yn-1-ol (**5**).[3] The ether (**6**), generated *in situ*, undergoes a facile Claisen rearrangement followed by sigmatropic H-shifts and finally an electrocyclic ring closure to afford the naphthopyran (Scheme 2).

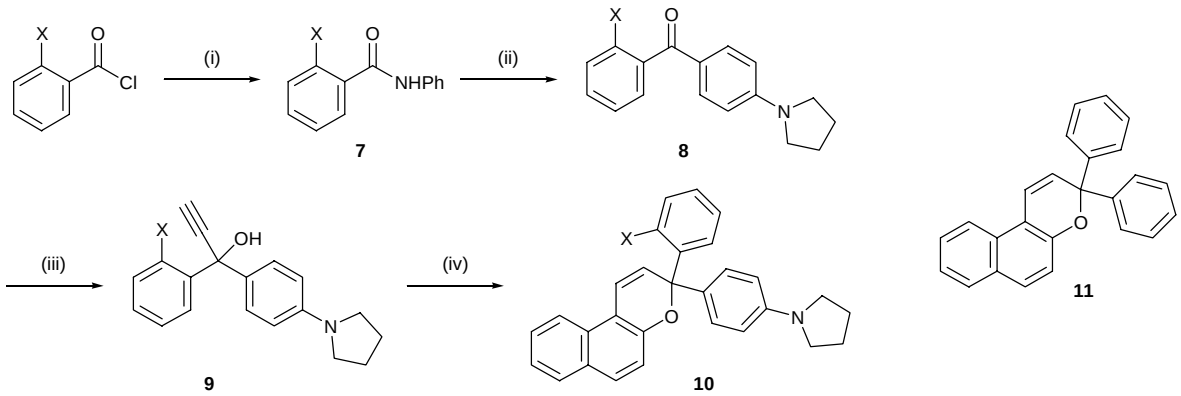


5 **6** **1**

Scheme 2

The *ortho* substituted benzophenones (**8**) required for the preparation of the substituted propynols (**9**) were readily obtained in moderate yield by the Vilsmeier-Haack reaction[6] of 1-phenylpyrrolidine with

an *N*-phenylbenzamides (**7**), which were derived from the acylation of aniline with *ortho* substituted benzoyl chlorides using a catalytic amount of DMAP in anhydrous pyridine (Scheme 3).[7] The 1,1-diarylprop-2-yn-1-ols (**9**) were obtained in excellent yield by the addition of lithium trimethylsilylacetylide (LTSA), derived from n-butyllithium and trimethylsilylacetylene, to a substituted benzophenone with subsequent unmasking of the terminal acetylene.[8] Both the methoxy- **9e** and methyl- **9f** substituted propynols darkened appreciably on rotary evaporation of the extraction solvent. These crude propynols were employed directly in the subsequent step without any purification.



a, X =F; b, X = Cl; c, X = Br; d, X = I; e, X = OMe; f, X = Me; g, X = H

Reagents and conditions: (i) $PhNH_2$, anhyd. py, DMAP (cat.), 0 ^oC - rt; (ii) $POCl_3$, *N*-phenylpyrrolidine, heat then 50% aq. HCl reflux; (iii) LTSA, THF 0 ^oC - rt then KOH, MeOH; (iv), 2-naphthol, acidic alumina, PhMe, reflux.

Scheme 3

The substituted naphthopyrans (**10**) were obtained according to the procedure outlined in Schemes 2 and 3. Yields for the formation of the *ortho* substituted naphthopyrans (**10a – f**) ranged from 26 – 68 %, somewhat lower than that obtained for the parent compound (**10g**) (82%). Evidently the presence of an *ortho* substituent in **9** hinders the formation of **10**.

It was interesting to note that the naphthopyrans (**10b – g**) showed the typical doublet for 2-H at *ca*. 6.5 ppm with $J \approx 10$ Hz in their ^{1}H NMR spectra as a consequence of coupling to 1-H which resonates further downfield due to its benzylic character.[9] The fluorine substituted compound (**10a**), afforded a double doublet at δ 6.43 for 2-H with J = 10.0, 4.6 Hz. This unexpected additional coupling is due to long range coupling of the proximal fluorine atom to 2-H.[10] Others have failed to recognise this feature, Carreira and Zhao incorrectly attributed long range ^{19}F – ^{1}H coupling in 5,5'-bis[3-(2-fluorophenyl)-3*H*-naphtho[2,1-*b*]pyran-3-yl]-2,2'-bithiophene to the presence of diastereoisomers,[11] Delbaere *et al*. also failed to report similar F – H coupling for 3-(2-fluorophenyl)-3-phenyl-3*H*-naphtho[2,1-*b*]pyran.[12] The ^{1}H NMR spectrum of **10a** is displayed in Figure 1, with an expansion of the double doublet assigned to 2-H (δ 6.43) and the aromatic protons that are *ortho* to the pyrrolidine ring (δ 6.48).

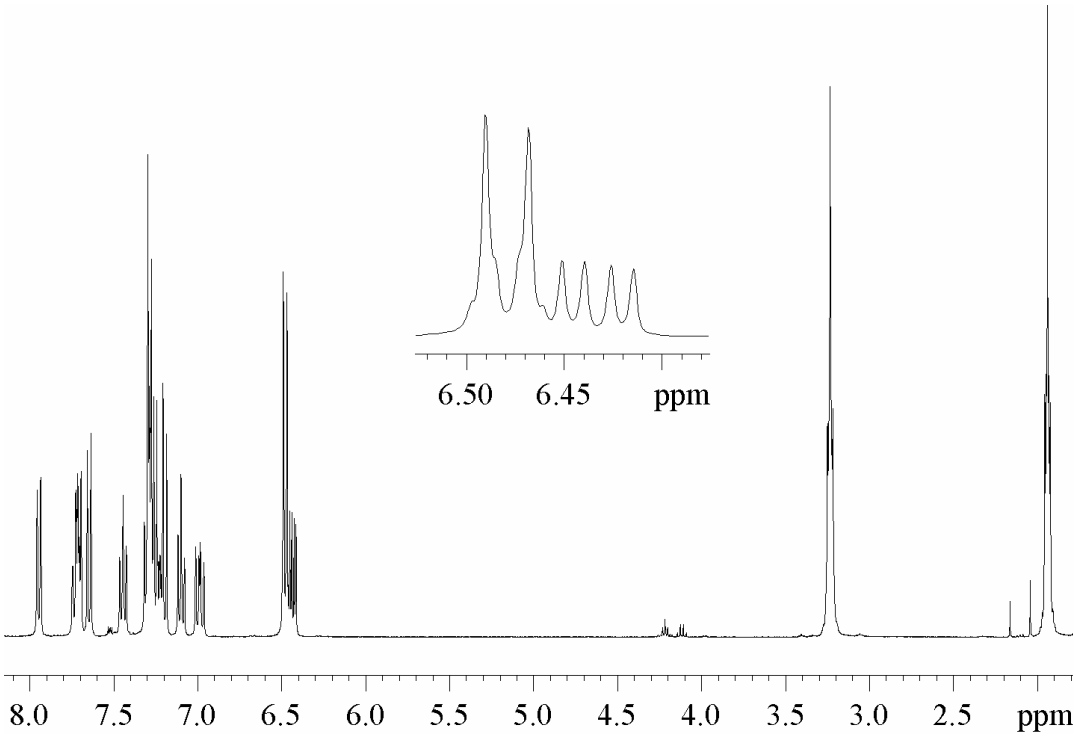


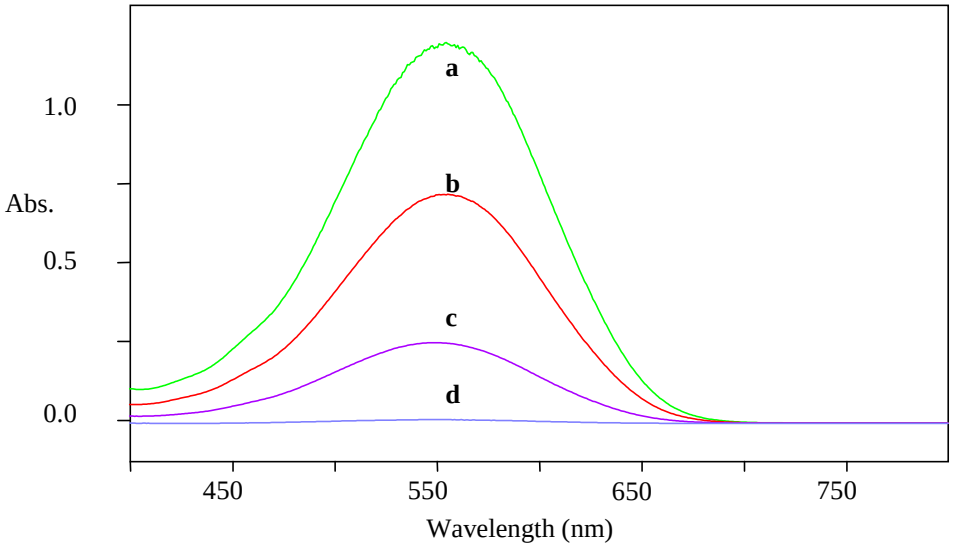
Figure 1. ^{1}H NMR spectrum of naphthopyran (**10a**).

The ring-opened products derived from the naphthopyrans (**10**) are intense purple in color. The data in Table 1 records the wavelength of maximum absorption (λ_{max}) of the ring-opened species formed when the naphthopyrans (**10**) are irradiated to a constant intensity with UV light in toluene solution at 20 °C. Additionally the time taken for the intensity of the photogenerated color to decrease to half of its original value (half-life, t½) is presented. For comparison purposes, the data are also given for 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran (**11**).

Table 1. Spectroscopic data for naphthopyrans (**10**) and (**11**).

	ortho substituent	λ_{max} (nm)	t½ (sec)
(**10a**)	F	554	40
(**10b**)	Cl	554	741
(**10c**)	Br	554	1024
(**10d**)	I	553	1167
(**10e**)	MeO	555	351
(**10f**)	Me	555	639
(**10g**)	H	538	5
(**11**)	—	430	10

Visible spectra of naphthopyran (**10a**) are displayed in Figure 2 to illustrate the decrease in intensity of absorption after cessation of UV irradiation.



Spectrum **a** recorded immediately after cessation of irradiation. Spectra **b** and **c** recorded at increasing times after cessation of irradiation. Spectrum **d** recorded prior to irradiation.

Figure 2. Visible spectra of naphthopyran (**10a**)

The data in Table 1 merit some comment. The introduction of a strongly electron donating pyrrolidine ring into **11** to afford **10g** induces a significant bathochromic shift in λ_{max} of 108 nm. A further bathochromic shift of 16 nm is noted on incorporation of an *ortho* fluorine atom (**10a**). The alternation of the *ortho* substituent through compounds (**10a** – **f**) has a negligible influence on λ_{max}. It is likely that this feature is a consequence of twisting of the aryl groups out of a near planar arrangement in the ring-opened form in order to alleviate the steric interaction between the *ortho* hydrogen atoms of one aryl ring and the *ortho* substituent on the alternate ring. Such twisting significantly reduces the p-orbital overlap in the conjugated system and diminishes the electronic properties of the *ortho* group. A similar twisting phenomena has been noted for triarylmethine dye systems.[13] In accord with previous observations[3] the introduction of an electron donating group into the *para* position of one of the aryl rings increases the rate of fade, reduces t½, (**10g** vs. **11**) leading to the perception of weak color generation. However, in marked contrast to this, the presence of an *ortho* substituent, irrespective of its electronic character increases t½. Furthermore, it is apparent from the series of halogeno substituted compounds (**10a** – **d**) that t½ increases as the size of the *ortho* substituent increases, leading to an observed increase in color intensity. It is likely that the steric demands made by the *ortho* substituent hinder the re-formation of the *cis*-isomer (Scheme 1) from which the electrocyclisation to the colorless pyran must occur.

EXPERIMENTAL

Melting points were determined in capillary tubes and are uncorrected. Visible spectra were recorded for solutions in spectroscopic grade toluene in 10 mm quartz cells at 20 °C using a Analytik Jena Specord S100 diode array spectrophotometer. Samples were irradiated to a steady state absorbance using a Spectroline 8 Watt lamp (365 nm). NMR spectra were recorded on either a Bruker Avance 400 MHz instrument for solutions in $CDCl_3$; *J* values are given in Hertz. Flash chromatographic separations were performed on chromatography silica gel (40 – 60 micron particle size distribution) as supplied by Fluorochem Ltd., according to the published procedure.[14] 4-Pyrrolidinobenzophenone was provided by James Robinson Ltd., Huddersfield, UK.

Preparation of 2-substituted *N*-phenylbenzamides (**7**)

The *o*-halogenobenzoyl chloride (200 mmol) was added dropwise to a cold (-5 °C) stirred solution of aniline (200 mmol) in anhydrous pyridine (60 mL) containing 4-dimethylaminopyridine (0.1g, cat.), at such a rate so as to maintain an internal temperature below 5 °C. Towards the end of the addition, anhydrous pyridine (10 mL) was added to improve the stirring of the resulting slurry. On completion of the addition of the acid chloride the reaction mixture was warmed to room temperature and stirred overnight. The mixture was transferred into water (800 mL) and dilute HCl (200 mL, 2M, aq.) was added. The resulting solid was collected by vacuum filtration, washed with dilute HCl (200 mL, 0.2M, aq.) followed by water (500 mL) and air-dried. A small sample of the crude product was recrystallised for characterisation. The following amides were prepared in this way.

1. 2-Fluoro-*N*-phenylbenzamide (**7a**) From 2-fluorobenzoyl chloride as an off-white powder (98%), mp 95 – 96 °C (lit.,[15] mp 99 °C).
2. 2-Chloro-*N*-phenylbenzamide (**7b**) From 2-chlorobenzoyl chloride as an off-white powder (97%), mp 116 – 118 °C (lit.,[15] mp 117 °C).
3. 2-Bromo-*N*-phenylbenzamide (**7c**) From 2-bromobenzoyl chloride as an off-white powder (99%), mp 114 – 116 °C (lit.,[15] mp 119 °C).
4. 2-Iodo-*N*-phenylbenzamide (**7d**) From 2-iodobenzoyl chloride as an off-white powder (93%), mp 143 – 145 °C (lit.,[16] mp 143 – 144 °C).
5. 2-Methoxy-*N*-phenylbenzamide (**7e**) From 2-methoxybenzoyl chloride as an off-white powder (90%), mp 76 – 78 °C (lit.,[17] mp 74 – 75 °C).
6. 2-Methyl-*N*-phenylbenzamide (**7f**) From 2-methylbenzoyl chloride as an off-white powder (99%), mp 124 – 126 °C (lit.,[18] mp 125 – 126 °C).

Preparation of 2-substituted benzophenones (**8**) by Vilsmeier-Haack reaction

Phosphorous oxychloride (104 mmol) was added dropwise over 30 min to a suspension of the *o*-substituted *N*-phenylbenzamide (77 mmol) in *N*-phenylpyrrolidine (111 mmol) at 50°C. On completion of the addition the resulting dark solution was heated to 150°C for 6 h. After cooling HCl (80 mL, 50% aq.) was added and the mixture was refluxed for 3 h. The cooled solution was poured into water (500 mL) and NaOH (100 mL, 2M, aq.) and extracted with dichloromethane (4 × 100 mL). The combined extracts were washed with NaOH (100 mL 0.2M, aq.), HCl (100 mL 0.2M, aq.) and finally with water (2 × 50 mL). The organic extracts were dried (anhyd. Na_2SO_4) and the solvent was removed to give the crude benzophenone. Purification was effected by either flash chromatography or by repeated recrystallisation. The following benzophenones were obtained in this way.

1. 2-Fluoro-4'-pyrrolidinobenzophenone (**8a**) From 2-fluoro-*N*-phenylbenzamide as pale yellow plates after recrystallisation from EtOAc / hexane (charcoal) (47%), mp 79 – 81 °C, ν_{max} (KBr) 1658, 1612, 1598, 1539 cm^{-1}, δ_H 2.04 (4H, m, $(CH_2)_2$), 3.38 (4H, m, $(NCH_2)_2$), 6.42 (2H, m, Ar-H), 7.21 (2H, m, Ar-H), 7.44 (2H, m, Ar-H), 7.77 (2H, m, Ar-H). Anal. Calcd for $C_{17}H_{16}NOF$: C, 75.8; H, 6.00; N, 5.2. Found: C, 75.7; H, 5.6; N, 5.0.

2. 2-Chloro-4'-pyrrolidinobenzophenone (**8b**) From 2-chloro-*N*-phenylbenzamide as pale yellow plates after flash chromatography (30% EtOAc / hexane) and recrystallisation from EtOAc / hexane (45%), mp 115 – 117 °C, ν_{max} (KBr) 1637, 1592, 1540 cm^{-1}, δ_H 2.04 (4H, m, $(CH_2)_2$), 3.38 (4H, m, $(NCH_2)_2$), 6.50 (2H, m, Ar-H), 7.37 (4H, m, Ar-H), 7.70 (2H, m, Ar-H). Anal. Calcd for $C_{17}H_{16}NOCl$: C, 71.4; H, 5.7; N, 4.9. Found: C, 71.3; H, 5.8; N, 4.9.

3. 2-Bromo-4'-pyrrolidinobenzophenone (**8c**) From 2-bromo-*N*-phenylbenzamide as off-white plates after flash chromatography (30% EtOAc / hexane) and recrystallisation from EtOAc / hexane (40%), mp 129 – 131 °C, ν_{max} (KBr) 1637, 1587, 1539 cm^{-1}, δ_H 2.03 (4H, m, $(CH_2)_2$), 3.36 (4H, m, $(NCH_2)_2$), 6.50 (2H, m, Ar-H), 7.28 (2H, m, Ar-H), 7.38 (1H, m, Ar-H), 7.61 (1H, dd, *J* 7.8, 0.7, Ar-H), 7.69 (2H, m, Ar-H). Anal. Calcd for $C_{17}H_{16}NOBr$: C, 61.8; H, 4.9; N, 4.2. Found: C, 61.6; H, 4.7; N, 4.2.

4. 2-Iodo-4'-pyrrolidinobenzophenone (**8d**) From 2-iodo-*N*-phenylbenzamide as pale yellow plates after recrystallisation from EtOAc / hexane (charcoal) (53%), mp 139 – 142 °C, ν_{max} (KBr) 1636, 1588, 1539 cm^{-1}, δ_H 2.04 (4H, m, $(CH_2)_2$), 3.35 (4H, m, $(NCH_2)_2$), 6.50 (2H, m, Ar-H), 7.09 (1H, m, Ar-H),

7.26 (1H, m, Ar-H), 7.40 (1H, m, Ar-H), 7.67 (2H, m, Ar-H), 7.87 (1H, dd, *J* 7.8, 3.0, Ar-H). Anal. Calcd for $C_{17}H_{16}NOI$: C, 54.1; H, 4.3; N, 3.7. Found: C, 54.0; H, 4.1; N, 3.7.

5. 2-Methoxy-4'-pyrrolidinobenzophenone (**8e**) From 2-methoxy-*N*-phenylbenzamide as pale yellow plates after recrystallisation from EtOAc / hexane (charcoal) (48%), mp 135 – 138 °C, ν_{max} (KBr) 1635, 1592, 1544 cm^{-1}, δ_H 2.03 (4H, m, $(CH_2)_2$), 3.37 (4H, m, $(NCH_2)_2$), 3.76 (3H, s, OMe), 6.49 (2H, m, Ar-H), 7.00 (2H, m, Ar-H), 7.28 (1H, dd, *J* 7.4, 1.7, Ar-H), 7.40 (1H, m, Ar-H), 7.74 (2H, m, Ar-H). Anal. Calcd for $C_{18}H_{19}NO_2$: C, 76.8; H, 6.8; N, 5.0. Found: C, 76.5; H, 7.0; N, 5.1.

6. 2-Methyl-4'-pyrrolidinobenzophenone (**8f**) From 2-methyl-*N*-phenylbenzamide as pale yellow plates after recrystallisation from EtOAc / hexane (charcoal) (60%), mp 95 – 97 °C, ν_{max} (KBr) 1631, 1591, 1541, 1525 cm^{-1}, δ_H 2.01 (4H, m, $(CH_2)_2$), 2.28 (3H, s, Me), 3.36 (4H, m, $(NCH_2)_2$), 6.48 (2H, m, Ar-H), 7.29 (4H, m, Ar-H), 7.72 (2H, m, Ar-H). Anal. Calcd for $C_{18}H_{19}NO$: C, 81.5; H, 7.2; N, 5.3. Found: C, 81.6; H, 7.4; N, 5.3.

Preparation of 1-aryl-1-(4-pyrrolidinophenyl)prop-2-yn-1-ols (**9**)

n-Butyllithium (2.5 M in hexanes) (33 mmol) was added slowly *via* syringe to a cold (-10 °C), stirred solution of trimethylsilylacetylene (33 mmol) in anhydrous tetrahydrofuran (100 mL) under a nitrogen atmosphere. On completion of the addition (*ca*. 5 min) the cold solution was allowed to stir for 1 h. The benzophenone (30 mmol) slurried in anhydrous tetrahydrofuran (50 mL) was then added in a single portion and the mixture stirred until TLC examination of the reaction mixture indicated that no benzophenone remained (*ca*. 3 h). The reaction mixture was then re-cooled to 0 °C and a solution of methanolic potassium hydroxide was added (from potassium hydroxide (60 mmol) in methanol (30 mL)) in a single portion. The cooling bath was removed and the mixture was warmed to rt, after *ca*. 15 min TLC indicated that de-protection was complete. The mixture was acidified to pH ~ 7 using glacial acetic acid and then poured into water (500 mL). The organic layer was separated and the aqueous layer was extracted with ethyl acetate (3 × 75 mL). The organic phases were combined, washed with water (2 × 100 mL) and dried (anhyd. Na_2SO_4). Removal of the solvent gave the prop-2-yn-1-ol that was sufficiently pure for subsequent use. Analytically pure samples were obtained by recrystallisation from hexane and ethyl acetate. The following alkynols were obtained in this way:

1. 1-(2-Fluorophenyl)-1-(4-pyrrolidinophenyl)prop-2-yn-1-ol (**9a**) From 2-fluoro-4'-pyrrolidino-benzophenone as a pale grey powder (82%), mp 145 – 148 °C, ν_{max} (KBr) 3372, 3295, 1613, 1601, 1537 cm^{-1}, δ_H 1.99 (4H, m, $(CH_2)_2$), 2.74 (1H, s, alkynic-H), 2.81 (1H, br s, OH), 3.25 (4H, m, $N(CH_2)_2$), 6.49 (2H, m, Ar-H), 7.03 (1H, m, Ar-H), 7.18 (1H, m, Ar-H), 7.29 (1H, m, Ar-H), 7.38 (2H, m, Ar-H), 7.70

(1H, m, Ar-H). Anal. Calcd for $C_{19}H_{18}NOF$: C, 77.2; H, 6.2; N, 4.7. Found: C, 77.0; H, 5.9; N, 4.4.

2. 1-(2-Chlorophenyl)-1-(4-pyrrolidinophenyl)prop-2-yn-1-ol (**9b**) From 2-chloro-4'-pyrrolidinobenzophenone as a pale grey powder (86%), mp 107 – 109 °C, ν_{max} (KBr) 3242, 1609, 1512 cm^{-1}, δ_H 1.98 (4H, m, $(CH_2)_2$), 2.83 (1H, s, alkynic-H), 3.10 (1H, br s, OH), 3.28 (4H, m, $N(CH_2)_2$), 6.51 (2H, m, Ar-H), 7.30 (5H, m, Ar-H), 7.99 (1H, m, Ar-H). Anal. Calcd for $C_{19}H_{18}NOCl$: C, 73.2; H, 5.8; N, 4.5. Found: C, 73.3; H, 5.7; N, 4.6.

3. 1-(2-Bromophenyl)-1-(4-pyrrolidinophenyl)prop-2-yn-1-ol (**9c**) From 2-bromo-4'-pyrrolidinobenzophenone as a pale grey powder (86%), mp 108 – 109 °C, ν_{max} (KBr) 3245, 1608, 1511 cm^{-1}, δ_H 1.98 (4H, m, $(CH_2)_2$), 2.84 (1H, s, alkynic-H), 3.10 (1H, br s, OH), 3.28 (4H, m, $N(CH_2)_2$), 6.50 (2H, m, Ar-H), 7.18 (1H, m, Ar-H), 7.32 (2H, m, Ar-H), 7.38 (1H, m, Ar-H), 7.55 (1H, dd, *J* 7.9, 1.2, Ar-H), 8.03 (1H, dd, *J* 7.9, 1.7, Ar-H). Anal. Calcd for $C_{19}H_{18}NOBr$: M^+, 355.0571(9) (^{79}Br). Found: M^+, 355.0574 (^{79}Br).

4. 1-(2-Iodophenyl)-1-(4-pyrrolidinophenyl)prop-2-yn-1-ol (**9d**) From 2-iodo-4'-pyrrolidinobenzophenone as an off-white powder (93%), mp 85 – 87 °C, ν_{max} (KBr) 3277, 1609, 1514 cm^{-1}, δ_H 1.99 (4H, m, $(CH_2)_2$), 2.85 (1H, s, alkynic-H), 2.93 (1H, br s, OH), 3.28 (4H, m, $N(CH_2)_2$), 6.49 (2H, m, Ar-H), 6.98 (1H, m, Ar-H), 7.28 (2H, m, Ar-H), 7.42 (1H, m, Ar-H), 7.92 (1H, dd, *J* 7.6, 1.2, Ar-H), 8.08 (1H, dd, *J* 7.8, 2.0, Ar-H). Anal. Calcd for $C_{19}H_{18}NOI$: C, 56.6; H, 4.5; N, 3.5. Found: C, 56.0; H, 4.2; N, 3.7.

5. 1-Phenyl-1-(4-pyrrolidinophenyl)prop-2-yn-1-ol (**9g**) From 4-pyrrolidinobenzophenone as a pale blue powder (96%), mp 138.5 – 140.0 °C, ν_{max} (Nujol) 3373, 3279, 2115, 1610, 1510 cm^{-1}, δ_H 1.72 (4H, m, $(CH_2)_2$), 2.54 (1H, br s, OH), 2.69 (1H, s, alkynic-H), 3.10 (4H, m, $N(CH_2)_2$), 6.35 (2H, m, Ar-H), 7.18 (5H, m, Ar-H), 7.45 (2H, m, Ar-H). Anal. Calcd for $C_{19}H_{19}NO$: C, 82.3; H, 6.9; N, 5.1. Found: C, 82.2; H, 6.6; N, 5.0.

Preparation of 3-aryl-3-(4-pyrrolidinophenyl)-3*H*-naphtho[2,1-*b*]pyrans (**10**)

A stirred solution of 2-naphthol (3.2 mmol) and the prop-2-yn-1-ol (3.2 mmol) in toluene (40 mL) was warmed to 50 °C. Acidic alumina (2.5g) was added and the mixture was refluxed until TLC indicated that none of the prop-2-yn-1-ol remained (*ca*. 1.5 h). The cooled mixture was filtered and the alumina was washed with hot toluene (2 × 50 mL). Removal of the toluene from the combined washings and filtrate gave a deep red gum that was eluted from silica (40% EtOAc / hexane) to afford the naphthopyran. The following naphthopyrans were obtained using this protocol:

1. 3-(2-Fluorophenyl)-3-(4-pyrrolidinophenyl)-3*H*-naphtho[2,1-*b*]pyran (**10a**) From 1-(2-fluorophenyl)-1-(4-pyrrolidinophenyl)prop-2-yn-1-ol and 2-naphthol as colorless microcrystals after recrystallisation from EtOAc / hexane (33 %), mp 186 – 189 °C, ν_{max} (KBr) 1611, 1520 cm^{-1}, δ_H 1.94 (4H, m, $(CH_2)_2$), 3.29 (4H, m, $N(CH_2)_2$), 6.43 (1H, dd, *J* 10.0, 4.6, 2-H), 6.48 (2H, m, Ar-H), 6.99 (1H, m, Ar-H), 7.10 (1H, m, Ar-H), 7.23 (6H, m, Ar-H, 1-H), 7.44 (1H, m, Ar-H), 7.64 (1H, d, *J* 8.8, Ar-H), 7.72 (2H, m, Ar-H), 7.94 (1H, d, *J* 8.5, Ar-H). Anal. Calcd for $C_{29}H_{24}NOF$: M^+, 421.1841(9); C, 82.6; H, 5.8; N, 3.3. Found: M^+, 421.1845; C, 82.5; H, 5.8; N, 3.3.

2. 3-(2-Chlorophenyl)-3-(4-pyrrolidinophenyl)-3*H*-naphtho[2,1-*b*]pyran (**10b**) From 1-(2-chlorophenyl)-1-(4-pyrrolidinophenyl)prop-2-yn-1-ol and 2-naphthol as pale purple microcrystals after recrystallisation from EtOAc / hexane (52%), mp 190 – 192 °C, ν_{max} (KBr) 1610, 1521 cm^{-1}, δ_H 1.98 (4H, m, $(CH_2)_2$), 3.24 (4H, m, $N(CH_2)_2$), 6.47 (2H, m, Ar-H), 6.60 (1H, d, *J* 10.4, 2-H), 7.28 (8H, m, Ar-H, 1-H), 7.47 (1H, m, Ar-H), 7.64 (1H, d, *J* 8.8, Ar-H), 7.71 (1H, d, *J* 8.0, Ar-H), 7.83 (1H, dd, *J* 7.3, 2.4, Ar-H), 7.95 (1H, d, *J* 8.4, Ar-H). Anal. Calcd for $C_{29}H_{24}NOCl$: $[M+H]^+$, 438.1624(7) (^{35}Cl); C, 79.5; H, 5.5; N, 3.2. Found: $[M+H]^+$, 438.1625 (^{35}Cl); C, 79.4; H, 5.4; N, 3.1.

3. 3-(2-Bromophenyl)-3-(4-pyrrolidinophenyl)-3*H*-naphtho[2,1-*b*]pyran (**10c**) From 1-(2-bromophenyl)-1-(4-pyrrolidinophenyl)prop-2-yn-1-ol and 2-naphthol as pale purple microcrystals after recrystallisation from EtOAc / hexane (68%), mp 174 – 176 °C, ν_{max} (KBr) 1609, 1520 cm^{-1}, δ_H 1.96 (4H, m, $(CH_2)_2$), 3.27 (4H, m, $N(CH_2)_2$), 6.48 (2H, m, Ar-H), 6.61 (1H, d, *J* 10.0, 2-H), 7.11 (1H, m, Ar-H), 7.21 (6H, m, Ar-H, 1-H), 7.46 (1H, m, Ar-H), 7.56 (1H, d, *J* 7.6, Ar-H), 7.65 (1H, d, *J* 8.8, Ar-H), 7.71 (1H, d, *J* 7.6, Ar-H), 7.81 (1H, dd, *J* 7.8, 1.6, Ar-H), 7.96 (1H, d, *J* 8.4, Ar-H). Anal. Calcd for $C_{29}H_{24}NOBr$: $[M+H]^+$, 482.1119(7) (^{79}Br); C, 72.2; H, 5.0; N, 2.9. Found: $[M+H]^+$, 482.1130 (^{79}Br); C, 72.0; H, 5.1; N, 2.6.

4. 3-(2-Iodophenyl)-3-(4-pyrrolidinophenyl)-3*H*-naphtho[2,1-*b*]pyran (**10d**) From 1-(2-iodophenyl)-1-(4-pyrrolidinophenyl)prop-2-yn-1-ol and 2-naphthol as pale purple microcrystals after recrystallisation from EtOAc / hexane (26%), mp 140 – 143 °C, ν_{max} (KBr) 1608, 1520 cm^{-1}, δ_H 1.96 (4H, m, $(CH_2)_2$), 3.25 (4H, m, $N(CH_2)_2$), 6.49 (3H, m, Ar-H, 2-H), 6.90 (1H, m, Ar-H), 7.34 (8H, m, Ar-H, 1-H), 7.64 (1H, d, *J* 8.8, Ar-H), 7.70 (2H, m, Ar-H), 7.95 (1H, m, Ar-H). Anal. Calcd for $C_{29}H_{24}NOI$: $[M+H]^+$, 530.0979(3); C, 65.8; H, 4.6; N, 2.6. Found: $[M+H]^+$, 530.0981; C, 65.5; H, 4.5; N, 2.4.

5. 3-(2-Methoxyphenyl)-3-(4-pyrrolidinophenyl)-3*H*-naphtho[2,1-*b*]pyran (**10e**) From 1-(2-methoxy-phenyl)-1-(4-pyrrolidinophenyl)prop-2-yn-1-ol and 2-naphthol as pale purple microcrystals

after recrystallisation from EtOAc / hexane (27%), mp 202 – 204 °C, ν_{max} (KBr) 1612, 1519 cm^{-1}, δ_H 1.93 (4H, m, $(CH_2)_2$), 3.22 (4H, m, $N(CH_2)_2$), 3.61 (3H, s, OMe), 6.43 (2H, m, Ar-H), 6.60 (1H, d, *J* 10.4, 2-H), 6.86 (1H, d, *J* 7.6, Ar-H), 6.93 (1H, m, Ar-H), 7.22 (6H, m, Ar-H, 1-H), 7.41 (1H, m, Ar-H), 7.62 (1H, d, *J* 8.4, Ar-H), 7.68 (1H, d, *J* 8.0, Ar-H), 7.73 (1H, dd, *J* 7.6, 1.6, Ar-H), 7.92 (1H, d, *J* 8.4, Ar-H). Anal. Calcd for $C_{30}H_{27}NO_2$ requires: $[M+H]^+$, 434.2120(1); C, 83.1; H, 6.3; N, 3.2. Found: $[M+H]^+$, 434.2122; C, 83.0; H, 6.3; N, 3.1.

6. 3-(2-Methylphenyl)-3-(4-pyrrolidinophenyl)-3*H*-naphtho[2,1-*b*]pyran (**10f**) From 1-(2-methylphenyl)-1-(4-pyrrolidinophenyl)prop-2-yn-1-ol and 2-naphthol as pale purple microcrystals after recrystallisation from EtOAc / hexane (42%), mp 163 – 165 °C, ν_{max} (KBr) 1611, 1520 cm^{-1}, δ_H 1.97 (4H, m, $(CH_2)_2$), 2.29 (3H, s, Me), 3.25 (4H, m, $N(CH_2)_2$), 6.16 (1H, d, *J* 10.0, 2-H), 6.48 (2H, m, Ar-H), 7.20 (8H, m, Ar-H, 1-H), 7.43 (1H, m, Ar-H), 7.49 (1H, m, Ar-H), 7.60 (1H, d, *J* 8.8, Ar-H), 7.68 (1H, d, *J* 8.0, Ar-H), 7.94 (1H, d, *J* 8.4, Ar-H). Anal. Calcd for $C_{30}H_{27}NO$: $[M+H]^+$, 418.21780(9); C, 86.3; H, 6.5; N, 3.4. Found: $[M+H]^+$, 418.2178; C,86.1 ; H, 6.5; N, 3.3.

7. 3-Phenyl-3-(4-pyrrolidinophenyl)-3*H*-naphtho[2,1-*b*]pyran (**10g**) From 1-phenyl-1-(4-pyrrolidino-phenyl)prop-2-yn-1-ol and 2-naphthol as off-white microcrystals after recrystallisation from EtOAc / hexane (82%), mp 187.5 – 189.5 °C, ν_{max} (KBr) 1613, 1519 cm^{-1}, δ_H 1.98 (4H, m, $(CH_2)_2$), 3.29 (4H, m, $N(CH_2)_2$), 6.28 (1H, d, *J* 9.9, 2-H), 6.55 (2H, m, Ar-H), 7.39 (11H, m, Ar-H, 1-H), 7.71 (2H, m, Ar-H), 7.99 (1H, m, Ar-H). Anal. Calcd for $C_{29}H_{25}NO$: C, 86.3; H, 6.3; N, 3.5. Found: C, 86.3; H, 6.1; N, 3.3.

CONCLUSION

A series of novel substituted 3*H*-naphtho[2,1-*b*]pyrans (**10**) has been obtained. On irradiation with UV light (**10**) undergo a reversible electrocyclic ring opening and isomerisation to the purple merocyanine valence tautomers. The steric effect of groups in the *ortho* position of a phenyl ring adjacent to the oxygen hetero-atom causes a dramatic increase in the lifetime of the colored form, which correlates with the size of the group.

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