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Synthesis and properties of thermo- and photochromic bisindolinobenzospiropyrans linked by thio- and carbonyl groups

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Abstract

Novel thermo- and photochromic thio- and carbonylated bisspiropyrans have been synthesized by the reaction of 5,5′-thiobissalicylaldehydes or the 5,5′-carbonyl analogue and Fischer's base derivatives in 1:2.5 mole ratios. For the synthesis of 5,5′-thio- or carbonylbissalicylaldehyde, 4,4′-thiodiphenol or 4,4′-carbonylbisphenol was formylated with paraformaldehyde. The synthesized dyes were characterized using ^{1}H NMR, IR, UV–vis and mass spectroscopy. The thio-bisspiropyrans showed no thermo- and photochromism whereas the carbonylated dyes showed weak thermo- and photochromism. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Thermo- and photochromic dyes; Thio-bisindolinobenzospiropyran; Carbonyl-bisspiropyran

1. Introduction

Thermo- and photochromic indolinobenzospiropyran dyes have recently become important in connection with the rapid development of information recording systems, such as high-density optical data storage, optical switching, displays and non-linear optics [1,2]. Structurally, spiropyran dyes consist of two *pi* systems linked by a tetrahedral spiro carbon. They form a coloured metastable state on heating or irradiation with UV light, while the reverse process to the colorless state (SP) is induced by visible light, heat or can occur spontaneously [1,2]. The metastable state is called *photo-merocyanine,* as it resembles the structure of merocyanine dyes (MC). The process is shown in Scheme 1.

Since the stability of the spiropyran structure, as well as the ultimate absorption associated with the merocyanine chromophore, is strongly dependent on the substituents present, it is of interest to investigate the influence of structural changes of the parent spiropyran. Structural modification of spiropyrans has thus been an active area of research [3–12].

A major effort in this laboratory has been in the structural modification of spiropyrans for special functionalities [5–12]. We previously reported the synthesis and characterization of the symmetric and unsymmetric bisindolinospirobenzopyrans (BSPs) which contain two spiropyran moieties connected through an alkyl- or arylamido group [6,8]. We

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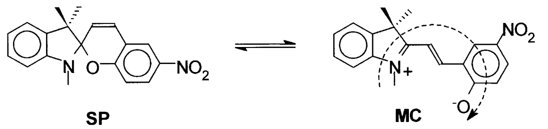
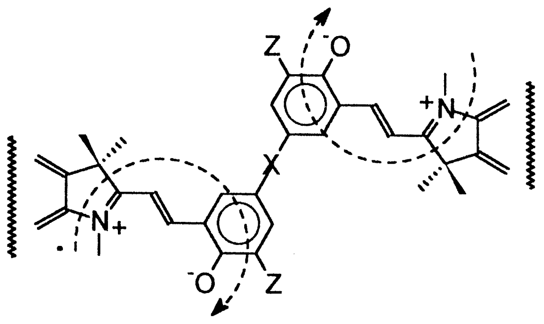
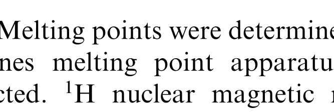


Scheme 1.

also reported the synthesis and characterization of dimeric spiropyrans, in which two spiropyran units were directly connected through each of the 6′-carbon [12]. Since two merocyanine chromorphores in the dimeric spiropyran systems were linked either directly or through a group, the two merocyanine chromorphores were expected to overlap each other.



In this paper, we describe the synthesis and properties of the bisspiropyrans, **1**–**6**, which have two spiropyran units connected through either a thio or a carbonyl group.



Dimer	X	Y	Z
1	S	H	H
2	CO	H	H
3	CO	Cl	H
4	S	H	NO_2
5	S	Cl	NO_2
6	S	NHCOPh	NO_2

2. Experimental

2.1. General

Melting points were determined using a Fischer–Jones melting point apparatus and are uncorrected. ^1H nuclear magnetic resonance (NMR) spectra were obtained using a Bruker AMX-500 spectrometer in deuterated chloroform. UV–visible absorption spectra were recorded using a Varian Cary 1E UV–visible spectrometer and IR spectra were recorded using an Analet instrument FT–IR (MAP-60) using KBr pellets. Photoirradiation was carried out by using a mercury lamp (Ushio, 1 kW) as the excitation light source. Electron impact (EI) mass spectra were recorded on a Schimadzu GCMS-QP1000 spectrophotometer.

2.2. Materials

The required 4,4′-thiodiphenol, Fischer base and 5-chlorinated Fischer base were purchased from Aldrich and were used without further purification. 5-Benzoylamino Fischer's base was prepared according to the known method [6].

2.2.1. Synthesis of 3-(p-hydroxyphenylsulfanyl) salicylaldehyde (HPS-SA) and 5,5′-thiobissalicylaldehyde (*SA-1*)

To a solution of 4,4′-thiodiphenol (3 g, 13.6 mmol) in 100 ml toluene was added $SnCl_4$ (0.35 ml, 2.99 mmol) and tributylamine (2.59 ml, 10.9 mmol) under N_2 at room temperature. After refluxing the reaction mixture for 30 min, paraformaldehyde (2.06 g, 65.3 mmol) was added under N_2 atmosphere and the mixture refluxed for 8 h. At the end of reaction the solution was neutralized with 2 M HCl. The solution was extracted with EtOAc, dried with $MgSO_4$ and finally concentrated in vacuo. Flash chromatography (EtOAc 20%–hexane 80% v/v%) and recrystallization from acetone–hexane afforded 1.38 g (41%) of HPS-SA and 0.38 g (10%) of **SA-1**. ^1H NMR (500 Mz, $CDCl_3$): δ 6.98 (*d*, 1H, J=8.7 Hz), 7 52 (*d*, 1H), 7 59 (*s*, 1H), 9.83 (*s*, 1H) 11.04 (*s*, 1H).

2.2.2. Synthesis of 5,5′-carbonylbissalicylaldehyde (*SA-2*)

The procedure used for the synthesis of 5,5′-carbonylbissalicylaldehyde was the same as that for the above **SA-1**, except for the use of 4,4′-dihydroxybenzophenone instead of 4,4′-thiodiphenol. Flash chromatography (EtOAc 20%–hexane 80%, v/v%) and recrystallization from acetone–hexane afforded white solid, **SA-2** (m.p. 173 °C, yield 5%). ^1H NMR (500 Mz, DMSO-d_6): δ 7.16 (*d*, 1H, J=8.6 Hz), 7.92 (*s*, 1H), 10.32 (*s*, 1H), 11.59 (*s*, 1H).

2.2.3. Synthesis of 5,5′-thiobis(3-nitrosalicylaldehyde) (*SA-3*)

To a solution of 5,5′-thiobissalicylaldehyde (0.5 g, 1.83 mmol) in 50 ml acetic acid, was added nitric acid (0.16 ml) slowly, keeping the solution temperature below 15 °C. The reaction mixture was refluxed for 1 h, after which time the yellow precipitate was filtered and washed thoroughly with water. The yellow solid was dissolved in EtOAc, dried with $MgSO_4$ and concentrated in vacuo. Flash chromatography (EtOAc 20%–hexane 80%, v/v%) and recrystallization from acetone–hexane afforded 0.3 g of **SA-3**. ^1H NMR (500 Mz, DMSO-d_6): δ 8.01 (*s*, 1H), 8.29 (*s*, 1H), 10.23 (*s*, 1H).

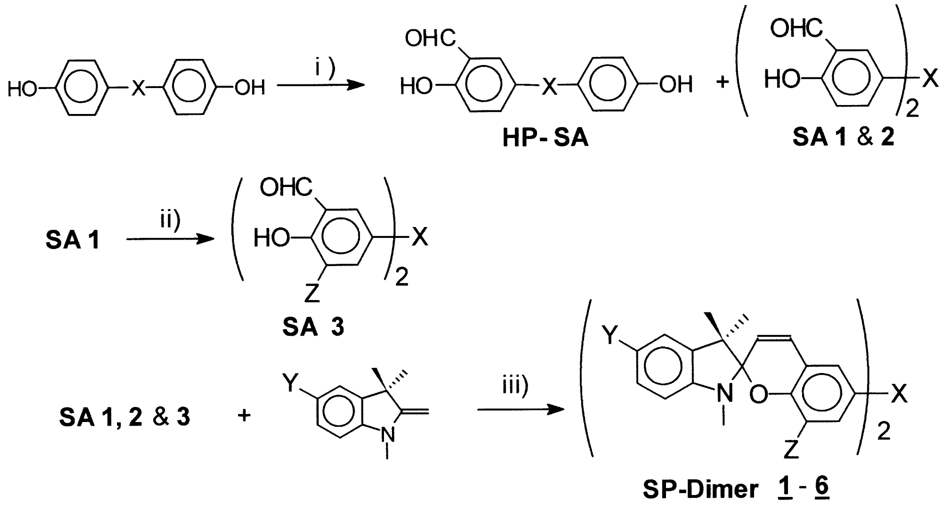
2.2.4. Synthesis of thio- and carbonylated bisspiropyrans (1–6)

Thio- and carbonylated bisspiropyrans were generally synthesized by the reaction of substituted 5,5′-thiobisalicylaldehydes or 5,5′-carbonylbissalicylaldehyde and Fischer's base derivatives in 1:2.5 mole ratios. according to the known procedure [5]. A representative example was: to a solution of 5,5′-thiobis(3-nitrosalicylaldehyde) (0.13 g, 0.357 mmol) in 30 ml methanol was added Fischer's base (0.133 ml, 0.75 mmol) and the mixture refluxed for 1 h. The ensuing solution was allowed to cool to room temperature and concentrated in vacuo. Flash chromatography (EtOAc 30%–hexane 70%, v/v%) and recrystallization from acetone–hexane afforded 0.226 g of bisspiropyran **4**.

3. Results and discussion

3.1. Synthesis of thio- and carbonylated bisspiropyrans (1–6)

Thio- and carbonylated bisspiropyrans (**1**–**6**) were generally synthesized by the reaction of 5,5′-thiobissalicylaldehydes (**SA-1** and **SA-3**) or the 5,5′-carbonyl analogue (SA-2) and Fischer's base derivatives (FB) in 1:2.5 mole ratios. For the synthesis of 5,5′-thio- or carbonylbissalicylaldehyde (**SA-1**, **SA-2**), 4,4′-thiobisphenol or 4,4′-carbonylbisphenol in toluene was reacted with $SnCl_4$/ tributylamine under N_2, followed by reaction with paraformaldehyde. Formylation of 4,4′-thiobisphenol gave the mono-formylated product, hydroxyphenylsulfanyl or hydroxyphenylcarbonylated salicylaldehyde (**HPS-SA** or **HPC-SA**) (Scheme 2) as a major product and the doubly formylated product (bissalicylaldehyde, **SA-1** or **SA-2**) as a minor product. Nitration of **SA-1** was



i) $SnCl_4$, n-Bu_3N / paraformaldehyde, toluene
ii) HNO_3, CH_3COOH
iii) MeOH, reflux

Scheme 2.

performed by reaction with nitric acid/acetic acid to yield **SA-3**. Characterization data of the synthesized bisspiropyrans are summarized in Table 1.

3.2. *Spectroscopic properties of the bis-spiropyrans (1–6)*

The IR spectral frequencies of the precursors (**SA-1**, **-2** and **-3**) and the synthesized bisspiropyrans **1**–**6** were obtained using KBr pellets, as shown in Table 2. The OH frequency of **SA-3** was observed at 3262 cm^{-1}, indicating intramolecular H-bond was present in the salicylaldehyde(ortho-carbonyl substituted phenol). This band did not change its position significantly even at high dilution, as expected. Characteristic carbonyl stretching absorptions were observed at 1656–1658 cm^{-1} for **SA-1** and **SA-2**, but at 1678 cm^{-1} for **SA-3**. The nitro substitutent of the salicylaldehyde, **SA-3**, may have interrupted the H-bonding between OH and C=O groups, and hence the bond-order of C=O was somewhat increased, compared to that of the non-nitrated SA. The nitro group of **SA-3** showed two strong bands at 1531 and 1355 cm^{-1}, for the asymmetric stretching vibration and the symmetric stretching vibration, respectively. The Cspiro-O stretching frequencies of the synthesized bis-spiropyrans, **1**–**6**, occurred at 921–956 cm^{-1}, typical of those found in the indolinobenzospiropyran compounds [5,6]. The nitro group of the bisspiropyrans, **4**–**6**, had two strong bands at 1527–1529 and 1346–1348 cm^{-1}, for asymmetric stretching vibration and the symmetric stretching vibration, respectively. Aromatic ring C=C stretching absorption occurred at 1601–1606 and 1469–1485 cm^{-1} and intense aryl C–O stretching absorption was found at 1233–1271 cm^{-1}.

The proton NMR spectral data of the bisspiropyrans, **1**–**6** in $CDCl_3$ are shown in Table 2. The proton NMR spectra of the symmetric bisspiropyrans showed N–Me peaks at 2.72–2.75 ppm, except for compound **6** (2.66 ppm, measured in DMSO-d_6). These values agree well with the 2.70 ppm value observed for 1,2,3,3-tetramethylindoline [13]. Two geminal methyl groups (prochiral center, C3′) occurred at 1.15–1.19 ppm and 1.28–1.38 ppm for the 9-methyl and 8-methyl groups, respectively. From the previous *n*Oe experimental study [15] of gem-dimethyl peaks of spiropyran systems, the relative stereochemistry of the indolino gem-dimethyl groups can be assigned. Methyl group C-9′ is located close to the olefinic proton H3 and methyl group C-8′ is located close to oxygen moiety of the pyranyl group, as shown in the Newman projection at the C3′–C2′ bond (Scheme 3). The chemical shift of C-8′ were expected to be in down field, compared to that of C-9′, via a through-space interaction between the oxygen atom of the pyran-ring and the C-8′ of indoline moiety.

The ^{1}H data for bisspiropyran **6** was different to that of the others since they were measured in DMSO-d_6. The olefinic protons appeared as double-

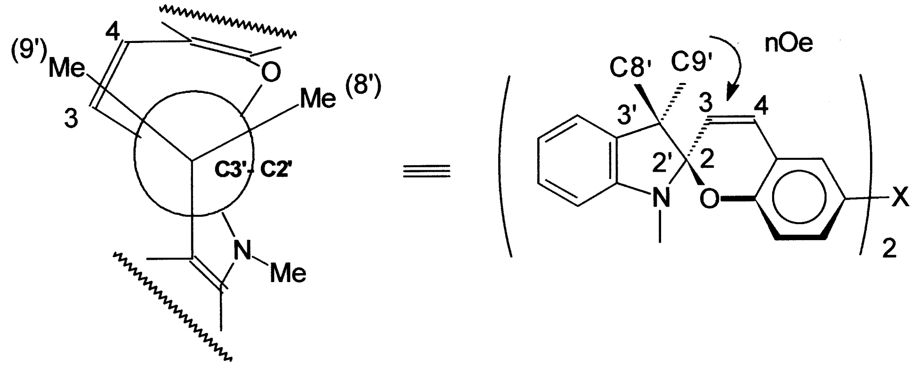
Table 1
M.p.'s and other characterization data for the precursors and bisspiropyrans

Compound	m.p. (°C)	Color[a]	Yield (%)	Mw	Molecular ion	
					(m/z)	Rel. int. (%)
SA-1	147 (lit.[b] 155–157)	Perm. Yellow	10	274.03	274	100
SA-2	173	White	5	270.05	270	78
SA-3	185 (dec.)	Perm. Yellow	45	364.00	364	100
1	88	Yellow	74	584.77	584	18
2	139	White	77	580.27	580	100
3	155	White	82	648.19	648	100
4	240 (dec.)	Compose Green	94	674.22.	674	82
5	248 (dec.)	Linden Green	91	742.14	742	51
6	231	Prussian Blue	76	913.01	913	11

[a] Colour in solid state.
[b] Datum from Ref. [14].

Table 2
IR and ^{1}H NMR spectroscopy data for the prepared bisspiropyrans

Dyes	IR (KBr pellet) (cm^{-1})	^{1}H NMR (500 MHz) δ
1	2961 (*w*), 1608 (*w*) 1460 (*s*), 1260 (*s*), 1122 (*m*), 960 (*s*)	1.15 (*s*, 3H), 1.30 (*s*, 3H), 2.72 (*s*, 3H), 5.69 (*d*, 1H, *J*=10.2 Hz), 6,52 (*d*, 1H, *J*=7.3 Hz), 6.58 (*d*, 1H, *J*=6.7 Hz), 6 67 (*d*, 1H), 6.72 (*s*, 1H), 6.78 (*d*. 1H), 7.04 (*t*, 1H, *J*=7.0 Hz), 7.06 (*d*, 1H, *J*=7.3 Hz), 7.17 (*t*, 1H, *J*=7.3 Hz).
2	1648 (*s*), 1604 (*s*), 1488 (*s*), 1264 (*s*), 1120 (*s*), 955 (*s*)	1.18 (*s*, 3H), 1.32 (*s*, 3H), 2.75 (*s*, 3H), 5.75 (*d*, 1H, *J*=10.3 Hz), 6.54 (*d*, 1H, *J*=7.7 Hz), 6.75 (*d*, 1H, *J*=8.3 Hz), 6.86 (*t*, 1H, *J*=6.8 Hz), 6.90 (*d*, 1H), 7.08 (*d*, 1H, *J*=7.3 Hz), 7.19 (*t*, 1H, *J*=7.7 Hz), 7.56 (*d*, 1H, *J*=8.3 Hz), 7.58 (*s*, 1H)
3	1646 (*s*), 1604 (*s*), 1484 (*s*), 1264 (*s*), 1121 (*s*), 957 (*s*)	1.15 (*s*, 3H), 1.28 (*s*, 3H), 2.72 (*s*, 3H), 5.74 (*d*, 1H, *J*=10.3 Hz), 6.45 (*d*, 1H, *J*=83 Hz), 6.76 (*d*, 1H, *J*=8.2 Hz), 6.95 (*d*, 1H), 7.01 (*s*, 1H), 7.13 (*d*, 1H), 7.59 (*s* 1H), 7.62 (*s*, 1H, *J*=8.2 Hz).
4	1606 (*w*), 1529 (*s*), 1485 (*s*), 1348 (*s*), 1271 (*s*), 1105 (*m*), 921 (*s*)	1.19 (*s*, 3H), 1.38 (*s*, 3H), 2.75 (*s*, 3H), 5.91 (*d*, 1H, *J*=10.4 Hz), 6.54 (*d*, 1H, *J*=7.7 Hz), 6.85 (*t*, 1H, *J*=7.6 Hz), 6.88 (*d*, 1H), 7.07 (*d*, 1H, *J*=7.3 Hz), 7.17 (*t*, 1H, *J*=7.7 Hz), 7.29 (*s*, 1H), 7.68 (*s*, 1H).
5	1602 (*m*), 1529 (*s*), 1484 (*s*), 1346 (*s*), 1267 (*s*), 1106 (*m*), 921 (*s*)	1.19 (*s*, 3H), 1.33 (*s*, 3H), 2 72 (*s*, 3H), 5.89 (*d*, 1H, *J*=10.4 Hz), 6.44 (*d*, 1H, *J*=83 Hz), 6.88 (*d*, 1H), 7.01 (*s*, 1H), 7.12 (*d*, 1H), 7.29 (*s*, 1H), 7.68 (*s*, 1H).
6	3417 (*s*), 1667 (*s*), 1601 (*s*), 1527 (*s*), 1469 (*s*), 1233 (*s*), 1110 (*w*), 956 (*w*)	1.14 (*s*. 3H), 1.25 (*s*, 3H), 2.66 (*s*, 3H), 6.01 (*d*, 1H, *J*=10.4 Hz), 6.59 (*d*, 1H, *J*=8.6 Hz), 7.17 (*d*, 1H), 7.46 (*s*, 1H), 7.50 (*d*, 1H), 7.56 (*s*, 1H), 7.70 (*s*, 1H).



Scheme 3.

doublets at 5.74–5.91 and 6.78–6.95 ppm for H3 and H4, respectively. Their peaks had large coupling constants *J*=10.2–10.4 Hz for both olefinic protons and hence the H3 and H4 signals were characteristic of spiropyran systems, as reported previously [15].

3.3. Photochromic properties of the compounds **1**–**6**

Photochromic properties of compounds **1**–**6** are summarized in Table 3. Thiobisspiropyran **1** showed no thermo- and photochromism. As expected, the nitro derivatives of thio-dyes, **4**–**6**, exhibited

Table 3
Photochromic behaviors of bisspiropyrans (BisSPs)

BisSP	Substituent			T/P[a]	
	X	Y	Z		MC[d] (λ_{max}, nm)[e]
	H	H	–	Non[b]	– (Ref. [12])
	Cl	Cl	–	Non	– (Ref. [12])
	H	H	–C≡C–	Non	– (Ref. [11])
1	S	H	H	Non	–
2	CO	H	H	T/P[c]	–
3	CO	Cl	H	T/P	–
4	S	H	NO_2	T/P	579
5	S	Cl	NO_2	T/P	583
6	S	NHCOPh	NO_2	T/P	587

[a] T and P denote the thermo- and photochromic behavior at room temperature, respectively.

[b] Ring-opening was not observed for this substrate.

[c] This substrate showed weak thermo- and photochromism.

[d] Ring-opened merocyanine species.

[e] Wavelength values (nm) in DMF.

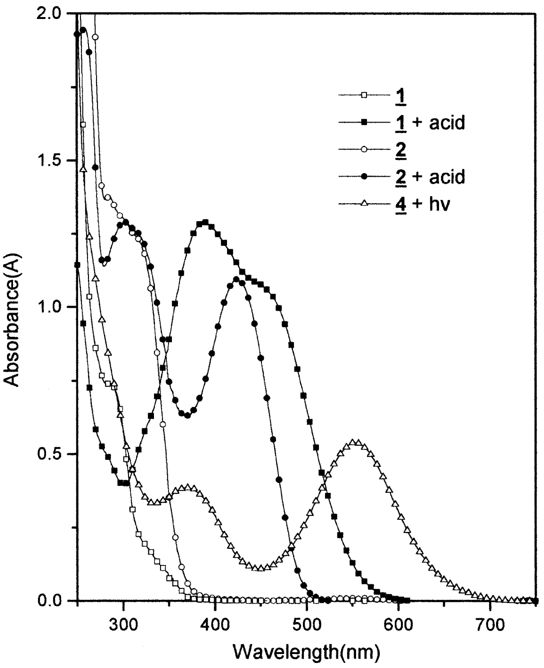


Fig. 1. UV–vis spectroscopic data of BisSPs, **1**, **2** and **4** in neutral and acidic EtOH.

thermo- and photochromism. As an example, irradiation of dye **4** in ethanol at room temperature resulted in λ_{max} wavelengths at 380 and 570 nm in UV–vis spectroscopy, which corresponded to their opened photomerocyanine. The prepared carbonylated dyes **2** and **3**, however, showed weak thermo- and photochromism; their opened-merocyanine form was formed only below 15 °C. The ring-opening behavior in acidic ethanol of **1** is shown in Fig. 1. UV–vis spectrum of **1** showed a double absorption maxima at 380–400 and 460–480 nm in the visible wavelength region, whereas bisspiropyrans **2** and **3** were at 440—450 nm in excess acidic ethanol, which is characteristic of UV–vis behavior of opened merocyanine compounds in acid [7]. Detailed kinetic studies of the spiro-ring cleavage of these bis-spiro dyes in excess acidic media will be carried out in due course.

Acknowledgements

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