Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006

To cite this article: Christopher D. Gabbutt, John D. Hepworth, B. Mark Heron & Steven M. Partington (2000): Protolysis of Spironaphtho(aza)pyranoindoles, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 345:1, 323-328

To link to this article: http://dx.doi.org/10.1080/10587250008023939

Mol. Cryst. and Liq. Cryst., 2000, Vol. 345, pp. 323-328
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Protolysis of Spironaphtho(aza)pyranoindoles

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Some novel amino-substituted spiroindolinonaphthopyrans have been synthesised. Whilst these compounds exhibit no observable photochromic properties at ambient temperature, protonation results in ring opening to give stable, intensely coloured dyes. Recyclisation and decolouration result on basification.

Keywords: Photochromism; (mero)cyanine dyes; nmr spectroscopy; spiroindolinonaphthopyran; spiroindolinonaphthoxazine; protolysis

INTRODUCTION

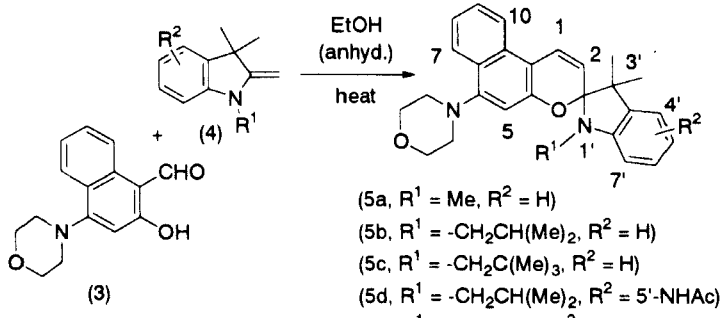
The synthesis and photochromic properties of spiroindolinobenzopyrans (BIPS) (1) has been the subject of several reviews.[1] The colouration process of the BIPS system (1) relies upon either the photolytic or thermal induced cleavage of the O—C bond to generate a merocyanine dye (2) (Scheme 1).

Scheme 1

We have recently reported the synthesis of some 6-aminospiroindolinonaphthopyrans (NIPS) and shown that these compounds were not photochromic at ambient temperature but could be reversibly ring opened to give stable (mero)cyanine dyes by control of the pH of their environment.[2] We now describe the synthesis of some analogues of these NIPS molecules and comment on the influence of alkyl groups located on the indoline nitrogen atom on the spectroscopic properties of these dyes.

DISCUSSION

Of the various syntheses of BIPS molecules, the most efficient route relies on the condensation of a Fischer's base with a substituted salicylaldehyde.[1] 2-Hydroxy-4-morpholino-1-naphthaldehyde (3), obtained by a regiospecific Vilsmeier-Haack formylation of 4-morpholino-2-naphthol,[2] gave the NIPS (5a - e) [3] (Scheme 2) in good yield (Table 1) on heating with a Fischer's base (4) in anhydrous ethanol.

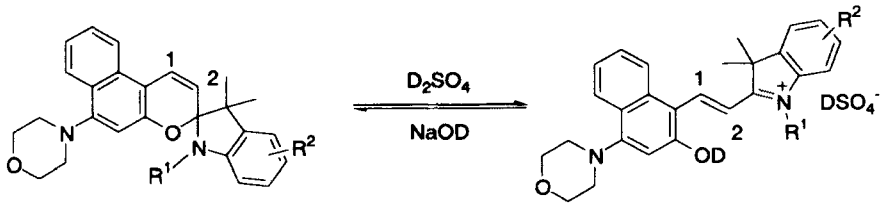


Scheme 2

In the ^{1}H nmr spectrum of (5) the presence of an AB system at *ca.* δ 5.7 (2-H) and *ca.* δ 7.5 (1-H) with a coupling constant of ~ 10.5 Hz is indicative of the *cis* arrangement of the pyran ring protons.[4] The signal associated with 1-H always appears downfield of 2-H as a consequence of its benzylic disposition. 5-H, flanked by the morpholine function and the oxygen heteroatom, resonates at *ca.* δ 6.0. The *geminal* methyl groups of the indoline ring are non-equivalent and afforded singlets in the range δ 1.2 - δ 1.4. The protons of the *N*-CH_2 unit are diastereotopic and in the case of (5c), where there are no adjacent protons, an AB system with J_{gem} = 15 Hz is present at δ 3.3.

These novel amino-substituted NIPS (5a - e) exhibited no observable photochromic or negative photochromic [5] properties at ambient temperatures. However, these molecules were converted to the (mero)cyanine dyes on protonation. Thus, treating solutions of (5) in acetone or toluene with one drop of aqueous hydrochloric or sulfuric acid resulted in the instantaneous development of an intense red colour. Furthermore, the ring opening process is reversed on neutralisation with consequent decolourisation.

The persistence of the coloured forms in acidic solution enabled their structure to 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 data for these transient species are relatively difficult to obtain; the spectra are invariably complex because of the ever present signals associated with the ring-closed form.[6] The ^{1}H nmr spectrum of (5) in the presence of D_2SO_4 was completely different from that of (5) alone and was consistent with a single *trans-trans-cis* rotameric dye structure (6).[2] An AB system was present with a coupling constant of *ca.* 16 Hz clearly indicating a *transoid* arrangement of 1-H and 2-H.[7] Of equal importance are the magnitudes of the downfield shifts of 1-H to *ca.* δ 9.0 and of 2-H to *ca.* δ 8.1, shifts of ~1.4 ppm and ~2.4 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 shifts of 1-H and 2-H are of comparable magnitude to those in numerous other cyanine and merocyanine dyes.[7] The *geminal* methyl groups are now equivalent, consistent with the planar arrangement of the rest of the species, and resonate at ~δ 1.9. The signal attributed to the *N*-CH_2-alkyl group of (6) is greatly simplified and resonates at ~δ 4.3 in complete agreement with an iminium ion structure.[8]



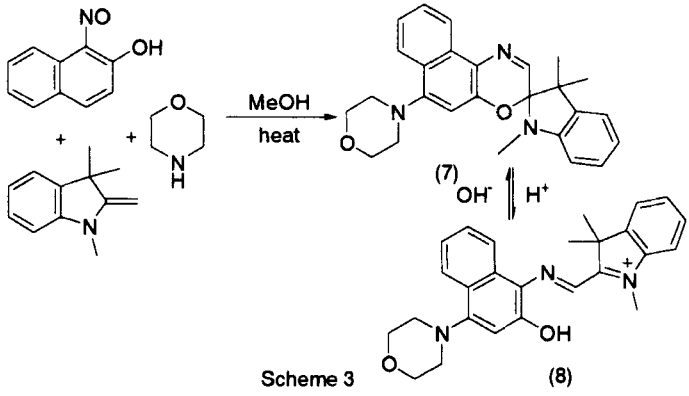
(5) (6)

Table 1. Selected Spectroscopic Data for NIPS (5) and Merocyanines (6)

	Yield	λ_{max} (6)	10^{-4} ε_{max} (6)	^{1}H nmr ($CDCl_3$) (5)			^{1}H nmr (acetone-d_6 + D_2SO_4) (6)		
	(%)	(nm)	($mol^{-1}dm^3cm^{-1}$)	$\delta_{1\text{-H}}$	$J_{1,2}$ (Hz)	$\delta_{2\text{-H}}$	$\delta_{1\text{-H}}$	$J_{1,2}$ (Hz)	$\delta_{2\text{-H}}$
5a	61	546	10.0	7.53	10.5	5.70	8.99	15.8	8.09
5b	67	560	11.7	7.48	10.5	5.71	8.95	15.4	8.13
5c	82	564	11.2	7.39	10.5	5.71	9.04	15.9	8.32
5d	76	555	10.1	7.46	10.5	5.68	9.00	15.9	8.20
5e	71	568	10.9	7.56	10.5	5.79	9.10	16.1	8.28
7	40	588	1.3	-	-	7.64	-	-	9.99

The increased intensity of the morpholine derivative (6a) relative to the 6-unsubstituted dye and attributed to the true cyanine nature of the former [2] is accentuated as the *N*-alkyl function becomes more sterically demanding. A further small red shift in λ_{max} is also noted.

The reversible pH switching of (5a – e) was also observed for the spiroindolinonaphthoxazine (SINO) (7), obtained in a one pot procedure by heating 1-nitroso-2-naphthol with Fischer's base and morpholine (Scheme 3) [9], though the lifetime of the corresponding azacyanine (8) was limited and appreciable decomposition was observed on standing. A pronounced shift $\Delta\delta$ = 2.35 ppm of the azomethine proton (2-H) of (7) in its ^{1}H NMR spectrum was observed on protonation [δ 7.64 in (7) to δ 9.99 in (8)], similar to those noted for (5) → (6).



Scheme 3 (8)

CONCLUSION

Some novel amino-substituted NIPS have been synthesised. Whilst these compounds exhibit no observable photochromic properties at ambient temperature, protonation gives intensely coloured dyes. Introduction of the 6-amino substituent into the NIPS system provides for an extended conjugation pathway and protonation consequently affords cyanine dyes that exhibit red shifts of λ_{max} and significantly enhanced ε_{max} values. A further enhancement of ε_{max} is observed when the indoline *N*-Me group is replaced by an *N*-alkyl function. Protolysis of the SINO (7) affords an azacyanine dye (8) with λ_{max} 588 nm.

However, the low value of ε_{max} of (8) is attributed to its relatively rapid decomposition in acidic media.

ACKNOWLEDGEMENT

We thank the EPSRC for provision of a HRMS service (University of Wales, Swansea).

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[3] Data for typical NIPS compound: 1′-Neopentyl-3′,3′-trimethyl-6-morpholino-1′,3′-dihydrospiro-{*3H*-naphtho[2,1-*b*]pyran-3,2′-(2*H*)-indole} (**5c**) (82%) as a pale pink foam after elution from silica with 40 % ethyl acetate in hexane, m.p. = 88 – 92 °C; ν_{max} (KBr) 1642, 1609, 1587 cm^{-1}; λ_{max} (acetone + H_2SO_4) 564 nm, ε_{max} = 111891 $mol^{-1}dm^3cm^{-1}$; δ_H ($CDCl_3$) 0.89 (9H, s, $C(Me)_3$), 1.19 (3H, s, 3′-Me), 1.24 (3H, s, 3′-Me), 2.82 and 3.80 (2H, AB, *J* 15.0, NCH_2tBu), 2.94 (4H, m, $N(CH_2)_2$), 3.84 (4H, m, $O(CH_2)_2$), 5.71 (1H, d, *J* 10.5, 2-H), 6.51 (1H, s, 5-H), 6.60 (1H, d, *J* 7.8, Ar-H), 6.79 (1H, m, Ar-H), 7.00 (1H, d, *J* 6.6, Ar-H), 7.09 (1H, m, Ar-H), 7.24 (1H, m, Ar-H), 7.39 (1H, d, *J* 10.5, 1-H), 7.40 (1H, m, Ar-H), 7.92 (1H, d, *J* 8.3, Ar-H), 8.00 (1H, d, *J* 8.0, Ar-H); δ_H(acetone-d_6 + D_2SO_4) 1.18 (9H, s, $C(Me)_3$), 1.97 (6, s, 3′-Me), 3.69 (4H, m, $N(CH_2)_2$), 4.14 (4H, m, $O(CH_2)_2$), 4.53 (2H, s, NCH_2tBu), 7.61 (4H, m, Ar-H), 7.75 (1H, m, Ar-H), 7.87 (1H, m, Ar-H), 7.96 (1H, m, Ar-H), 8.29 (2H, m, Ar-H), 8.32 (1H, d, *J* 15.9, 2-H), 9.04 (1H, d, *J* 15.9, 1-H) (Found: C, 79.3; H, 7.7; N, 6.0; M^+, 468.2790. $C_{31}H_{36}N_2O_2$ requires C, 79.4; H, 7.8 ; N, 6.0 %; M^+, 468.2778).

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