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Spectral Assignments and Reference Data

Complete ^{1}H and ^{13}C NMR spectral assignment of symmetric and asymmetric bis-spiropyran derivatives

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^{1}H and ^{13}C NMR spectra of symmetric and asymmetric bis-spiropyrans, Series 1-3, were completely assigned. Especially, the ^{1}H assignment of asymmetric spiropyrans was achieved by utilizing ^{1}H–^{1}H COSY and nOe experiments. All of the carbons in the dye molecules were investigated through a combination of heteronuclear 2D-shift correlation spectroscopy (HETCOR), together with an attached proton test (APT). Copyright © 2005 John Wiley & Sons, Ltd.

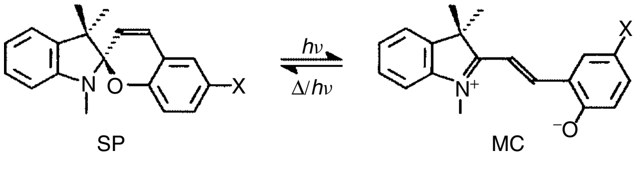
KEYWORDS: NMR; ^{1}H NMR; ^{13}C NMR; 2DNMR; APT; symmetric bis-spiropyrans; asymmetric bis-spiropyrans

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 nonlinear optics.[1,2] Structurally, spiropyran dyes consist of two π systems linked by a tetrahedral spiro carbon. They form a colored metastable state on heating or irradiation with UV light, while the reverse process is induced spontaneously or by visible light and heat. The metastable state is called *photomerocyanine,* 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. A major effort of this laboratory has been in the structural modification of spiropyrans for special functionalties.[3–7]

Previously, our laboratory reported synthesis and solvatokinetic studies of symmetric and asymmetric bis-indolinospirobenzopyrans (BSPs), which contain two spiropyran moieties connected at C-6, either directly or through a connecting group, such as a thio- or carbonyl group.[6] Since two merocyanine chromorphores in the dimeric spiropyran systems are linked, either directly or through a linking group, the two merocyanine chromorphores are expected to overlap, and hence induce a bathochromic shift of their maximum wavelengths. For studying this connection, the detailed ^{1}H and ^{13}C NMR spectroscopic data of those bis-spiropyrans prepared symmetric (Series 1–2) and asymmetric (Series 3) were examined, whose chemical structures are shown in Scheme 2.



Photochromism of spiropyrans

Scheme 1

These symmetric and asymmetric BSPs are the potent key materials for the synthesis of bent-shaped (banana shaped) liquid crystals,[8] in the cases when X and Y are long alkyl-chained linkages, as in Scheme 3.

RESULTS AND DISCUSSION

Symmetric bis-spiropyrans (Series 1–2) were generally synthesized by the reaction of 5,5′-substituted bis-salicylaldehyde and Fischer base (FB) derivatives, in a 1 : 2.5 mole ratio. The asymmetric bis-spiropyrans (Series 3) were prepared by a two-step reaction, using two differently substituted Fischer bases. As a representative example, bis-spiropyranyl sulfides were synthesized by the reaction of 5,5′-thiobis(3-nitrosalicylaldehyde) and Fischer base derivatives in a 1 : 2.5 mole ratio. For the synthesis of the doubly formylated bis-salicylaldehyde, 4,4′-thiobisphenol in toluene was reacted with $SnCl_4$/tributylamine under N_2, followed by reaction with paraformaldehyde. The formylation of 4,4′-thiobisphenol gave the monoformylated product, hydroxyphenylsulfanyl salicylaldehyde as the major product and the doubly formylated bis-salicylaldehyde as a minor product.

The symbols, melting points (mp) and other characteristics of the symmetric (Series 1–2) and asymmetric (Series 3) bis-spiropyrans examined are summarized in Table 1.

^{1}H NMR assignment of the symmetric and asymmetric bis-spiropyrans (Series 1–3) were very straightforward, as found from the known chemical shifts and coupling constants of the mono-spiropyrans.[9] The proton NMR spectral data of bis-spiropyrans (Series 1), bis(8-nitrospiropyranyl) sulfides (Series 2) and asymmetric bis-spiropyran (Series 3) in DMSO are given in Table 2. The proton NMR spectra of these materials showed *N*–Me peaks at 2.61–2.67 ppm, with the exception of compound SP-ASP (2.72–2.75 ppm, measured in $CDCl_3$). Two geminal methyl groups (prochiral center, C3′) appeared at 1.08–1.12 and 1.20–1.24 ppm for the 9-methyl and 8-methyl groups, respectively, with the exception of compound SP-ASP (1.19 and 1.31–1.34 ppm, measured in $CDCl_3$). From the nOe experimental study of the *gem*-dimethyl peaks of the bis-spiropyran systems, the relative stereochemistry of the indolino *gem*-dimethyl groups can be assigned, as in mono-spiropyrans.[8] By analyzing the nOe enhancement study, the protons of the SP unit 1, such as H-3, H-4, H-8′, H- 9′ and H-10′, etc. could not be differentiated from the protons of the SP unit 2, such as H-3″, H-4″, H-8‴, H-9‴ and H-10‴, etc. The olefinic protons appeared as pairs of doublets at 5.73–5.80 and 6.90–7.08 ppm for H3 and H4, respectively. Their peaks had large coupling constants, *J* = 10.1–10.2 Hz, for both olefinic protons, with the H3 and H4 signals very characteristic of bis-spiropyran systems, as in mono-SP.[9]

These results were corroborated by the ^{1}H–^{1}H COSY plot of SP-ASP, which showed cross peaks for H-3,3″ and H-4,4″, H-7‴ and H-6‴, H- 7′ and H-6′, H-8,8″ and H-7,7″, and for H- 5′ and H-6′.

From the heteronuclear 2D-shift correlation spectrum (HETCOR)[10] for the prepared SP-ASP, a direct ^{13}C–^{1}H correlation for SP-ASP could be established. The 12 carbons in each unit of bis-SPs were coupled with 12 previously assigned protons. These carbons were C-3, 4, 5, 7, 8, 4′, 5′, 6′, 7′, 8′, 9′ and 10′ in each unit. These carbons have now been assigned, and are summarized in Tables 3 and 4.

Geminal methyl peaks are shown at 25–26 and 19.8–20.6 ppm for C-8′ and C-9′, respectively. Interestingly, the pro-*R* methyl carbon (C8′) resonates at a lower frequency than that of the pro-*S* methyl carbon (C9′). In fact, it has been reported[9] that for the *S*-epimer of 6-nitrospirobenzopyran the pro-*R* methyl group (H9′) resonates at 1.24 ppm, while the pro-*S* methyl group (H8′) appears at 1.37 ppm in their ^{1}H NMR spectra. To assign the residual six quaternary aromatic carbons, use was made of substituent-induced shift increments for C-2, 2′, 4a, 6, 8a, 3′, 3′a, 5′ and 7′a from the benzene and coupled

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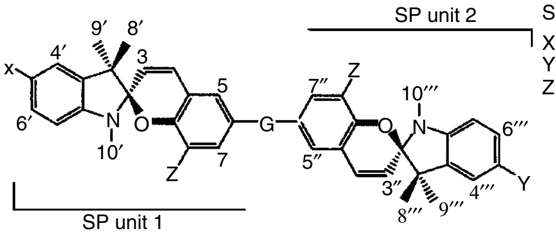
Spectral Assignments and Reference Data



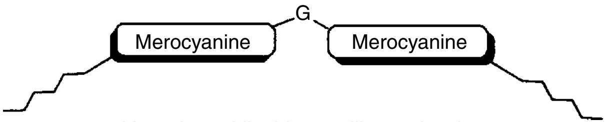
Series 1: G = – and X = Y
Series 2: G = S or CO and X = Y
Series 3: G = – and X ≠ Y
X = H, Cl, NHCOR
Y = H, Cl, NHCOR
Z = –, NO_2

Structures of bis-spiropyrans
Scheme 2

Table 1. Symbols and characterization of the bis-spiropyrans examined

		Substituents			Melting			
	Symbols[a]	G	X and Y	Z	point (mp)	Yield	Color	Note[b]
Series 1	Bis-SP	–	H	H	260–262	87	Yellow	–
	Bis-CSP	–	Cl	H	280–282	75	White	–
	Bis-ASP	–	NHCOMe	H	221–224	62	Green	–
Series 2	TBis-NSP	S	H	NO_2	240[c]	94	Green	P,T
	TBis-CNSP	S	Cl	NO_2	248[c]	91	Green	P,T
	TBis-ANSP	S	NHCOPh	NO_2	231[c]	76	Blue	P,T
	C_bBis-SP	CO	H	H	139	77	White	–
	C_bBis-CSP	CO	Cl	H	155	82	White	–
Series 3	SP-ASP	–	H and NHCOMe	H	121	82	Violet	–
	SP-CSP	–	H and Cl	H	239	87	Yellow	–
	CSP-ASP	–	Cl and HCOMe	H	129	79	Yellow Green	–

[a] T- and $C_b$bis-SP denote thio- and carbonylated bis-spiropyran, and A- and C-, NSP, amido-, chloro- and nitrospiropyran, respectively.
[b] P and T denote photochromic and thermochromic dyes, respectively.
[c] Literature data obtained from Ref. 6(d).



Vent-shaped-liquid crystalline molecules
Scheme 3

spectra. For calculation of the chemical shifts of these carbons, by comparison of the substituted benzenes, the increment method[10] was employed. The calculated values of the above carbons were 104, 119, 132, 153, 51, 138.7, 123 and 146.7 ppm for C-2, 2′, 4a, 6, 8a, 3′, 3′a, 5′ and 7′a, respectively. The calculated values were reasonably close to the experimental chemical shifts. Both the values of the calculated and experimental chemical shifts deviated by no more than 1%. Because of the ambiguity of the chemical shift of C-4a, the attached proton test spectra (APT)[11] of SP-ASP were used. The chemical shifts of C-6′ and C-4a were too close to be separated in the HETCOR spectrum, whereas they were well separated in the APT spectrum. Tables 3 and 4 summarize the ^{13}C NMR chemical shifts for the symmetric (Series 1–2) and asymmetric bis-spiropyrans (Series 3) examined.

EXPERIMENTAL

Materials

Symmetric (Series 1–2) and asymmetric bis-spiropyrans (Series 3) were prepared according to the previously described methods.[6] Commercially available Fluka grade Fischer base (1,3,3-trimethyl-2-methyleneindoline) was nitrated with H_2SO_4/HNO_3, and then reduced with stannous chloride dihydrate and conc. HCl. ASP was obtained from the reaction of alkyl- or arylamido-Fischer base (RCONH-FB) with an equimolecular amount of salicylaldehyde.

Samples for the ^{1}H,^{13}C NMR determination were prepared as 1 M solutions in either $CHCl_3$-*d* or DMSO-d_6, as mentioned elsewhere.

NMR spectra

The one- and two-dimensional ^{1}H and ^{13}C NMR spectra were recorded with a Varian Mercury 300 NMR spectrometer, operating at 300.07 MHz for the ^{1}H and 75.46 MHz for the ^{13}C resonances, respectively. The samples used were 0.1 M solutions in DMSO-d_6 for both the ^{1}H and ^{13}C, prepared in 5 mm NMR tubes at 298 K. The ^{1}H and ^{13}C chemical shifts were referred to $SiMe_4$ in $CDCl_3$ as an internal standard, or to the residual solvent signal in DMSO-d_6 (^{1}H = 2.50 ppm and ^{13}C = 39.52 ppm). The digital resolutions of the ^{1}H and ^{13}C NMR spectra were 0.25 and 0.6 Hz per point, respectively. The narrower spectral region of special interest was also measured, but with a smaller spectral width and greater digital resolution (down to 0.2 Hz). The following techniques were used: proton-noise decoupling, APT, ^{1}H–^{1}H COSY and ^{1}H–^{13}C HETCOR. The ^{1}H–^{1}H COSY spectra were obtained in the magnitude mode, with 1024 points in the F_2 dimension and 256 increments in the F_1 dimension. Each increment was obtained with 16 scans, a spectral width of 4500 Hz and a relaxation delay of 1 s. The resolutions were 5.4 and 10.7 Hz per point in the F_1 and F_2 dimensions, respectively. The ^{1}H–^{13}C HETCOR spectra were measured with the one-bond C–H

Table 2. ^{1}H-NMR data for the bis-spirobenzopyrans in DMSO-d_6

	Series 1			Series 2			Series 3[a]		
Protons	Bis-SP	Bis-CSP	Bis-ASP[b]	TBis-NSP[b]	TBis-CNSP[b]	C_bBis-CS[b]	SP-CSP	SP-AS[b,c]	C_bSP-ASP[b]
H-4′,4‴	7.11	7.17	7.30	7.07	7.01	7.01	7.09, 7.17	7.09, 7.28	7.15, 7.28
H- 5′	6.77	–	–	6.85	–	–	6.77	6.86	–
H-6′,6‴	7.13	7.15	7.23	7.17	7.12	7.13	7.11, 7.13	7.17	7.11, 7.25
H-7′,7‴	6.56	6.59	6.49	6.54	6.44	6.45	6.56	6.54, 6.46	6.55, 6.48
H-8′,8‴	1.11	1.12	1.08	1.19	1.19	1.15	1.10	1.19	1.09
H-9′,9‴	1.22	1.24	1.20	1.38	1.33	1.28	1.21	1.31, 1.34	1.20, 1.19
H-10′,10‴	2.66	2.67	2.63	2.75	2.72	2.72	2.64	2.72, 2.75	2.63, 2.61
H-3,3″	5.80	5.80	5.80	5.91	5.89	5.74	5.79, 5.80	5.73, 5.71	5.77
H-4,4″	7.06	7.08	7.05	6.88	6.88	6.95	7.06, 7.07	6.90	7.05, 7.03
H-5,5″	7.43	7.45	7.42	7.29	7.29	7.59	7.44, 7.43	7.19	7.42
H-7,7″	7.32	7.35	7.31	7.68	7.68	7.62	7.31, 7.34	7.24	7.31, 7.29
H-8,8″	6.71	6.74	6.72	–	–	6.76	6.71, 6.72	6.76, 6.74	6.71
J(3-H,4-H)	10.2	10.2	10.2	10.4	10.4	10.3	10.2	10.1	10.1
J(7-H,8-H)	8.4	8.5	8.4	–	–	8.2	8.4	8.1	8.4

[a] Numbers are unduplicated, if chemical shifts of SP units 1 and 2 are coincident.

[b] Protons of aceto- and amide groups resonate at 1.98–2.15 and 9.67 ppm, respectively.

[c] Data in CDCl$_3$.

Table 3. ^{13}C-NMR data for the symmetric bis-spirobenzopyrans (series 1–2) in $CHCl_3 - d$, including data for a mono-spiropyran for comparison

		Series 1		Series 2				
Carbons	Mono-SP[a]	Bis-SP[b]	Bis-ASP[b]	TBis-SP	TBis-NSP	TBis-CNSP	C_bBis-SP	C_bBis-CSP
C-2,2′	106.5	104.1	104.3	104.9	107.3	107.2	105.3	105.8
C-3′	51.92	51.38	51.42	52.23	52.32	52.34	51.9	52.44
C-3′a	136.0	136.3	136.4	137.0	137.4	137.7	136.4	138.8
C-4′	n/a	121.5	114.3	121.9	121.4	121.9	121.5	122.5
C-5′	131.7	118.9	131.6	119.6	120.0	124.6	119.4	124.5
C-6′	118.9	127.5	118.9	128.0	127.8	127.5	127.7	127.8
C-7′	106.8	106.8	106.5	107.2	107.1	108.1	106.9	108.2
C-7′a	144.1	147.8	144.0	148.5	147.3	145.9	147.9	147.1
C-8′	25.67	25.69	25.62	26.27	26.00	25.82	25.9	26.11
C-9′	19.68	19.88	19.84	20.57	20.02	19.79	20.00	20.28
C-10′	28.70	28.58	28.75	29.34	28.87	28.98	28.86	29.40
C-3	121.3	119.6	119.5	120.5	122.5	122.0	120.1	120.1
C-4	128.4	129.4	129.4	129.4	127.9	128.2	129.1	129.8
C-4a	120.6	118.8	118.8	120.0	122.7	122.5	118.4	118.8
C-5	125.8	124.6	124.6	130.1	133.9	134.0	129.0	129.5
C-6	140.5	132.0	131.9	126.8	125.1	125.4	130.1	130.7
C-7	122.9	127.4	127.4	133.4	128.1	128.2	132.4	133.0
C-8	115.4	114.7	114.7	116.4	135.8	137.4	114.6	115.0
C-8a	159.4	153.1	153.1	154.4	148.1	147.9	158.0	158.2

[a] Data of 5′-acetamido-6-nitro SP for comparison from Ref. 6(a).

[b] Data in DMSO-d_6.

coupling value set to 140 Hz, using 2048 points in the F_2 dimensions and 256 increments in the F_1 dimension, with a relaxation delay of 1 s. The spectral width was 20 000 Hz in the F_2 and 4500 Hz in the F_1 dimensions. The resulting resolution was 19.53 Hz per point in the F_2 and 17.6 Hz per point in the F_1 dimensions. All two-dimensional experiments were performed by standard pulse sequences, using the Mercury Data System software Version VNMR 6.1B. For proton decoupling, Waltz 16 modulation was used.

Spectral Assignments and Reference Data

Table 4. ^{13}C-NMR data for asymmetric bis-spirobenzopyrans (Series 3) in DMSO-d_6

	SP unit 1				SP unit 2		
Carbons	SP-CSP	SP-ASP[a]	CSP-ASP	Carbons	SP-CSP	SP-ASP[a]	CSP-ASP
C-2,2′	104.1	104.3	104.1	C-2″,2‴	104.1	104.5	104.3
C-3′	51.40	51.71	51.51	C-3‴	51.56	51.80	51.42
C-3′a	136.3	136.7	138.7	C-3‴a	138.7	137.4	136.4
C-4′	121.5	121.5	121.9	C-4‴	122.0	115.6	114.3
C-5′	119.0	119.1	122.5	C-5‴	122.5	129.8	131.6
C-6′	127.5	127.6	127.0	C-6‴	127.1	120.4	118.9
C-7′	106.8	106.7	108.0	C-7‴	108.1	106.6	106.5
C-7′a	147.9	148.2	146.7	C-7‴a	146.8	145.5	143.9
C-8′	25.70	25.85	25.26	C-8‴	25.31	25.71	25.60
C-9′	19.89	20.16	19.54	C-9‴	19.59	20.06	19.83
C-10′	28.60	28.92	28.60	C-10‴	28.65	29.07	28.73
C-3	119.2	119.7	119.5	C-3″	119.7	119.5	119.1
C-4	129.4	129.4	129.4	C-4″	129.7	129.5	129.6
C-4a	118.9	118.9	118.7	C-4″a	118.7	118.8	118.8
C-5	124.6	124.7	124.6	C-5″	124.7	124.7	124.6
C-6	131.9	132.7	132.1	C-6″	132.1	132.6	131.8
C-7	127.5	127.9	127.5	C-7″	127.5	127.8	127.4
C-8	114.7	115.2	114.7	C-8″	114.7	115.2	114.7
C-8a	153.1	153.5	152.9	C-8″a	152.9	153.6	153.1

[a] Data in $CDCl_3$.

Acknowledgments

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