Ring contraction during the 6π-electrocyclisation of naphthopyran valence tautomers†

Christopher D. Gabbutt,[a] B. Mark Heron,*[a] Suresh B. Kolla,[a] Colin Kilner,[b] Simon J. Coles,[c] Peter N. Horton[c] and Michael B. Hursthouse[c]

Received 7th May 2008, Accepted 9th June 2008
First published as an Advance Article on the web 9th July 2008
DOI: 10.1039/b807744d

The thermal and photochemical ring-opening of spiro(3*H*-naphtho[2,1-*b*]pyran-3,9′-thioxanthene-10,10-dioxide) **3** results in the facile ring-contraction to 9-(naphtho[2,1-*b*]furan-2-yl)-9*H*-thioxanthene-10,10-dioxide **6**. Similar behaviour is displayed by the isomeric spiro(2*H*-naphtho[1,2-*b*]pyran-2,9′-thioxanthene-10,10-dioxide) **9** affording 9-(naphtho[1,2-*b*]furan-2-yl)-9*H*-thioxanthene-10,10-dioxide **12**, though more severe reaction conditions were required. The comparative ease of this rearrangement for the isomers **3** and **9** was rationalised on the basis of the relative isomer populations of the ring-opened naphthopyrans. The rearrangement of simple mono- and bis-methylsulfonylphenyl substituted photochromic naphthopyrans **18**, **20** was examined; the former failed to rearrange whereas the latter could be induced to rearrange only under prolonged UV irradiation. The photochromism of diastereoisomerically pure sulfoxides derived from the oxidation of spiro(3*H*-naphtho[2,1-*b*]pyran-3,9′-thioxanthene) **2a** and spiro(2*H*-naphtho[1,2-*b*]pyran-2,9′-thioxanthene) **2b** resulted in conversion to the most thermodynamically stable *trans*-isomer in each case.

Introduction

The reversible 6π electrocyclic opening of the pyran ring has attracted considerable attention particularly when the pyran ring is fused to a naphthalene unit and where the photochemical ring-opening–thermal ring-closing sequence is accompanied by a change in colour.[1] There are numerous reports concerning the influence of substituents on the photochromic properties of diarylnaphthopyrans.[2] However, none of these accounts[3] discusses the influence of a single strong conjugating electron withdrawing substituent in one of the *geminal* aryl rings upon the photochromism of the pyran unit since such groups are difficult to incorporate using the standard Claisen rearrangement route[4] and suitable staring materials are not readily available for the $Ti(OEt)_4$ promoted route.[5] We were interested in investigating the synthesis of such substituted naphthopyrans and thought that the use of electron donating thioether substituents, which could be subsequently oxidised to a sulfone unit, would be a convenient strategy to access such compounds.

Results and discussion

An obvious starting point was the preparation of the known spirothioxanthene substituted compounds **2a**, **b**[6] (Scheme 1), which could be readily oxidised in a later step.

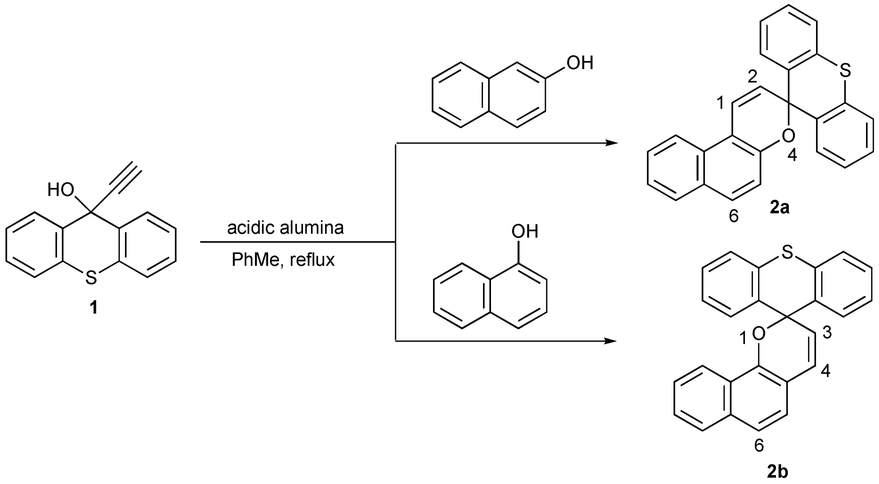
Addition of lithium trimethylsilylacetylide (LiTMSA) to thioxanthone, followed by base-promoted unmasking of the terminal acetylene unit, proceeded cleanly to afford propynol **1** in excellent yield (94%). Heating a PhMe solution of 2-naphthol with **1** in the presence of acidic alumina for 1 h afforded **2a** in 55% yield [$\delta_{2\text{-H}} = 6.18$, d, $\delta_{1\text{-H}} = 7.03$, d ($J = 10.2$ Hz)].[6] Our attempts to oxidise **2a** with excess peracetic acid were unsuccessful, but oxidation of a CH_2Cl_2 solution of **2a** with 1.5 equivalents of *m*-CPBA gave three new components, which were readily separated by flash chromatography (Scheme 2). The use of greater amounts of *m*-CPBA for the oxidation of **2a** resulted in the formation of trace amounts of by-products, which proved difficult to remove by flash column chromatography.

The compounds resulting from the oxidation were characterised as the sulfone **3** (17%) [$\delta_{2\text{-H}} = 6.36$, d, $\delta_{1\text{-H}} = 7.08$, d ($J = 10.2$ Hz)], the *cis*-sulfoxide **4** (28%) [$\delta_{2\text{-H}} = 5.59$, d, $\delta_{1\text{-H}} = 7.05$, d ($J = 10.0$ Hz), Fig. 1][7] and the *trans*-sulfoxide **5** (20%) [$\delta_{2\text{-H}} = 6.58$, d, $\delta_{1\text{-H}} = 7.78$, d ($J = 10.2$ Hz), Fig. 2].[8] The pronounced deshielding of the alkene protons in the *trans*-sulfoxide **5** compared to the *cis*-isomer **4** ($\Delta\delta_{2\text{-H}} = 0.99$; $\Delta\delta_{1\text{-H}} = 0.73$) presumably stems from their proximity to the anisotropic S=O unit. It is also noteworthy that 2-H in **4** resonates at an unusually high field position (δ 5.59) compared to those in **2a** and **3** ($\delta \sim 6.2$). A possible explanation for this anomalous shift is provided by the X-ray crystal structure (Fig. 1), which indicates that 2-H not only lies within a shielding zone of one of the thioxanthene rings but also is in close proximity to the sulfur lone pair of the sulfoxide unit.

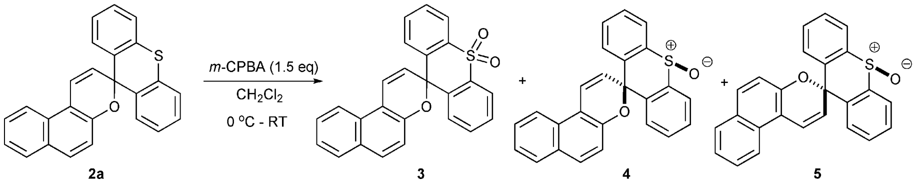
---

[a] *Department of Colour Science, School of Chemistry, University of Leeds, Leeds, UK LS2 9JT. E-mail: b.m.heron@leeds.ac.uk; Fax: +44 (0)113 3432947; Tel: +44 (0)113 3432925*
[b] *School of Chemistry, University of Leeds, Leeds, UK LS2 9JT*
[c] *Department of Chemistry, University of Southampton, Highfield, Southampton, UK SO17 1BJ*

† Electronic supplementary information (ESI) available: ^{1}H, ^{13}C NMR and UV–visible spectra for compounds. CCDC reference numbers 670085, 670086, 661552, 663292. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b807744d



Scheme 1 Preparation of spiro(naphthopyranthioxanthenes) **2a**, **b**.



Scheme 2 Oxidation of spiro(3*H*-naphtho[2,1-*b*]pyran-3,9′-[9*H*]-thioxanthene) **2a**.

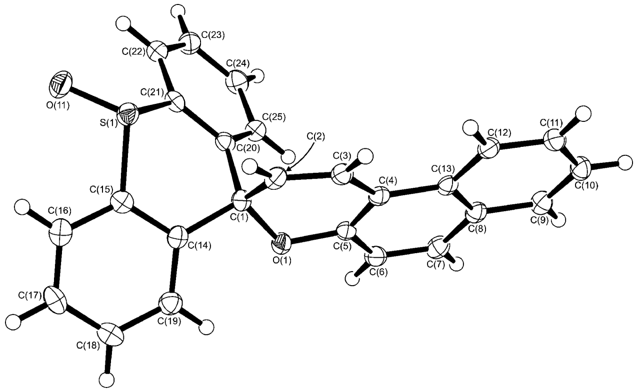


Fig. 1 X-Ray crystal structure of compound **4**.

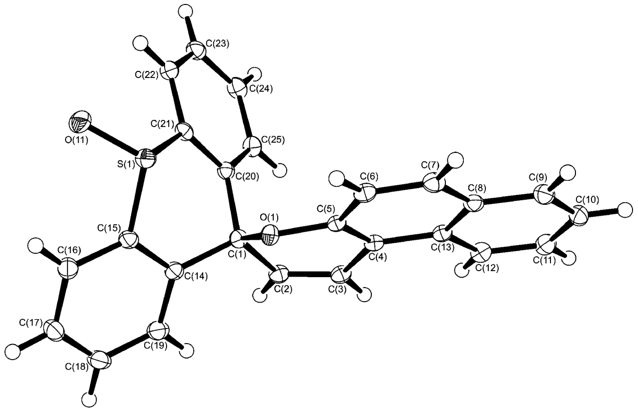


Fig. 2 X-Ray crystal structure of compound **5**.

In both sulfoxide diastereoisomers **4** and **5** the sulfoxide oxygen prefers a pseudo equatorial site with stereochemical differentiation occurring through the arrangement of the pyran ring oxygen and C-2 atoms about the spiro carbon (C-1, crystallographic numbering). This preference for the equatorial orientation of the sulfoxide oxygen atom in each of the isomers **4** and **5** precludes the potential photochemical isomerisation of the sulfoxide group.[9] The thioxanthene moiety adopts the typical boat conformation leading to a ridge tile or 'V-shaped' arrangement.[10]

Attempts to obtain crystals of the sulfone **3** for a comparative crystal study were unsuccessful due to the appreciable thermal lability of this compound. Even brief heating during recrystallisation (EtOAc–hexane) resulted in formation of a significant quantity (TLC) of a new, non-photochromic product. Quantitative conversion could be achieved by heating a solution of **3** in EtOAc–hexane, 1 : 1 under reflux for 45 min. The instability of **3** stems from its proclivity to undergo an irreversible ring contraction and aromatisation to the naphtho[2,1-*b*]furan **6**[11] [$\delta(\mathrm{CDCl_3})_{9\text{-H}}$ = 5.92, s, $\delta_{1'\text{-H}}$ = 7.10, s], the constitution of which was established by X-ray crystallography (Fig. 3).[12]

Each of the new naphthopyrans **3**–**5** displayed photochromism and reversibly developed a yellow colour, with *ca.* $\lambda_{\max}$ 426 nm, on irradiation of a toluene solution with a TLC inspection lamp (365 nm, 8 Watt); $\lambda_{\max}$ is shifted hypsochromically relative to **2a** (481 nm) in keeping with the decrease in electron donating ability of the S atom upon oxidation. Interestingly, the photochromism of **3** was particularly short-lived with irradiation (TLC inspection lamp, 365 nm) of a d_8-toluene solution (*ca.* 20 mg/2.5 mL) resulting in the complete loss of photochromism in less than 90 s (*cf.* Fig. 4). Examination of the ^{1}H NMR spectrum of this solution revealed that facile ring contraction had again occurred to afford **6**. Irradiation (365 nm, 180 s) of a d_8-toluene solution of **4** resulted in the complete isomerisation of **4** into **5**, whereas

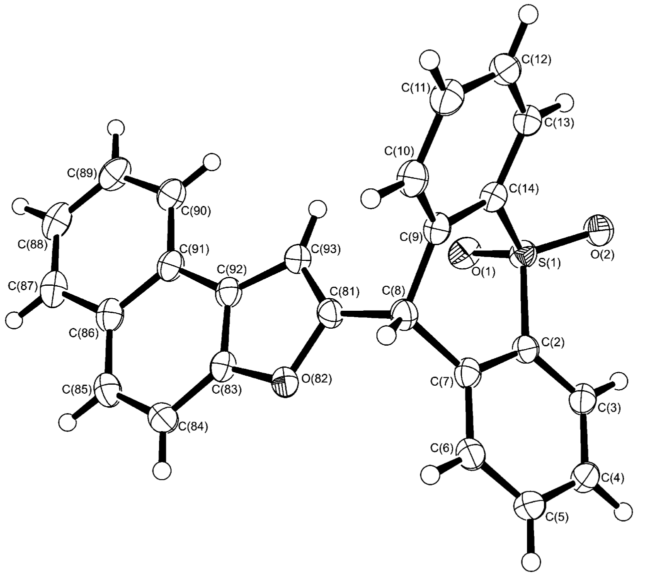


Fig. 3 X-Ray crystal structure of compound **6**.

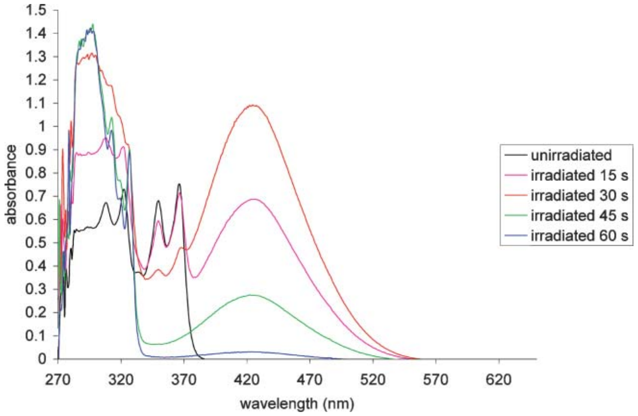
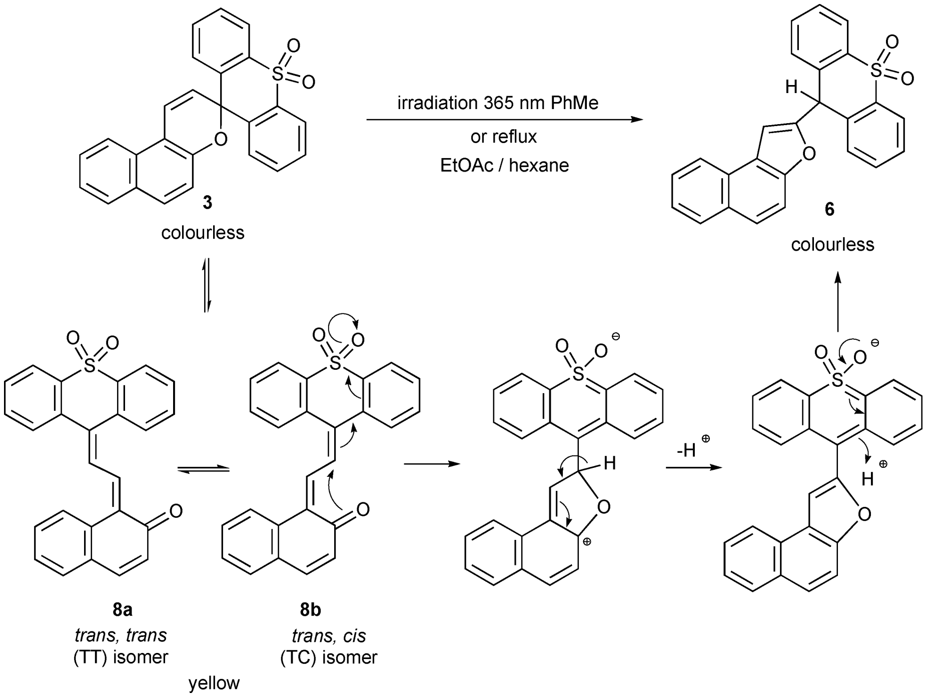


Fig. 4 UV–Visible spectra of naphthopyran **3** in toluene at various irradiation times.

similar treatment of **5** resulted in no change, which suggests that the *trans*-diastereoisomer **5** is the more thermodynamically stable of the pair.

A mechanism for the facile ring contraction of **3** to **6** is presented in Scheme 3. Thermal and photochemical ring-opening of the pyran unit affords the isomeric dienones **8a**, **b**. The ratio of these two isomers is presumed to favour the less sterically congested isomer **8b** and is supported by studies on the photochemical ring-opening of 3*H*-naphtho[2,1-*b*]pyrans, which have established the predominance of the *trans*,*cis*-isomer (TC) *cf.* **8b**, using NMR spectroscopy.[13] The geometry of **8b** favours the intervention of a rapid 5-*exo-trig* ring closure over the usual isomerisation and 6π-electrocylisation sequence to generate the aromatic thiaanthracene and thence the thioxanthene upon proton transfer.

The isomeric 2*H*-naphtho[1,2-*b*]pyran **2b** [$\delta_{3\text{-H}} = 6.16$, d, $\delta_{4\text{-H}} = 6.43$, d ($J = 9.9$ Hz)][6] was obtained from 1-naphthol and alkynol **1** in 45% yield. Oxidation of **2b** with *m*-CPBA resulted in a similar mixture of compounds, sulfone **9** (28%) [$\delta_{3\text{-H}} = 6.31$, d, $\delta_{4\text{-H}} = 6.50$, d ($J = 9.9$ Hz)], *cis*-sulfoxide **10** (24%) [$\delta_{3\text{-H}} = 5.55$, d, $\delta_{4\text{-H}} = 6.47$, d ($J = 9.7$ Hz)] and *trans*-sulfoxide **11** (43%) [$\delta_{3\text{-H}} = 6.46$, d, $\delta_{4\text{-H}} = 7.19$, d ($J = 10.0$ Hz), Fig. 5][14] (Scheme 4). It is noteworthy that again the *cis*-sulfoxide **10** exhibits anomalous shifts of the pyran ring protons in accord with those of *cis*-isomer **4**. UV irradiation of a toluene solution of each of the new naphthopyrans resulted in the reversible development of an orange-yellow colour (*ca.* $\lambda_{\max} = 470$ nm), again shifted hypsochromically relative to the unoxidised compound **2b** ($\lambda_{\max} = 503$ nm). Interestingly, for the naphtho[1,2-*b*]pyrans **9–11**, the hypsochromic shift is *ca.* 30 nm, significantly



Scheme 3 Proposed mechanism for the ring contraction of naphthopyran **3** to naphthofuran **6**.

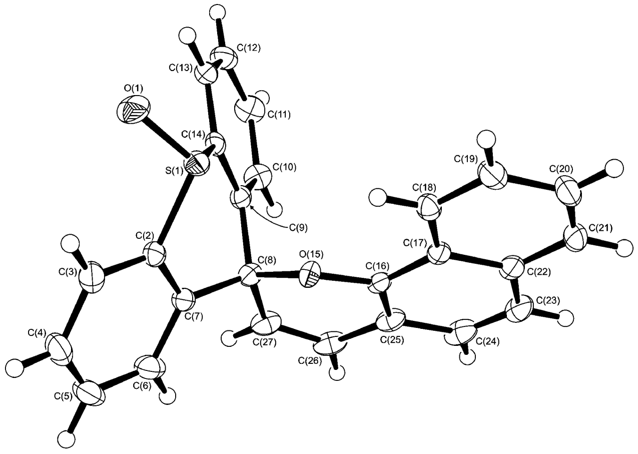
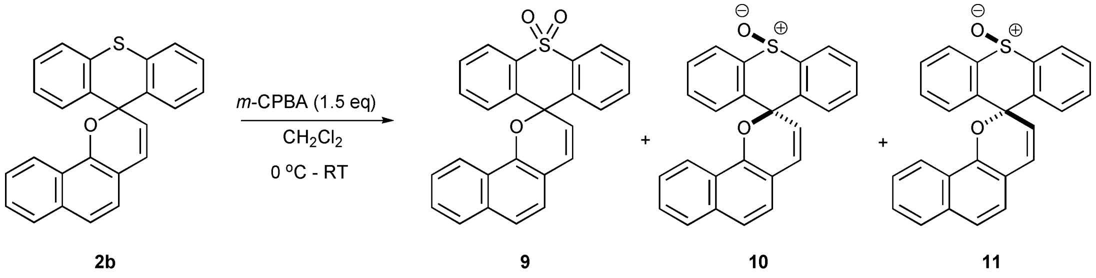


Fig. 5 X-Ray crystal structure of compound **11**.

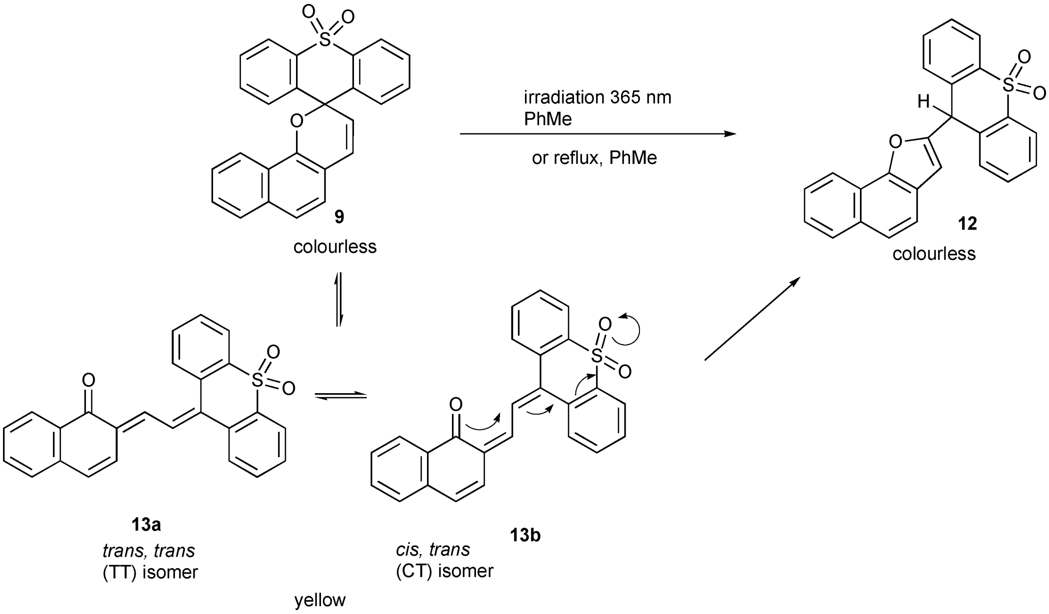
smaller than that for the alternative series **2a**, **3–5** of *ca.* 50 nm. Irradiation of a d_8-toluene solution of the sulfoxides **10** and **11** resulted in the complete isomerisation of the former into the most stable diastereoisomer **11**, whilst the *trans*-sulfoxide **11** remained unchanged. Interestingly, for this naphtho[1,2-*b*]pyran isomer, the sulfone **9** proved to be more resistant to ring contraction and heating in toluene for 26 h was required in order to effect the contraction to naphthofuran **12** (72%) [$\delta(\mathrm{CDCl_3})_{9\text{-H}} = 5.93$, s, $\delta_{1'\text{-H}} = 6.77$, s] (Scheme 5). A longer period of UV irradiation (3600 s, 8 Watt TLC lamp) was also required to effect the efficient contraction to **12**.

The reluctance of **9**, compared with isomer **3**, to undergo ring contraction may be explained by considering the likely geometry and relative abundance of the ring-opened coloured forms **13a**, **b** (Scheme 5). Steady state spectroscopic investigations of 2*H*-naphtho[1,2-*b*]pyrans have revealed that ring-opened species with *trans*,*trans*- (TT) geometries corresponding to **13a** are longer lived (more stable) than their *cis*,*trans*- (CT) isomers *cf.* **13b**.[15] Isomer **13a** does not posses the appropriate geometry for a facile ring contraction, however, the relatively small proportion of **13b** under the applied irradiation conditions can undergo ring contraction with the result that the isomer ratio gradually adjusts to compensate for the removal of **13b**, which is manifest in the slow conversion of **9** into **12**.

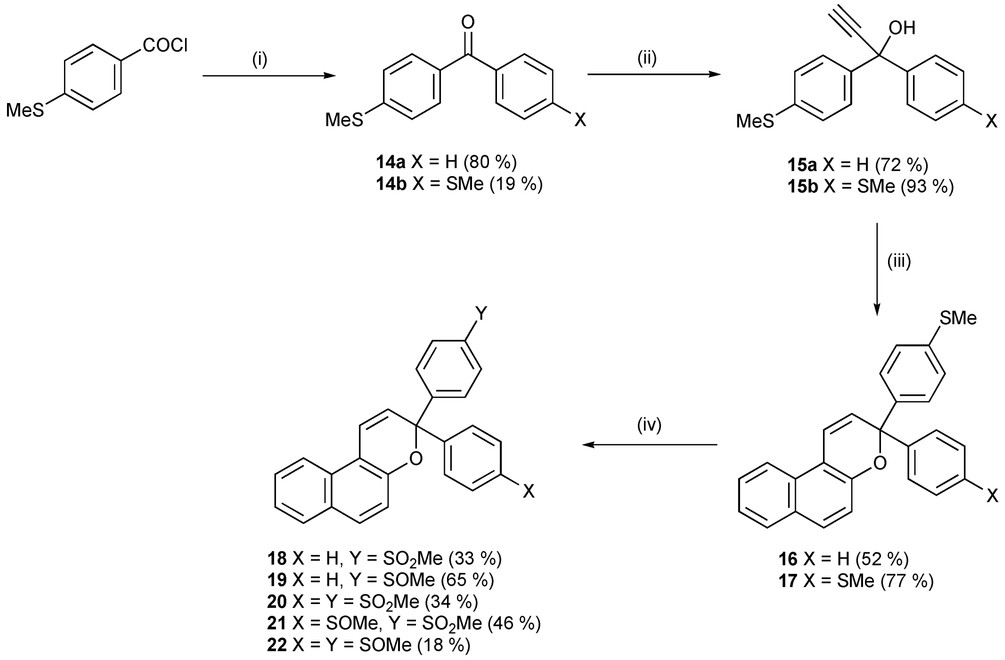
We were interested to explore whether this rearrangement was a consequence solely of the thioxanthene dioxide unit or was more general and would operate with simple electron withdrawing methylsulfonyl groups. Thus the monomethylthio- and bismethylthio- naphtho[2,1-*b*]pyrans **16** and **17**, respectively, were obtained according to Scheme 6. (Methylthio)benzophenones **14a**, **b** were obtained by a standard Friedel–Crafts acylation procedure



Scheme 4 Oxidation of spiro(2*H*-naphtho[1,2-*b*]pyran-2,9′-[9*H*]-thioxanthene) **2b**.



Scheme 5 Proposed mechanism for the ring contraction of naphthopyran **9** to naphthofuran **12**.



Reagents: (i) $AlCl_3$, PhH or PhSMe; (ii) TMS-acetylide, THF, N_2, 0 °C - RT then KOH, MeOH RT;
(iii) 2-naphthol, acidic alumina, PhMe, reflux; (iv) *m*-CPBA, CH_2Cl_2

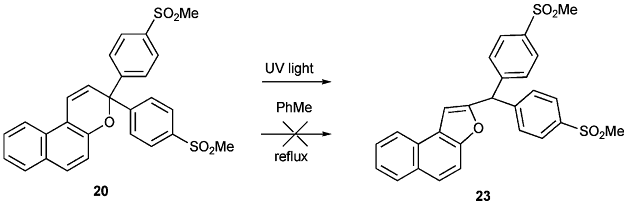
Scheme 6 Preparation of intermediates and naphthopyrans **16**, **17** and their oxidised analogues **18–22**.

and were converted to propynols **15a**, **b** in excellent yield using the preferred method of addition of LiTMSA with subsequent *in situ* base promoted desilylation.[4] Propynols **15a**, **b** were directly converted into the naphthopyrans **16** and **17** respectively, upon heating in toluene containing 2-naphthol and suspended acidic alumina. Naphthopyran **17** has recently been prepared in 36% yield through the addition of excess 4-methythiophenylmagnesium bromide to 3*H*-naphtho[2,1-*b*]pyran-2-one,[16] whilst **16** is surprisingly unknown.

Oxidation of **16** gave the sulfone **18** [$\delta_{\text{2-H}}$ 6.25, d, J = 9.9 Hz, δ_{Me} 3.01] together with an inseparable mixture of diastereoisomeric sulfoxides **19** [$\delta_{\text{2-H}}$ 6.25 and 6.26, d, J = 9.9 Hz, δ_{SOMe} 2.686 and 2.691]. Similarly, **17** gave the bis-sulfone **20** [$\delta_{\text{2-H}}$ 6.22, d, J = 9.9 Hz, δ_{Me} 3.02], the diastereoisomeric mixed sulfoxide-sulfones **21** [$\delta_{\text{2-H}}$ 6.23 and 6.24, d, J = 9.9 Hz, δ_{SOMe} 2.70 and 2.71, δ_{Me} 3.02] and the bis-sulfoxide **22** as an inseparable mixture of diastereoisomers [$\delta_{\text{2-H}}$ 6.24 m, δ_{SOMe} 2.702 and 2.705]. The hypsochromic shifts noted in λ_{max} upon oxidation of the S-atom(s) were *ca.* 35 nm and 60 nm respectively, for the series derived from **16** and **17**. This *ca.* 60 nm shift in λ_{max} upon oxidation of bis-methylthio substituted naphthopyran **17** confirms the approximate additive effect of substituents in the geminal aryl rings.[1]

Heating a solution of **18** in toluene under reflux for either 24 h or irradiation for 15 min in an immersion well photochemical reactor (125 Watt, medium pressure Hg lamp) failed to effect the ring contraction to the naphthofuran. However, similar irradiation of bis-sulfone **20** resulted in the contraction to **23**, though all attempts to effect the thermal contraction failed (Scheme 7).

The ring contraction of sulfones **3** and **9** that contain the thioxanthene 10,10-dioxide moiety is far more facile than that of **18** and **20**. This may be a consequence of either a more favourable cyclisation geometry for the 5-*exo*-*trig* closure when the *geminal* aryl rings are conformationally constrained in a thioxanthene unit or the stabilising influence of the aromatic thiaanthracene intermediate.



Scheme 7 Photochemical ring contraction of naphthopyran **20**.

Conclusion

The synthesis of naphthopyrans bearing electron withdrawing substituents can be conveniently accomplished by manipulation of the oxidation state of thioether units. Oxidation of the thioether unit of the spiro(naphthopyran–thioxanthenes) **2a**, **2b** affords sulfones and separable mixtures of the respective diasteroisomeric sulfoxides. The former, **3** and **9**, display only transient photochromism (UV irradiation) before efficient ring contraction supervenes in the normal cyclisation process and results in the formation of a naphthofuran in each case. Thermally induced ring contraction of these sulfones to the respective naphthofurans was also facile. Differentiation between the 3*H*-naphtho[2,1-*b*]- **3** and 2*H*-naphtho[1,2-*b*]- **9** pyran systems was observed, with the latter requiring longer irradiation/heating times for complete ring contraction to be observed, a feature attributed to the established valence isomer distribution under irradiation. The sulfoxides derived from each naphthopyran isomer display good photochromism with the reversible generation of yellow solutions.

UV irradiation of the *cis*-isomer of each sulfoxide results in the irreversible isomerisation to the more thermodynamically stable *trans*-isomer. Different behaviour under UV irradiation was noted for the mono- and bis-sulfones, **18** and **20** respectively, with **18** proving resistant to ring contraction under the applied conditions, whereas **20** afforded naphthofuran **23** but only photochemically and under more severe conditions.

Experimental

Unless otherwise stated, reagents were used as supplied. NMR spectra were recorded on a 400 MHz spectrophotometer (^{1}H NMR 400 MHz, ^{13}C NMR 100 MHz) for sample solution in $CDCl_3$ with tetramethylsilane as an internal reference. FT-IR spectra were recorded on either a spectrophotometer system equipped with a diamond probe ATR attachment (neat sample) or in KBr discs. UV–visible spectra were recorded for spectroscopic grade toluene solutions of the naphthopyrans (*ca.* 1×10^{-5}mol dm^{-3}) using a diode array spectrophotometer with activating irradiation provided by a TLC inspection lamp (Spectroline E Series 365 nm, 8 Watt). An immersion well photochemical reactor (Photochemical Reactors Ltd. UK) equipped with a 125 Watt, medium pressure Hg lamp was used for the ring contraction of **20**. Naphthopyrans **2a** (mp 154–156 °C) and **2b** (mp 161–163 °C) had physical and spectroscopic data in good agreement with that reported by Coelho *et al.*[6] and methylthio substituted benzophenones **14a**[17] and **14b**[18] had similar good agreement with literature reported data. All compounds were homogeneous by TLC using a range of eluent systems of differing polarity.

General method for the preparation of prop-yn-1-ols (15a) (15b)

n-Butyllithium (1.6 M in hexanes) (9.4 mL, 15 mmol) was added slowly *via* syringe to a cold (−10 °C), stirred solution of trimethylsilylacetylene (2.12 mL, 15 mmol) in anhydrous tetrahydrofuran (60 mL) under a nitrogen atmosphere. On completion of the addition (*ca.* 5 min) the cold solution was allowed to stir for 1 h. The benzophenone **14a** or **14b** (12 mmol) was added in a single portion and the mixture stirred until TLC examination of the reaction mixture indicated that none of the benzophenone remained (*ca.* 3 h). The reaction mixture was re-cooled to 0 °C and a solution of methanolic potassium hydroxide (from potassium hydroxide (1.74 g, 31 mmol) in methanol (20 mL)) was added in a single portion. The cooling bath was then removed and the mixture warmed to room temperature; after *ca.* 15 min, TLC examination indicated that deprotection was complete. The mixture was acidified to pH ~ 7 using glacial acetic acid and then poured into water (500 mL). The organic layer was separated and the aqueous layer extracted with ethyl acetate (3 × 100 mL). The organic phases were combined, washed with water (3 × 50 mL) and dried (anhyd. Na_2SO_4). Removal of the solvent gave the prop-2-yn-1-ol, which was used directly without further purification.

1-(4-Methylthiophenyl)-1-phenylprop-2-yn-1-ol (15a)

(2.20 g, 72%) as a pale yellow oil, ν_{max} 3450, 3244, 1595, 1483, 1398, 995 cm^{-1}, δ_H 2.45 (3H, s, SMe), 2.86 (1H, s, alkyne-H), 2.87 (1H, bs, OH), 7.18 (2H, m, Ar–H), 7.29 (3H, m, Ar–H), 7.50 (2H, m, Ar–H), 7.58 (2H, m, Ar–H).

1,1-Bis(4-methylthiophenyl)prop-2-yn-1-ol (15b)

(3.35 g, 93%) as colourless microcrystals, mp 75.0–77.0 °C, ν_{max} 3453, 3246, 1594, 1488, 1432, 1396, 1090, 1061, 993 cm^{-1}, δ_H 2.46 (6H, s, SMe), 2.76 (1H, s, alkyne-H), 2.87 (1H, s, OH), 7.20 (4H, m, Ar–H), 7.49 (4H, m, Ar–H).

General method for the preparation of methylthio substituted naphthopyrans (16) and (17)

A stirred solution of 2-naphthol (1.89 g, 13.1 mmol) and the prop-2-yn-1-ol (13.1 mmol) in toluene (60 mL) was warmed to 50 °C. Acidic alumina (2.0 g) was added and the mixture was refluxed until TLC examination indicated that none of the prop-2-yn-1-ol remained (*ca.* 1.5 h). The mixture was cooled to ~50 °C, filtered and the alumina was washed with hot toluene (2 × 30 mL). Removal of the toluene from the combined washings and filtrate gave a red gum that was eluted from silica (50% ethyl acetate in hexane), followed by recrystallisation from MeOH to afford the naphthopyran.

3-(4-Methylthiophenyl)-3-phenyl-3*H*-naphtho[2,1-*b*]pyran (16)

(2.59 g, 52%) as off-white microcrystals, mp 120–121 °C, λ_{max}(PhMe) 464 nm, ν_{max} 1634, 1489, 1223, 1090, 1079, 1002, 950, 812, 751, 736, 707, 696 cm^{-1}, δ_H 2.44 (3H, s, SMe), 6.22 (1H, d, J = 9.8 Hz, 2-H), 7.19 (3H, m, Ar–H, 5-H), 7.25 (1-H, m, Ar–H), 7.33 (4H, m, Ar–H, 1-H), 7.39 (2H, m, Ar–H), 7.48 (3H, m, Ar–H), 7.65 (1H, d, J = 8.8 Hz, 6-H), 7.73 (1H, d, J = 8.8 Hz, 7-H), 7.95 (1H, d, J = 8.8 Hz, 10-H), δ_C 15.6, 82.3, 114.0, 118.3, 119.7, 121.3, 123.6, 126.0, 126.6, 126.9, 127.5, 127.6, 127.6, 128.1, 128.5, 129.3, 129.8, 129.9, 137.9, 138.1, 141.6, 144.7, 150.5. Found M$^+$ = 380.1228. $C_{26}H_{20}OS$ requires M$^+$ = 380.1229.

3,3-Bis(4-methylthiophenyl)-3*H*-naphtho[2,1-*b*]pyran (17)

(4.3 g, 77%) as colourless microcrystals, mp 171–173 °C (mp apparatus, uncorrected), 174 °C (DSC) [lit. mp = 142–143 °C[16]], λ_{max}(PhMe) 478 nm, ν_{max} 1627, 1486, 1093, 1082, 1002, 955, 820, 740 cm^{-1}, δ_H 2.45 (6H, s, SMe), 6.18 (1H, d, J = 9.9 Hz, 2-H), 7.18 (5H, m, Ar–H, 5-H), 7.31 (2H, m, Ar–H, 1-H), 7.38 (4H, m, Ar–H), 7.46 (1H, m, Ar–H), 7.65 (1H, d, J = 8.8 Hz, 6-H), 7.72 (1H, d, J = 8.1 Hz, 7-H), 7.94 (1H, d, J = 8.5 Hz, 10-H), δ_C 15.6, 82.0, 114.0, 118.3, 119.8, 121.3, 123.7, 126.0, 126.7, 127.3, 127.5, 128.5, 129.3, 129.7, 129.9, 137.9, 141.5, 150.4. Found M$^+$ = 426.1112. $C_{27}H_{22}OS_2$ requires M$^+$ = 426.1107.

General method for the oxidation of thioether substituted naphthopyrans (2a, 2b, 19, 20).

m-Chloroperoxybenzoic acid (1.34 g, 5.95 mmol, 77%,) was added portionwise over 5 min to a cold (0 °C) stirred solution of the photochromic thioether (3.97 mmol) in CH_2Cl_2 (25 mL). On completion of the addition, the cooling bath was removed and the solution was stirred until TLC examination of the reaction mixture indicated that no further thioether remained (15 min). The reaction mixture was poured into water (200 mL) and the organic layer separated. The aqueous layer was extracted with CH_2Cl_2 (2 × 50 mL) and the combined CH_2Cl_2 layers were washed with aqueous Na_2SO_3 solution (2 × 50 mL, 2 M), saturated $NaHCO_3$ solution (2 × 50 mL) and water (50 mL). Removal of the dried (anhydrous Na_2SO_4) CH_2Cl_2 gave the crude product, which was purified by flash column chromatography.

From spiro(3*H*-naphtho[2,1-*b*]pyran-3,9′-[9*H*]-thioxanthene) (**2a**) after elution with 25% EtOAc–hexane as three fractions:

Fraction 1: spiro(3*H*-naphtho[2,1-*b*]pyran-3,9′-[9*H*]-thioxanthene-10,10-dioxide) (3). (0.27 g, 17%) as pale yellow microcrystals, mp 209–210 °C, λ_{max}(PhMe) 426 nm, ν_{max} 1639, 1590, 1296, 1163, 1132, 1095, 1071, 1011, 806, 751 cm^{-1}, δ_H 6.36 (1H, d, J = 10.2 Hz, 2-H), 7.08 (1H, d, J = 10.2 Hz, 1-H), 7.35 (1H, d, J = 8.8 Hz, 5-H), 7.41 (1H, m, Ar–H), 7.49 (1H, m, Ar–H), 7.57 (4H, m, Ar–H), 7.85 (2H, m, Ar–H), 7.93 (3H, m, 10-H, Ar–H), 8.18 (2H, m, Ar–H), δ_C 78.1, 110.6, 116.4, 116.6, 121.1, 123.8, 124.2, 125.0, 126.5, 127.2, 128.7, 129.0, 129.7, 129.8, 130.8, 133.3, 133.9, 138.1, 143.3, 150.9. Found C, 75.6; H, 4.0; S, 8.0; M + Na$^+$ = 419.0714. $C_{25}H_{16}O_3S$ requires C, 75.7; H, 4.1; S, 8.1%; M + Na$^+$ = 419.0712.

Fraction 2: *cis*-spiro(3*H*-naphtho[2,1-*b*]pyran-3,9′-[9*H*]-thioxanthene-10-oxide) (4). (0.42 g, 28%) as pale yellow microcrystals from EtOAc–hexane, mp 205–206 °C, λ_{max}(PhMe) 426 nm, ν_{max} 1632, 1588, 1239, 1204, 1098, 1045, 1011, 811, 749, 546 cm^{-1}, δ_H 5.59 (1H, d, J = 10.0 Hz, 2-H), 7.05 (1H, d, J = 10.0 Hz, 1-H), 7.40 (1H, m, Ar–H), 7.50 (4H, m, Ar–H), 7.57 (2H, m, Ar–H), 7.86 (5H, m, Ar–H), 8.04 (2H, m, Ar–H), δ_C 78.8, 111.5, 116.9, 117.9, 121.2, 122.4, 124.18, 124.21, 124.7, 127.2, 128.4, 128.7, 129.7, 129.8, 130.5, 131.0, 137.5, 138.5, 151.1. Found M + H$^+$ = 381.0942. $C_{25}H_{16}O_2S$ requires M + H$^+$ = 381.0944.

Fraction 3: *trans*-spiro(3*H*-naphtho[2,1-*b*]pyran-3,9′-[9*H*]-thioxanthene-10-oxide) (5). (0.30 g, 20%) as pale yellow microcrystals from EtOAc–hexane, mp 210–211 °C, λ_{max}(PhMe) 427 nm, ν_{max} 1632, 1587, 1510, 1445, 1239, 1219, 1082, 1059, 1035, 1000, 930, 807, 777, 751, 736 cm^{-1}, δ_H 6.58 (1H, d, J = 10.2 Hz, 2-H), 6.90 (1H, d, J = 8.8 Hz, 5-H), 7.37 (1H, m, Ar–H), 7.45 (2H, m, Ar–H), 7.53 (3H, m, Ar–H), 7.59 (1H, d, J = 8.8 Hz, 6-H), 7.71 (1H, d, J = 8.1 Hz, Ar–H), 7.76 (2H, dd, J = 7.6, 1.2 Hz, Ar–H), 7.78 (1H, d, J = 10.2 Hz, 1-H), 8.05 (1H, d, J = 8.5 Hz, 10-H), 8.12 (2H, dd, J = 7.6, 1.3 Hz, Ar–H), δ_C 77.8, 113.3, 117.5, 119.8, 121.1, 123.7, 124.1, 125.6, 127.03, 127.04, 128.7, 128.9, 129.6, 129.7, 130.0, 130.5, 135.8, 144.8, 149.9. Found M + H$^+$ = 381.0943. $C_{25}H_{16}O_2S$ requires M + H$^+$ = 381.0944.

From spiro(2*H*-naphtho[1,2-*b*]pyran-2,9′-[9*H*]-thioxanthene) (**2b**) after elution with 25% EtOAc–hexane as three fractions:

Fraction 1: spiro(2*H*-naphtho[1,2-*b*]pyran-2,9′-[9*H*]-thioxanthene-10,10-dioxide) (9). (0.42 g, 28%) as pale yellow microcrystals, mp 198–199 °C, λ_{max}(PhMe) 472 nm, ν_{max} 1646, 1569, 1466, 1440, 1393, 1295, 1264, 1164, 1147, 1134, 1104, 1068, 974, 920, 809, 765, 755, 723 cm^{-1}, δ_H 6.31 (1H, d, J = 9.9 Hz, 3-H), 6.50 (1H, d, J = 9.9 Hz, 4-H), 7.20 (1H, d, J = 8.3 Hz, 5-H), 7.55 (7H, m, Ar–H), 7.86 (3H, m, Ar–H), 8.20 (2H, m, 4′, 5′-H), 8.27 (1H, m, Ar–H), δ_C 78.7, 112.4, 121.2, 121.3, 121.6, 123.3, 123.8, 124.8, 124.8, 126.3, 126.7, 126.9, 128.0, 128.9, 133.4, 134.0, 135.1, 143.5, 147.6. Found C, 75.7; H, 4.0; S, 7.8; M$^+$ = 396.0817. $C_{25}H_{16}O_3S$ requires C, 75.7; H, 4.1; S, 8.1%; M$^+$ = 396.0815.

Fraction 2: *cis*-spiro(2*H*-naphtho[1,2-*b*]pyran-2,9′-[9*H*]-thioxanthene-10-oxide) (10). (0.36 g, 24%) as pale yellow microcrystals from EtOAc–hexane, mp 204–206 °C, λ_{max}(PhMe) 471 nm, ν_{max} 1651, 1617, 1568, 1442, 1392, 1265, 1206, 1108, 1087, 1070, 1040, 984, 817, 758, 733 cm^{-1}, δ_H 5.54 (1H, d, J = 9.7 Hz, 3-H), 6.47 (1H, d, J = 9.7 Hz, 4-H), 7.17 (1H, d, J = 8.3 Hz, 5-H), 7.53 (7H, m, Ar–H), 7.78 (2H, dd, J = 7.8, 1.1 Hz, Ar–H), 7.89 (1H, m, Ar–H), 8.06 (2H, dd, J = 7.7, 1.1 Hz, Ar–H), 8.42 (1H, m, Ar–H), δ_C 79.5, 113.1, 121.4, 121.6, 122.3, 122.4, 123.5, 124.2, 124.7, 124.8, 126.4, 127.0, 128.1, 128.4, 130.7, 135.2, 137.7, 138.5, 147.9. Found C, 78.7; H, 4.2; S, 8.2; M + H$^+$ = 381.0939. $C_{25}H_{16}O_2S$ requires C, 78.9; H, 4.3; S, 8.4%; M + H$^+$ = 381.0944.

Fraction 3: *trans*-spiro(2*H*-naphtho[1,2-*b*]pyran-2,9′-[9*H*]-thioxanthene-10-oxide) (11). (0.65 g, 43%) as pale yellow microcrystals from EtOAc–hexane, mp 157–158 °C, λ_{max}(PhMe) 473 nm, ν_{max} 1650, 1619, 1444, 1374, 1264, 1168, 1094, 1054, 1036, 946, 924, 822, 770, 765, 754, 739, 659 cm^{-1}, δ_H 6.46 (1H, d, J = 10.0 Hz, 3-H), 7.19 (1H, d, J = 10.0 Hz, 4-H), 7.22 (1H, d, J = 8.3, 5-H), 7.36 (3H, m, Ar–H), 7.50 (4H, m, Ar–H), 7.65 (1H, m, Ar–H), 7.76 (2H, dd, J = 7.6, 1.1 Hz, Ar–H), 8.05 (1H, m, Ar–H), 8.14 (2H, dd, J = 7.6, 1.3 Hz, Ar–H), δ_C 78.4, 114.6, 119.4, 121.2, 122.2, 124.4, 124.5, 125.5, 125.9, 126.7, 127.2, 127.5, 128.5, 128.9, 130.0, 134.8, 136.0, 144.8, 147.2. Found M + H$^+$ = 381.0941. $C_{25}H_{16}O_2S$ requires M + H$^+$ = 381.0944.

From 3-(4-methylthiophenyl)-3-phenyl-3*H*-naphtho[2,1-*b*]pyran (**16**) after elution with 25% EtOAc–hexane as two fractions:

Fraction 1: 3-(4-methylsulfonylphenyl)-3-phenyl-3*H*-naphtho-[2,1-*b*]pyran (18). (0.54 g, 33%) as colourless microcrystals from EtOAc–hexane, mp 180–181 °C, λ_{max}(PhMe) 425 nm, ν_{max} 1631, 1587, 1513, 1489, 1310, 1295, 1246, 1217, 1148, 1089, 1081, 1008, 957, 821, 775, 756, 723, 711 cm^{-1}, δ_H 3.01 (3H, s, SO_2Me), 6.25 (1H, d, J = 9.9 Hz, 2-H), 7.21 (1H, d, J = 8.8, 5-H), 7.28 (1H, m, Ar–H), 7.36 (3H, m, Ar–H), 7.38 (1H, d, J = 9.9 Hz, 1-H), 7.47 (3H, m, Ar–H), 7.68 (1H, d, J = 8.7 Hz, Ar–H), 7.72 (3H, m, Ar–H), 7.87 (2H, m, Ar–H), 7.96 (1H, d, J = 8.6 Hz, 10-H), δ_C 44.5, 82.0, 114.1, 118.1, 120.7, 121.3, 124.0, 126.6, 126.9, 126.9, 127.3, 127.9, 128.1, 128.4, 128.6, 129.5, 129.7, 130.3, 139.5, 143.7, 150.2, 151.0. Found C, 75.5; H, 4.8; S, 7.7; M + $NH_4{}^+$ = 430.1473. $C_{26}H_{20}O_3S$ requires C, 75.7; H, 4.9; S, 7.8%; M + $NH_4{}^+$ = 430.1471.

Fraction 2: 3-(4-methylsulfinylphenyl)-3-phenyl-3*H*-naphtho[2,1-*b*]pyran (19). As an inseparable mixture of two diastereoisomers (1.03 g, 65%) as colourless microcrystals from EtOAc–hexane, mp 195–197 °C, λ_{max}(PhMe) 429 nm, ν_{max} 1629, 1586, 1447, 1394, 1243, 1220, 1079, 1048, 1007, 957, 819, 762, 751, 744, 734, 697 cm^{-1}, δ_H all signals, 2.686 (3H, s, SOMe), 2.691 (3H, s, SOMe), 6.25 (1H, d, J = 9.9 Hz, 2-H), 6.26 (1H, d, J = 9.9 Hz, 2-H), 7.20 (1H, d, J = 8.8 Hz, 5-H), 7.21 (1H, d, J = 9.1 Hz, 5-H), 7.27 (1H, m, Ar–H), 7.33 (4H, m, Ar–H, 1-H), 7.46 (3H, m, Ar–H), 7.59 (2H, m, Ar–H), 7.67 (3H, m, Ar–H), 7.72 (1H, d, J = 8.3 Hz, Ar–H), 7.96 (1H, d, J = 8.5 Hz, 10-H), δ_C all signals, 43.8, 82.1, 114.0, 118.2, 120.3, 121.3, 123.5, 123.8, 126.8, 126.9, 127.0, 127.9, 128.0, 128.3, 128.6, 129.4, 129.7, 130.1, 138.1, 144.1, 144.1, 144.7, 148.2, 150.3. Found C, 78.6; H, 5.0, S, 8.1; M + H$^+$ = 397.1258. $C_{26}H_{20}O_2S$ requires C, 78.7; H, 5.1; S, 8.1%; M + H$^+$ = 397.1257.

From 3,3-bis(4-methylthiophenyl)-3*H*-naphtho[2,1-*b*]pyran (**17**) after elution with 25% EtOAc–hexane as three fractions:

Fraction 1: 3,3-bis(4-methylsulfonylphenyl)-3*H*-naphtho[2,1-*b*]pyran (20). (0.66 g, 34%) as colourless microcrystals from EtOAc–hexane, mp 171–172 °C, λ_{max}(PhMe) 415 nm, ν_{max} 1633, 1588, 1395, 1311, 1291, 1146, 1086, 1007, 952, 769 cm^{-1}, δ_H 3.02 (6H, s, SO_2Me), 6.22 (1H, d, J = 9.9 Hz, 2-H), 7.22 (1H, d, J = 8.8 Hz, 5-H), 7.37 (1H, m, Ar–H), 7.45 (1H, d, J = 9.9 Hz, 1-H), 7.52 (1H, m, Ar–H), 7.70 (6H, m, Ar–H), 7.92 (4H, m, Ar–H), 7.97 (1H, d, J = 8.4 Hz, 10-H), δ_C 44.4, 81.5, 114.2, 117.9, 121.3, 121.8, 124.3, 125.4, 127.2, 127.6, 127.8, 128.7, 129.6, 129.7, 130.8, 138.1, 140.1, 149.7, 149.8. Found C, 66.1; H, 4.5; S, 13.0; $M + NH_4^+$ = 508.1249. $C_{27}H_{22}O_5S_2$ requires C, 66.1; H, 4.5; S, 13.1%; $M + NH_4^+$ = 508.1247.

Fraction 2: 3-(4-methylsulfinylphenyl)-3-(4-methylsulfonylphenyl)-3*H*-naphtho[2,1-*b*]pyran (21). As an inseparable mixture of two diastereoisomers (0.86 g, 46%) as colourless microcrystals from EtOAc–hexane, mp 207.0–209.0 °C, λ_{max}(PhMe) 423 nm, ν_{max} 1633, 1394, 1307, 1293, 1147, 1084, 1047, 1006, 951, 827, 812, 774 cm^{-1}, δ_H all signals 2.704 (3H, s, SOMe), 2.706 (3H, s, SOMe), 3.02 (3H, s, SO_2Me), 6.23 (1H, d, J = 9.9 Hz, 2-H), 6.24 (1H, d, J = 9.9 Hz, 2-H), 7.21 (1H, d, J = 8.8 Hz, 5-H), 7.22 (1H, d, J = 8.9 Hz, 5-H), 7.37 (1H, m, 8-H), 7.43 (1H, d, J = 9.9 Hz, 1-H), 7.51 (1H, m, 9-H), 7.63 (4H, m, Ar–H), 7.72 (3H, m, Ar–H), 7.74 (1H, d, J = 8.1 Hz, Ar–H), 7.90 (2H, m, Ar–H), 7.97 (1H, d, J = 8.6 Hz, 10-H), δ_C all signals 43.8, 44.4, 81.6, 114.1, 118.0, 121.3, 121.4, 123.8, 124.2, 125.8, 127.1, 127.5, 127.9, 128.0, 128.6, 129.6, 129.7, 130.6, 139.9, 145.5, 146.9, 149.9, 150.2. Found C, 68.1; H, 4.6, S, 13.5; M^+ = 474.0952. $C_{27}H_{22}O_4S_2$ requires C, 68.3; H, 4.7; S, 13.5%; M^+ = 474.0954.

Fraction 3: 3,3-bis(4-methylsulfinylphenyl)-3*H*-naphtho[2,1-*b*]pyran (22). As an inseparable mixture of diastereoisomers (0.32 g, 18%) as colourless microcrystals from EtOAc–hexane, mp 191–193 °C, λ_{max}(PhMe) 426 nm, ν_{max} 1629, 1214, 1084, 1044, 1006, 950, 813, 741 cm^{-1}, δ_H all signals 2.702 (3H, s, SOMe), 2.705 (3H, s, SOMe), 6.24 (1H, m, 2-H), 7.20 (1H, d, J = 8.7 Hz, Ar–H), 7.36 (1H, m, Ar–H), 7.41 (1H, d, J = 9.6 Hz, 1-H), 7.50 (1H, m, Ar–H), 7.62 (8H, m, Ar–H), 7.70 (1H, d, J = 9.2 Hz, Ar–H), 7.74 (1H, d, J = 8.0 Hz, Ar–H), 7.97 (1H, d, J = 8.4 Hz, 10-H), δ_C all signals 43.8, 43.8, 81.8, 114.1, 118.1, 121.0, 121.3, 123.7, 124.1, 126.2, 127.0, 127.9, 128.6, 129.5, 129.7, 130.4, 145.3, 147.4, 150.0. Found M^+ = 458.1006. $C_{27}H_{22}O_3S_2$ requires M^+ = 458.1005.

Procedure for the thermal rearrangement of spiro(3*H*-naphtho[2,1-*b*]pyran-3,9′-thioxanthene-10,10-dioxide (3)

A solution of naphthopyran (**3**) (0.25 g, 0.63 mmol) in EtOAc (30 mL) and hexane (30 mL) was heated under reflux until TLC examination of the mixture indicated that no reactant remained (*ca.* 45 min). Removal of the solvent gave:

9-(naphtho[2,1-*b*]furan-2-yl)-9*H*-thioxanthene-10,10-dioxide (6). (0.25 g, 100%) as pale brown plates from EtOAc–hexane, mp 239–241 °C, ν_{max} 1566, 1445, 1385, 1293, 1270, 1163, 1143, 1129, 797, 740, 726, 578, 567, 499 cm^{-1}, δ_H 5.92 (1H, s, 9-H), 7.10 (1H, s, 1′-H), 7.42 (2H, m, Ar–H), 7.48 (1H, m, Ar–H), 7.58 (6H, m, Ar–H), 7.73 (1H, d, J = 8.9 Hz, Ar–H), 7.93 (1H, d, J = 8.1 Hz, Ar–H), 8.07 (1H, d, J = 8.2 Hz, Ar–H), 8.21 (2H, m, Ar–H), δ_C 43.5, 106.4, 112.2, 123.4, 123.5, 124.1, 124.7, 125.5, 126.5, 127.6, 128.4, 128.7, 129.3, 130.3, 132.7, 137.3, 138.0, 152.7, 153.1. Found $M + NH_4^+$ = 414.1158. $C_{25}H_{16}O_3S$ requires $M + NH_4^+$ = 414.1158.

Procedure for the thermal rearrangement of spiro(2*H*-naphtho[1,2-*b*]pyran-2,9′-thioxanthene-10,10-dioxide (9)

A solution of naphthopyran (**9**) (0.25 g, 0.63 mmol) in toluene (75 mL) was heated under reflux until TLC examination of the mixture indicated that no reactant remained (*ca.* 26 h). Removal of the solvent gave:

9-(naphtho[1,2-*b*]furan-2-yl)-9*H*-thioxanthene-10,10-dioxide (12). (0.18 g, 72%) as pale brown plates upon recrystallisation from PhMe, mp 243–244 °C, ν_{max} 1581, 1570, 1472, 1445, 1385, 1290, 1273, 1158, 1142, 1124, 1056, 962, 807, 760, 745, 734, 680 cm^{-1}, δ_H 5.93 (1H, s, 9-H), 6.77 (1H, s, 3′-H), 7.42 (3H, m, Ar–H), 7.50 (1H, m, Ar–H), 7.56 (5H, m, Ar–H), 7.66 (1H, d, J = 8.3, Ar–H), 7.91 (1H, d, J = 8.1, Ar–H), 8.21 (3H, m, Ar–H), δ_C 43.5, 108.4, 119.7, 119.9, 121.2. 123.6, 123.8, 124.1, 125.3, 126.4, 128.4, 128.4, 129.2, 131.5, 132.7, 137.3, 138.1, 150.9, 153.0. Found C, 75.7; H, 4.0; S, 7.9; M^+ = 396.0817. $C_{25}H_{16}O_3S$ requires C, 75.7; H, 4.1; S, 8.1%; M^+ = 396.0815.

Photochemical rearrangement of (20)

A stirred solution of naphthopyran (**20**) (0.40 g, 0.81 mmol) in toluene (100 mL) in an immersion well photochemical reactor was degassed with nitrogen and irradiated until TLC examination of the reaction mixture indicated that no further change in the composition of the reaction mixture had occurred (*ca.* 15 min). The toluene was removed and the crude product was recrystallised from EtOAc and hexane to afford:

2-[1,1-bis(4-methylsulfonylphenyl)methyl]naphtho[2,1-*b*]furan (23). (0.34 g, 85%) as colourless microcrystals from PhMe, mp 235–237 °C, ν_{max} 1593, 1302, 1144, 1089, 954, 805, 762 cm^{-1}, δ_H 3.09 (6H, s, SO_2Me), 5.86 (1H, s, methine), 6.84 (1H, s, 1-H), 7.47 (5H, m, Ar–H), 7.57 (1H, m. Ar–H), 7.59 (1H, d, J = 9.2, 5-H), 7.73 (1H, d, J = 9.0, Ar–H), 7.95 (5H, m, Ar–H), 8.03 (1H, d, J = 8.0, 9-H), δ_C 44.5, 50.9, 105.7, 112.1, 123.1, 123.3, 124.8, 125.6, 126.6, 127.4, 128.1, 128.8, 129.9, 130.3, 139.8, 146.1, 152.8, 155.6. Found C, 65.9; H, 4.5; S, 12.9; $HM + NH_4^+$ = 508.1253. $C_{27}H_{22}O_5S_2$ requires C, 66.1; H, 4.5; S, 13.1%; $M + NH_4^+$ = 508.1247.

Acknowledgements

The authors thank Yorkshire Forward and James Robinson Ltd. (Huddersfield, UK) for a research studentship to SBK and the EPSRC for access to the National Mass Spectrometry Service (Swansea) and the National X-Ray Crystallography Service (Southampton, UK). The Clothworkers′ of the City of London are thanked for a millennium grant for the purchase of a Bruker Avance NMR spectrophotometer.

References

1 For recent reviews see: J. D. Hepworth and B. M. Heron, in *Functional Dyes*, ed. S.-H. Kim, Elsevier, Amsterdam, 2006, pp. 85–135 and B. Van Gemert, in *Organic Thermochromic and Photochromic Compounds,*

Volume 1 Main Photochromic Families, ed. J. C. Crano and R. J. Guglielmetti, Plenum Press, New York, 1999, pp. 111–140.

2 P. J. Coelho, M. A. Salvador, B. M. Heron and L. M. Carvalho, *Tetrahedron*, 2005, **61**, 11730; C. D. Gabbutt, B. M. Heron and A. C. Instone, *Tetrahedron*, 2006, **62**, 737; S. Delbaere, G. Vermeersch, M. Frigoli and G. H. Mehl, *Org. Lett.*, 2006, **8**, 4931; J. N. Moorthy, P. Venkatakrishnan, S. Sengupta and M. Baidya, *Org. Lett.*, 2006, **8**, 4891; W. Zhao and E. M. Carreira, *Chem.–Eur. J.*, 2007, **13**, 2671; E. A. Shilova, V. P. Perevalov, A. Samat and C. Moustrou, *Tetrahedron Lett.*, 2007, **48**, 4127.

3 Examples of the Claisen route to naphthopyrans are known, however, in these instances, the electron withdrawing aryl group is partnered with an electron rich aryl unit to improve reactivity *e.g.* J. Momoda, S. Matsuoka, H. Nagou, PCT WO 2000075238 (2000); J. Momota, T. Hara, Japanese Patent, JP 09124645 (1997).

4 C. D. Gabbutt, B. M. Heron, A. C. Instone, D. A. Thomas, S. M. Partington, M. B. Hursthouse and T. Gelbrich, *Eur. J. Org. Chem.*, 2003, 1220.

5 J.-L. Pozzo, V. A. Lokshin and R. Guglielmetti, *J. Chem. Soc., Perkin Trans. 1*, 1994, 2591.

6 P. Coelho, L. M. Carvalho, S. Abrantes, M. M. Oliveira, A. M. F. Oliveira-Campos, A. Samat and R. Guglielmetti, *Tetrahedron*, 2002, **58**, 9505; A. Mustafa, *J. Chem. Soc.*, 1949, 2295.

7 Crystallographic data for compound **4** (CCDC670085): formula $C_{25}H_{16}O_2S$; formula weight, 380.44; T = 120(2) K; λ = 0.71073 Å; crystal system = monoclinic; space group, $P2_1/n$; unit cell dimensions, a = 11.1939(5) Å, α = 90°; b = 14.0344(4) Å, β = 101.498(2)°; c = 11.7187(5) Å, γ = 90°; volume = 1804.06(12) Å^3; Z = 4; density (calculated) = 1.401 Mg m^{-3}; absorption coefficient = 0.198 mm^{-1}; F(000) = 792; crystal, shard; colourless; crystal size = 0.08 × 0.07 × 0.04 mm^3 θ range for data collection = 3.16–27.48°; index ranges = $-14 \leq h \leq 14$, $-18 \leq k \leq 16$, $-15 \leq l \leq 15$; reflections collected = 21913; independent reflections = 4135 [R_{int} = 0.0999]; completeness to θ = 27.48° = 99.8%; absorption correction = semi-empirical from equivalents; max. and min. transmission = 0.9921 and 0.9843; refinement method = full-matrix least-squares on F^2; data/restraints/parameters = 4135/0/253; goodness-of-fit on F^2 = 1.065; final R indices [$F^2 > 2\sigma(F^2)$] = R_1 = 0.0671, wR_2 = 0.1124; R indices (all data) = R_1 = 0.1094, wR_2 = 0.1255; largest diff. peak and hole = 0.369 and −0.361 e Å^{-3}.

8 Crystallographic data for compound **5** (CCDC670086): formula $C_{25}H_{16}O_2S$; formula weight = 380.44; T = 120(2) K; λ = 0.71073 Å; crystal system = monoclinic; space group = $P2_1/n$; unit cell dimensions, a = 11.3454(2) Å, α = 90°; b = 13.4896(2) Å, β = 96.3650(10)°; c = 11.5736(3) Å, γ = 90°; volume = 1760.36(6) Å^3; Z = 4; density (calculated) = 1.435 Mg m^{-3}; absorption coefficient = 0.203 mm^{-1}; F(000) = 792; crystal = prism; colourless; crystal size = 0.30 × 0.30 × 0.20 mm^3 θ range for data collection = 3.02–27.49°; index ranges = $-14 \leq h \leq 14$, $-17 \leq k \leq 17$, $-15 \leq l \leq 14$; reflections collected = 22230; independent reflections = 4007 [R_{int} = 0.0303]; completeness to θ = 27.49° = 99.3%; absorption correction = semi-empirical from equivalents; max. and min. transmission = 0.9605 and 0.9415; refinement method = full-matrix least-squares on F^2; data/restraints/parameters = 4007/0/253; goodness-of-fit on F^2 = 1.059; Final R indices [$F^2 > 2\sigma(F^2)$] = R_1 = 0.0364, wR_2 = 0.0930; R indices (all data) = R_1 = 0.0389, wR_2 = 0.0948; largest diff. peak and hole = 0.360 and −0.470 e Å^{-3}.

9 For examples of photochemical isomerisation of sulfoxides see: A. A. Rachford and J. J. Rack, *J. Am. Chem. Soc.*, 2006, **128**, 14318; T. Fujita, H. Kamiyama, Y. Osawa, H. Kawaguchi, B. J. Kim, A. Tatami, W. Kawashima, T. Maeda, A. Nakanishi and H. Morita, *Tetrahedron*, 2007, **63**, 7708.

10 J. A. Gillean III, D. W. Phelps and A. W. Cordes, *Acta Crystallogr., Sect. B*, 1973, **29**, 2296.

11 Crystallographic data for compound **6** (CCDC661552): formula $C_{25}H_{16}O_3S$; formula weight = 396.44; T = 150(2) K; λ = 0.71073 Å [Mo-K$_\alpha$]; crystal system = monoclinic; space group = $P2_1/n$; unit cell dimensions, a = 7.97170(10) Å, α = 90°; b = 20.6854(3) Å, β = 101.1430(7)°; c = 11.1804(2) Å, γ = 90°; volume = 1808.87(5) Å^3; Z = 4; density (calculated) = 1.456 Mg m^{-3}; absorption coefficient = 0.205 mm^{-1}; F(000) = 824; crystal = pale brown plate; crystal size = 0.31 × 0.20 × 0.08 mm; θ range for data collection = $2.71 \leq \theta \leq 26$°; index ranges = $-9 \leq h \leq 9$, $-25 \leq k \leq 25$, $-13 \leq l \leq 13$; reflections collected = 34563; independent reflections = 3553 [R(int) = 0.084]; absorption correction = none; refinement method = full-matrix least-squares on F^2; data/restraints/parameters = 3553/0/262; goodness-of-fit = 1.058; Final R indices [$I > 2\sigma(I)$] = R_1 = 0.0396, wR_2 = 0.1011; R indices (all data) = R_1 = 0.0483, wR_2 = 0.1084; largest diff. peak and hole = 0.298 and −0.545 e Å^{-3}.

12 There is only one previous report describing the contraction of 8-ethenyl-3,3-diphenyl-3H-naphtho[2,1-b]pyran, which was accomplished under prolonged intense irradiation in either cyclohexane or ethanol leading to a dihydronaphthofuran, which was accompanied by benzophenone: S. Coen, N. Lehadus, C. Moustrou, A. Samat and R. Guglielmetti, *Heterocycl. Commun.*, 2002, **8**, 27.

13 S. Delbaere, B. Luccioni-Houze, C. Bochu, Y. Teral, M. Campredon and G. Vermeersch, *J. Chem. Soc., Perkin Trans. 2*, 1998, 1153; X. Sallenave, S. Delbaere, G. Vermeersch, A. Saleh and J.-L. Pozzo, *Tetrahedron Lett.*, 2005, **46**, 3257; M. Frigoli and G. H. Mehl, *Chem. Commun.*, 2004, 2040.

14 Crystallographic data for *trans*-sulfoxide **11** (CCDC663292): formula $C_{25}H_{16}O_2S$; formula weight = 380.44; T = 150 K; λ = 0.71073 Å [Mo-K$_\alpha$]; crystal system = monoclinic; space group = $C2/$; unit cell dimensions, a = 19.3719(8) Å, α = 90°; b = 11.5100(5) Å, β = 99.926(2)°; c = 16.4409(6) Å, γ = 90°; volume = 3611.0(3) Å^3; Z = 8; density (calculated) = 1.4 Mg m^{-3}; absorption coefficient = 0.198 mm^{-1}; F(000) = 1584; crystal = pale brown fragment; crystal size 0.29 × 0.26 × 0.21 mm; θ range for data collection = $2.32 \leq \theta \leq 28.3$°; index ranges = $-25 \leq h \leq 25$, $-15 \leq k \leq 15$, $-18 \leq l \leq 21$; reflections collected = 29976; independent reflections = 4465 [R(int) = 0.0437]; absorption correction = none; refinement method = full-matrix least-squares on F^2; Data/restraints/parameters = 4465/0/253; Goodness-of-fit = 1.025; Final R indices [$I > 2\sigma(I)$] = R_1 = 0.0370, wR_2 = 0.0875; R indices (all data) = R_1 = 0.0486, wR_2 = 0.0936; largest diff. peak and hole = 0.309 and −0.541 e Å^{-3}.

15 S. Jockusch, N. J. Turro and F. R. Blackburn, *J. Phys. Chem. A*, 2002, **106**, 9236.

16 T.-F. Tan, J. Han, M.-L. Pang, Y.-F. Fu, H. Ma, Y.-X. Ma and J.-B. Meng, *Tetrahedron*, 2006, **62**, 4900.

17 L. C. Schmidt, V. Rey and A. B. Peñéñory, *Eur. J. Org. Chem.*, 2006, 2210.

18 P. Lucas, N. El Mehdi, H. A. Ho, D. Bélanger and L. Breau, *Synthesis*, 2000, 1253.