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An NMR investigation of the merocyanine dyes generated by protolysis of some novel spironaphthopyranoindoles

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Dedicated to Dr. Geoff Hallas in celebration of his 65th birthday.

Abstract

Two novel amino-substituted spiroindolinonaphthopyrans have been synthesised. Whilst these compounds exhibit no observable photochromic properties at ambient temperature, protonation gives stable, intensely coloured dyes. ^{1}H nmr spectroscopy has been used to establish the configuration of these dyes. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Photochromism; Merocyanine dyes; nmr spectroscopy; Synthesis; Spiroindolinonaphthopyran (NIPS); Protolysis

1. Introduction

The phenomenon of photochromism, originally demonstrated by Fritsch in 1867 [1], is well documented and has been the subject of several reviews [2]. Known organic photochromic systems include azobenzenes [3], stilbenes and the related diheteroarylethenes [4], fulgides [5], spirodihydroindolizines [6], oxazines [7] and pyrans [3,8]. Of these systems, the oxazines and pyrans have attracted particular attention because of the wide range and intensity of colours which can be developed, their fatigue resistance and the ease with which their rate of fade can be controlled [9]. The design of photochromic pyrans has evolved from the originally conceived spiroindolinobenzopyrans (1) [10] often abbreviated to BIPS, through to the isomeric, angularly fused, 2,2-diaryl-2*H*-naphtho[1,2-*b*]-(Ref. [11]) and 3,3-diaryl-3*H*-naphtho [2,1-*b*]-pyrans [12]. The colouration process of the pyran system relies upon photolytic or thermal induced cleavage of the O–C bond to generate a merocyanine dye (Scheme 1). Cleavage of this O–C bond in a variety of benzopyran derivatives under various conditions is known and the corresponding valence isomerism of simple 2*H*-pyrans to afford a dienal is well documented [13]. There has been considerable speculation concerning the number and distribution of possible isomers contributing to the overall observed colour, with the application of molecular modelling [14] and nmr studies of transient intermediates [15,16] being employed.

Of the many developments of the BIPS molecule recorded, perhaps the most important is the presence of the 6-nitro substituent which is essential for intense colour generation [16]. Simple benzologues of BIPS compounds have been described [16,17].

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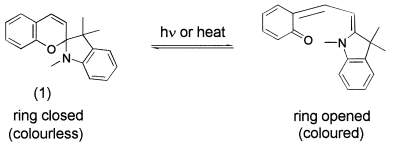
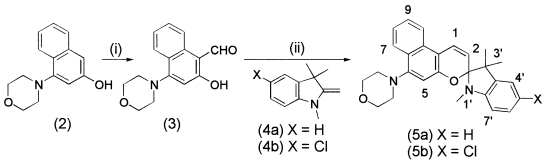


Scheme 1.



Reagents: (i) $POCl_3$, DMF, Δ; (ii) (4), EtOH anhyd., Δ.

Scheme 2.

However, our extensive synthetic programme on photochromic naphthopyrans and naphthoxazines has shown that the presence of an amino substituent *meta* to the pyran and oxazine oxygen atom is particularly beneficial for intense colour development [18]. Bearing this feature in mind, we commenced a synthetic programme to obtain some novel amino substituted spiroindolinonaphtho[2,1-*b*]pyrans (NIPS).

2. Results and discussion

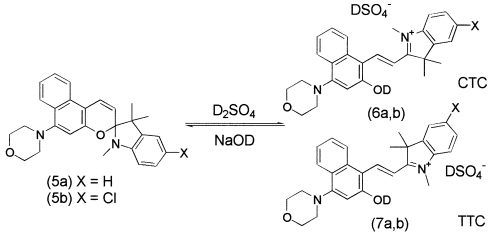
The synthesis of BIPS molecules is well established, with the most efficient route relying upon the condensation of a Fischer's base with a salicylaldehyde [16]. For example, compound (1) results from the condensation of Fischer's base, 1,3,3-trimethyl-2-methyleneindoline, with a salicylaldehyde. The key starting material required for our synthetic study was a 4-amino-2-hydroxy-1-naphthaldehyde. From our previous work on photochromic naphthopyrans we had ready access to 4-morpholino-2-naphthol (2) [18]. Vilsmeier–Haack formylation [19] of (2) proceeded smoothly to afford 2-hydroxy-4-morpholino-1-naphthaldehyde (3) regiospecifically and in excellent yield. The ^{1}H nmr spectrum of this compound clearly showed the presence of a formyl proton at δ 10.6 and a low field signal at δ 13.6 attributed to the hydrogen bonded hydroxyl proton; 3-H appeared as a singlet at δ 6.63.

Heating (3) in anhydrous ethanol containing Fischer's base (4a) gave NIPS [(5a) Scheme 2] as pale pink micro-crystals after elution from silica and recrystallisation. The chloro-compound (5b) was obtained in a similar fashion, though recrystallisation alone was sufficient to obtain pure material. In the ^{1}H nmr spectrum of (5a), the presence of an AB system at δ 5.70 (2-H) and δ 7.53 (1-H) with a coupling constant of 10.5 Hz is indicative of the *cis* arrangement of the pyran ring protons [13,20]. The signal associated with 1-H always appears downfield of 2-H as a consequence of its benzylic disposition. 5-H, *ortho* to both the morpholine function and the oxygen heteroatom resonates at δ 6.63 as in the parent aldehyde (3). The geminal methyl groups of the indoline ring are non-equivalent affording singlets at δ 1.21 and δ 1.34 and the signal for the *N*-methyl group appears within the expected range at *δ* 2.74. The ^{1}H nmr data obtained for (5b) closely resembles that of (5a). Complete assignment of the indoline ring protons is possible with the introduction of the 5′-chlorine atom. Predictably, 7′-H resonates furthest upfield of the aromatic signals (δ 6.43) since it is *ortho* to the indoline ring nitrogen.

Surprisingly, these novel amino substituted NIPS (5a,b) exhibited no observable photochromic or negative photochromic [21] properties at ambient temperatures. However, these molecules are reversibly converted to the merocyanine dyes by adjusting the pH of their environment. Thus, treating solutions of (5a) and (5b) in acetone or toluene with one drop of aqueous hydrochloric or sulfuric acid resulted in the instantaneous development of an intense red colour. It is noteworthy that the intense colour persisted and was not reduced after 1 week. Subsequent neutralisation of the solution with aqueous sodium hydroxide effected the discharge of the red colour and the return to the original weakly coloured solution.

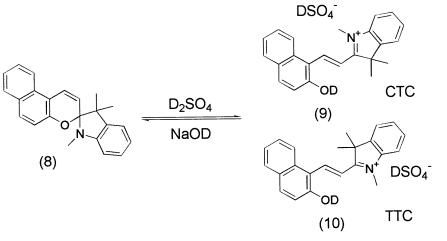
The persistence of the developed red colour, presumably due to the acid-promoted ring opening of the NIPS compounds to generate a merocyanine dye, seeded the thought that the coloured species could be probed by ^{1}H nmr spectroscopy. The study of the ring-opened forms of photochromic dyes by ^{1}H nmr spectroscopy has been reported, though the data for these transient species is relatively difficult to obtain and spectra

are invariably complex due to the ever present signals associated with the ring closed form [15]. Our initial attempts to record the ^{1}H spectra of the coloured species were unsuccessful because the suspension of tiny droplets of acid in the $CDCl_3$ solution caused poor resolution. This problem was obviated by using deuterioacetone as the solvent, the minute amount of acid required to cause the colour change now being fully miscible. The change from $CDCl_3$ to acetone-d_6 has minimal effect on δ for the ring closed form. The ^{1}H nmr spectrum of (5a) in the presence of D_2SO_4 was completely different from that of (5a) recorded in acetone-d_6 alone and was consistent with rotameric dye structures [(6a, 7a), Scheme 3]. An AB system was present with a coupling constant of 15.8 Hz clearly indicating a *transoid* arrangement of 1-H and 2-H [for simplicity the atom numbers used for the NIPS (5a,b) have been retained for the cyanines (6a,b and 7a,b)] [22]. Of equal importance are the magnitudes of the downfield shifts of 1-H to δ 8.99 and of 2-H to δ 8.09, shifts of 1.30 ppm and 2.32 ppm, respectively. It is thought that 2-H is more significantly affected by the transformation to the open form because it lies in the deshielding zone of the anisotropic iminium group. The chemical shift of 1-H and 2-H are of comparable magnitude to those of numerous other cyanine and merocyanine dyes [22]. The *N*-methyl group resonates at δ 4.13, in complete agreement with an iminium ion structure [23]. The geminal methyl groups are now equivalent, consistent with the planar arrangement of the rest of the species, and resonate at δ 1.91. The signals for the morpholine ring protons have also undergone a downfield shift, with the $N(CH_2)_2$ function being affected by the greatest amount, Δδ 0.41 ppm. It was thought possible that this latter shift may be a consequence



Scheme 3.

of protonation at the morpholine ring nitrogen, which would have a marked influence on the position of the signals of the neighbouring aromatic protons. However, a sample of (8), a known spiroindolinonaphthopyran, readily prepared from 2-hydroxynaphthaldehyde and (4a), also generated an intense coloured species (9,10) on protonation. The ^{1}H nmr spectrum of the latter was comparable with that recorded for (6a,b and 7a,b) (Table 1).



It is pertinent to note that protonation converts the NIPS (5a,b and 8) exclusively to their ring opened forms since there are no residual signals in the ^{1}H nmr spectra which can be attributed to the spiropyran structures. Furthermore, the ^{1}H nmr spectra of the ring opened forms are consistent with the presence of a single rotamer, the precise configuration of which cannot be ascertained from simple nmr experiments alone. However, 2D ^{1}H-^{1}H NOESY experiments on protonated (8) revealed cross-peaks for interactions between 2-H and the NMe group, the NMe group and 7′-H, 1-H and the geminal 3′-Me groups, and 1-H and 10-H. The presence of such through space interactions is consistent with the structure of the *trans-trans-cis* (TTC) rotamer (10) rather than the *cis-trans-cis* (CTC) rotamer (9). An analogous TTC configuration pertains for the cyanine dyes (7a,b).

Table 1
Selected ^{1}H nmr data (acetone-d_6) for (5a), (5b) and (8)

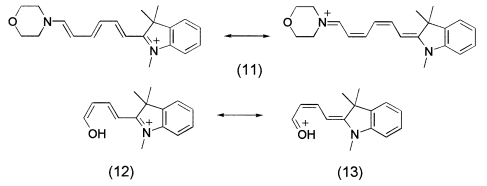
	δ 1-H[a]	$J_{1,2}$ (Hz)	δ 2-H	δ 3′-Me	δ NMe
(8)	7.78	10.5	5.89	1.19, 1.31	2.73
(10)	9.05	16.1	8.25	1.99	4.23
(5a)	7.69	10.5	5.77	1.18, 1.30	2.71
(7a)	8.99	15.8	8.09	1.91	4.13
(5b)	7.71	10.5	5.76	1.20, 1.31	2.72
(7b)	8.98	16.1	8.15	1.90	4.24

[a]The atom numbers employed for the naphthopyrans have been retained for the merocyanine dyes.

To further characterise these new merocyanine dyes we attempted to record their ^{13}C nmr spectra. However, to our disappointment we were unable to obtain sufficiently well resolved spectra for either (7a) or (7b). During the long acquisition period required to record sufficient data from these dilute solutions, the protonated dyes gradually precipitated out of the acetone-$^{d}6$ solution. However, respectable ^{13}C nmr data were obtained for (10), which indicated that prominent downfield shifts of a number of carbon atoms had occurred on protonation relative to their position in (8).

The spectral parameters for the dyes (7a), (7b) and (10) are presented in Table 2. The changes in both λ_{max} and ε_{max} consequent on the introduction of the morpholino function merit some discussion.

The pronounced increase in the intensity of absorption is particularly significant and it is instructive to compare the chromogen in the two odd alternant dyes (7a) and (10). That of (7a), resonance hybrid (11), is a true cyanine with the two terminal nitrogen atoms having a similar tendency to release electrons. On the other hand, (10) is clearly different, with a much smaller contribution expected from (12) than from (13), and therefore possesses merocyanine characteristics.



The high absorption intensity of (7a) (ε_{max} $10.1\times10^4\,mol^{-1}\,dm^3\,cm^{-1}$) combined with its brightness is typical of a cyanine dye [22].

Irrespective of the exact designation of the chromogen, an appreciable red shift of λ_{max} is expected because of the extended conjugation in (11) compared to (12) and $\Delta\lambda$ of $+68$ nm is not an inappropriate shift.

The influence of the 5′-chloro substituent is small, even though it is conjugated with the indoline N atom and can therefore influence its basicity. An enhanced red shift is observed but the reduction in intensity is more marked, perhaps implying a further imbalance between the contributions from the two resonance forms of (11).

It is noteworthy that the spiroindolinonaphthopyrans are also peizochromic, changing colour from pale pink to deep red on grinding.

Table 2
Spectral parameters for protonated dyes in acetone

Dye	λ_{max} (nm)	$\varepsilon_{max}\times10^4$ ($mol^{-1}\,dm^3\,cm^{-1}$)
(7a)	546	10.0
(7b)	557	7.88
(10)	478	3.59

3. Experimental

Flash chromatography was performed using silica gel grade C-560 as supplied by Fluorochem Ltd. according to the published procedure [24]. Melting points were recorded in capillaries and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 882 infrared spectrophotometer in KBr discs. Nmr spectra were recorded in $CDCl_3$ and $^{d}6$-acetone using a Jeol lambda series 400 MHz instrument, coupling constants are quoted in Hz. Visible spectra were recorded in spectroscopic grade acetone in 1 cm quartz cells using a Perkin Elmer λ5 spectrophotometer.

3.1. Formylation of 4-morpholino-2-naphthol

Phosphorus oxychloride (23 mmol) was added dropwise over 10 min to cold stirred anhydrous *N,N*-dimethylformamide (40 cm^3). The resulting solution was allowed to warm to room temperature over 20 min. 4-Morpholino-2-naphthol (22 mmol) was added portionwise over 5 min to the Vilsmeier reagent and the resulting pale green/yellow solution was heated at 100°C for 5 h. The cooled solution was poured into ice water (300 cm^3) and extracted with ethyl acetate ($4\times50\,cm^3$). The combined extracts were washed sequentially with brine ($3\times50\,cm^3$) and water ($2\times50\,cm^3$) and then dried (Na_2SO_4) and evaporated to give a green gum. Elution from a short silica gel column with 40% ethyl acetate in hexane and recrystallisation from ethyl acetate and hexane gave 2-hydroxy-4-morpholino-1-naphthaldehyde (3)

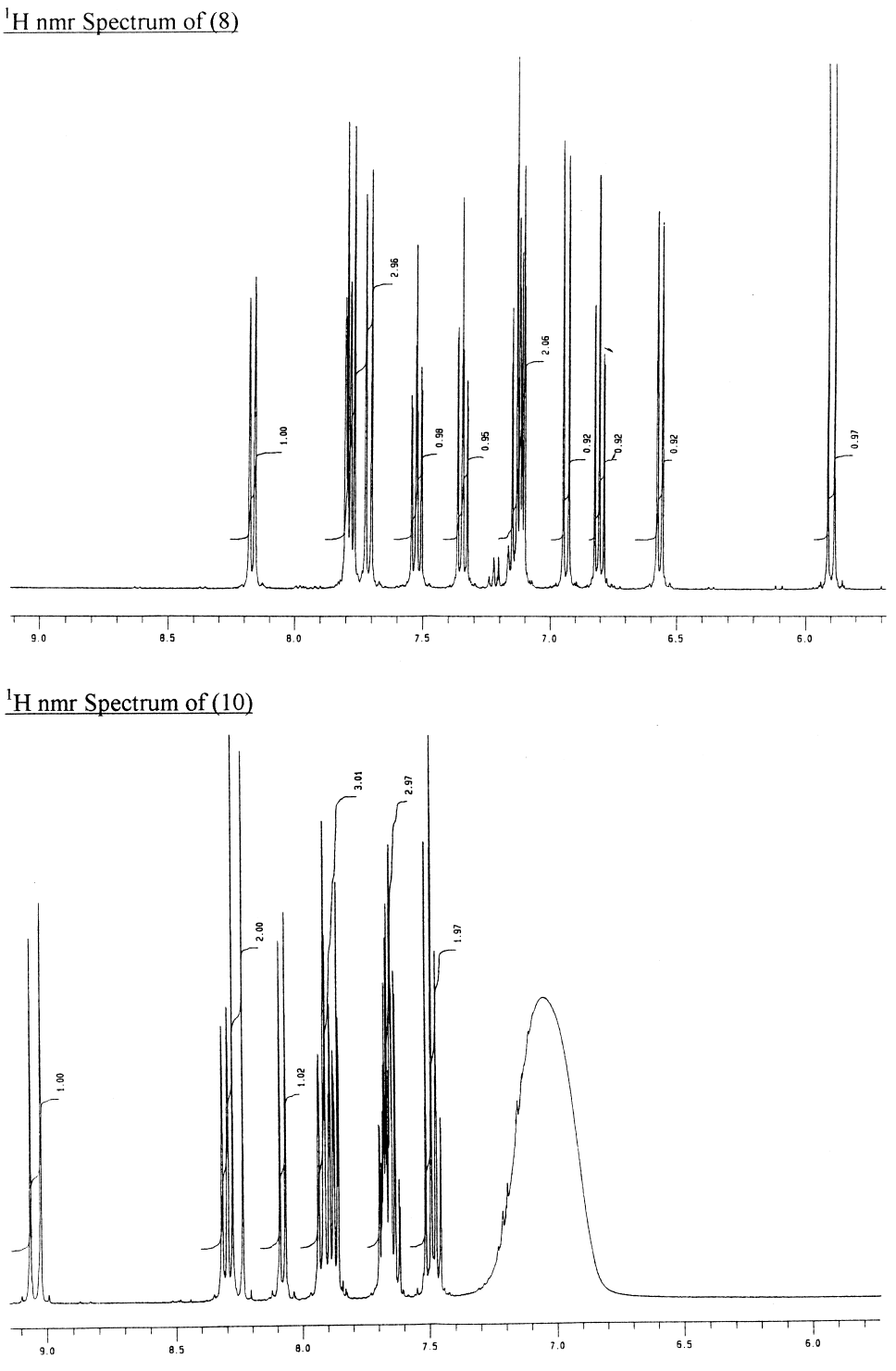


Fig. 1. Aromatic region of the ^{1}H nmr spectra of (8) and (10) in acetone-d_6.

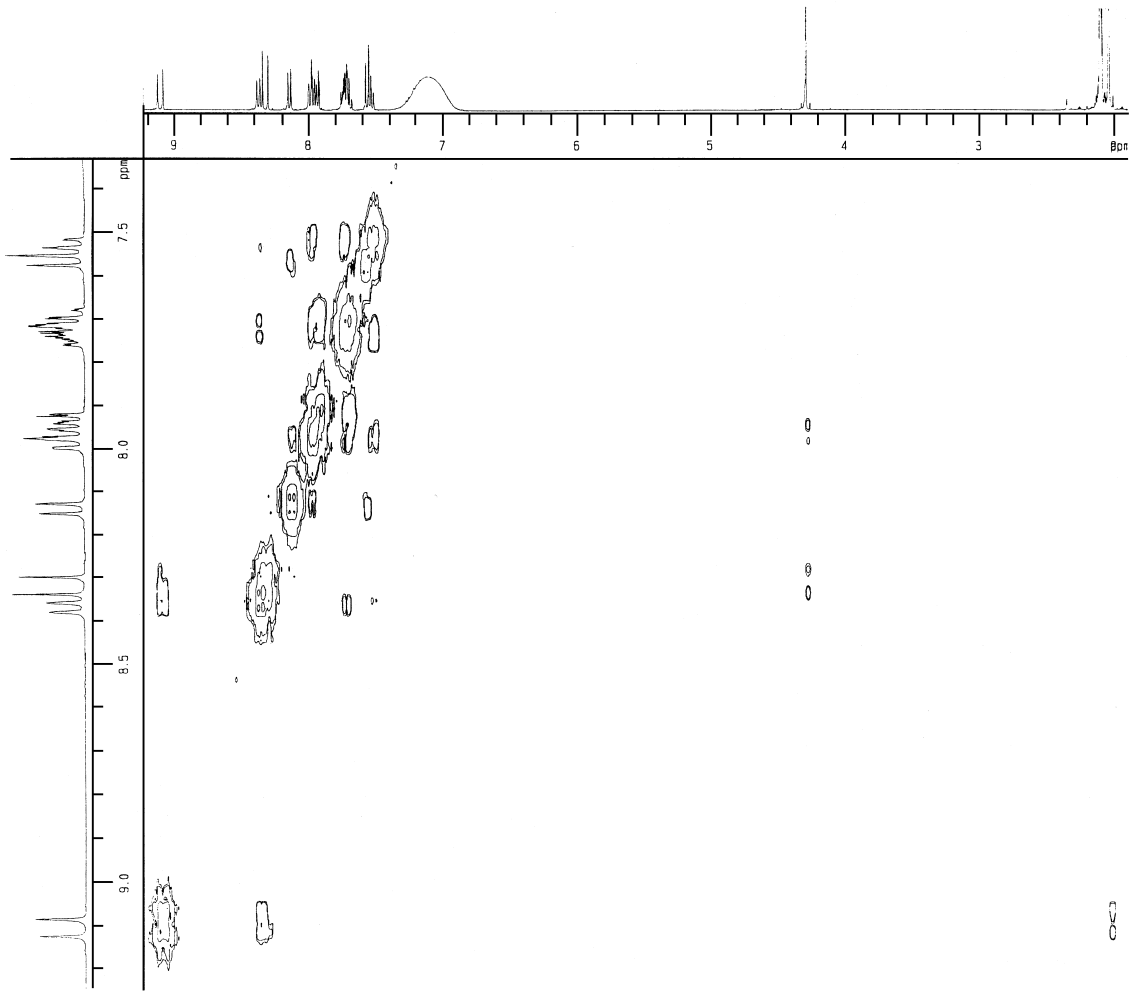


Fig. 2. ^{1}H-^{1}H NOESY spectrum of (10) in acetone-d_6.

(72%) as pale green plates, m.p. = 128.5–130.5°C; ν_{max} (KBr) 1631, 1581, 1444, 1394, 1196, 1117; $^{\delta}H$ ($CDCl_3$) 3.23 (4H, m, $N(CH_2)_2$), 3.99 (4H, m, $O(CH_2)_2$), 6.63 (1H, s, 3-H), 7.40 (1H, m, Ar-H), 7.58 (1H, m, Ar-H), 8.03 (1H, m, 5-H), 8.30 (1H, m, 8-H), 10.62 (1H, s, CHO), 13.56 (1H, s, OH) (Found: C, 69.9; H, 5.9; N, 5.3. $C_{15}H_{15}NO_3$ requires C, 70.0; H, 5.9; N, 5.4%).

3.2. Preparation of NIPS compounds (5a,b) and (8)

A solution of the 2-hydroxy-1-naphthaldehyde (8 mmol) and the 1,3,3-trimethyl-2-methyleneindoline (8 mmol) in anhydrous ethanol (50 cm^3) was refluxed for 6 h. After cooling the solvent was removed and the resulting bright pink gum was purified by either column chromatography and/or by recrystallisation. This protocol was used to prepare the following compounds:

1. 1′,3′,3′-Trimethyl-1′,3′-dihydrospiro{(3*H*)-naphtho[2,1-*b*]pyran-3,2′-(2*H*)indole} (8) (54%) as colourless micro-crystals after elution from silica gel with 20% ethyl acetate in hexane and recrystallisation from hexane and ethyl acetate, m.p. = 181.5–182.5°C, lit. m.p. = 181–182°C [17]; λ_{max} (acetone + H_2SO_4) 478 nm, ε_{max} = 35905 $mol^{-1}\,dm^3\,cm^{-1}$; δ_H

($CDCl_3$) 1.22 (3H, s, 3′-Me), 1.34 (3H, s, 3′-Me), 2.74 (3H, s, NMe), 5.79 (1H, d, *J* 10.5, 2-H), 6.53 (1H, d, *J* 7.6, Ar-H), 6.85 (1H, m, Ar-H), 6.97 (1H, d, *J* 9.0, Ar-H), 7.09 (1H, m, Ar-H), 7.18 (1H, m, Ar-H), 7.33 (1H, m, Ar-H), 7.50 (1H, m, Ar-H), 7.59 (1H, d, *J* 10.5, 1-H), 7.61 (1H, d, *J* 8.9, Ar-H), 7.72 (1H, m, Ar-H), 8.02 (1H, d, *J* 8.3, Ar-H), δ_C ($CDCl_3$) 20.2, 25.8, 28.9, 51.5, 104.2, 106.7, 110.6, 117.4, 117.7, 119.1, 120.6, 121.5, 123.2, 124.9, 126.7, 127.6, 128.6, 129.8, 130.0, 136.7, 148.1, 152.6.

δ_H (acetone-d_6) 1.19 (3H, s, 3′-Me), 1.31 (3H, s, 3′-Me), 2.73 (3H, s, NMe), 5.89 (1H, d, *J* 10.5, 2-H), 6.56 (1H, d, *J* 7.7, Ar-H), 6.81 (1H, m, Ar-H), 6.93 (1H, m, Ar-H), 7.13 (2H, m, Ar-H), 7.35 (1H, m, Ar-H), 7.52 (1H, m, Ar-H), 7.71 (1H, d, J 8.8, Ar-H), 7.78 (2H, m, Ar-H and d, *J* 10.5, 1-H), 8.17 (1H, d, *J* 8.5, Ar-H), δ_C (acetone-d_6) 20.6, 26.3, 52.4, 105.4, 107.8, 111.8, 118.0, 118.9, 120.2, 121.9, 122.4, 124.4, 126.0, 127.9, 128.5, 129.6, 131.0, 131.2, 137.7, 149.2, 153.6.

δ_H (acetone-d_6 + D_2SO_4) 1.99 (6H, s, 3′-Me), 4.23 (3H, s, NMe), 7.49 (2H, m, Ar-H), 7.66 (3H, m, Ar-H), 7.90 (3H, m, Ar-H), 8.08 (1H, d, *J* 9.0, Ar-H), 8.25 (1H, d, *J* 16.1, 2-H), 8.31 (1H, d, *J* 8.9, Ar-H), 9.05 (1H, d, *J* 16.1, 1-H), δ_C (acetone-d_6 + D_2SO_4) 27.0, 34.8, 53.1, 114.3, 115.6, 116.4, 119.4, 122.9, 123.7, 125.3, 129.7, 129.9, 130.0, 130.1, 130.3, 134.0, 137.5, 143.2, 144.3, 147.8, 161.1, 184.2.

2. 1′,3′,3′-Trimethyl-6-morpholino-1′,3′-dihydrospiro{(3*H*)-naphtho[2,1-*b*]pyran-3,2′-(2*H*)indole} (5a) (61%) as pale pink micro-crystals after elution from silica gel with 30% ethyl acetate in hexane and recrystallisation from hexane and ethyl acetate, m.p. = 193.5–194.5°C; ν_{max} (KBr) 1640, 1610, 1585, 1488, 1453, 1364, 1141, 1113, 745; λ_{max} (acetone + H_2SO_4) 546 nm, ε_{max} = 100150 $mol^{-1}\,dm^3\,cm^{-1}$; δ_H ($CDCl_3$) 1.21 (3H, s, 3′-Me), 1.34 (3H, s, 3′-Me), 2.74 (3H, s, NMe), 3.03 (4H, m, $N(CH_2)_2$), 3.93 (4H, m, $O(CH_2)_2$), 5.70 (1H, d, *J* 10.5, 2-H), 6.54 (1H, d, *J* 7.6, Ar-H), 6.63 (1H, s, 5-H), 6.86 (1H, m, Ar-H), 7.10 (1H, dd, *J* 7.4, 1.0, Ar-H), 7.20 (1H, m, Ar-H), 7.32 (1H, m, Ar-H), 7.49 (1H, m, Ar-H), 7.53 (1H, d, *J* 10.5, 1-H), 8.01 (1H, d, *J* 8.5, Ar-H), 8.07 (1H, m, Ar-H), δ_C ($CDCl_3$) 14.1, 20.2, 25.8, 28.9, 51.4, 53.4, 67.3, 104.5, 106.7, 106.8, 115.7, 119.1, 121.2, 121.5, 122.7, 123.9, 124.1, 124.9, 126.8, 127.6, 130.9, 136.8, 148.1, 151.4, 153.0 (Found: C, 78.6, H, 6.7; N, 6.7; M^+ 412.2170. $C_{27}H_{28}N_2O_2$ requires C, 78.6; H, 6.9; N, 6.8%; M^+, 412.2151).

δ_H (acetone-d_6) 1.18 (3H, s, 3′-Me), 1.30 (3H, s, 3′-Me), 2.71 (3H, s, NMe), 3.01 (4H, m, $N(CH_2)_2$, 3.85 (4H, m, $O(CH_2)_2$), 5.77 (1H, d, *J* 10.5, 2-H), 6.56 (2H, overlapping s and d, 5-H and Ar-H), 7.13 (2H, m, Ar-H), 7.34 (1H, m, Ar-H), 7.51 (1H, m, Ar-H), 7.69 (1H, d, *J* 10.5, 1-H), 8.13 (2H, m, Ar-H).

δ_H (acetone-d_6 + D_2SO_4) 1.91 (6H, s, 3′-Me), 3.42 (4H, m, $N(CH_2)_2$), 4.00 (4H, m, $O(CH_2)_2$), 4.13 (3H, s, NMe), 7.25 (1H, s, 5-H), 7.50 (1H, m, Ar-H), 7.59 (2H, m, Ar-H), 7.70 (1H, m, Ar-H), 7.81 (1H, m, Ar-H), 8.09 (1H, d, *J* 15.8, 2-H), 8.18 (1H, d, *J* 8.3, Ar-H), 8.32 (1H, d, *J* 9.7, Ar-H), 8.99 (1H, d, *J* 15.8, 1-H).

3. 5′-Chloro-1′,3′,3′-trimethyl-6-morpholino-1′,3′-dihydrospiro{(3*H*)-naphtho[2,1-*b*]pyran-3,2′-(2*H*)indole} (5b) (68%) as pink needles after recrystallisation from ethyl acetate and hexane, m.p. = 222.0–223.5°C; ν_{max} (KBr) 1639, 1588, 1482, 1449, 1368, 1169, 1117, 863, 746; λ_{max} (acetone + H_2SO_4) 557 nm, ε_{max} = 78810 $mol^{-1}\,dm^3\,cm^{-1}$; δ_H ($CDCl_3$) 1.20 (3H, s, 3′-Me), 1.32 (3H, s, 3′-Me), 2.71 (3H, s, NMe), 3.04 (4H, bs, $N(CH_2)_2$), 3.93 (4H, m, $O(CH_2)_2$), 5.66 (1H, d, *J* 10.5, 2-H), 6.43 (1H, d, *J* 8.1, 7′-H), 6.61 (1H, s, 5-H), 7.03 (1H, d, *J* 2.1, 4′-H), 7.12 (1H, dd, *J* 8.0, 2.2, 6′-H), 7.33 (1H, m, Ar-H), 7.48 (1H, m, Ar-H), 7.53 (1H, d, *J* 10.5, 1-H), 8.01 (1H, d, *J* 8.3, Ar-H), 8.08 (1H, d, *J* 8.3, Ar-H), δ_C ($CDCl_3$) 20.0, 25.6, 29.0, 51.5, 53.4, 67.3, 104.6, 106.4, 106.7, 107.6, 115.1, 121.2, 122.1, 122.9, 123.8, 123.9, 124.1, 125.1, 126.9, 127.3, 130.9, 138.8, 146.8, 151.6, 152.9 (Found: C, 72.4; H, 6.1; N, 6.3; M^+ 446.1758. $C_{27}H_{27}ClN_2O_2$ requires C, 72.5; H, 6.1; N, 6.3%; M^+, 446.1761(1)).

δ_H (acetone-d_6) 1.20 (3H, s, 3′-Me), 1.31 (3H, s, 3′-Me), 2.72 (3H, s, NMe), 3.01 (4H, m, $N(CH_2)_2$), 3.86 (4H, m, $O(CH_2)_2$), 5.76 (1H, d, *J* 10.5, 2-H), 6.56 (1H, d, *J* 8.1, 7′-H), 6.60 (1H, s, 5-H), 7.13 (2H, m, Ar-H), 7.34 (1H, m, Ar-H), 7.51 (1H, m, Ar-H), 7.71 (1H, d, *J* 10.5, 1-H), 8.14 (2H, m, Ar-H)

δ_H (acetone-d_6 + D_2SO_4) 1.90 (6H, s, 3′-Me), 3.60 (4H, bm, $N(CH_2)_2$), 4.10 (4H, m, $O(CH_2)_2$), 4.24 (3H, s, NMe), 7.61 (1H, m, Ar-H), 7.69 (1H, m, Ar-H), 7.77 (2H, m, Ar-H), 7.91 (1H, d, *J* 8.8, Ar-H), 7.96 (1H, d, *J* 2.2, Ar-H), 8.15 (1H, d, *J* 16.1, 2-H), 8.34 (1H, d, *J* 8.3, Ar-H), 8.40 (1H, *d*, *J* 8.3, Ar-H), 8.98 (1H, d, *J* 16.1, 1-H).

4. Conclusions

Two novel amino-substituted spiroindolinonaphthopyrans have been synthesised. Whilst these compounds exhibit no observable photochromic properties at ambient temperature, protonation gives intensely coloured dyes. The configuration of these dyes has been established exclusively as *trans-trans-cis* by NOESY. This form of the dye is configurationally stable with no evidence for the interconversion to either the *cis-trans-cis* rotamer or the spiropyran. Introduction of the 6-amino substituent into the NIPS system provides for an extended conjugation pathway and protonation consequently affords dyes which exhibit bathochromically shifted λ_{max} (ca. 75 nm) and significantly enhanced ε_{max} values.

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