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Photochromism of some thienobenzopyrans

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Dedicated to Dr. A.T. Peters in appreciation of his contributions to colour chemistry

Abstract

Some novel thienobenzopyrans have been synthesised and their photochromic properties are discussed.

Keywords: Photochromism; Thienobenzopyrans; NMR spectroscopy

1. Introduction

The synthesis and photochromic properties of naphthopyrans has been the subject of several reviews [1–3]. Much of the early work focused on the synthesis of 3-spirocycloalkane- and 3-alkyl-3-aryl-3*H*-naphtho[2,1-*b*]pyrans **1** [4]. The move to 3,3-diaryl substitution led to significant improvements in both fatigue resistance and the intensity of photo-generated colour [5]. The isomeric 2,2-diaryl-2*H*-naphtho[1,2-*b*]pyrans **2** were initially much less studied probably as a consequence of the very slow rate of fade of the photo-generated colour when compared to **1**. However, this problem of slow fade was addressed in our research disclosure [6] which demonstrated that a substituent at the 5-position of **2** brings about a dramatic increase in the rate of fade, such that 2*H*-naphtho [1,2-*b*]pyrans are often the compounds of choice for imparting photochromic properties to ophthalmic lenses [7].

The intense activity directed towards the synthesis of novel 5-substituted photochromic 2*H*-naphtho [1,2-*b*]pyrans stimulated by this disclosure [6] has led to a variety of substituted naphthopyrans [7], pyrans fused to carbocyclic rings [8], indenopyrans [9] and some heterobenzopyrans e.g. pyranocarbazoles [10] and thieno- and furo-benzopyrans [11]. We now report some of our earlier findings on the synthesis and photochromic properties of some heterobenzopyrans.

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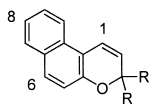

3*H*-naphtho[2,1-*b*]pyran

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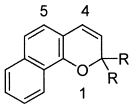


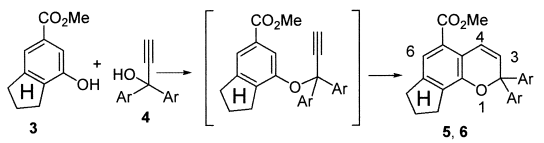
2*H*-naphtho[1,2-*b*]pyran

2

2. Results and discussion

The most convenient synthetic route to thienobenzopyrans **5** and **6** relies upon the one-pot, acid-catalysed etherification of a hydroxybenzothiophene **3** with a 1,1-diarylprop-2-yn-1-ol **4**. An initially formed ether readily undergoes a Claisen rearrangement followed by sigmatropic H-shifts and a subsequent electrocyclic ring closure to afford **5** and **6** (Scheme 1, Table 1). The hydroxybenzo-thiophenes **3** were readily obtained by extending the established Stobbe condensation-ring closure route to naphthols from an aromatic aldehyde [12] to heteroaromatic aldehydes.

The signal for 3-H in the ^{1}H NMR spectra of **5** and **6** appears as a doublet in the range δ 6.0 to δ 6.5 with $J_{3,4}$ ca. 10Hz. 4-H resonates downfield of 3-H at ~δ 7.6 as a consequence of its benzylic disposition and is relatively unaffected by the *peri* carbonyl function. Interestingly, in the ^{1}H NMR spectra of the aminoaryl substituted thieno[2,3-*h*]benzopyrans **5c–f** 6-H appears as a doublet at ca. δ 8.0 with $J_{6,9}$~0.7 Hz, the magnitude of this coupling is comparable with that observed for simple 4-hydroxy substituted benzo[*b*]thiophenes [13]. No such coupling was observed between 6-H and 9-H for **5a,b** or the [3,2-*h*] fused isomers **6a,b**. The remaining signals in the ^{1}H NMR spectrum of **5** and **6** appear in the regions expected for the individual structural types and in accord with the nature of the substituents.

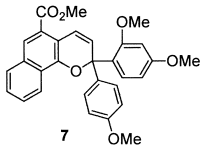


3 **4** **5, 6**

Scheme 1.

The photochromic process of the naphtho[1,2-*b*]pyran unit is well documented [2,3] and relies upon a reversible 6 π electrocyclic ring opening of the pyran ring under UV irradiation to afford an intensely coloured dienone that can interconvert to a number of isomers and rotamers (Scheme 2).

The model naphthopyran **7** with λ_{max} 490 nm and $t_{1/2}$, 450 s was the standard chosen to assess the influence of hetero-ring fusion [14].



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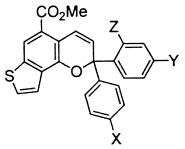
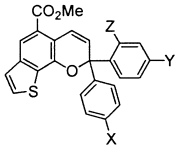
A direct comparison of the photochromic properties of the 2,2-di(4-methoxyphenyl) derivatives of the thiophene fused systems **5a** and **6a** is only of qualitative value since the lifetime of the ring opened forms of **6a** was short. Nonetheless, it is clear that there is a major difference in stability of the coloured forms of the two thienobenzopyran isomers **5a** and **6a**.

In order to obtain more meaningful spectroscopic data, an *o*-methoxy substituent was incorporated into one of the *gem*. aryl rings. It is well established that the presence of an *ortho*-substituent on a 3-aryl substituent in naphtho[2,1-*b*]pyrans decreases the rate of ring closure of the coloured form [15] and a similar situation obtains for the 2-aryl substituents in the [1,2-*b*] isomers. The data in Table 1 for compounds **5b** and **6b** further substantiate this feature. It is noted that an *o*-methoxy group has only a small effect on λ_{max} of the open form.

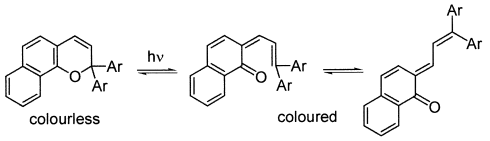
The π-electron rich nature of the thiophene ring brings about a red shift of λ_{max}, with both isomers **5b** and **6b** absorbing at ca. 15 nm longer wavelength than the naphthopyran **7**. However, the mode of fusion has a pronounced effect on the rate of fade with the [2,3-*h*] isomer **5b** fading two orders of magnitude slower than the [3,2-*h*] analogue **6b**.

The influence of substitution in the *geminal* diaryl function by groups other than methoxy on the photochromic properties of the thieno[2,3-*h*][1]benzopyrans **5** was also explored. The introduction of NMe_2 groups in the *para* positions of the diaryl

Table 1
Spectroscopic data for thienobenzopyrans **5** and **6**

Structure	No.	X	Y	Z	λ_{max}[a]	$t_{1/2}$[a] (s)
	**5a**	MeO	MeO	H	503	640
	5b	MeO	MeO	MeO	504	1550
	5c	Me_2N	Me_2N	H	605	< 0.5
	5d	Me_2N	Me_2N	Me	600	2
	5e	Morph[b]	H	H	545	< 0.5
	5f	Morph[b]	H	Cl	548	270
	**6a**	MeO	MeO	H	498	< 0.5
	6b	MeO	MeO	MeO	507	15

[a] λ_{max} and $t_{1/2}$ were obtained for solutions of **5–6** in spectroscopic grade toluene at 20°C after irradiation to a constant intensity.
[b] Morph represents a morpholino substituent.



Scheme 2.

groups **5c** resulted in a dramatic decrease in $t_{1/2}$, such that λ_{max} could only be obtained on cooling the solution. The incorporation of an *ortho* methyl group **5d** increased $t_{1/2}$ to 2 s with a λ_{max} of 600 nm. The observation that each NMe_2 function induces a bathochromic shift of λ_{max} of ~50 nm is in accord with our previous observations [3].

A cyclic amino function exerts a similar effect to a dimethylamino group, with one morpholine substituent bringing about a red shift of 42 nm in **5e** relative to **5a**. The enhanced kinetics of ring closure associated with a 4-aminophenyl group and its modification by an *ortho* substituent are again apparent, cf. **5f** vs. **5e**.

3. 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 using a Hewlett Packard 8452A diode array spectrophotometer. Samples were irradiated using a Spectroline 8 W lamp (366 nm). NMR spectra were recorded on a Jeol λ 400 MHz instrument for solutions in $CDCl_3$; *J* values are given in Hz. Flash chromatographic separations were performed on Sorbsil™ C560 silica gel as supplied by Fluorochem Ltd.

3.1. General method for the preparation of the thienobenzopyrans 5 and 6

Aluminium oxide, activated, acidic, Brockmann 1, ~150# (5 g) was added to a stirred solution of the hydroxybenzothiophene **3** (6.9 mmol) and the 1,1-diarylprop-2-yn-1-ol **4** (6.9 mmol) in anhydrous toluene (75 cm^3). The mixture was then heated until TLC examination of the reaction mixture indicated that no hydroxybenzothiophene remained (ca. 2 h). The mixture was allowed to cool and then diluted with water (100 cm^3). The organic phase was separated and the aqueous phase extracted with ethyl acetate (50 cm^3). The combined organic extracts were washed with water (50 cm^3), dried and evaporated to give a red/brown gum which was purified by flash chromatography and recrystallisation. The following thienobenzopyrans were obtained by this protocol.

*3.1.1. Methyl 2,2-di(4-methoxyphenyl)thieno[2,3-*h*][1]benzopyran-5-carboxylate* **5a**

As colourless micro-crystals (59%) after elution from silica with 30% ethyl acetate in hexane and recrystallisation from EtOAc and hexane, m.p. = 95.0–97.0°C; ν_{max} (KBr) 1715, 1609, 1511, 1280, 1251, 1036; δ_H 3.75 (6H, s, OMe), 3.89 (3H, s, CO_2Me), 6.14 (1H, d, *J* 10.3, 3-H), 6.81 (4H, m, Ar-H), 7.36 (4H, m, Ar-H), 7.46 (1H, d, *J* 5.5, 8-H), 7.55 (1H, d, *J* 5.4, 9-H), 7.64 (1H, d, *J* 10.3, 4-H), 8.05 (1H, s, 6-H) (Found: C, 70.6; H, 4.8; S, 7.0; MH^+, 459.1261. $C_{27}H_{22}O_5S$ requires C, 70.7; H, 4.85; S, 7.0 %; MH^+, 459.1266).

*3.1.2. Methyl 2-(2,4-dimethoxyphenyl)-2-(4-methoxyphenyl)thieno[2,3-*h*][1]benzopyran- 5-carboxylate* **5b**

As colourless micro-crystals (64%) after elution from silica with 30% ethyl acetate in hexane and recrystallisation from EtOAc and hexane, m.p. 143.0–144.5°C; ν_{max} (KBr) 1713, 1608, 1503, 1285, 1033; δ_H 3.56 (3H, s, OMe), 3.74 (3H, s, OMe), 3.76 (3H, s, OMe), 3.90 (3H, s, CO_2Me), 6.43 (3H, m, Ar-H, 3-H), 6.78 (2H, m, Ar-H), 7.35 (2H, m, Ar-H), 7.46 (1H, d, *J* 5.4, 8-H), 7.57 (2H, m, Ar-H, 9-H) 7.58(1H, *d*, *J* 10.3, 4-H), 8.05 (1H, s, 6-H) (Found: C, 68.75; H, 5.0; S. 6.55. $C_{28}H_{24}O_6S$ requires C, 68.8; H, 5.0; S, 6.6%).

*3.1.3. Methyl 2,2-di(4-dimethylaminophenyl)thieno [2,3-*h*][1]benzopyran-5-carboxylate* **5c**

As off-white micro-crystals (51%) after elution from silica with 25% ethyl acetate in hexane and recrystallisation from EtOAc and hexane, m.p. = 189.0–190.5°C; ν_{max} (KBr) 1716, 1611, 1507, 1281, 1031; δ_H 2.89 (12H, s, NMe_2), 3.89 (3H, s, CO_2Me), 6.15(1H, d, *J* 10.2, 3-H), 6.63 (4H, m, Ar-H), 7.31 (4H, m, Ar-H), 7.43 (1H, d, *J* 5.4, 8-H), 7.55 (1H, dd, *J* 5.4, 0.7, 9-H), 7.60 (1H, d, *J* 10.2, 4-H), 8.01 (1H, d, *J* 0.7, 8-H) (Found: C, 71.7; H, 5.85; N, 5.6; S, 6.6. $C_{29}H_{28}N_2O_3S$ requires C, 71.9; H, 5.8; N, 5.8; S, 6.6%).

*3.1.4. Methyl 2-(4-dimethylaminophenyl)-2-(4-dimethylamino-2-methylphenyl)thieno[2,3-*h*][1]benzopyran-5-carboxylate* **5d**

As pale blue micro-crystals (53%) after elution from silica with 30% ethyl acetate in hexane and recrystallisation from EtOAc and hexane, m.p. = 198.5–199.5°C; ν_{max} (KBr) 1717, 1610, 1503, 1280, 1035; δ_H 2.27 (3H, s, Ar-Me), 2.90 (6H, s, NMe_2), 2.92 (6H, s, NMe_2), 3.91 (3H, s, CO_2Me), 6.03 (1H, d, *J* 10.3, 3-H), 6.43 (1H, m, Ar-H), 6.51 (1H, m, Ar-H), 6.66 (2H, m, Ar-H), 7.28 (2H, m, Ar-H), 7.31 (1H, d, *J* 8.7, Ar-H), 7.43 (1H, d, *J* 5.5, 8-H), 7.53 (1H, dd, *J* 5.5, 0.8, 9-H), 7.58 (1H, d, *J* 10.3, 4-H), 8.02 (1H, d, *J* 0.8, 6-H) (Found: C, 72.1; H, 6.0; N, 5.6; S, 6.1. $C_{30}H_{30}N_2O_3S$ requires C, 72.3; 11, 6.1; N, 5.6; S, 6.4%).

*3.1.5. Methyl 2-(4-morpholinophenyl)-2-phenylthieno[2,3-*h*][1]benzopyran-5-carboxylate* **5e**

As colourless micro-crystals (42%) after elution from silica with 30% ethyl acetate in hexane and recrystallisation from EtOAc and hexane, m.p. = 202.0–203.5°C; ν_{max} (KBr) 1712, 1608, 1508, 1247, 1030; δ_H 3.12 (4H, m, $N(CH_2)_2$), 3.81 (4H, m, $O(CH_2)_2$), 3.91 (3H, s, CO_2Me), 6.18 (1H, d, *J* 10.3, 3-H), 6.81 (2H, m, ArH), 7.30 (5H, m, Ar-H), 7.47 (3H, m, Ar-H, 8-H), 7.58 (1H, dd, *J* 5.5, 0.8, 9-H), 7.67 (1H, d, *J* 10.3, 4-H), 8.06 (1H, d, *J* 0.8, 6-H) (Found: 71.7; H, 5.2; N, 2.8; S, 6.5. $C_{29}H_{25}NO_4S$ requires C, 72.0; H, 5.2; N, 2.9; S, 6.6%).

*3.1.6. Methyl 2-(2-chlorophenyl)-2-(4-morpholinophenyl)thieno[2,3-*h*[1]benzopyran-5-carboxylate* **5f**

As colourless micro-crystals (57%) after elution from silica with 20% ethyl acetate in hexane and recrystallisation from EtOAc and hexane, m.p. = 194.0–195.5°C; ν_{max} (KBr) 1714, 1608, 1513, 1279, 1248, 1035; δ_H 3.14 (4H, m, $N(CH_2)_2$), 3.81 (4H, m, $O(CH_2)_2$), 3.92 (3H, s, CO_2Me), 6.39 (1H, d, *J* 10.2, 3-H), 6.81 (2H, m, Ar-H), 7.28 (5H, m, Ar-H), 7.47 (1H, d, *J* 5.4, 8-H), 7.59 (1H, dd, *J* 5.4, 0.7, 9-H), 7.70 (1H, d, *J* 10.2, 4-H), 7.81 (1 H, m, Ar-H), 8.08 (1H, d, *J* 0.7, 6-H) (Found: 67.0; H, 4.6; N, 2.7; S, 6.1. $C_{29}H_{24}ClNO_4S$ requires C, 67.2; H, 4.7; N, 2.7; S. 6.2%).

*3.1.7. Methyl 2,2-di(4-methoxyphenyl)thieno[3,2-*h*][1]benzopyran-5-carboxylate* **6a**

As colourless micro-crystals (62%) after elution from silica with 25% ethyl acetate in hexane and recrystallisation from EtOAc and hexane,

m.p. = 103.0–104.5°C; ν_{max} (KBr); δ_H 3.76 (6H, s, OMe), 3.91 (3H, s, CO_2Me), 6.20 (1H, d, *J* 10.3, 3-H), 6.83 (4H, m, Ar-H), 7.28 (1H, d, *J* 5.4, 7-H), 7.38 (4H, m, Ar-H), 7.44 (1H, d, *J* 5.4, 8-H), 7.67 (1H, d, *J* 10.3, 4-H), 8.03 (1H, s, 6-H) (Found: C, 70.7; H, 4.65; S, 6.9. $C_{27}H_{22}O_5S$ requires C, 70.7; H, 4.85; S, 7.0%).

*3.1.8. Methyl 2-(2,4-dimethoxyphenyl)-2-(4-methoxyphenyl)thieno[3,2-*h*][1]benzopyran-5-carboxylate* **6b**

As colourless micro-crystals (56%) after elution from silica with 30% ethyl acetate in hexane and recrystallisation from EtOAc and hexane, m.p. = 115.5–116.5°C; δ_H 3.57 (3H, s, OMe), 3.74 (3H, s, OMe), 3.76 (3H, s, OMe), 3.91 (3H, s, CO_2Me), 6.45 (2H, m, Ar-H), 6.50 (1H, d, *J* 10.2, 3-H), 6.77 (2H, m, Ar-H), 7.28 (1H, d, *J* 5.4, 7-H), 7.38 (2H, m, Ar-H), 7.43 (1H, d, *J* 5.4, 8-H), 7.58 (1H, d, *J* 8.1, Ar-H), 7.60 (1H, d, *J* 10.2, 4-H), 8.02 (1H, s, 6-H) (Found: C, 68.8; H, 4.9; S, 6.5. $C_{28}H_{24}O_6S$ requires C, 68.8; H, 5.0; S, 6.6%).

4. Conclusions

Some novel photochromic thienobenzopyrans have been synthesised. The presence of the thiophene ring brings about a red shift of λ_{max}. The mode of ring fusion of the thiophene ring has a profound effect on the rate of fade of the photogenerated species.

Acknowledgements

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