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Photochromic bi-naphthopyrans

Stuart Aiken [a], Christopher D. Gabbutt [a], B. Mark Heron [a, *], Suresh B. Kolla [b]

[a] Department of Chemical Sciences, School of Applied Sciences, University of Huddersfield, Queensgate, Huddersfield HD1 3DH, UK
[b] School of Chemistry, The University of Leeds, Woodhouse Lane, Leeds LS2 9JT, UK

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ABSTRACT

A series of novel 3-aryl-(3,3-diaryl-3*H*-naphtho[2,1-*b*]pyran-8-yl)-3*H*-naphtho[2,1-*b*]pyrans has been accessed from 6-bromo-2-naphthol *via* a four step transformation. Acylation of the dianion derived from the treatment of 6-bromo-2-naphthol with *n*-butyllithium with Weinreb amides and subsequent reaction with a 1,1,-diarylprop-2-yn-1-ol gave 8-aroyl-3*H*-naphtho[2,1-*b*]pyrans in good yield. Addition of lithium trimethylsilylacetylide to the foregoing 8-aroylnaphthopyrans proceeded smoothly with base-mediated desilyation to afford the target bi-naphthopyrans upon acid-catalysed reaction with 2-naphthol. Preliminary evaluation of the photochromic response of the new bi-naphthopyrans revealed reversible independent naphthopyran ring-opening leading to a complex photochromic signature.

1. Introduction

There has been sustained interest in the design and synthesis of photochromic naphthopyrans for commercial application in ophthalmic lenses for at least the last 20 years [1]. The synthesis and photochromic response (in a variety of solvents and polymers and at differing temperatures) of an increasing number of more structurally complex naphthopyrans has appeared in the scientific literature over the last few years [2–5]. Amongst these examples are systems in which two 3*H*-naphtho[2,1-*b*]pyran units are linked together through one of the C-3 substituents e.g. **1** [6], **2** [7], **3** [8] and **4** [9] (Fig. 1) to afford bi-naphthopyrans.

Two examples of symmetrical bi-naphthopyrans linked through the 8,8′-positions (**5** and **6**) have been described in the literature to date (Fig. 2). In **5** competition between fluorescence and photochromism was observed which was dependent upon the number of thienyl units [10]. The latter weakly photochromic example, **6**, was accessed by an electrochemical dimerisation [11].

Attracting somewhat lesser attention, perhaps as a consequence of their relative inaccessibility, are bi-naphthopyrans in which the two naphthopyran units bear different *geminal* aryl groups and thus provide the opportunity to develop different coloured photomerocyanines upon irradiation. Furthermore, as far as we are able to ascertain there appear to be no examples of bi-naphthopyrans in which one naphthopyran unit serves as the '3-aryl substituent' on a second naphthopyran unit.

Previous studies of substituent effects on the photochromism of 3*H*-naphtho[2,1-*b*]pyrans have revealed that the presence of a methoxy group at the 8-position leads to a bathochromic shift in absorption maximum of the photomerocyanine coupled with enhanced intensity [3,4]. Given this interesting photochromic response of 8-substituted naphtho[2,1-*b*]pyrans we were interested in examining the influence on the photochromic properties of linking two naphthopyran units together involving the 8-position of one naphthopyran and the *para*-position of one of the *geminal* aryl groups of the second naphthopyran. This study predominantly describes our investigation of the synthesis and a preliminary survey of absorption properties of a series of novel linked naphthopyrans wherein the typical C-2 aryl substituent of a 3*H*-naphtho[2,1-*b*]pyran is replaced by a 3,3-diaryl-3*H*-naphtho[2,1-*b*]pyran-8-yl unit leading to a molecule that contains two different photoactive pyran rings.

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 $CDCl_3$

* Corresponding author. Tel.: +44 (0)1484 471728.
E-mail addresses: m.heron@hud.ac.uk, b_mark_heron@hotmail.co.uk (B.M. Heron).

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0143-7208/

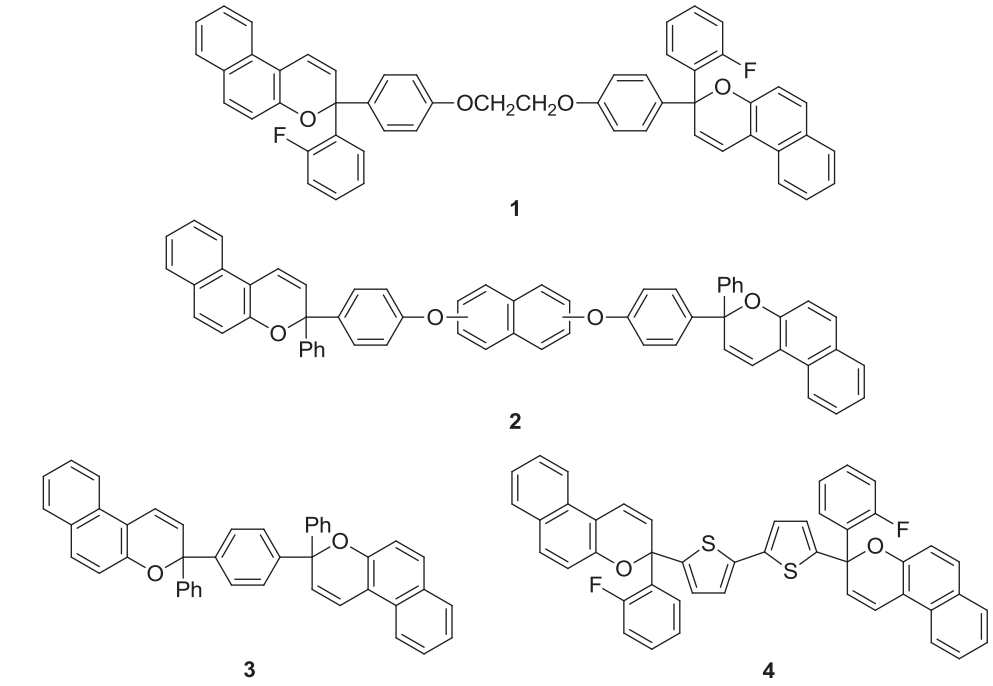

Fig. 1. Selected examples of bi-naphthopyrans.

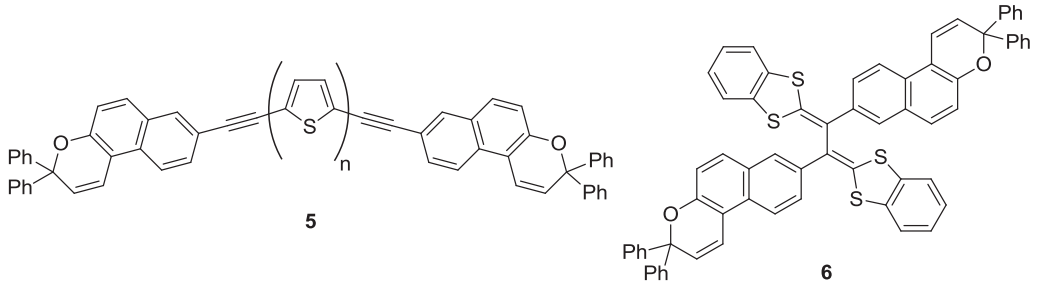

Fig. 2. Symmetrical 8,8′-bi-naphthopyrans.

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.* $1 \times 10^{-4} - 10^{-6}$ moldm^{-3}) using a Cary 50 Probe spectrophotometer equipped with a single cell Peltier temperature controlled (10 and 22 °C) stirred cell attachment with activating irradiation provided by a Spectroline 8 W lamp. All 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 independently at the National EPSRC Mass Spectrometry Service Centre, Swansea. 1-Phenyl-1-(4-pyrrolidinophenyl)prop-2-yn-1-ol **11a** [12] 1-(2-fluorophenyl)-1-(4-pyrrolidinophenyl)prop-2-yn-1-ol **11b** [12] and 1-(4-fluorophenyl)-1-(4-phenyl)prop-2-yn-1-ol **11c** [6] were prepared according to our published procedures.

2.2. Preparation of Weinreb amides *7a, b*

4-Fluorobenzoyl chloride (15 g, 94.6 mmol) and *N,O*-dimethylhydroxylamine hydrochloride (10.1 g, 104 mmol) were dissolved in $CHCl_3$ (200 mL) and stirred at room temperature. The solution was cooled to 0 °C and pyridine (17.3 mL, 230 mmol) was added. The mixture was warmed and stirred at room temperature for 1 h and then poured into aq. sat. NaCl solution (300 mL). The organic layer was separated and the aqueous layer extracted with CH_2Cl_2 (3 × 100 mL). The combined organic layers were washed with water (3 × 50 mL), dried (anhyd. Na_2SO_4) and then evaporated. The crude *4-fluoro-N-methoxy-N-methylbenzamide* **7a** was purified *via* distillation under vacuum to afford a colourless liquid (96%), bp = 120 °C at 0.3 mmHg (lit. b.p. 70 °C at 0.1 mmHg [13]); ν_{max} 583, 905, 918, 1262, 1375, 1508, 1582, 1630, 2972, 3274 cm^{-1}; δ_H 3.34 (3H, s, CH_3), 3.52 (3H, s, OCH_3), 7.08 (2H, m, Ar–H), 7.73 (2H, m, Ar–H).

2.2.1. 2,4-diflouro-N-methoxy-N-methylbenzamide *7b*

From 2,4-difluorobenzoyl chloride using an identical protocol as for amide **7a**, as a colourless liquid after vacuum distillation in 89% yield, bp = 125 °C at 0.3 mmHg; ν_{max} 489, 583, 679, 852, 967, 984, 1099, 1207, 1613, 2939 cm^{-1}; δ_H 3.35 (3H, s, CH_3), 3.56 (3H, bs, OMe), 6.91 (2H, m, Ar–H), 7.51 (1H, m, Ar–H). Key ^{1}H NMR signals were in agreement with those reported in the literature [14].