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Symmetric and unsymmetric indolinobenzospiropyran dimers: synthesis and characterization

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Abstract

Symmetric and unsymmetric spiropyran dimers(1-6) have been synthesized. Symmetric spiropyran dimers were synthesized by the one-step reaction of substituted 5,5′-bisalicylaldehydes (BSA) and Fischer's Base derivatives (FB), whereas unsymmetric spiropyran dimers were synthesized in a two consecutive step reaction. The synthesized dyes were characterized by ^{1}H NMR, IR UV-Vis. and mass spectroscopy. UV-Visible spectra of these dimers in excess acid ethanol showed twin absorption maxima at 380–400 and 460–480 nm in the visible region, unlikely in the case of bis-spiropyrans which have two merocyanine chromophores connected through a non-conjugated linkage. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Thermochromic; Photochromic; Symmetric and unsymmetric spiropyran dimer; Optical switching

1. Introduction

Thermo- and photochromic indolinobenzospiropyran dyes are currently receiving considerable attention, due to their application in the area of high-density optical data storage, optical switching, displays and non-linear optics [1–3]. Structurally, spiropyran dyes consist of two pi-systems linked by a tetrahedral spiro carbon. They form coloured merocyanine (MC) species on heating or irradiation with UV light, while the reverse process to the colorless spiro form (SP) is induced by visible light, heat or can occur spontaneously (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, 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.

A major effort in our laboratory has been in structural modification of spiropyrans for special functionalities [4–8]. We have previously reported the synthesis and properties of symmetric and unsymmetric bis-indolinospirobenzopyrans (BSPs) in which two spiropyran functions are linked through an amide linkage [9]. Two merocyanine chromorphores are now directly linked and hence two merocyanine chromorphore may overlap each other.

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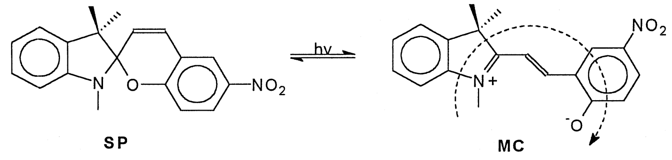
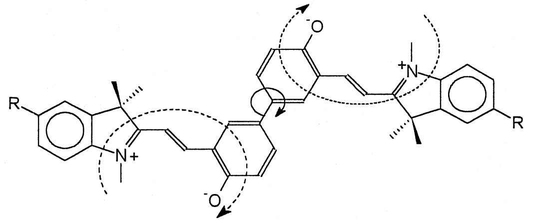
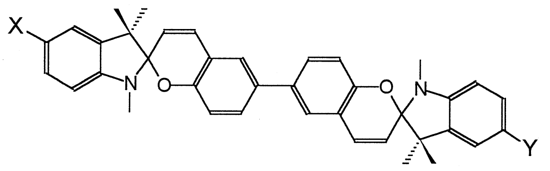


Scheme 1.



Herein, we describe the synthesis and characterization of dimeric spiropyrans, **1**–**6**, in which two spiropyran units are directly connected through both 6′-carbons, and hence two merocyanine chromorphores are directly linked in their opened merocyanine forms. To the best of our knowledge, this is first examination of dimeric spiropyrans, although there has been a synthetic report on **1** and **4** [10].



Dimer	Symbol	X	Y
1	$[SP]_2$	H	H
2	SP-SP(Cl)	H	Cl
3	SP-SP(Acta)	H	NHCOMe
4	$[SP(Cl)]_2$	Cl	Cl
5	(Cl)SP-SP(Acta)	Cl	NHCOMe
6	$[SP(Acta)]_2$	NHCOMe	NHCOMe

2. Experimental

2.1. General

Melting points were determined using a Fischer-Jones melting point apparatus and are uncorrected. ^{1}H NMR spectra were obtained in deuterated chloroform on a Bruker AMX-500 spectrometer, UV-Vis absorption spectra on a Varian Cary 1E UV-visible spectrometer and IR spectra with an Analet Instrument FT-IR (MAP-60) using KBr pellets. Electron Impact (EI) mass spectra were recorded on a Schimadzu GCMS-QP1000 spectrophotometer.

2.2. Materials

The required 4,4′-biphenol, Fischer base and 5-chlorinated Fischer base were purchased from Aldrich Chemical Inc. and used without further purification. 5-Acetaminated Fischer base was prepared, according to Keum's method [4].

2.3. Synthesis of 5,5′-bisalicylaldehyde(BiSA)

To a solution of 4,4′-biphenol (0.97 g) and NaOH (3.3 g) in 30 ml water was added chloroform (3.36 ml) slowly, keeping the solution temperature at 60–65°C. The reaction mixture was refluxed for 3 h. After reaction was complete, unreacted material was removed via steam distillation. The mixture was allowed to cool to room temperature and neutralized with dil. HCl to give a yellow precipitate. Flash chromatography (EtOAc 25%–hexane 75%, v/v%) and recrystallization from acetone–hexane afforded 0.49 g (44%) of HPSA and 0.11 g (9%) of BiSA. Further reaction with HPSA gave BiSA in 92% yield.

2.4. Synthesis of symmetric spiropyran dimers (1, 4, & 6)

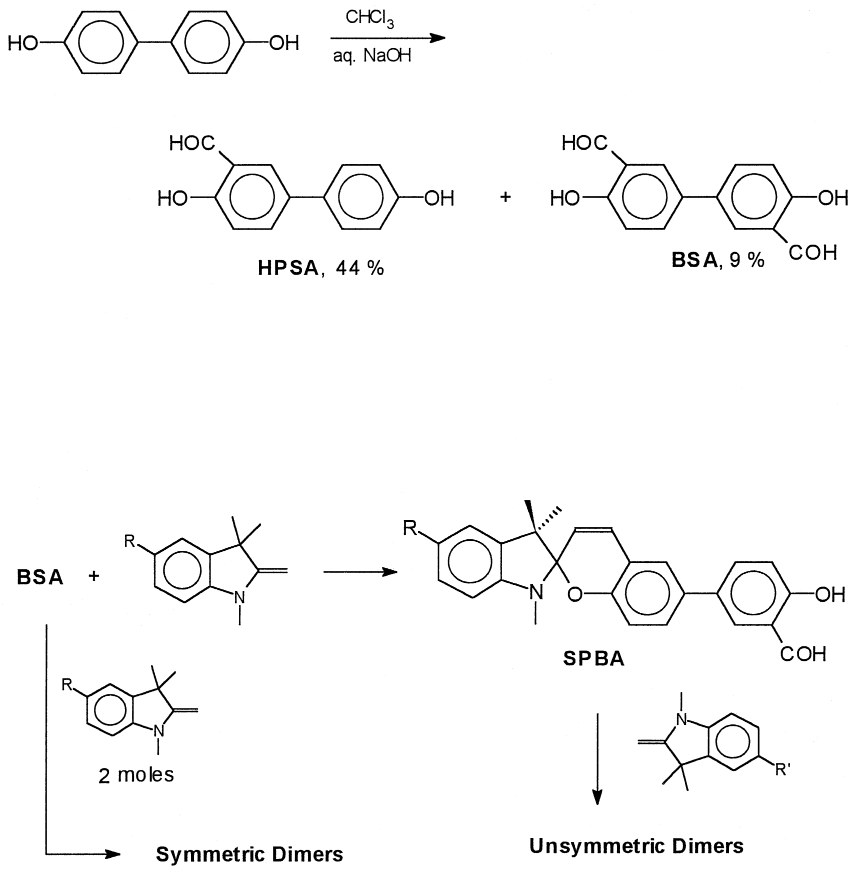
Symmetric spiropyran dimers were synthesized by the reaction of substituted 5,5′-bis-salicylaldehydes and Fischer's Base derivatives in 1:2.5 mole ratios, according to the known procedure [4]. A representative synthesis is as follows:

To a solution of 5,5′-bis-salicylaldehyde (0.1 g, mmol) in 50 ml ethanol Fischer's Base (0.15 ml) was added. The mixture was refluxed for 2 h using a Dean-Stark trapt. After the reaction was complete, the liquor was cooled to room temperature and concentrated in vacuo. Flash chromatography (EtOAc 20%–hexane 80%, v/v%) and recrystallization from acetone–hexane afforded 0.199 g of spiropyran dimer **1**.

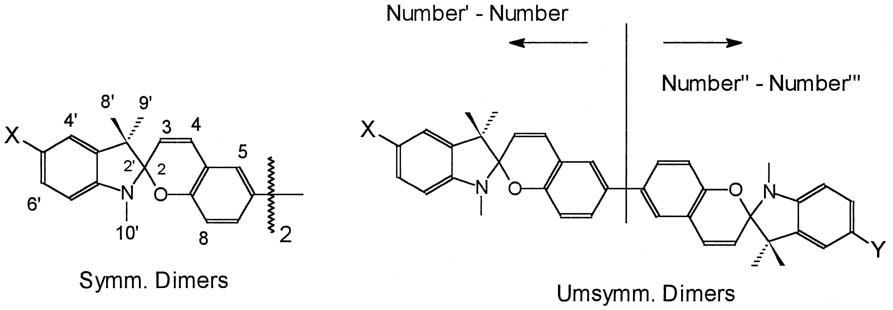
2.5. Synthesis of unsymmetric spiropyran dimers (2, 3 & 5)

Unsymmetric spiropyran dimers were synthesized in two consecutive steps, viz., after the reaction of the substituted 5,5′-bis-salicylaldehydes and Fischer's Base derivatives in 1:1.2 mole ratios, a further reaction was carried out with the second molecule of Fischer's Base derivatives in a 1:1.5 mole ratio. A typical procedure is as follows:

To a solution of 5,5′-bis-salicylaldehyde (0.102 g) in 50 ml ethanol was added 5-chloro-Fischer's Base (90 ul). The mixture was refluxed for 2 h using a Dean-Stark trap. After the reaction was complete, the liquor was allowed to cool to room temperature and concentrated in vacuo. Flash chromatography (EtOAc 20%–hexane



Scheme 2.



Scheme 3.

Table 1
Characterization data for the precursors and spiropyran dimers

Compound	m.p. (°C)	Color	Yield (%)	Mw	Molecular ion	
					(m/z)	Rel.int (%)
HPSA	165	Permanent yellow	44	214.22	214	100
BiSA	219	Lemon yellow	37	242.23	242	100
(Cl)SPSA	74	Naples yellow	62	431.13	431	100
SPSA	78–81	Naples yellow	65	397.17	397	100
1	260–262	White	87	552.28	522	100
2	239	Lemon yellow	87	586.24	586	100
3	121	Icy violet	82	609.30	609	83
4	280–282 (decomp)	White	75	620.20	620	100
5	129	Pastel yellow green	79	643.26	643	100
6	221∼224	Olive green	62	666.32	666	58

80%, v/v%) and recrystallization from acetone–hexane afforded 0.112 g (62%) of 2-hydroxy-5-[5″-chloro-1.3.3-trimethylspiro(2H-1-benzopyran-2,2′-indoline)-6′-yl] benzaldehyde [(Cl)SPSA]. The prepared (Cl)SPSA (0.196) was dissolved in 20 ml of MeOH and FB (81 ul) was added. The mixture solution was refluxed for 2.5 h and the resulting white precipitate filtered, washed with cold ether and concentrated in vacuo. Flash chromatography (EtOAc 5%–hexane 95%, v/v%) and recrystallization from methylene–hexane afforded 0.231 g of the spiropyran dimer, 2.

3. Results and discussion

3.1. Synthesis of symmetric and unsymmetric dyes

Symmetric spiropyran dimers were generally synthesized by a one-step reaction of substituted 5,5′-bis-salicylaldehydes(BSA) and Fischer's Base derivatives (FB) in 1:2.5 mole ratios, whereas unsymmetric spiropyran dimers were obtained in two consecutive steps. The reaction of BSA with one mole of FB formed the spiropyranyl salicyaldehyde (SPSA); further reaction of SPSA with a second molecule of FB yielded the unsymmetric dimers, as shown in Scheme 2. Characterization data of the synthesized dimeric spiropyrans are summarized in Table 1.

3.2. Spectroscopic properties of compounds, 1–6

Table 2 summarizes the IR spectral frequencies of the synthesized HPSA, BiSA, SPSA and spiropyran dimers. The OH frequencies of HPSA is observed at 3255 cm^{-1}, indicating that an intramolecular H-bond is present in the salicylaldehyde(ortho-carbonyl substituted phenol). This band did not change its position significantly even at

Table 2
IR spectroscopy data for salicylaldehyde-derivatives and spiropyrans

Compound	Frequency (cm^{-1})
HPSA	3255(s), 2885(w), 1654(s), 1485(m), 1268(m), 1104(w), 828(m)
BiSA	3251(s), 2866(s), 1665(s), 1474(m), 1283(m), 1185(w), 835(w)
(Cl)SPSA	3436(w), 2963(w), 2870(w), 1661(s), 1479(s), 1258(m), 964(m)
SPSA	3427(w), 2923(w), 2868(w), 1660(s), 1480(s), 1261(s), 962(m)
1	2960(w), 1608(m), 1481(s), 1259(m), 951(m), 817(m), 744(m)
2	2961(w), 1606(m), 1483(s), 1255(s), 1128(m), 960(s), 746(w)
3	3445(s), 2963(m), 1656(m), 1611(m), 1484(s), 1257(s), 1122(m), 962(m), 817(w), 744(w)
4	2965(w), 1604(m), 1482(s), 1253(s), 1126(m), 961(s), 818(m)
5	3458(w), 2964(m), 1658(m), 1609(m), 1481(s), 1256(s), 1124(m), 962(s), 813(m), 720(w)
6	3294(m), 2965(m), 1658(s), 1488(s), 1255(s), 1121(w), 961(s), 813(m)

The symbols denoted as follows: s = strong and sharp, m = medium, w = weak.

Table 3
^{1}H NMR data for the prepared spriopyran dimers in DMSO-d_6

	Spiropyran dimers					
Proton	**1**	**2**	**3**[a]	**4**	**5**	**6**
4′-H	7.11	7.09	7.09	7.17	7.15	7.30
5′-H	6.77	6.77	6.86	—	—	—
6′-H	7.13	7.11	7.17	7.15	7.11	7.23
7′-H	6.56	6.56	6.54	6.59	6.55	6.49
8′,8″-Me	1.11	1.10	1.19	1.12	1.09	1.08
9′,9″-Me	1.22	1.21	1.31,1.34	1.24	1.20,1.19	1.20
10′,10″-Me	2.66	2.64	2.72,2.75	2.67	2.63,2.61	2.63
3-H	5.80	5.79	5.73	5.80	5.77	5.80
4-H	7.06	7.06	6.90	7.08	7.05	7.05
5-H	7.43	7.43	7.19	7.45	7.42	7.42
7-H	7.32	7.31	7.24	7.35	7.31	7.31
8-H	6.71	6.71	6.76	6.74	6.71	6.72
4‴-H	–	7.17	7.28	–	7.28	–
5‴-H	–	–	–	–	–	–
6‴-H	–	7.13	7.17	–	7.25	–
7‴-H	–	6.58	6.46	–	6.48	–
3″-H	–	5.80	5.71	–	5.77	–
4″-H	–	7.07	6.90	–	7.03	–
5″-H	–	7.44	7.19	–	7.42	–
7″-H	–	7.34	7.24	–	7.29	–
8″-H	–	6.72	6.74	–	6.71	–
-COCH$_3$	–	–	2.15	–	1.99	1.98
-NHCO-	–	–	–	–	9.67	9.67
J(6′-H,7′-H)	7.5	7.4	7.7	8.2	8.3	8.2
J(3-H,4-H)	10.2	10.2	10.1	10.2	10.1	10.2
J(7-H,8-H)	8.4	8.4	8.1	8.5	8.4	8.4
J(6‴-H,7‴-H)	–	8.0	8.2	–	8.3	–
J(3″-H,4″-H)	–	10.2	10.1	–	10.2	–
J(7″-H,8″-H)	–	8.4	8.1	–	8.4	–

[a] Data in CDCl$_3$.

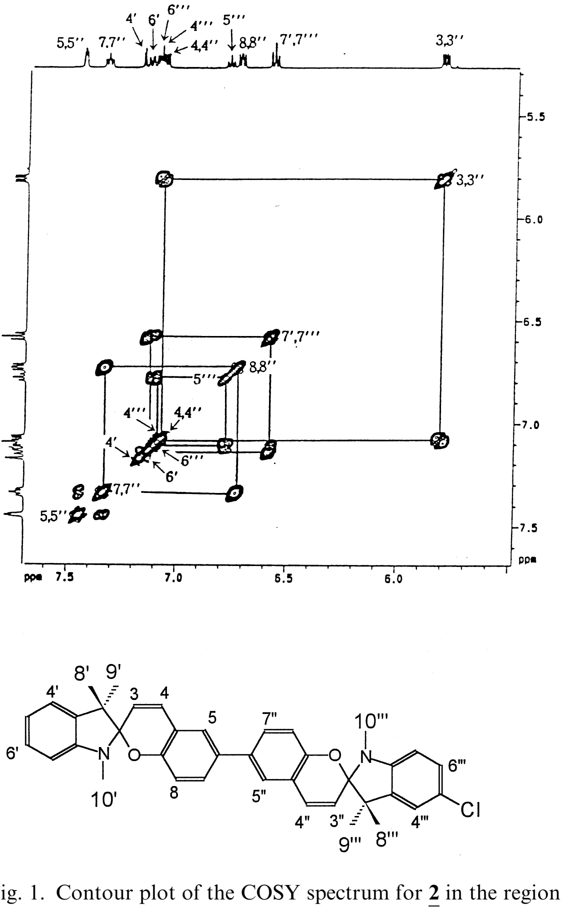


Fig. 1. Contour plot of the COSY spectrum for 2 in the region of 5.5–7.5 ppm.

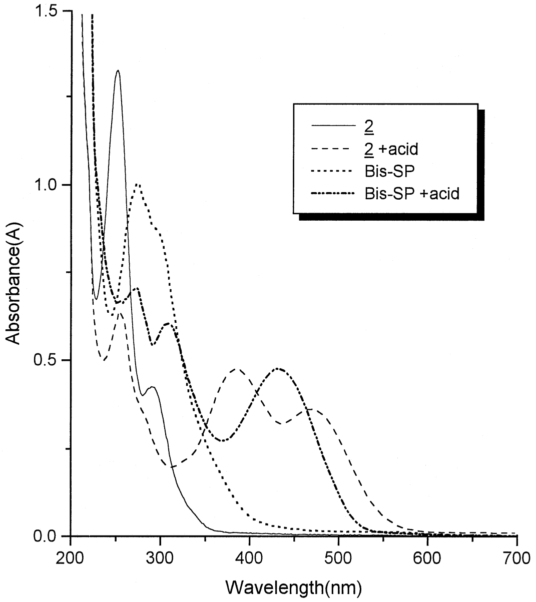


Fig. 2. UV-Vis. spectra of Dimer 2 and Bis-SP in EtOH.

high dilution, as expected. The C–H stretching vibration was observed in SA's at about 2866–2885 cm^{-1}, and these compounds also showed characteristic carbonyl absorption at 1654–1665 cm^{-1}.

The spiropyran dimers showed aryl C–N frequencies at 1253–1259 cm^{-1}. These C–N frequencies were very sensitive to the substituents at the C-4′ position; thus dimers 1 show at 1259 cm^{-1} whereas dimers 4, which have two Cl substituents at both of the C4′ positions, show at 1253 cm^{-1}. The C$_{spiro}$–O stretching frequencies occur at 951–962 cm^{-1}; these are generally found in indolinobenzospiropyran compounds.

^{1}H NMR spectral data of the SP dimers in DMSO-d_6 are given in Table 3. The NMR spectra of the symmetric SP dimers are straightforward with respect to their for the interpretation, whereas those of unsymmetric SP dimers are complicated, and hence aided by 2D NMR (Fig. 1). The numbering systems are shown as in Scheme 3.

The SP dimers prepared show N-Me peaks at 2.61–2.67 ppm. Two geminal methyl groups (pro chiral center, C3′) occur at 1.08–1.11 ppm and 1.19–1.21 ppm for the pro-S, 9-methyl and pro-R, 8-methyl groups, respectively. ^{1}H data for the dimer 3 was deviated from the others since they were measured in $CDCl_3$. The olefinic protons appear at 5.77–5.80 and 6.90–7.80 ppm for H3 and H4, and at 5.71–5.79 and 6.90–7.06 ppm for H3″ and H4″, respectively. Both olefinic protons have large coupling constants $J = 10.1$–$10.2\,H_Z$ and hence they (H3 and H3″) are a very characteristic signal of spiropyrans, as reported previously [11].

UV-Visible spectra for the synthesized dimers in excess acidic ethanol showed double absorption maxima at 380–400 and 460–480 nm in the visible wavelength region, as shown in Fig. 2.

This is of interest, since it has been shown that bis-spiropyrans, whose structure shown below, in the same medium show only one absorption maximum at 450–460 nm in the visible wavelength region [12]. This may indicate that the two merocyanine chromorphores of the SP dimer synthesized overlap each other, and hence bathochromic shifts are expected in the absorption maxima of the MC forms of these dimers.

$$[\mathrm{SP{-}NHCO} - (\mathrm{CH_2})_8 - \mathrm{CONH} - \mathrm{SP}]$$

Bis – spiropyran

Further detailed studies on the determination of UV-Vis spectral data of these dimers, whose MC have very short life time and of the spiro-ring cleavage of these dimers in excess acidic media, will be reported in due course.

Acknowledgements

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