Benzopentalenonaphthalenones from the intramolecular capture of a merocyanine derived from a naphthopyran†

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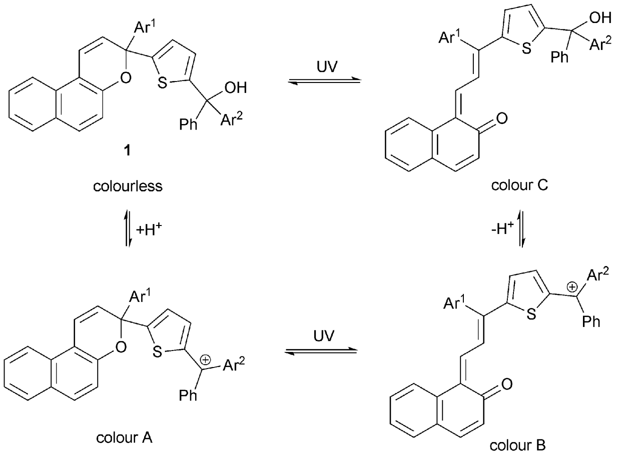
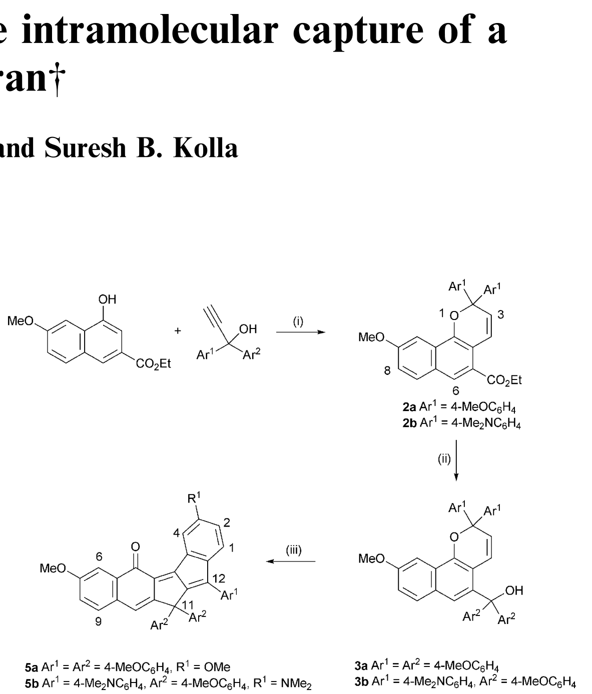
Novel, highly coloured benzopentalenonaphthalenones result from a cascade process initiated by the thermally-induced ring-opening of diarylmethanol substituted 2*H*-naphtho[1,2-*b*]pyrans in the presence of acid.

Interest in the design and properties of new functional dye systems[1] has increased at a steady rate over the last few years as a consequence of emerging technologies including dye sensitised solar cells[2] and organic conducting and emitting systems.[3] More established functional dye systems, such as those used for photochromism,[4,5] photodynamic therapy[6] and assorted sensor systems,[7] continue to attract attention. In particular, the control of various phenomena through the cycling sequence of a photochromic unit has recently been reviewed.[8]

Our interest of late has focussed upon cationic dye systems whose colour can be modulated by the switching of a photochromic naphthopyran unit.[9] 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 (Scheme 1). We now report our observations on the naphtho[1,2-*b*]pyran system **3**, wherein the cationic centre is generated adjacent to the naphthalene unit in close proximity to the photomerocyanine moiety.



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



Reagents and conditions: (i) acidic Al_2O_3, PhMe, reflux, ~ 2h; (ii) 4 eq. Ar^2Li, THF, N_2, -78 °C to rt then aq NH_4Cl; (iii) cat. 4-TsOH, PhMe, 60 °C overnight (Ar^1 = 4-$MeOC_6H_4$) or reflux 48 h (Ar^1 = 4-$Me_2NC_6H_4$)

Scheme 2 Synthesis of benzopentalenonaphthalenones **5**.

Alkyl 2,2-diaryl-2*H*-naphtho[1,2-*b*]pyran-5-carboxylates **2a, b** were readily prepared using the established acid-catalysed route from a 1,1-diarylprop-2-yn-1-ol and an alkyl 4-hydroxynaphthalene-2-carboxylate.[10] The addition of excess 4-methoxyphenyllithium to **2** at low temperature gave the diarylmethanols **3a, b** in good yield (Scheme 2).[11] The ^1H NMR spectra of these compounds displayed a readily identifiable doublet at δ 5.8 (J = 10.1 Hz) for the pyran ring proton, 3-H.[5]

Examination of the photochromic response of the new diarylmethanol substituted naphthopyran **3a** in CH_2Cl_2 solution (*ca.* 1×10^{-5} mol dm^{-3}) under irradiation with ultraviolet light (275–375 nm) resulted in the generation of a red solution with λ_{max} 514 nm which faded gradually to colourless upon cessation of irradiation. A solution of **3b** developed a weak blue colour with 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 donation 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.[5] Treatment of the colourless solutions of **3a, b** in CH_2Cl_2 with $MeSO_3H$ (98%, 2 μL injected directly into 10 mm path length cuvette) resulted in the development of an intense violet shade derived from the two new strong bands in the absorption spectrum [**3a** λ_{max} = 498 nm, ε_{max} = 7.87×10^4 mol^{-1} dm^3 cm^{-1}, λ_{max} = 648 nm, ε_{max} = 1.26×10^4 mol^{-1} dm^3 cm^{-1}, **3b** λ_{max} = 476 nm, ε_{max} = 5.11×10^4 mol^{-1} dm^3 cm^{-1}, λ_{max} = 568 nm, ε_{max} = 1.72×10^4 mol^{-1} dm^3 cm^{-1}, after dilution to *ca.* 1×10^{-6} mol dm^{-3}]. These bands are considered to arise from cation generation and compare favourably with unsymmetrically substituted

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triarylmethine dyes.[12] In marked contrast to the behaviour of **1**, irradiation of these acidic solutions of **3a, b** resulted in no appreciable change in their absorption spectra.†

In order to further explore this unexpected phenomenon, toluene solutions of **3** containing a catalytic amount of 4-TsOH were examined. Upon warming, the initial colour gradually intensified and after stirring at 60 °C for 20 h **3a** had been irreversibly converted into a new, intense coloured, turquoise species **5a** (76%) (Scheme 2).[13] The ^{1}H NMR spectrum of **5a** displayed signals at *ca.* δ 3.8 for four non-equivalent methoxy groups and a distinct singlet at δ 6.42. Additionally the ^{13}C NMR spectrum displayed a signal at δ 184 which is attributed to an α,β-unsaturated C=O group. The absence of any ^{1}H NMR signals that could be attributed to the pyran ring combined with a hydrogen atom count that was two hydrogen atoms too few for the predicted species **4** resulting from intramolecular trapping of the cation by the proximal extended π-system was also of note. Mass spectrometry confirmed the molecular formula of the product as $C_{43}H_{34}O_6$ and the pentacyclic structure **5a** was established by X-ray crystallography (Fig. 1).[14] Naphthopyran **3b** underwent a similar cyclisation process to afford **5b** (58%) though more forcing reaction conditions were required (48 h, 100 °C). Pentalenones **5a, b** exhibited two absorption bands with the longer wavelength band bathochromically shifted relative to that of their respective precursors with **5a** (turquoise) λ_{max} = 586 nm, ε_{max} = 1.06 × 10^4 mol^{-1} dm^3 cm^{-1}, λ_{max} = 376 nm, ε_{max} = 1.59 × 10^4 mol^{-1} dm^3 cm^{-1} and **5b** (violet) λ_{max} = 545 nm, ε_{max} = 1.61 × 10^4 mol^{-1} dm^3 cm^{-1}, λ_{max} = 370 nm, ε_{max} = 1.04 × 10^4 mol^{-1} dm^3 cm^{-1} (CH_2Cl_2), respectively, which is presumably a consequence of the extended conjugated pathway coupled with the fixed planar arrangement of the fused rings. There was no evidence of any aggregation of these dyes in CH_2Cl_2 solution from dilution experiments, a feature attributed to the geminal diaryl groups (Ar^2) which are directed above and below the main plane of the molecule.

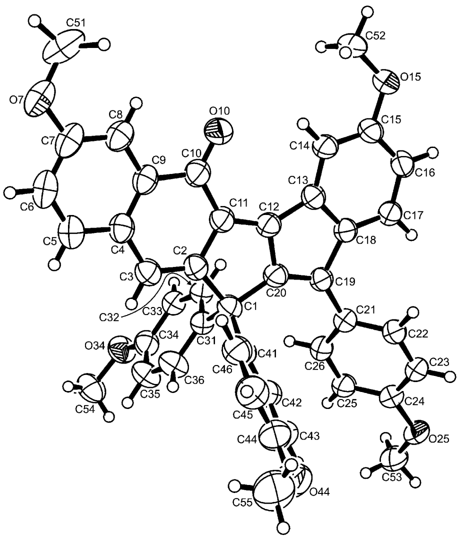
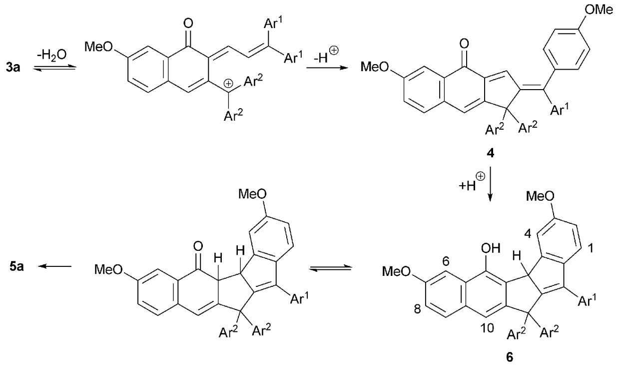
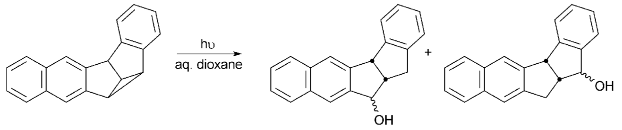


Fig. 1 X-Ray crystal structure of **5a** with thermal ellipsoids scaled at the 50% probability level.



Scheme 3 Proposed mechanism for the formation of **5a**.



Scheme 4 Photochemical rearrangement of the benzo-2,3-naptho-barrelene sysetm.

The formation of **5** may be rationalised by a cascade process involving initial intramolecular trapping of the cation to presumably afford **4**. The latter subsequently undergoes a second intramolecular cyclisation to the naphthol **6**, tautomerisation of which followed by aerial oxidation results in the generation of the stabilising, extended conjugated π system (Scheme 3). In order to establish the proposed mechanism, a solution of **3a** in degassed toluene under N_2 containing 4-TsOH was stirred for 5 days at rt; work-up and column chromatography afforded a pale blue solid whose initial ^{1}H NMR spectrum indicated the presence of a small amount of **5a** [*ca.* 3%, δ_H 7.80 (d, 6-H), 8.51 (1H, d, 4-H)] together with the major component which was identified as the naphthol **6** [^{1}H NMR δ 5.23 (s) 4_b-H, δ 5.55 (s) OH (D_2O exchange) and δ 7.12 (s) 10-H]. An OH stretch at 3372 cm^{-1} and the absence of a significant C=O signal in the ^{13}C NMR spectrum supported this assignment. Interestingly, re-recording the ^{1}H NMR spectrum of the initial solution after 16 hours indicated an increased proportion (*ca.* 15%) of **5a**, presumably generated by the facile air oxidation process.

The thermally induced ring-opening of a naphthopyran unit and subsequent trapping of the merocyanine with a proximal cationic centre provides a reasonably efficient route to this unusual unsaturated pentacyclic system and interesting new dyes. To our knowledge the only other report of the benzo[5,6]pentaleno[1,2-*b*]naphthalene ring system appears in an exploratory mechanistic study concerned with the photochemical rearrangement of the benzo-2,3-naphthobarrelene system (Scheme 4).[15] The conversion of pyrans and their benzologues into carbocycles is particularly rare although examples are known.[16] Further examination of the synthesis of these systems and their application are ongoing.

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11 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/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} = 514, 429 nm (CH_2Cl_2) then 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 (1 H, s, OH), 3.76 (6 H, s, OMe), 3.82 (6 H, s, OMe), 3.92 (3 H, 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 $[M + Na]^+$ = 689.2503 $C_{43}H_{38}O_7$ requires $[M + Na]^+$ = 689.2510.

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13 3,7-Dimethoxy-11,11,12-tris(4-methoxyphenyl)-11*H*-benzo[5,6]-pentaleno[1,2-*b*]naphthalene-5-one **5a** as deep purple microcrystals 0.37 g (76%) after elution from silica with 5% ethyl acetate in toluene and recrystallisation from acetone/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 $[M + H]^+$ = 647.2419 $C_{43}H_{34}O_6$ requires $[M + H]^+$ = 647.2428.

14 Crystal data for **5a** crystallised from CH_2Cl_2/hexane by vapour diffusion: $C_{43}H_{34}O_6$, M = 646.7, monoclinic, space group $C2/c$, a = 23.5830(17) Å, α = 90°, b = 16.0599(13) Å, β = 96.983(3)°, c = 17.8227(15) Å, γ = 90°, volume = 6700.1(9) Å^3, ρ_{calcd} = 1.282 Mg m^{-3}, T = 150(2) K, Z = 8, 51 816 reflections measured, independent reflections 7460 $R_{(int)}$ = 0.0785, R_1 = 0.0611 ($I > 2\sigma(I)$), wR_2 (all data) = 0.1930. Full data are provided in the ESI†.

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