Thermo- and Photochromic Dyes: Spiro(indolinebenzopyrans)

2*—Detailed Assignment of the ¹H NMR Spectra and Structural Aspects of the Closed Form of 1,3,3-Trimethylspiro(indoline-2,2'-benzopyrans)

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The proton NMR assignments for a series of 12 thermo- and photochromic 1,3,3-trimethylspiro(indoline-2,2'benzopyrans) dyes is reported. All of the protons in the dye molecule were assigned through a combination of homonuclear decoupling experiments and correlation spectroscopy. The relative stereochemistry of the indolino gem-dimethyl groups was assigned so that, for the S-epimer, the pro-R methyl was found to resonate at 1.24 ppm while the pro-S methyl appeared at 1.37 ppm for compound 1.

KEY WORDS Thermo- and photochromic dyes Spiro(indoline-2,2'-benzopyrans) ¹H NMR assignments

INTRODUCTION

Thermo- and photochromic spiropyrans² are of significant practical interest, since they form coloured species on heating or irradiation with UV light.



A typical example of an organic thermo- and photochromic compound which continues to enjoy active interest is the spiropyran derivative 1,3,3-trimethyl-6'nitrospiro(indoline-2,2'-benzopyran) (2, $R_1 = H$, $R_2 = NO_2$, $R_3 = H$).



* For part 1, see Ref. 1.

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0749-1581/92/111128-04 \$07.00 © 1992 by John Wiley & Sons, Ltd. Since the discovery of the spiropyran-merocyanine transformation by Fischer and Hirshberg in 1952³ and independently by Chaude and Rumpf in 1953,⁴ the details of the photochemical processes associated with this interconversion⁵⁻⁸ have received considerable attention. Further, many practical applications of these interesting materials have been reported.⁹⁻¹⁵ However, many unsolved problems still remain, such as the identity of the colourless and photochemically produced coloured species, the mechanistic process involved in the equilibrium between the two species and the structural identification of the dicondensed product formed from the reaction of Fischer's base and salicylaldehydes.

The use of photochromic materials for dyeing applications in which the dye is intended to change colour reversibly on exposure to light requires that the spiropyran and the merocyanine form should be reasonably stable at ordinary temperatures in the absence of illumination, and that photochemical interconversion of these states should also be possible at ordinary temperatures. It is known¹ that the thermal stability of the merocyanine can be affected by the specific choice of substituents R_1 , R_2 and R_3 .

In order to design new materials with the required stability, it was decided to examine these thermo- and photochromic functional dyes further, including detailed ¹H NMR structural analysis of related species and UV-visible spectroscopic studies to determine the influence of solvent on the equilibrium.¹

Structurally, spiropyran dyes consist of two π systems linked by a tetrahedral spiro carbon. Since the stability of the spiropyran structure, and also the absorption

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		Substituent					
Compound	R,	R ₂	R ₃	M.p. (lit.)* (°C)	Colour ^b	Yield (%)°	T/Pª
1	н	$-N=NPh(p-NO_2)$	н	200-202 (205-206)	y. red	85	e
2	н	NO ₂	н	178 (177–178)	yellow	83	Т, Р
3	н	NO ₂	Br	245-247 (254-256)	purple	77	Т, Р
4	н	NO ₂	t	227 (228–229)	d. brown	78	Т, Р
5	н	NO ₂	OMe	180–184 (185–190)	g. yellow	89	Т, Р
6	н	NO ₂	NO ₂	269–270 (270)	green	70	t
7	CI	NO ₂	н	145146 (147148)	brown	80	Т, Р
8	н	Br	н	86 (86–87)	purple	70	T, P ⁹
9	н	CI	н	82-81 (89-92)	p. yellow	51	Τ, Ρ ⁹
10	н	Cl	Cl	123-124 (124-125)	p. pink	71	T, P ⁹
11	н	1	I	181 (182–183)	white	70	Т, Р ⁹
12	н	н	н	9798 (9597)	p. pink	47	—e

Table 1. Characterization of spiro(indolinebenzopyrans)

* Ref. 2 pertains to compounds 1, 7 and 9-12 and Refs 5 and 26 report compounds 2-6 and 8.

^b Colour in the solid state is reported (y. = yellowish; d. = dark; g. = golden; p. = pale).

^c The yield, based on the moles of indoline used, is reported.

^d T and P denote the thermo- and photochromic behaviour at room temperature, respectively.

^e Ring opening was not observed for this substrate.

^f The rate of ring opening is solvent dependent.

⁹ This substrate showed weak thermo- and photochromism.

associated with the merocyanine chromophore, is strongly dependent on the substituents, it is of interest to investigate the influence of substituents on the conformation of the parent spiropyran. An NMR structural investigation of the precursor spiropyran would be particularly valuable, since it would lead to an understanding of the conformational consequences of substituent changes on the parent spiropyran, and provide a basis for understanding the role of spiropyran substituent stabilization or destabilization in the overall ring opening process. This paper reports the results of our ¹H NMR structural investigation.

RESULTS AND DISCUSSION

Of the spiropyrans (1-12) described in Table 1 the 6'nitrospiropyrans exhibited very strong photochromism, with very large molar extinction coefficients for the open chain merocyanines, whereas in contrast, others (notably the halo and phenylazo derivatives) showed either very weak molar extinction coefficients or no such photochromic behaviour at room temperature.

Table 2 summarizes the 400 MHz ¹H NMR chemical shifts for all of the compounds in the present study.

Table 2. 'H NMR chemical shifts and coupling co	onstants (in ppm) of the spiropyrans 1–12 in acetone-d.
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	Compound											
Proton	1	2	3	4	5	6	7	8	9°	10°	11	12
H-4	7.19	7.16	7.15	7.16	7.12	7.14	6.62	7.07	7.02	7.17	7.11	7.13
H-5	6.88	6.83	6.84	6.85	6.82	6.85	—	6.86	6.88	6.87	6.80	7.11
H-6	7.15	7.12	7.16	7.16	7.12	7.14	6.86	7.17	7.19	7.21	7.13	7.24
H-7	6.69	6.60	6.64	6.64	6.61	6.54	6.60	6.59	6.65	6.55	6.59	6.75
8-CH3	1.37	1.28	1.31	1.31	1.29	1.34	1.29	1.26	1.30	1.32	1.29	1.36
9-CH ₃	1.24	1.17	1.20	1.20	1.17	1.20	1.20	1.13	1.17	1.18	1.16	1.21
10-CH ₃	3.16	2.74	2.75	2.72	2.76	2.78	2.75	2.70	2.73	2.73	2.68	2.70
H-3′	5.83	6.01	6.08	6.04	5.99	6.24	6.00	5.72	5.74	5.79	5.87	5.71
H-4′	7.07	7.20	7.23	7.19	7.15	7.38	7.22	6.79	6.77	6.77	6.95	6.98
H-5′	7.80	8.13	8.16	8.17	7.67	8.43	8.15	7.16	7.04	7.16	7.53	6.83
H-6′		_	_		·	_					_	6.78
H-7′	7.94	8.03	8.25	8.42	7.81	8.57	8.06	7.19	7.08	7.19	7.84	7.08
H-8′	6.75	6.83					6.89	6.53	6.54		_	6.57
A(H)°	8.03	_	_	—			_				_	—
B(H)	8.40	_		_	_			-				
J(H-3′, H-4′)⁵	10.5	10.5	10.5	10.5	10.5	10.5	10.5	10.0	10.0	10.0	10.5	10.5
J(H-5′, H-7′)⁵	2.0	3.0	2.5	2.5	2.5	2.5	3.0	1.0	1.0	1.0	2.0	1.0
J(H-7′, H-8′)⁵	8.0	9.0	_				7.5	7.5	8.0	—		8.0
J(H-6', H-7') ^ь	8.5	8.0	7.5	8.0	7.5	8.0	7.5	9.0	9.5	7.5	8.0	8.0

^a in $-N=NPh(p-NO_2)$, J(H-A, H-B) = 9.10 Hz.

^b in Hz to the nearest 0.5 Hz.

° in CDCl₃.



Figure 1. Observed NOEs in spiropyrans 1, 2 and 4.

Some of the chemical shift values, e.g. for 2 and 7, had been reported previously at 60 MHz.¹⁶ The spiropyrans 1–12 show N-methyl peaks at 2.68–3.16 ppm and two geminal methyl groups at 1.1–1.24 and 1.28–1.37 ppm, respectively. The olefinic proton (H-3'), appearing at 5.71–6.24 ppm, is well separated from the other absorptions and has a coupling constant (AX) ${}^{3}J = 10.0-10.5$ Hz. All other protons on sp² carbons, including the olefinic proton at H-4, absorb at 7–9 ppm.

The values of the N-methyl chemical shifts agree well with the 2.70 ppm value observed for 1,2,3,3-tetra-methylindoline,¹⁷ except for that of 1 (3.16 ppm). The remaining proton signals are in the 8-9 ppm region. The assignment of these protons was facilitated by the COSY-90 (correlated spectroscopy, two-dimensional homonuclear shift experiment) spectra¹⁷ in the range 2128.8-3433.4 Hz shown in Fig. 2. From the COSY¹⁸⁻²⁰ analysis, a pairwise coupling could be established: A-E, B-F, C-I, H-I and J-K. Since peak A is shown to be from H-3', peak E (7.07 ppm) must be from H-4'. The remainder of the coupled peaks can be assigned by first dividing the peaks into two groups, those in the nitroaromatic ring (three protons: C, H and I) and those in the indole ring (four protons: B, D, G and F). In the first group, the chemical shift of peak C and the ortho and meta couplings associated with it clearly allow the assignment of this absorption to H-8'. Consequently, H-7' corresponds to peak I and H-5' corresponds to peak H. In the indole ring aromatic moiety two protons show large ortho couplings. These protons can readily be distinguished on the basis of chemical shift and, consequently, H-7 corresponds to peak B, while H-4 is assigned to peak E. Decoupling then leads to the assignment of peak D as H-6 and peak G as H-5. This assignment is confirmed by the respective chemical shifts. Similar arguments can be applied to compounds 2-12 and these results are summarized in Table 2.

The excellent separation observed for the gemdimethyl peaks has made it possible to assign the resonances using NOE experiments. The ¹H{¹H} NOE enhancements are summarized in Fig. 1. Only one NOE was found between the gem-dimethyl groups and the vinylic proton H-3', consistent with a spiropyran structure where the planar components, i.e. the plane formed by the indoline unit and the plane formed by the pyran/ nitrophenyl ring, are orthogonal. Evaluation of the parent ring system (R₁, R₂, and R₃ = H) and 2 using



Figure 2. Contour plot of the COSY spectrum for 1 in the region 3433.4–2128.8 Hz.

PCMODEL^{21, 22} indicates that methyl group C-9 has a C—H distance to H-3' of 2.8–3.0 Å (for low-energy deformations of the five-membered pyrrolidine ring), whereas methyl group C-8 has a C—H distance to H-3' of 4.2–4.4 Å. Hence the relative stereochemistry of the indolino *gem*-dimethyl groups was assigned so that for the S-epimer the pro-R methyl group was found to resonate at 1.24 ppm, while the pro-S methyl appeared at 1.37 ppm for 1.

EXPERIMENTAL

Compounds

Salicylaldehydes. Bromination of 5-nitrosalicylaldehyde gave 3-bromo-5-nitrosalicylaldehyde, m.p. 147–148 °C (lit.²³ 147–148 °C), 3-iodo-5-nitrosalicylaldehyde was prepared by the iodination of 5-nitrosalicylaldehyde with iodine monochloride in glacial acetic acid, m.p. 164–166 °C (lit.²⁴ 166 °C) and 3-methoxy-5-nitrosalicylaldehyde was obtained from the nitration of 3-methoxysalicylaldehyde with aluminium nitrate in acetic anhydride.²⁵ The reaction of salicylaldehyde with 4-nitrophenyldiazonium chloride gave 5-(4-nitrophenylazo)salicylaldehyde.

Unsubstituted 5-nitro-, 5-chloro-, 5-bromo-, 3,5dibromo-, 3,5-dichloro-, 3,5-diiodo- and 3,5-dinitrosalicylaldehydes were available from Aldrich Chemical and were used without further purification.

2-Methylene-1,3,3-trimethylindoline and its 5-chloro derivative. These were available from Aldrich Chemical Co. and were used without further purification.

1,3,3-Trimethylspiro(indolinebenzopyrans). These were all prepared by a common procedure.^{26,27} An equimolar mixture of salicylaldehyde and 2-methylene-1,3,3-trimethylindoline in either ethanol or DMF (30-40 ml per 0.01 mol of aldehyde) was refluxed for 2-4 h. The crystalline product was separated from the highly coloured reaction mixture by filtration, washed with cold ethanol and purified by recrystallization from ethanol or ethanol-water mixtures. The yields, melting points, colours and thermo/photochromic behaviour are summarized in Table 1.

Bruker 400 MHz spectrometer operating at 298 K using a digital resolution of 0.3 Hz per point. Samples were not degassed. Chemical shifts are reported in parts per million (ppm) downfield from TMS. In all experiments 5 mm o.d. NMR tubes (Wilmad 507-PP) were used. The one-dimensional NOE difference experiments consisted of a single irradiation frequency at each multiplet. A pre-irradiation time of 2 s was used.

Representative parameters used to obtain the twodimensional absolute value ¹H-¹H COSY¹⁸⁻²⁰ spectrum were taken from Sanders and Hunter²⁰ and are summarized as follows: spectral width 2000 Hz, 256 experiments, each consisting of 8 scans stored in 1K of data, incrementable delay beginning at 3 μ s with data processing accomplished using a sine-bell window in F_1 and F_2 with zero filling in F_1 and a resolution of 4 Hz per point. The transformed spectrum was symmetrized about the diagonal.

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Spectra

The ¹H NMR spectra were recorded for 10 wt.% solutions in acetone- d_6 , unless stated otherwise, on a

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