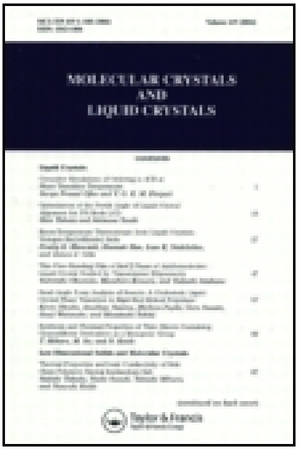

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Synthesis and Photochromic Properties of 2H,9H-Indeno[1,2-f]- and 3H,7H-Indeno[2,1-i]- naphtho[2,1-b]pyrans

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Synthesis and Photochromic Properties of 2*H*,9*H*-Indeno[1,2-*f*]- and 3*H*,7*H*-Indeno[2,1-*i*]-naphtho[2,1-*b*]pyrans

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Expedient syntheses of the 3-hydroxy- and 6-hydroxy- derivatives of 11H-benzo[a]-fluoren-11-one, obtained via Suzuki-Miyaura couplings are described. Reactions of these phenols with 1,1-diarylprop-2-yn-1-ols give indeno[2,1-i]- and indeno[1,2-f]-naphtho[2,1-b]pyranones respectively. The photochromic properties of these and the reduced derivatives are reported. A rationale for the pronounced hypsochromic shift in λ_{max} *of the photomerocyanine from a 2H,9H-indeno[1,2-f]naphtho[2,1-b]pyran is presented.*

Keywords: indenonaphthopyran; naphthopyran; photomerocyanine; Suzuki coupling

INTRODUCTION

The isomeric naphthopyrans **1** and **2** are currently the most commercially important class of photochrome and are extensively employed in a variety of variable transmission devices. Both **1** and **2** exhibit T-type (thermally reversible) photochromism [1], due to electrocyclic ring opening to a merocyanine valence tautomer 3 (Scheme 1).

The photomerocyanines from **1** exhibit slower fading kinetics, greater colourability and have $\lambda_{\max}$ bathochromically shifted compared to those from **2** (i.e. **3**). Much work has centred on efforts to improve the fading

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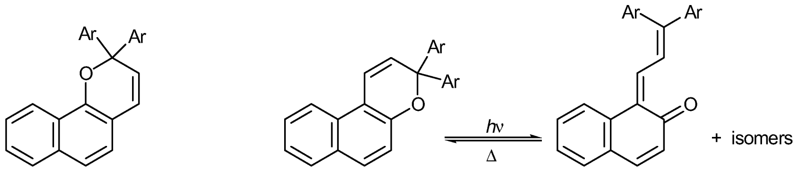


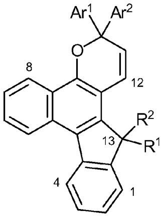
1
2*H*-Naphtho[1,2-*b*]pyran

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

3
Merocyanine
coloured form

SCHEME 1

kinetics of **1** and enhance the colourability of **2**. In particular, a considerable number of fused-ring naphthopyrans has been obtained. Thus, the indenonaphthopyrans **4** [2] ($R^1 = H$, alkyl, $R^2 = H$, alkyl, aryl; $R^1 = R^2 = NR_2$) containing an embedded naphtho[1,2-*b*]pyran core have been obtained. The isomeric systems 5 have also been described [3]. The pyran moiety in **5** can be reconfigured to give an alternative series of indenonaphthopyrans exemplified by **6** [3], **7** [4a] and **8** [4b]. Heterocyclic analogues of **8** have recently been reported [4c].



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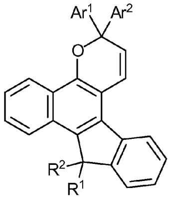

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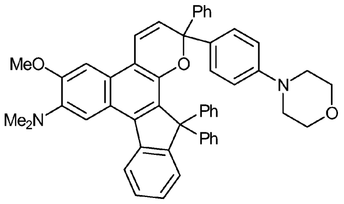

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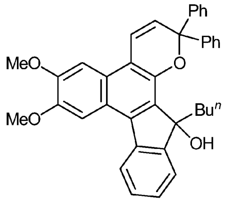

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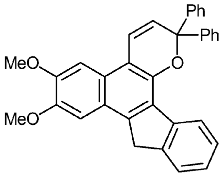

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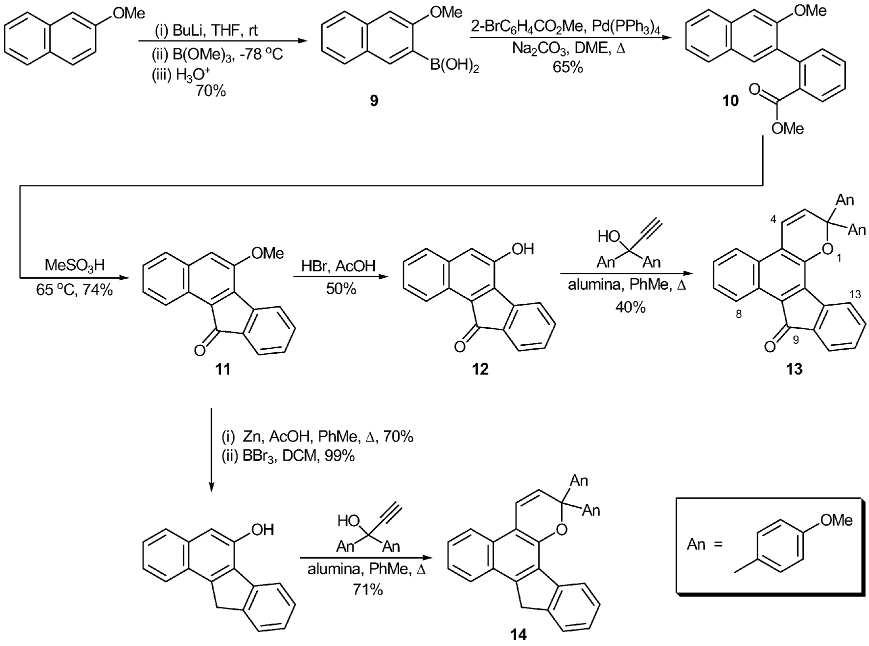
RESULTS AND DISCUSSION

The indeno[1,2-*f*]naphtho[2,1-*b*]pyran **8** has been obtained *via* acylation of 2-indanone with 3,4-dimethoxyphenylacetyl chloride [4b]. We now report an alternative route to indeno systems (cf. **8**) which offers greater flexibility in terms of accessibility of starting materials and substitution patterns which may be achieved. The requisite starting material, 6-hydroxy-11*H*-benzo[*a*]fluoren-11-one is obtained *via* Suzuki-Miyaura coupling of methyl 2-bromobenzoate to the readily available boronic acid **9**. Subsequent intramolecular Friedel-Crafts acylation provides **11** and thus **12** in high yield (Scheme 2). This approach to **11** represents an alternative to the current literature procedure, which utilises the directed remote metallation of an analogue of **10** in which the CO_2Me function is replaced by $CONPr^{i}_{2}$ [5].

Acid catalysed condensation of **12** with 1,1-di(4-methoxyphenyl)-prop-2-yn-1-ol gave the 2*H*,9*H*-indeno[1,2-*f*]naphtho[2,1-*b*]pyran-9-one **13** [6] in moderate yield.

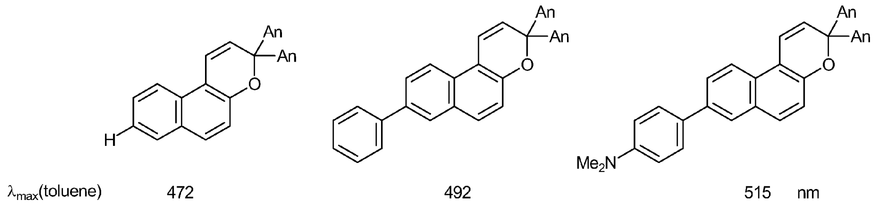
The reduced system **14** could be efficiently obtained by reduction and demethylation of **11** to give 6-hydroxy-11*H*-benzo[*a*]fluorene and subsequent reaction with the propynol.

Electron donating substituents at C-8 in naphtho[2,1-*b*]pyrans induce bathochromic shifts in λ_{max} of the photomerocyanine valence isomer [1,7]. The route outlined in Scheme 2 provides an efficient

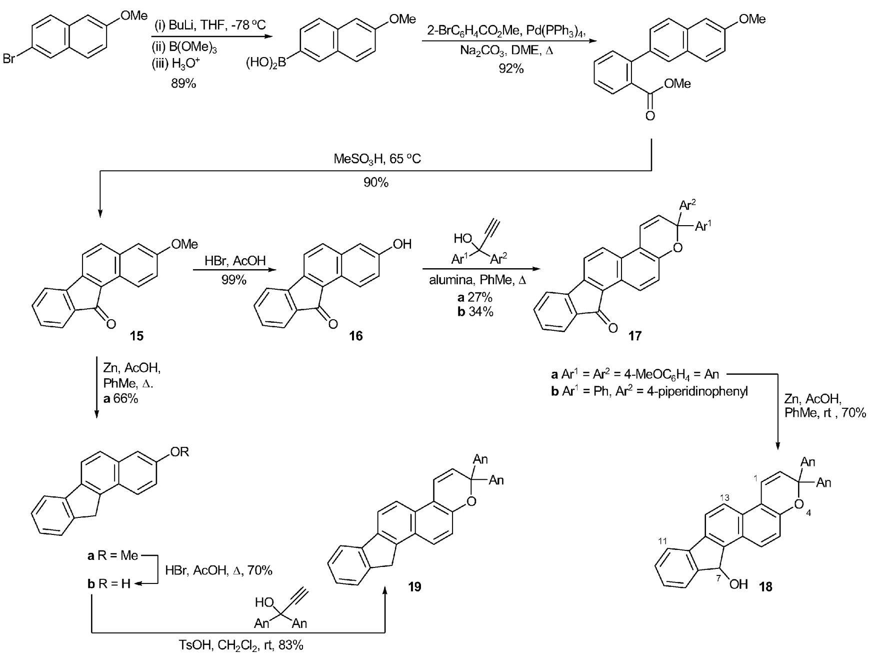


SCHEME 2

entry to the hitherto inaccessible compounds **13** and **14**. With access to these systems it was of interest to extend this approach to the synthesis of indeno[2,1-*i*][2,1-*b*]napthopyrans, conformationally rigid analogues of 8-phenylnaphtho[2,1-*b*]pyrans.

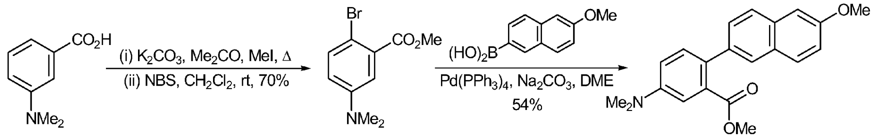


The required starting materials, 3-(alk)oxy-11*H*-benzo[*a*]fluorenes **15** and **16** were obtained via Suzuki methodology from 6-bromo-2-methoxynaphthalene (Scheme 3) and subsequently converted to the fluorenones **17a** [8] and **17b**, fluorenol **18** and the fluorene derivative **19**.



SCHEME 3

Attempts to obtain 9-dialkylamino derivatives of e.g. **17** or **19**, could not be realised owing to the reluctance of the ester **20**, or its derivatives to cyclise. Further studies in this area are in progress.



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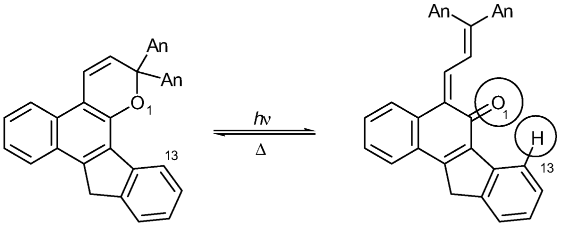
PHOTOCHROMIC PROPERTIES

Surprisingly, the indenonaphthopyranone **13** did not exhibit any observable photochromic response at ambient temperature, the compound was strongly coloured and gave a yellow-orange solution [λ_{max}(PhMe) = 443 nm]. In contrast, the fluorene **14** exhibited colourless → orange photochromism (λ_{max} = 461 nm, $t_{1/2}$ = 2 s). In the case of the indeno[2,1-*i*]-naphthopyranones **17a** and **17b**, the former exhibited a very weak photochromic response (λ_{max} = 463 and 584 nm, $t_{1/2}$ = 50 s), whereas the latter provided only an orange solution (λ_{max} = 457 nm). The reduced derivatives **18** (λ_{max} = 492 nm, $t_{1/2}$ = ca. 1.5 s) and **19** (λ_{max} = 495 nm, $t_{1/2}$ = ca. 1.5 s) exhibit identical properties to the 3,3-dianisyl-8-phenylnaphtho[2,1-*b*]pyran (*vide supra*). The effective absence of a photochromic response in the fluorenones **13** and **17a,b** is remarkable and merits further investigation. The pronounced hypsochromic shift of λ_{max} of the photomerocyanine **13A** presumably stems from steric destabilisation arising from interaction of O-1 with H-13.



13 **13A**

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[6] ^{1}H NMR data for 2,2-di(4-methoxyphenyl)-2*H*,9*H*-indeno[1,2-*f*]naphtho [2,1-*b*] pyran-9-one 13, δ_{H}(DMSO-d_6, 400 MHz) 8.65 (1H, m, H-8), 8.04 (1H, m, H-5), 7.82 (1H, br.d, H-10), 7.55–7.45 (3H, m, Ar-H), 7.43–7.35 (2H, m, Ar-H), 7.32–7.23 (5H, m, 1 × Ar-H and 4 × C_6H_4OMe), 6.82, (4H, AA′BB′, $J_{\mathrm{app.}} = 8.8$ Hz, C_6H_4OMe), 6.64 (1H, d, $J = 10.0$ Hz, H-3), 3.59 (6H, s, OMe).

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[8] ^{1}H NMR data for 3,3-di(4-methoxyphenyl)-3*H*,7*H*-indeno[2,1-*i*]naphtho[2,1-*b*]pyran-7-one **17a**, δ_{H}(CDCl$_3$, 400 MHz) 8.82 (1H, d, $J = 9.2$ Hz, H-6), 8.10 (1H, br.d, Ar-H), 7.62–7.54 (2H, m, Ar-H), 7.46–7.35 (6H, m, 2 × Ar-H and 4 × C_6H_4OMe), 7.29–7.19 (3H, m, Ar-H), 6.85 (4H, AA′BB′, $J_{\mathrm{app.}} = 8.8$ Hz, C_6H_4OMe), 6.24 (1H, d, $J = 10.0$ Hz, Hz, H-2).