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Synthesis and photochromic properties of some fluorine-containing naphthopyrans

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Abstract

A series of novel naphthopyrans containing fluorine substituents has been prepared and their behaviour following irradiation with UV light has been investigated. The colourless naphthopyrans exhibit photochromism through electrocyclic opening of the pyran ring. The spectral properties of the resulting coloured naphthalene-based dienones are discussed.

Keywords: Naphthopyrans; Fluorine; Photochromism; X-ray crystallography; Synthesis; Spectroscopy

1. Introduction

The relatively small size and high electronegativity of the fluorine atom often imparts unusual properties to organic molecules into which it is incorporated. Mention can be made of the useful effects noted when fluorine is included into biomolecules [1], alkanes and alkenes [2], liquid crystals [3], polymers [4], and more recently photochromic molecules [5]. The facile displacement of fluoride ion from electron deficient aromatic systems by nucleophiles has been extensively utilised in organic synthesis [6]. The fact that the ^{19}F nucleus, spin quantum number $= \frac{1}{2}$, can be studied by NMR spectroscopy is also advantageous [7]. This feature has been used to illustrate the presence of isomers of the ring opened form of some photochromic naphthopyrans [8] and selected ^{1}H and ^{13}C NMR data have also been reported for these compounds [9]. We now report the synthesis and spectroscopic properties of a range of fluorine containing photochromic naphthopyrans.

2. Results and discussion

The synthesis of photochromic diaryl naphthopyrans **1** has been accomplished by a number of routes [10–12]. Mention can be made of the addition of aryl Grignard reagents to naphthopyranones (benzocoumarins) **2**, a process that suffers from low yields and extensive by-product formation

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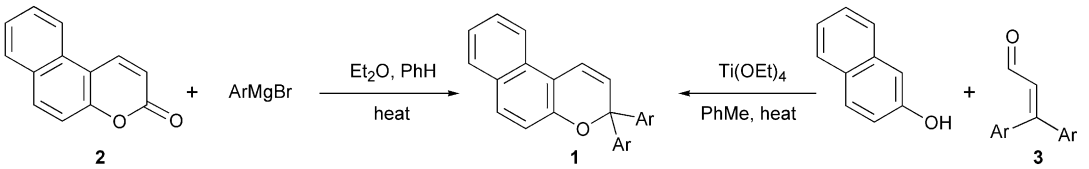
(Scheme 1) [13]. Pyran benzologues have been obtained from the reaction of titanium phenolates, derived from phenols [14] and naphthols (Scheme 1) [15] and titanium (IV) ethoxide, with β-phenylcinnamaldehydes **3**. This latter approach suffers from the use of aryl substituted cinnamaldehydes of which there are few readily available examples. It should be noted however, that this titanium (IV) ethoxide promoted route is often successful when other strategies fail, for example with electron deficient, hydroxy substituted heterocycles [15].

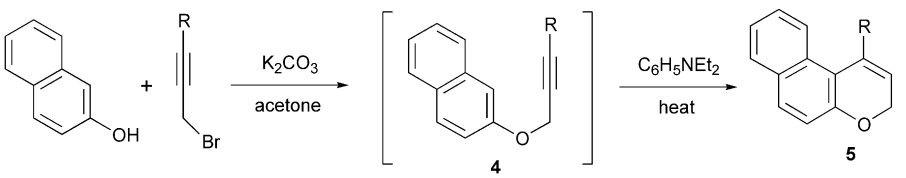
Perhaps the most expeditious route to diaryl substituted naphthopyrans that offers good flexibility is based on the thermal rearrangement of naphthyl propargyl ethers **4** to substituted naphthopyrans **5** first reported by Iwai and Ide in 1962 (Scheme 2) [16]. Diarylnaphthopyrans can be prepared in a single step using a substantially modified version of this protocol. Thus heating 1,1-diarylprop-2-yn-1-ols with a naphthol in toluene containing an acidic catalyst, required to promote the initial naphthyl propargyl ether formation, affords the naphthopyrans directly in good yield [10]. This protocol has been applied by us [17] and others [18] to a number of hydroxy substitued heterocyclic systems and has recently been adapted for the solid state synthesis of naphthopyrans [19].

The prop-2-yn-1-ols required for this route are conveniently prepared by the addition of lithium trimethylsilylacetylide (LTSA), derived from the deprotonation of trimethylsilylacetylene with *n*-butyllithium, to a substituted benzophenone with subsequent fluoride-promoted removal of the trimethylsilyl group [20]. The yields for this two step transformation are generally high and the crude product is often sufficiently pure for direct use in the formation of the naphthopyran. Yields of the fluorine-containing prop-2-yn-1-ols **6** prepared using this protocol for the current study were typically in excess of 85% after purification (Scheme 3). The ^{1}H NMR spectra of these compounds merit some comment. Both the hydroxyl and the alkynic protons resonate at ca. δ 2.9. Attempts to assign the signals by D_2O exchange were hindered by the relatively slow H–D exchange. However, variable temperature ^{1}H NMR spectroscopy enabled unequivocal assignment of these signals since the chemical shift of the hydroxyl proton exhibited the expected temperature dependence. Long range coupling between the alkynic proton and fluorine atom ($^6J_{H,\ F}$) and between the hydroxyl proton and the fluorine atom ($^4J_{OH,\ F}$) of ~0.5 and ~3 Hz respectively, were observed for those propynols with at least one *o*-fluorophenyl ring **6a, b, e, g, h, i**. The $^6J_{H,\ F}$ coupling must be through bond coupling since the H and F atoms are well removed from one another. However, the $^4J_{OH,\ F}$ coupling may be either through bond or through space [21].

The presence of a sharp band at ca. 3300 cm^{-1} (alkynic C–H stretch) together with a weak band at ca. 2100 cm^{-1} (C≡C stretch) in the infrared spectra of the propynols **6** confirm the presence of



Scheme 1.

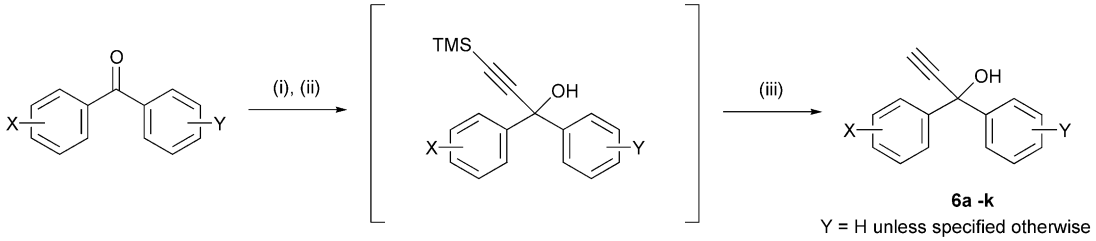


Scheme 2.

the alkyne function [22]. The band for the hydroxyl function appears slightly broadened at ca. 3500 cm^{-1} and a sharp band at ca. 1620 cm^{-1} is attributed to the aromatic C=C stretch.

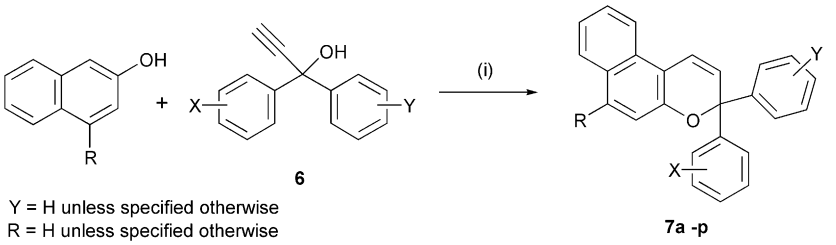
The addition of a catalytic quantity of 4-toluenesulfonic acid monohydrate to a stirred solution of the propynol **6a** and 2-naphthol in anhydrous toluene at ca. 40 °C resulted in the gradual development of a yellow colour. TLC examination of the reaction mixture after 30 min stirring at 40 °C revealed that a significant amount of the propynol and naphthol remained unreacted and thus the reaction mixture was heated to reflux until TLC revealed that no starting materials remained (ca. 90 min). Aqueous work-up and removal of the solvent gave the crude product as a red-brown gum that was purified by column chromatography to afford the colourless 3*H*-naphtho[2,1-*b*]pyran **7a** in 41% yield (Scheme 4).

It was interesting to note that the ^1H NMR spectrum of **7a** displayed a double doublet at δ 6.40, a chemical shift which is typical for 2-H in naphthopyrans [17,18,23] with $J = 10.2$ and 4.1 Hz. The larger of these coupling constants confirms the *cis* relationship between 1-H and 2-H, and is typical for the alkenic protons in both benzo- and naphtho- pyrans [17,18,24]. The second coupling constant is attributed to coupling to the fluorine atom ($^5J_{H;F}$). This feature was confirmed by a fluorine-decoupled ^1H NMR spectrum which displayed the signal for 2-H as a doublet with $J = 10.2$ Hz. It is noteworthy that during the complete assignment of the ^1H, ^{13}C and ^{19}F NMR spectra of some fluorine containing naphthopyrans including compound **7a** no reference was made to this unusual long range ^1H–^{19}F coupling between 2-H and the *ortho* fluorine atom [25]. The signal for 1-H appeared further downfield



6a: X = 2-F; 6b: X = 2,6-F; 6c: X = 3,4-F; 6d: X = 4-F; 6e: X = 2-F, Y = 4-F; 6f: X = Y = 4-F;6g: X = 2-F, Y = 4-OMe
6h: X = 2-F, 4-OMe, Y = 4-OMe; 6i: X = Y = 2-F, 4-OMe; 6j: X = 3-F, 4-morpholino; 6k: X = 2-CF_3

Scheme 3. Reagents and conditions: (i) LTSA, THF, N_2, -10 °C, (ii) H_3O^+, (iii) $(nBu)_4N^+F$-, THF, 0 °C.



7a: X = 2-F; 7b: X = 2,6-F; 7c: X = 3,4-F; 7d: X = 4-F; 7e: X = 2-F, Y = 4-F; 7f: X = Y = 4-F; 7g: X = 2-F, Y = 4-OMe;
7h: X = 2-F, Y = 4-OMe, R = morpholino; 7i: X = 2-F, 4-OMe, Y = 4-OMe; 7j: X = 2-F, 4-OMe, Y = 4-OMe, R = morpholino;
7k: X = Y = 2-F, 4-OMe; 7l: X = 3-F, 4-morpholino; 7m: X = 2-CF_3; 7n: X = 4-CF_3; 7o: X = 4-OMe; 7p: X = Y = 4-OMe

Scheme 4. Reagents and conditions: (i) 4-TsOH, PhMe, heat.

consistent with its benzylic disposition, but was not resolved from the complex pattern associated with the aromatic signals which appear in the range δ 6.99–7.95. The ^{19}F NMR spectrum displayed a signal at δ –110.7 for the *ortho*-fluorine atom.

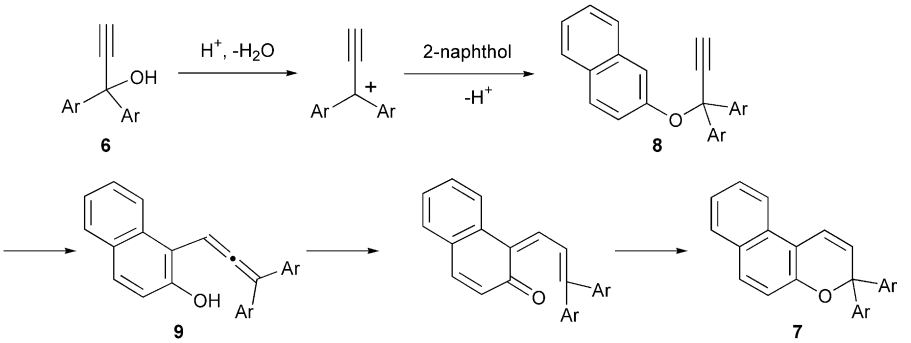
The 3*H*-naphtho[2,1-*b*]pyrans **7b–h** were isolated in moderate yields (29–44%) using the foregoing protocol. Improved yields (55–65%) were noted for those naphthopyrans **7i–l** derived from the alkynols **6h–j** which contained two electron donating methoxy groups or an amino function. This increase in yield may be rationalised by considering the mechanism outlined in Scheme 5. Initial protonation of the propynol **6** followed by loss of water generates a resonance stabilised carbocation. This species is further stabilised by electron donating groups and thus its formation is facilitated. Interception of the carbocation affords the naphthyl propargyl ether **8**, which undergoes a Claisen rearrangement and subsequent tautomerisation to the allenyl naphthol **9**. A 1,5-hydrogen shift and a 6π electrocyclisation complete the sequence to afford **7**.

Comparable ^1H NMR data with that obtained for **7a** was noted for these products with $^5J_{2\text{-H, F}}$ coupling (3.1–5.0 Hz) observed for examples **7b**, **e**, **g–k**. The low field region of the ^1H NMR spectrum of **7e** is displayed in Fig. 1. The loss of fluorine coupling to the signal for 2-H at δ 6.36 on recording the fluorine decoupled ^1H NMR spectrum is clearly evident from Fig. 1, with the signal now appearing as a doublet ($J = 10$ Hz) because of residual coupling to 1-H.

The ^{19}F NMR spectrum of **7e** displayed signals at δ–110.7 for the *ortho*- and at δ–115.0 for the *para*- fluorine atoms. Comparison of the ^{19}F NMR data for some of the other naphthopyrans revealed that the *o*-fluorine atoms typically resonate at ca. –110 ppm. The presence of a second *o*-fluorine atom in the same ring (**7b**) results in a marginal downfield shift to –107 ppm. Fluorine atoms located in *para* positions typically resonate at ca. –115 ppm except for that in compound **7c** where the F atoms resonate at –138 and –140 ppm, shifted significantly upfield.

The ^1H NMR spectrum of **7b** and **k** merit additional comment, since both contain two *ortho*-fluorine atoms. The signal for 2-H of **7b** appears at δ 6.36 as a double triplet with $^3J_{2\text{-H, 1-H}} = 10.0$ Hz and $^5J_{2\text{-H, F}} = 5.0$ Hz; evidently the two fluorine atoms are magnetically equivalent. A similar situation pertains for **7k**, in which 2-H resonates at δ 6.36 as a dt ith $^3J_{2\text{-H, 1-H}} = 10.0$ Hz and $^5J_{2\text{-H, F}} = 3.1$ Hz.

TLC examination of the reaction mixture from 2-naphthol and the trifluoromethyl-substituted alkynol **6k** indicated that only a trace amount of a yellow photochromic material had formed after prolonged reflux (54 h) in toluene. Attempts to isolate this material were unsuccessful. It seems likely that the carbocation that would result from the loss of water from this alkynol is so destabilised by the proximity of the electron withdrawing CF_3 group that its formation is unfavourable. That the steric factor is critical follows from the reported synthesis of 3-phenyl-3-(4-trifluoromethylphenyl)-3*H*-naphtho[2,1-*b*]pyran **7m** [26].



Scheme 5.

The availability of ethylene glycol bis[4-(2-fluorobenzoyl)phenyl] ether [27] prompted an investigation of its transformation into an ether-linked 3*H*-naphtho[2,1-*b*]pyran. Treatment of the ethylene derivative with an excess of lithium trimethylsilylacetylide and subsequent deprotection of the alkyne groups with TBAF gave the bis-alkynol **6l** in 54% yield as a pale yellow viscous gum after elution from silica. Reaction of TMSA at each of the carbonyl centres was confirmed by ^{1}H NMR spectroscopy which showed a doublet ($J = 0.7$ Hz) at δ 2.88 for the alkyne protons, consistent with our observations for the simple alkynols e.g. **6a**, and a broad singlet for the hydroxyl protons at δ 3.35. The protons of the ethylene bridge appeared as a slightly broadened singlet at δ 4.27.

Heating this bis-alkynol **6l** with 2-naphthol gave the photochromic naphthopyran **10**. The ^{1}H NMR spectrum of **10** was remarkably simple as a consequence of its symmetrical structure, and does not differentiate between the two possible diastereoisomers. The signal for 2-H appeared as the expected dd at δ 6.39 ($J = 10.0$, 4.2 Hz) and a singlet at δ 4.25 was attributed to the equivalent ethylene bridge protons. Unequivocal proof for the proposed bis-naphthopyran structure was provided by HRMS which indicated a molecular ion of $M^+ = 762.2574$ (required $M^+ = 762.2582$) (Scheme 6).

To assist in the analysis of the properties of some of the fluorine-containing photochromes, some methoxy-substituted naphtho[2,1-*b*]pyrans **7o**, **p** were obtained. Extension of this study to the synthesis of an isomeric 2,2-diaryl-2*H*-naphtho[1,2-*b*]pyran was undertaken. Heating 1-naphthol and propynol **6h** according to the above procedure gave the 2*H*-naphtho[1,2-*b*]pyran **11b** in 29% yield. The ^{1}H NMR spectrum of **11b** displayed a signal at δ 6.23 assigned to 3-H which appeared as a double doublet through coupling to 4-H ($J = 9.8$ Hz) and to the fluorine atom ($J = 3.4$ Hz). As is typical for the 2*H*-naphtho[1,2-*b*]pyran isomers, 4-H is well resolved from the aromatic protons and appears as a doublet, $J = 9.8$ Hz, at δ 6.69 [23]. The furthest downfield signal in the ^{1}H NMR spectrum of **11b** appeared at δ 8.3 which is assigned to 10-H on the basis of its proximity to the pyran ring oxygen atom. It is noteworthy that the chemical shift of this signal is ~0.3 ppm

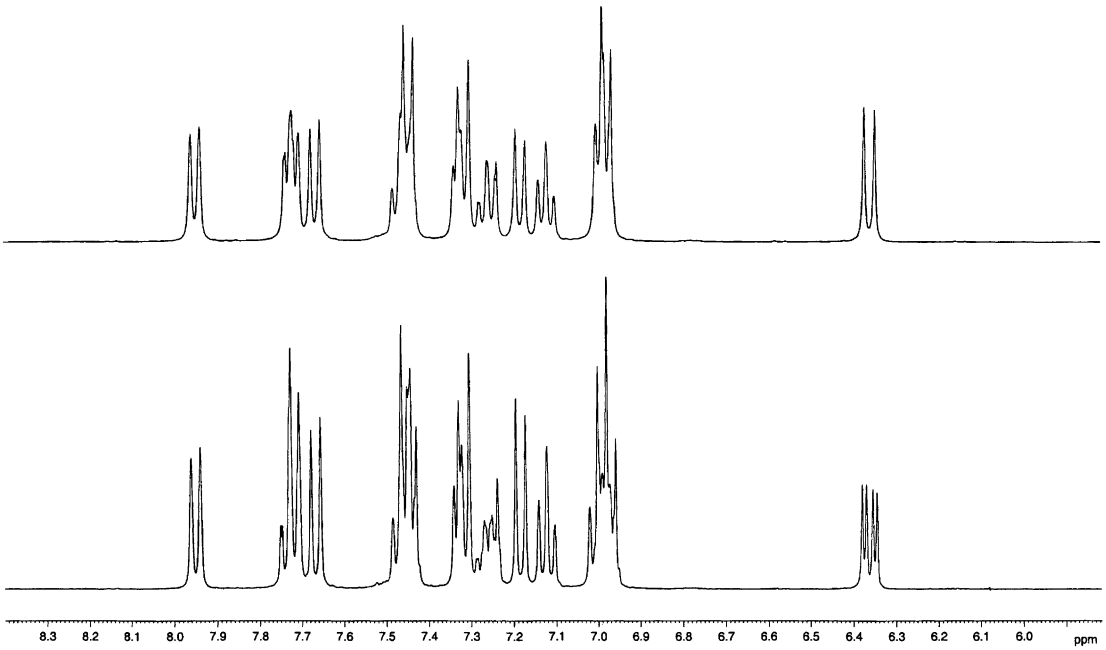
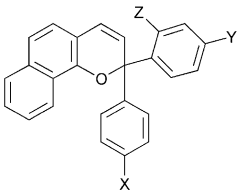
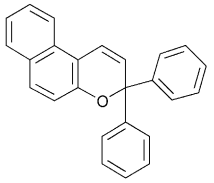


Fig. 1. Lower: 400 MHz ^{1}H NMR spectrum of compound **7e**; upper: ^{19}F decoupled spectrum of compound **7e**.

further downfield than the furthest downfield signal associated with the isomeric naphthopyrans **7.**



11a: X = Y = OMe, Z = H
11b: X = Y = OMe, Z = F



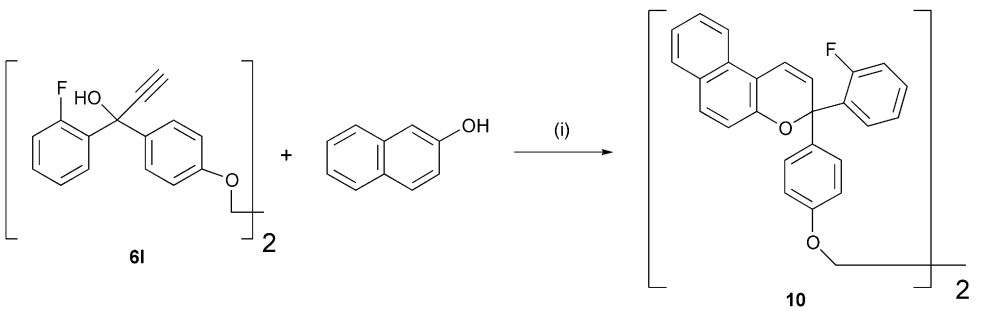
12

It is well known that the O-2C bond in 2*H*-pyrans is readily broken and indeed 2*H*-pyran itself remains unknown, existing preferentially as the acyclic dienone [20,28]. Irradiation of 2*H*-[1]benzopyrans with UV light induces an electrocyclic ring opening to a quinone methide, though in the absence of a trapping reagent only unchanged 2*H*-[1]benzopyran can be detected when irradiation ceases [29].

In the case of naphthopyrans, the quinone methide is sufficiently stable to be seen at ambient temperatures and can exist for some time after cessation of irradiation (Scheme 7). The ring opening process, which is the reverse of the final step of the synthesis (Scheme 5), leads to the dienone **14**, though transient absorption studies indicate that the rapid (picosecond) formation of **14** is followed by isomerisation to the transoid form **15** in the nanosecond time regime [30].

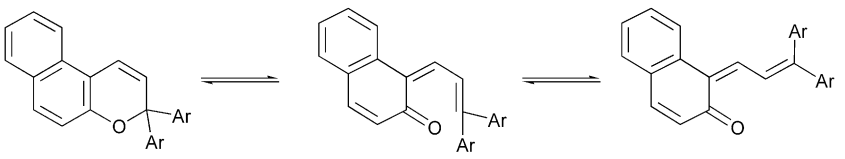
The ring-opened products derived from the colourless naphthopyrans **7** are yellow to orange in colour. The data in Table 1 records the wavelength of maximum absorption of the ring opened species formed when the naphthopyrans **7a–p** are irradiated with UV light in toluene solution at 20 °C. For comparison purposes, the data are also given for 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran **12** and 2,2-di(4-methoxyphenyl)-2*H*-naphtho[1,2-*b*]pyran **11a**.

Incorporation of a fluoro substituent in the phenyl rings of the naphtho[2,1-*b*]pyran results in a blue shift of λ_{max}. A 2-fluoro substituent (**7a**) brings about a shift of 9 nm and the effect of a second *ortho*-fluorine in the same ring is additive, **7b** absorbing a further 10 nm to the blue. The influence of a *para*-fluorine substituent is much less pronounced, $\Delta\lambda$ being only 2 nm, and the addition of a similar substituent in the second phenyl ring (**7f**) has no further effect on λ_{max}. Additivity, however, applies when there is unsymmetrical fluorine substitution in the two phenyl rings, since **7e** absorbs at 419 nm. From the data obtained for **7c**, it appears that a bathochromic



6l **10**

Scheme 6. Reagents and conditions: (i) 4-TsOH, PhMe, heat.



7 **14** **15**

Scheme 7.

shift of 7 nm is brought about by a *meta*-fluorine substituent.

The bisnaphthopyran **10** may be thought of as two units of **7g** isolated from each other by the ethylene bridge and this view is supported by the spectral data for **10** for which λ_{max} 450 nm compares favourably with λ_{max} 456 nm for **7g**.

Although it was not possible to synthesise the 2-trifluoromethylphenyl naphthopyran derivative **7m**, the absorption at 422 nm ($\Delta\lambda$ 8 nm) exhibited by 3-(4-trifluoromethylphenyl)-3*H*-naphtho[2,1-*b*]pyran **7n** clearly indicates the influence of the electron withdrawing nature of the CF_3 group.

The very limited data presented in Table 1 for the isomeric 2*H*-naphtho[1,2-*b*]pyran system indicates that the introduction of one *ortho*-fluoro substituent **11b** causes a small blue shift ($\Delta\lambda = 7$ nm) in the long wavelength band compared with **11a** and has a negligible influence on the short wavelength band.

The presence of an electron-releasing group in the 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyrans causes a red shift in λ_{max}. Thus, the 3-(4-methoxyphenyl) derivative **7o** absorbs at 460 nm and the 3,3-di(4-methoxyphenyl) compound **7p** at 472 nm.

Table 1
Spectroscopic data for naphthopyrans **7**, **10–12**

No.	λ_{max} (nm)
7a	421
7b	411
7c	421
7d	428
7e	419
7f	428
7g	456
7h	432
7i	463
7j	440
7k	445
7l	473
7n	422
7o	460
7p	472
10	450
11a	414, 495
11b	415, 488
12	430

λ_{max} Recorded for solutions irradiated to a constant intensity in toluene at 20 °C.

Consistently, introduction of *ortho*-fluorine substituents into **7o** and **7p** results in blue shifts, 4 nm for **7g** but a more significant shift of 9 nm for **7i** which absorbs at 463 nm. The introduction of a second *ortho*-fluorine substituent into **7i** to afford **7k** results in a further blue shift in λ_{max} of 18 nm.

The influence of an electron donating amino function at the 6-position of a naphtho[2,1-*b*]pyran was briefly examined, since it is known that this is an important position for the development of favourable photochromic properties in the system [31]. It is clear from a comparison of the spectral data for **7g** and **7h** that the 6-morpholino substituent exerts a blue shift ($\Delta\lambda = 24$ nm) and this is corroborated by the data for **7i** and **7j** for which $\Delta\lambda$ is 23 nm.

Unsuccessful attempts were made to obtain accurate and reproducible half-lives for the naphthopyrans. After irradiation of a standard solution of the naphthopyran in toluene at 20 °C to constant intensity, the irradiation was switched off and the time taken for the optical density to fall to a half of its equilibrium value was noted. Unfortunately, the data obtained were not reproducible. Consequently, only general comments can be made about the influence of substituents on the rate of fade of irradiated 3*H*-naphtho[2,1-*b*]pyrans based on a visual comparison with the behaviour of **12**.

An electron-donating group in the 4-position of a 3-phenyl ring results in an increase in the rate of decolouration; the 3-(4-methoxyphenyl) derivative **7o** fades faster than **12**. An additional methoxy substituent in the second phenyl ring enhances this effect, and the dimethoxyphenyl compound **7p** fades very rapidly. Conversely, an electron-withdrawing group in the same position stabilises the open form of the naphthopyran, with the influence varying with the withdrawing strength of the substituent. Thus, the trifluoromethyl derivative **7n** fades at a slower rate than the corresponding fluoro compound **7d**.

These observations are contrary to the normal view that an electron-donating group will stabilise an electron-demanding conjugated system such as the dienone **14**.

The most significant influence on the lifetime of the open form is brought about by an *ortho*

substituent, e.g. fluorine, in the phenyl ring, when the half-life is increased e.g. **7a**, **e**. A more significant increase in the half-life was observed when a second *ortho* fluorine substituent was present, **7b**. When a donor group is additionally present **7g**, **i**, **k**, the influence of the *ortho*-substituent is moderated to some extent. This *ortho* effect has been noted previously for some naphthopyrans imbibed in diethyleneglycol bis(allyl carbonate) [26]. It is evident that an *ortho*-substituent causes some steric hindrance to ring closure.

It should be noted that, irrespective of the electronic properties of a substituent, a slower fade rate is associated with the development of a greater intensity of colour on irradiation.

X-Ray crystal structures were obtained for compounds **7b** [32] and **7g** [33] (see Figs. 2 and 3). Pyran **7b** exists as two crystallographically independent

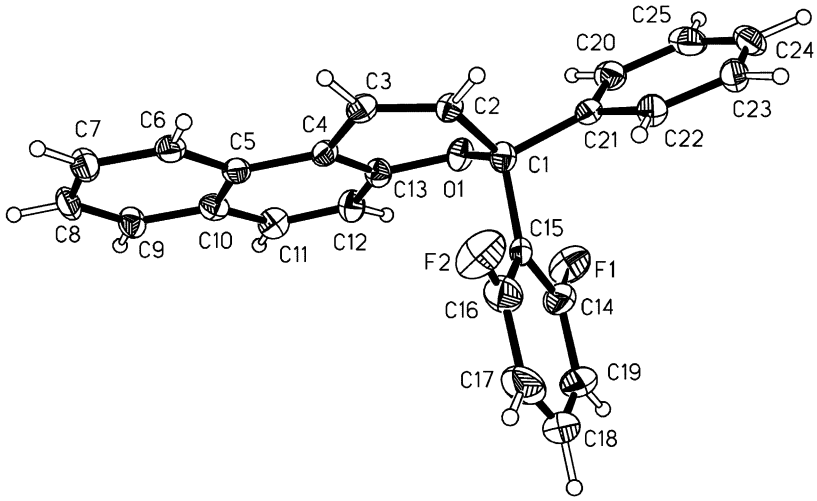


Fig. 2. X-ray crystal structure of **7b**.

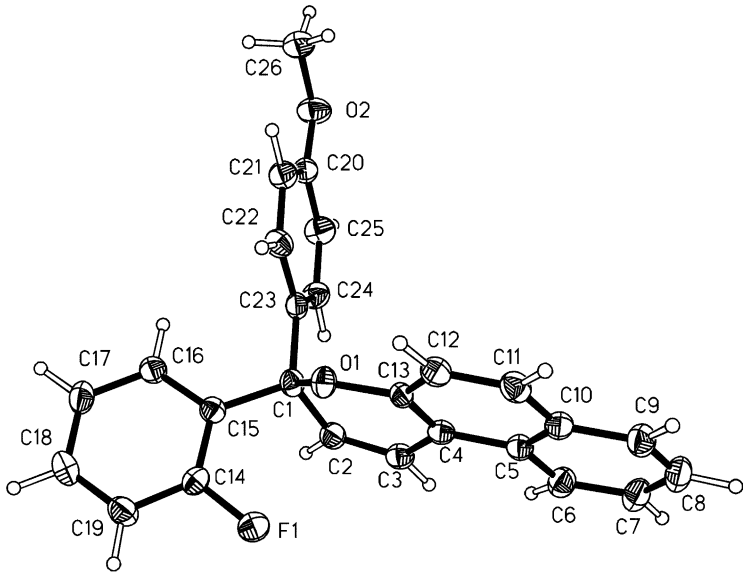


Fig. 3. X-ray crystal structure of **7g**.

molecules, only one of which is shown in Fig. 2. The pyran ring in each of the crystal structures is puckered to accommodate the O–sp^3 hybridised carbon unit. The arrangement of the aryl groups on C1 (crystal structure numbering) merits some comment. In **7b** the 2,6-difluorophenyl ring has adopted a pseudo axial disposition. Whereas in the latter structure, **7g**, the 2-fluorophenyl ring is pseudo equatorially disposed. The reason for the differing conformational preferences of these F-containing rings is, so far unclear. Comparison of the data obtained for **7b** with that for **12** [34] revealed that replacement of one phenyl ring with a 2,6-difluorophenyl unit significantly reduces the C_1–O_1 bond length but has a negligible effect on the O_1–$C_{naphthyl}$ bond length. Both of the C_1–C_{aryl} bond lengths are increased with the C_1–C_{phenyl} by the greater extent (0.016Å). The Ar–C_1–Ar angle is reduced by 2.4° to 108.1°. When the crystallographic data for **7g** are compared with that for **12** it is apparent that both the C_1–O_1 and O_1–$C_{naphthyl}$ bond lengths are increased to 1.464 and 1.380 Å, respectively. The C_1–C_{anisyl} bond is unchanged but the C_1–$C_{F\text{-}aryl}$ bond is slightly shorter. In contrast to **7b** the Ar–C_1–Ar angle is increased by 2.6° to 113.1° (Table 2).

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 with a thermostatted cell block. Samples were irradiated to a steady state absorbance using a Spectroline 8 Watt lamp (366 nm). NMR spectra were recorded on either a Jeol λ series or a Bruker Avance 400 MHz instrument for solutions in $CDCl_3$ (unless stated otherwise); J values are given in Hertz. $CFCl_3$ was used as an internal reference for the ^{19}F NMR spectra. X-ray crystallographic data were obtained using an Enraf Nonius Kappa CCD area detector (Ø scans and ω scans to fill Ewald sphere) [35]. Flash chromatographic separations were performed on Sorbsil™ C560 silica gel as supplied by Fluorochem Ltd., according to the published procedure [36]. 4-Morpholino-2-naphthol and photochromic naphthopyrans **7n–p**, **11a** and **12** were obtained from James Robinson Ltd., (Huddersfield). Distillations were performed using a Buchi GKR glass tube oven and all boiling points relate to the temperature at which distillation commenced.

Table 2
Selected bond lengths and angles for naphthopyrans **7b**, **g** and **12**

No.	Bond lengths Å				Bond angle°
	O_1–C_1	O_1–$C_{naphthyl}$	C_1–$C_{F\text{-}aryl}$	C_1–C_{aryl}	Ar–C_1–Ar
7b	1.440(4)	1.369(4)	1.538(5)	1.543(5)	108.1
7g	1.464(2)	1.380(2)	1.525(3)	1.527(3)	113.1
12[a]	1.458(2)	1.372(2)	1.530(2)	1.527(2)[b]	110.5

[a] Data obtained from [34].
[b] Bond length for C_1–C_{Ph}.

3.1. General method for the preparation of 1,1-diarylprop-2-yn-1-ols **6**

n-Butyllithium (2.5 M in hexanes) (32 mmol) was added slowly via syringe to a cold (−10 °C), stirred solution of trimethylsilylacetylene (32 mmol) in anhydrous tetrahydrofuran (100 cm^3) under a nitrogen atmosphere. On completion of the addition (ca. 5 min) the cold solution was stirred for 30 min. The benzophenone (30 mmol) was added in a single portion to the solution and the resulting mixture stirred until TLC examination indicated that no benzophenone remained (typically 2 h). The solution was then diluted with water (50 cm^3) and aqueous saturated ammonium chloride solution (50 cm^3). The organic phase was separated and the aqueous phase extracted with ethyl acetate (2×50 cm^3). The combined organic extracts were dried (anhydrous Na_2SO_4) and evaporated to give the crude 1,1-diaryl-3-trimethylsilylprop-2-yn-1-ol. A solution of tetra-n-butylammonium fluoride (1 M in THF) (36 mmol) was added to a cold (0 °C) stirred solution of the foregoing crude 1,1-diaryl-3-trimethylsilylprop-2-yn-1-ol in tetrahydrofuran (75 cm^3). The mixture was stirred until TLC examination of the mixture indicated that no silyl alcohol remained (ca. 15 min). The mixture was poured into water (200 cm^3)

and extracted with ethyl acetate (4×75 cm^3). The combined organic extracts were washed with water (5×50 cm^3), dried (anhydrous Na_2SO_4) and evaporated to give the 1,1-diarylprop-2-yn-1-ol which was sufficiently pure for subsequent use. Analytically pure material was obtained by either distillation under reduced pressure or by recrystallisation from light petroleum (b.p. 40–60 °C) and ethyl acetate. The following alkynols were obtained in this way:

3.1.1. 1-(2-Fluorophenyl)-1-phenylprop-2-yn-1-ol **6a**

From 2-fluorobenzophenone as a pale yellow oil (87%), b.p. 135–140 °C at 0.16 mmHg; ν_{max} 3559, 3500, 3300, 2105, 1615, 1586, 1489 cm^{-1}; δ_H 2.84 (1H, *d*, *J* = 0.5, C≡CH), 3.08 (1H, *d*, *J* = 2.9, OH), 6.98 (1H, *ddd*, *J* = 11.4, 8.0, 1.2, Ar-H), 7.14 (1H, *dt*, *J* = 7.6, 1.2, Ar-H), 7.30 (4H, *m*, Ar-H), 7.57 (2H, *m*, Ar-H), 7.21 (1H, *dt*, *J* = 7.9, 1.7, Ar-H), (Found: C, 79.5; H, 4.9. $C_{15}H_{11}FO$ requires C, 79.6; H, 4.9%).

3.1.2. 1-(2,6-Difluorophenyl)-1-phenylprop-2-yn-1-ol **6b**

From 2,6-difluorobenzophenone as a pale yellow oil (89%), b.p. 155–160 °C at 0.16 mmHg, m.p. 47.0–49.0 °C; ν_{max} 3500, 3450, 3320, 2098, 1607, 1570 cm^{-1}; δ_H 2.65 (1H, *t*, *J* = 0.8, C≡CH), 3.31 (1H, *t*, *J* = 3.8, OH), 6.64 (2H, *m*, Ar-H), 7.01 (1H, *m*, Ar-H), 7.11 (3H, *m*, Ar-H), 7.44 (2H, *m*, Ar-H), (Found: C, 73.6; H, 4.0. $C_{15}H_{10}F_2O$ requires C, 73.8; H, 4.1%).

3.1.3. 1-(3,4-Difluorophenyl)-1-phenylprop-2-yn-1-ol **6c**

From 3,4-difluorobenzophenone as a pale yellow oil (94%), b.p. 150–155 °C at 0.16 mmHg, ν_{max} 3510, 3439, 3301, 2112, 1602, 1580 cm^{-1}; δ_H 2.88 (1H, *s*, C≡CH), 2.93 (1H, *s*, OH), 7.07 (1H, *m*, Ar-H), 7.30 (4H, *m*, Ar-H), 7.42 (1H, *ddd*, *J* = 11.5, 7.6, 2.2, Ar-H), 7.56 (2H, *m*, Ar-H), (Found: C, 73.7; H, 4.0. $C_{15}H_{10}F_2O$ requires C, 73.8; H, 4.1%).

3.1.4. 1-(4-Fluorophenyl)-1-phenylprop-2-yn-1-ol **6d**

From 4-fluorobenzophenone as a pale yellow oil (81%), b.p. 160–165 °C at 0.16 mmHg; ν_{max} 3550, 3444, 3303, 2120, 1606, 1509 cm^{-1}; δ_H 2.84 (1H, *bs*, OH), 2.87 (1H, *s*, C≡CH), 6.98 (2H, *m*, Ar-H), 7.30 (3H, *m*, Ar-H), 7.56 (4H, *m*, Ar-H), (Found: C, 79.4; H, 4.8. $C_{15}H_{11}FO$ requires C, 79.6; H, 4.9%).

3.1.5. 1-(2-Fluorophenyl)-1-(4-fluorophenyl)prop-2-yn-1-ol **6e**

From 2,4′-difluorobenzophenone as a pale yellow oil (94%), b.p. 140–145 °C at 0.16 mmHg; ν_{max} 3580, 3440, 3310, 2105, 1615, 1499 cm^{-1}; δ_H 2.87 (1H, *d*, *J* = 0.6, C≡CH), 3.12 (1H, *d*, *J* = 3.0, OH), 7.00 (3H, *m*, Ar-H), 7.16 (1H, *m*, Ar-H), 7.30 (1H, *m*, Ar-H), 7.56 (2H, *m*, Ar-H), 7.70 (1H, *dt*, *J* = 8.1, 1.7, Ar-H), (Found: C, 73.6; H, 3.9. $C_{15}H_{10}F_2O$ requires C, 73.8; H, 4.1%).

3.1.6. 1,1-Bis(4-fluorophenyl)prop-2-yn-1-ol **6f**

From 4,4′-difluorobenzophenone as a pale yellow oil (88%), b.p. 150–155 °C at 0.16 mmHg (lit. b.p. 98 °C at 0.05 mmHg [37]); ν_{max} 3570, 3456, 3307, 2116, 1606, 1509 cm^{-1}; δ_H 2.87 (1H, *s*, C≡CH), 2.94 (1H, *s*, OH), 6.99 (4H, *m*, Ar-H), 7.52 (4H, *m*, Ar-H), (Found: C, 73.7; H, 4.0. $C_{15}H_{10}F_2O$ requires C, 73.8; H, 4.1%).

3.1.7. 1-(2-Fluorophenyl)-1-(4-methoxyphenyl)prop-2-yn-1-ol **6g**

From 2-fluoro-4′-methoxybenzophenone as a colourless viscous oil (94%), b.p. 220–225 °C at 0.16 mmHg; ν_{max} 3452, 3301, 2092, 1619, cm^{-1}; δ_H 2.84 (1H, *d*, *J* = 0.5, C≡CH), 3.17 (1H, *bs*, OH), 3.77 (3H, *s*, OMe), 6.84 (2H, *m*, Ar-H), 6.99 (1H, *m*, Ar-H), 7.14 (1H, *m*, Ar-H), 7.28 (1H, *m*, Ar-H), 7.49 (2H, *m*, Ar-H), 7.70 (1H, *m*, Ar-H), (Found: C, 74.8; H, 5.0. $C_{16}H_{13}FO_2$ requires C, 75.0; H, 5.1%).

3.1.8. 1-(2-Fluoro-4-methoxyphenyl)-1-(4-methoxyphenyl)prop-2-yn-1-ol **6h**

From 2-fluoro-4,4′-dimethoxybenzophenone as a pale yellow oil (89%), m.p. 100.0–102.5 °C; ν_{max} 3475, 3257, 2102, 1624, 1585, 1508 cm^{-1}; δ_H 2.84 (1H, *d*, *J* = 0.7, C≡CH), 2.96 (1H, *d*, *J* = 2.9, OH), 3.78 (3H, *s*, OMe), 3.80 (3H, *s*, OMe), 6.57 (1H, *dd*, *J* = 13.1, 2.5, Ar-H), 6.67 (1H, *ddd*, *J* = 8.7, 2.5, 0.9, Ar-H), 6.85 (2H, *m*, Ar-H), 7.49 (2H, *m*, Ar-H), 7.56 (1H, *t*, *J* = 9.0, Ar-H), (Found: C, 71.1; H, 5.0. $C_{17}H_{15}FO_3$ requires C, 71.3; H, 5.3%).

3.1.9. 1,1-Bis(2-fluoro-4-methoxyphenyl)prop-2-yn-1-ol ***6i***

From 2,2′-difluorobenzophenone as a pale yellow oil (85%), m.p. 99.5–101.5 °C; ν_{max} 3455, 3217, 2087, 1614, 1505 cm^{-1}; δ_H 2.86 (1H, *d*, $J=0.4$, C≡CH), 3.13 (1H, *t*, $J=2.2$, OH), 3.79 (6H, *s*, OMe), 6.56 (2H, *dd*, $J=13.1$, 2.7, Ar-H), 6.69 (2H, *dd*, $J=8.6$, 2.7, Ar-H), 7.65 (2H, *t*, $J=8.6$, Ar-H), (Found: C, 67.0; H, 4.5. $C_{17}H_{14}F_2O_3$ requires C, 67.1; H, 4.7%).

3.1.10. 1-(3-Fluoro-4-morpholinophenyl)-1-phenyl-prop-2-yn-1-ol ***6j***

From 3-fluoro-4-morpholinobenzophenone as a pale cream solid (92%), m.p. 157.5–158.5 °C; ν_{max} 3339, 3280, 2118, 1510, 1244 cm^{-1}; δ_H($CDCl_3$, d_6-DMSO) 2.81 (1H, *s*, C≡CH), 2.92 (4H, *m*, $N(CH_2)_2$), 3.71 (4H, *m*, $O(CH_2)_2$), 6.03 (1H, *s*, OH), 6.74 (1H, *m*, Ar-H), 7.18 (5H, *m*, Ar-H), 7.50 (2H, *m*, Ar-H), (Found: 73.2; H, 5.6; N, 4.4. $C_{19}H_{18}FNO_2$ requires C, 73.3; H, 5.8; N, 4.5%).

3.1.11. 1-Phenyl-1-(2-trifluoromethylphenyl)prop-2-yn-1-ol ***6k***

From 2-trifluoromethylbenzophenone as a pale yellow oil (79%), b.p. 135–145 °C at 0.16 mmHg; ν_{max} 3460, 3315, 2089, 1621, 1504 cm^{-1}; δ_H 2.88 (1H, *s*, C≡CH), 3.02 (1H, *s*, OH), 7.29 (3H, *m*, Ar-H), 7.44 (3H, *m*, Ar-H), 7.56 (1H, *m*, Ar-H), 7.74 (1H, *m*, Ar-H), 8.07 (1H, *d*, $J=8.0$, Ar-H), (Found: C, 69.3; H, 3.8. $C_{16}H_{11}F_3O$ requires C, 69.6; H, 4.0%).

3.1.12. Ethylene glycol bis {4-[1-(1-(2-fluorophenyl)-1-hydroxyprop-2-ynyl)]phenyl} ether[1] ***6l***

From ethylene glycol bis[4-(2-fluorobenzoyl)phenyl] ether as a pale yellow viscous gum (54%) after elution from silica with 30% EtOAc in hexane, δ_H 2.88 (2H, *d*, $J=0.7$, C≡CH), 3.35 (2H, *bs*, OH), 4.27 (4H, *s*, $O(CH_2)_2$), 6.87 (4H, *m*, Ar-H), 6.97 (2H, *m*, Ar-H), 7.16 (2H, *m*, Ar-H), 7.29 (2H, *m*, Ar-H), 7.47 (4H, *m*, Ar-H), 7.74 (2H, *m*, Ar-H), (Found: C, 75.1; H, 4.7. $C_{32}H_{24}F_2O_4$ requires C, 75.3; H, 4.8%).

3.2. General method for the preparation of the naphthopyrans 7

4-Toluenesulfonic acid monohydrate (ca. 0.05 g) was added to a stirred solution of the naphthol (6.9 mmol) and the 1,1-diarylprop-2-yn-1-ol **6** (6.9 mmol) in anhydrous toluene (75 cm^3). The mixture was then heated until TLC examination of the reaction mixture indicated that no naphthol remained. 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 (2×50 cm^3). The combined organic extracts were washed with aqueous saturated sodium hydrogen carbonate solution (2×50 cm^3) and water (50 cm^3). Removal of the dried (anhydrous Na_2SO_4) solvent gave a deep red / brown gum which was purified by flash chromatography and recrystallisation. The following naphthopyrans were obtained by this protocol:

3.2.1. 3-(2-Fluorophenyl)-3-phenyl-3H-naphtho[2,1-b]pyran ***7a***

From **6a** and 2-naphthol as colourless microcrystals (41%) after elution from silica with 2.5% EtOAc in hexane and recrystallisation from light petroleum (b.p. 40–60 °C) and diethyl ether, m.p. = 133.0–134.5 °C; δ_H 6.40 (1H, *dd*, $J=10.2$, 4.1, 2-H), 6.99 (1H, *ddd*, $J=11.4$, 8.2, 1.2, Ar-H), 7.11 (1H, *m*, Ar-H), 7.28 (7H, *m*, Ar-H), 7.46 (3H, *m*, Ar-H, 1-H), 7.66 (1H, *d*, $J=8.8$, Ar-H), 7.72 (2H, *m*, Ar-H), 7.95 (1H, *d*, $J=8.5$, Ar-H), δ_F −110.5 (*m*), (Found: M^+, 352.1262; C, 85.0; H, 4.8. $C_{25}H_{17}FO$ requires M^+, 352.1263; C, 85.2; H, 4.9%).

3.2.2. 3-(2,6-Difluorophenyl)-3-phenyl-3H-naphtho[2,1-b]pyran ***7b***

From **6b** and 2-naphthol as colourless microcrystals (34%) after elution from silica with 5% EtOAc in hexane and recrystallisation from light petroleum (b.p. 40–60 °C) and diethyl ether, m.p. = 86.0–87.5 °C; δ_H 6.36 (1H, overlapping *dt*, $J=10.0$, 5.0, 2-H), 6.75 (2H, *m*, Ar-H), 7.24 (7H,

[1] Melting point not determined as sample remained as a viscous gum despite all attempts to obtain a crystalline form.

m, Ar-H, 1-H), 7.45 (1H, *m*, Ar-H), 7.55 (2H, *m*, Ar-H), 7.66 (1H, *d*, $J=8.8$, Ar-H), 7.72 (1H, *d*, $J=8.1$, Ar-H), 7.94 (1H, *d*, $J=8.6$, Ar-H), δ_F–107.1 (*m*), (Found: M^+, 370.1169; C, 81.1; H, 4.3. $C_{25}H_{16}F_2O$ requires M^+, 370.1169; C, 81.1; H, 4.4%).

3.2.3. 3-(3,4-Difluorophenyl)-3-phenyl-3H-naphtho [2,1-b]pyran 7c

From **6c** and 2-naphthol as pale yellow microcrystals (44%) after elution from silica with 30% EtOAc in hexane and recrystallisation from light petroleum (b.p. 40–60 °C) and diethyl ether, m.p. = 111.5–113.0 °C; δ_H 6.16 (1H, *d*, $J=9.8$, 2-H), 7.05 (1H, *m*, Ar-H), 7.24 (8H, *m*, Ar-H, 1-H), 7.45 (3H, *m*, Ar-H), 7.65 (1H, *d*, $J=9.0$, Ar-H), 7.70 (1H, *m*, Ar-H), 7.93 (1H, *d*, $J=8.0$, Ar-H), δ_F–137.7 (*m*), −139.6 (*m*), (Found: M^+, 370.1163; C, 80.9; H, 4.2. $C_{25}H_{16}F_2O$ requires M^+, 370.1169; C, 81.1; H, 4.4%).

3.2.4. 3-(4-Fluorophenyl)-3-phenyl-3H-naphtho [2,1-b]pyran 7d

From **6d** and 2-naphthol as colourless microcrystals (37%) after elution from silica with 5% EtOAc in hexane and recrystallisation from light petroleum (b.p. 40–60 °C) and diethyl ether, m.p. = 116.0–117.0 °C; δ_H 6.21 (1H, *d*, $J=9.8$, 2-H), 6.99 (2H, *m*, Ar-H), 7.17 (1H, *d*, $J=8.8$, Ar-H), 7.27 (1H, *m*, Ar-H), 7.32 (4H, *m*, Ar-H, 1-H), 7.45 (5H, *m*, Ar-H), 7.65 (1H, *d*, $J=9.0$, Ar-H), 7.71 (1H, *d*, $J=8.1$, Ar-H), 7.95 (1H, *d*, $J=8.5$, Ar-H), δ_F −115.4 (*m*), (Found: M^+, 352.1261; C, 85.1; H, 4.9. $C_{25}H_{17}FO$ requires M^+, 352.1263; C, 85.2; H, 4.9%).

3.2.5. 3-(2-Fluorophenyl)-3-(4-fluorophenyl)-3H-naphtho[2,1-b]pyran 7e

From **6e** and 2-naphthol as colourless microcrystals (34%) after elution from silica with 5% EtOAc in hexane and recrystallisation from light petroleum (b.p. 40–60 °C), m.p. = 109.0–110.5 °C; δ_H 6.36 (1H, *dd*, $J=10.0$, 3.9, 2-H), 6.99 (3H, *m*, Ar-H), 7.12 (1H, *t*, $J=8.1$, Ar-H), 7.18 (1H, *d*, $J=8.8$, Ar-H), 7.29 (3H, *m*, Ar-H, 1-H), 7.46 (3H, *m*, Ar-H), 7.67 (1H, *d*, $J=8.8$, Ar-H), 7.73 (2H, *m*, Ar-H), 7.95 (1H, *d*, $J=8.3$, Ar-H), δ_F −110.8 (*m*), −115.0, (*m*), (Found: M^+, 370.1164; C, 81.0; H, 4.2. $C_{25}H_{16}F_2O$ requires M^+, 370.1169; C, 81.1; H, 4.4%).

3.2.6. 3,3-Bis(4-Fluorophenyl)-3H-naphtho[2,1-b] pyran 7f

From **6f** and 2-naphthol as colourless microcrystals (29%) after elution from silica with 5% EtOAc in hexane and recrystallisation from light petroleum (b.p. 40–60 °C) and diethyl ether, m.p. = 123.0–124.0 °C; δ_H 6.17 (1H, *d*, $J=9.8$, 2-H), 6.99 (4H, *m*, Ar-H), 7.15 (1H, *d*, $J=8.8$, Ar-H), 7.32 (2H, *m*, Ar-H, 1-H), 7.43 (5H, *m*, Ar-H), 7.66 (1H, *d*, $J=9.0$, Ar-H), 7.71 (1H, *d*, $J=8.0$, Ar-H), 7.95 (1H, *d*, $J=8.5$, Ar-H), δ_F −115.2 (*m*), (Found: M^+, 370.1170; C, 81.0; H, 4.4. $C_{25}H_{16}F_2O$ requires M^+, 370.1169; C, 81.1; H, 4.4%).

3.2.7. 3-(2-Fluorophenyl)-3-(4-methoxyphenyl)-3H-naphtho[2,1-b]pyran 7g

From **6g** and 2-naphthol as pale yellow cubes (31%) after elution from silica with 30% EtOAc in hexane and recrystallisation from EtOAc and hexane, m.p. = 124.5–126.5 °C; δ_H 3.74 (3H, *s*, OMe), 6.40 (1H, *dd*, $J=10.0$, 4.4, 2-H), 6.83 (2H, *m*, Ar-H), 6.99 (1H, *m*, Ar-H), 7.11 (1H, *m*, Ar-H), 7.25 (4H, *m*, Ar-H, 1-H), 7.38 (2H, *m*, Ar-H), 7.45 (1H, *m*, Ar-H), 7.65 (1H, *d*, $J=8.8$, Ar-H), 7.73 (2H, *m*, Ar-H), 7.94 (1H, *d*, $J=8.3$, Ar-H), (Found: M^+, 382.1370; C, 81.4; H, 4.9. $C_{26}H_{19}FO_2$ requires M^+, 382.1369; C, 81.6; H, 5.0%).

3.2.8. 3-(2-Fluorophenyl)-3-(4-methoxyphenyl)-6-morpholino-3H-naphtho[2,1-b] pyran 7h

From **6g** and 4-morpholino-2-naphthol as yellow microcrystals (38%) after elution from silica with 35% EtOAc in hexane and recrystallisation from EtOAc and hexane, m.p. 161.0–162.5 °C; δ_H 3.08 (4H, *m*, $N(CH_2)_2$), 3.76 (3H, *s*, OMe), 3.94 (4H, *m*, $O(CH_2)_2$), 6.28 (1H, *dd*, $J=10.0$, 4.2, 2-H), 6.84 (2H, *m*, Ar-H, 1H, *s*, 5-H), 6.99 (1H, *m*, Ar-H), 7.12 (1H, *m*, Ar-H), 7.29 (3H, *m*, Ar-H, 1-H), 7.38 (2H, *m*, Ar-H), 7.45 (1H, *m*, Ar-H), 7.71 (1H, *m*, Ar-H), 7.94 (1H, *d*, $J=8.6$, Ar-H), 8.07 (1H, *d*, $J=7.8$, Ar-H), (Found: M^+, 467.1897; C, 77.0; H, 5.5; N, 2.8. $C_{30}H_{26}FNO_3$ requires M^+, 467.1893; C, 77.1; H, 5.6; N, 3.0%).

*3.2.9. 3-(2-Fluoro-4-methoxyphenyl)-3-(4-methoxyphenyl)-3H-naphtho[2,1-b] pyran **7i***

From **6h** and 2-naphthol as pale yellow microcrystals (63%) after recrystallisation from hexane and EtOAc, m.p. = 130.0–132.5 °C; δ_H 3.74 (3H, *s*, OMe), 3.76 (3H, *s*, OMe), 6.33 (1H, *dd*, *J* = 10.0, 3.9, 2-H), 6.60 (2H, *m*, Ar-H), 6.83 (2H, *m*, Ar-H), 7.17 (1H, *m*, Ar-H), 7.26 (1H, *d*, *J* = 10.0, 1-H), 7.31 (1H, *m*, Ar-H), 7.38 (2H, *m*, Ar-H), 7.45 (1H, *m*, Ar-H), 7.55 (1H, *t* *J* = 8.9, Ar-H), 7.64 (1H, *d*, *J* = 8.8, Ar-H), 7.70 (1H, *d*, *J* = 8.1, Ar-H), 7.94 (1H, *d*, *J* = 8.5, Ar-H), (Found: M^+, 412.1471; C, 78.5; H, 5.1. $C_{27}H_{21}FO_3$ requires M^+, 412.1475; C, 78.6; H, 5.1%).

*3.2.10. 3-(2-Fluoro-4-methoxyphenyl)-3-(4-methoxyphenyl)-6-morpholino-3H-naphtho[2,1-b] pyran **7j***

From **6h** and 4-morpholino-2-naphthol as a colourless 'fluffy' solid (55%) recrystallisation from hexane and EtOAc, m.p. = 195.5–196.5 °C; δ_H 3.09 (4H, *m*, $N(CH_2)_2$), 3.76 (3H, *s*, OMe), 3.77 (3H, *s*, OMe), 3.96 (4H, *m*, $O(CH_2)_2$), 6.21 (1H, *dd*, *J* = 10.1, 3.9, 2-H), 6.57 (1H, *dd*, *J* = 12.9, 2.4, Ar-H), 6.64 (1H, *dd*, *J* = 8.8, 2.4, Ar-H), 6.84 (3H, *m*, Ar-H), 7.21 (1H, *d*, *J* = 10.1, 1-H), 7.29 (1H, *m*, Ar-H), 7.37 (2H, *m*, Ar-H), 7.45 (1H, *m*, Ar-H), 7.54 (1H, *t*, *J* = 8.8, Ar-H), 7.94 (1H, *d*, *J* = 8.3, Ar-H), 8.07 (1H, *d*, *J* = 8.3, Ar-H), (Found: M^+, 497.1997; C, 74.7; H, 5.6; N, 2.8. $C_{31}H_{28}FNO_4$ requires M^+, 497.2002; C, 74.8; H, 5.7; N, 2.8%).

3.2.11. 3,3-Bis(2-Fluoro-4-methoxyphenyl)-3H-naphtho[2,1-b]pyran[2] ***7k***

From **6i** and 2-naphthol as a pale orange foam (56%) after elution from silica with 30% EtOAc in hexane; δ_H 3.73 (6H, *s*, OMe), 6.36 (1H, *dt*, *J* = 10.0, 3.1, 2-H), 6.59 (4H, *m*, Ar-H), 7.20 (1H, *d*, *J* = 8.8, Ar-H), 7.25 (1H, *d*, *J* = 10.0, 1-H), 7.31 (1H, *m*, Ar-H), 7.44 (3H, *m*, Ar-H), 7.65 (1H, *d*, *J* = 8.8, Ar-H), 7.70 (1H, *d*, *J* = 8.6, Ar-H), 7.94 (1H, *d*, *J* = 8.3, Ar-H), δ_F −109.4 (*m*), (Found: M^+, 430.1379; C, 75.0; H, 4.5. $C_{27}H_{20}F_2O_3$ requires M^+, 430.1381; C, 75.3; H, 4.7%).

[2] Melting point not determined as sample remained as a pale orange foam despite all attempts to obtain a crystalline form.

*3.2.12. 3-(3-Fluoro-4-morpholinophenyl)-3-phenyl-3H-naphtho[2,1-b]pyran **7l***

From **6j** and 2-naphthol as pale orange microcrystals (65%) after recrystallisation from EtOAc and hexane, m.p. = 113.0–115.0 °C; δ_H 3.03 (4H, *m*, $N(CH_2)_2$), 3.81 (4H, *m*, $O(CH_2)_2$), 6.19 (1H, *d*, *J* = 10.0, 2-H), 6.83 (1H, *t*, *J* = 8.5, Ar-H), 7.15 (3H, *m*, Ar-H), 7.24 (2H, *m*, Ar-H), 7.31 (3H, *m*, Ar-H, 1-H), 7.46 (3H, *m*, Ar-H), 7.65 (1H, *d*, *J* = 8.8, Ar-H), 7.70 (1H, *d*, *J* = 8.1, Ar-H), 7.94 (1H, *d*, *J* = 8.1, Ar-H), (Found: M^+, 437.1791; C, 79.5; H, 5.4; N, 3.0. $C_{29}H_{24}FNO_2$ requires M^+, 437.1791; C, 79.6; H, 5.5; N, 3.2%).

*3.2.13. Ethylene glycol bis{4-[3-(2-fluorophenyl)-3H-naphtho[2,1-b]pyran-3-yl) phenyl]}ether **10***

From **6l** and 2-naphthol as colourless microcrystals (28%) after elution from silica with 30% EtOAc in hexane and recrystallisation from hexane and EtOAc, m.p. = 146.5–149.5 °C; δ_H ($CDCl_3$/d_6-DMSO) 4.25 (4H, *s*, $O(CH_2)_2$), 6.39 (2H, *dd*, *J*, 10.0, 4.2, 2-H), 6.84 (4H, *m*, Ar-H), 7.00 (2H, *m*, Ar-H), 7.15 (4H, *m*, Ar-H), 7.30 (10H, *m*, Ar-H, 1-H), 7.48 (2H, *m*, Ar-H), 7.70 (6H, *m*, Ar-H), 7.95 (2H, *m*, Ar-H), (Found: M^+, 762.2574; C, 81.7; H, 4.7. $C_{52}H_{36}F_2O_4$ requires M^+, 762.2582; C, 81.9; H, 4.8%).

*3.2.14. 2-(2-Fluoro-4-methoxyphenyl)-2-(4-methoxyphenyl)-2H-naphtho[1,2-b]pyran **11b***. From **6h** and 1-naphthol as pale pink microcrystals (29%) after elution from silica with 30% EtOAc in hexane and recrystallisation from hexane and EtOAc, m.p. = 109.5–110.0 °C; δ_H 3.73 (3H, *s*, OMe), 3.76 (3H, *s*, OMe), 6.23 (1H, *dd*, *J* = 9.8, 3.4, 3-H), 6.59 (2H, *m*, Ar-H), 6.69 (1H, *d*, *J* = 9.8, 4-H), 6.83 (2H, *m*, Ar-H), 7.14 (1H, *d*, *J* = 8.3, Ar-H), 7.33 (1H, *d*, *J* = 8.3, Ar-H), 7.41 (4H, *m*, Ar-H), 7.57 (1H, *t*, *J* = 9.0, Ar-H), 7.70 (1H, *m*, Ar-H), 8.30 (1H, *d*, *J* = 7.6, 10-H), (Found: M^+, 412.1472; C, 78.4; H, 5.0. $C_{27}H_{21}FO_3$ requires M^+, 412.1475; C, 78.6; H, 5.1%).

4. Conclusion

On irradiation with UV light, naphthopyrans undergo an electrocyclic ring opening to the

coloured quinone methides. Substituents containing fluorine cause a blue shift of the absorption band, but electron donating groups bring about a red shift. The photochromic properties are also influenced by substituents, with electron-withdrawing groups stabilising the ring opened valence tautomer. Conversely, electron-releasing groups decrease the half-life of the coloured form. The steric effect of groups in the *ortho* position of the phenyl groups adjacent to the hetero oxygen atom causes a dramatic increase in the lifetime of the coloured form.

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[32] X-ray crystallographic data for **7b**: empirical formula $C_{25}H_{16}F_2O$; formula weight 370.38; temperature 150(2) K; wavelength 0.71073 Å; crystal system monoclinic; space group $P2_1$; unit cell dimensions $a=16.4423(9)$ Å, $\alpha=90°$, $b=6.6345(4)$ Å, $\beta=102.851(3)°$, $c=17.1129(9)$ Å, $\gamma=90°$; Volume 1820.03(18) Å^3; Z 4; density (calculated) 1.352 Mg/m^3; Absorption coefficient 0.095 mm^1; $F(000)$ 768; crystal colourless prism; crystal size $0.10\times0.10\times0.10$ mm^3; θ range for data collection 2.4425.00°; Index ranges $-19\leqslant h\leqslant 19$, $-7\leqslant k\leqslant 7$, $-20\leqslant l\leqslant 20$; Reflections collected 27388; independent reflections 6342 [$R_{int}=0.0926$]; Completeness to $\theta=25.00°$ 99.7%; max and min transmission 0.9905 and 0.9905; Refinement method full-matrix least-squares on F^2; data/restraints/parameters 6342/13/601; goodness-of-fit on F^2 0.948; final R indices [$F^2>2\sigma(F^2)$] $R1=0.0596$, $wR2=0.1279$; R indices (all data) $R1=0.1162$, $wR2=0.1456$; Absolute structure parameter 0.2(11); extinction coefficient 0.0050(14); largest diff. peak and hole 0.338 and 0.222 e Å^{-3}. Asymmetric unit contains two molecules.
[33] X-ray crystallographic data for **7g**: empirical formula $C_{26}H_{19}FO_2$; formula weight 382.41; temperature 150(2) K; wavelength 0.71073 Å; crystal system monoclinic; space group $P2_1/n$; unit cell dimensions $a=14.2749(5)$ Å, $\alpha=90°$, $b=8.9694(4)$ Å, $\beta=91.397(3)°$, $c=14.5901(5)$ Å, $\gamma=90°$; volume 1867.52(12) Å^3; Z 4; density (calculated) 1.360 Mg/m^3; absorption coefficient 0.092 mm^{-1}; $F(000)$ 800; crystal colourless pyramid; crystal size $0.20\times0.20\times0.15$ mm^3; θ range for data collection 2.6726.00°; index ranges $-17\leqslant h\leqslant 17$, $-11\leqslant k\leqslant 11$, $-17\leqslant l\leqslant 17$; reflections collected 13902; independent reflections 3656 [$R_{int}=0.0692$]; completeness to $\theta=26.00°$ 93.5%; max and min transmission 0.9864 and 0.9819; refinement method full-matrix least-squares on F^2; data/restraints/parameters 3656/0/339; goodness-of-fit on F^2 0.968; final R indices [$F^2>2\sigma(F^2)$] $R1=0.0484$, $wR2=0.1071$; R indices (all data) $R1=0.0907$, $wR2=0.1196$; extinction coefficient 0.0051(15); largest diff. peak and hole 0.211 and 0.186 e Å^{-3}.
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