Dyes and Pigments **25** (1994) 21-29
1994 Elsevier Science Limited
Printed in Great Britain
0143-7208/94/$7.00

Synthesis and Characterization of Bis-indolinospirobenzopyrans, New Photo- and Thermochromic Dyes

Sam-Rok Keum, Jeong-Hoon Lee & Moon-Ki Seok

Department of Chemistry, College of Science and Technology, Korea University,
Jochiwon, Choong-Nam, 339-700 South Korea

(Received 22 November 1993; accepted 7 January 1994)

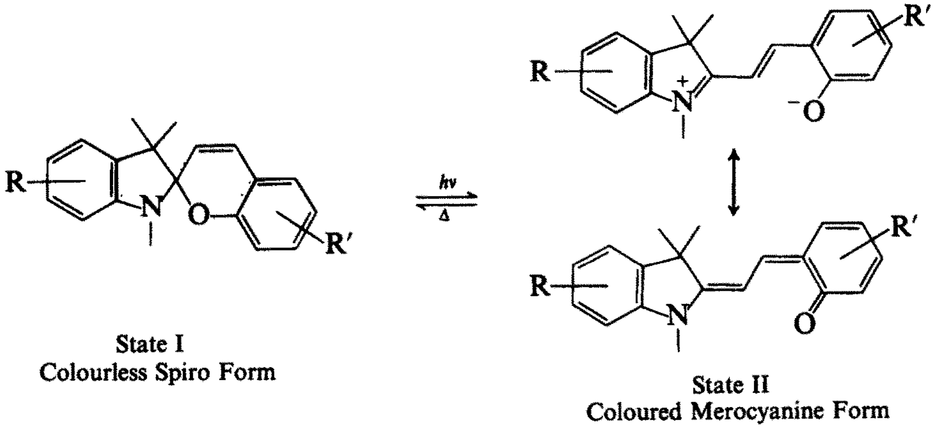
ABSTRACT

New thermo- and photochromic dyes, viz. bis-indolinospirobenzopyrans (BSPs, 3a–c) have been synthesized by the reaction of bis-Fischer bases (BFBs, 2a–c) with 2-hydroxy-5-nitrobenzaldehyde. The BFBs were prepared from the reaction of 5-amino-Fischer base with the corresponding diacyl halides. The synthesized BSPs have been characterized by 1H-NMR, IR, UV-VIS, and mass spectroscopy.

1 INTRODUCTION

During the last decade, many studies[1-13] have been made on the behavior of thermo- and photochromic indolinospirobenzopyran dyes. Interest in these compounds is connected with the reversibility between the colorless spiro forms and the merocyanine colored forms, as shown in Scheme 1. Absorption of ultraviolet light shifts the equilibrium towards the merocyanine colored form, State II, while the reverse process to the colorless form, State I, is induced by visible light, by heat, or spontaneously.

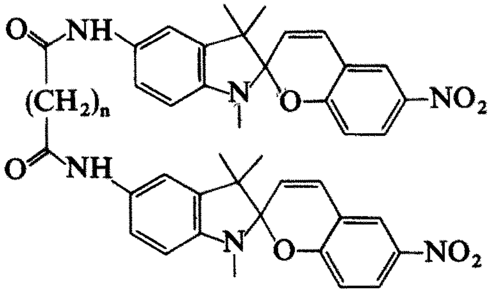
Basically, the spiropyran dyes consist of two π-systems linked by a tetrahedral spiro carbon atom, while substituents modify the stability of the spiropyran, as well as the long wavelength absorption associated with the π-system. Structural modification of these dyes has been an active area of research since the compounds were found to be useful due to the practical applications that these dyes can be used for[3-7] including recording, copying and preparation of display materials. It has also been reported[14-16]



Scheme 1.

that the merocyanine dyes are capable of giving 'giant' molecular aggregates, including spiropyran–merocyanine complexes. In order to control the aggregate growth and hence to prepare a novel dimer, the authors thus undertook synthetic work on bis analogues of indolinospirobenzopyrans by synthesizing a 'dimeric' dye which is obtained by connecting the 5-amino group of amino-Fischer base, **1c**, to the carbonyl group of diacid halide molecules. A major goal of this investigation was to demonstrate that these dyes are capable of intra- and intermolecular π-stacking via merocyanine units in nonpolar solvents.

The synthesized structures in this preliminary study are as follows:

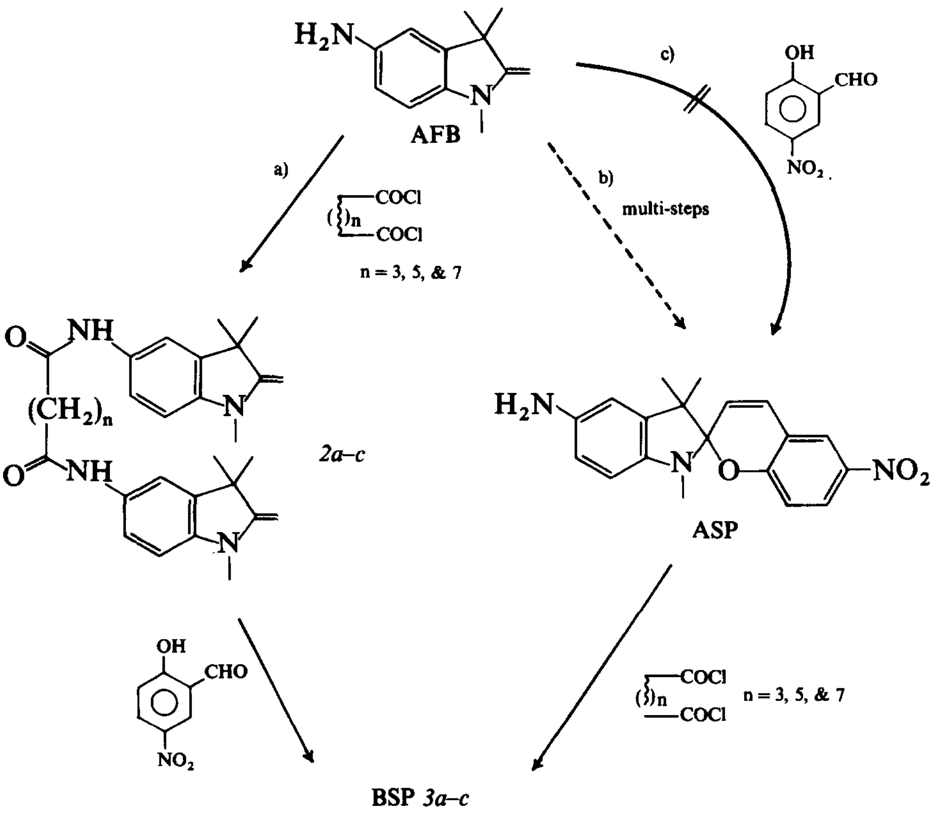


3a n = 3
3b = 5
3c = 7

2 RESULTS AND DISCUSSION

2.1 Synthesis

It is well established that substituted Fischer bases, 2-methylene-1,3,3-trimethylindoline, **1a**, react with various salicylaldehydes in 1 : 1 mole ratio to give the indolinobenzospiropyran derivatives (SP).[9,17] One



Scheme 2.

would hence expect that 5-amino-6'-nitro-1,3,3-trimethylspiro(indolino-2,2'-benzopyran) (ASP) would react with various diacid halides in the synthesis of a series of bis spiropyran dyes (BSPs), i.e. bis[5-{1,3,3-trimethylspiro(indolino-2,2'-benzopyranyl)}]-α,ω-dicarboxamides via route (b) in Scheme 2. It has been reported,[18] however, that ASP requires a multistep synthesis from 5-amino-Fischer base, **1c**. Several tedious steps for blocking of the amino group and deblocking were needed in the reaction with salicylaldehydes, since **1c** has an extra nucleophilic center in the amino group in addition to the methylene group or Fischer base. This may be the reason why route (c) in Scheme 2, i.e. the reaction of **1c** with nitrosalicylaldehyde, was not recommended for use in the synthesis of ASP.[18]

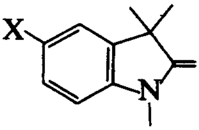
The authors thus undertook a synthetic study using diacid halides as both blocking group of the amino function and as carbon chains to make the connection between two spiropyranyl groups, as shown in route (a) in Scheme 2. Bis-Fischer bases [bis{5-(2-methylene-

TABLE 1
Characterization Data for BSPs (**3a**, **3b** and **3c**)

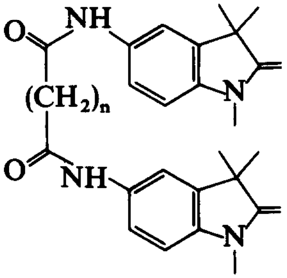
Compound		*Analysis*			*Mw*	*Molecular ion*	
		C.	*H.*	*N.*		*(m/z)*	*Relative intensity (%)*
3a	Calc.	67·00,	5·49,	10·90	770·88	771·1	100
	Found	67·01,	5·52,	10·68			
3b	Calc.	67·65,	5·80,	10·52	798·93	799·6	24·24
	Found	67·51,	5·64,	10·43			
3c	Calc.	68·26,	6·09,	10·16	826·98	827·0	8·80
	Found	68·57,	6·18,	9·98			

Calc., Calculated.

1,3,3-trimethylindoline)}-α,ω-dicarboxamides] were obtained from the reaction of diacid halides with 2–3 molar ratio of AFB, **1c**, which was prepared by adapting Gale's method.[19] The BFBs were then reacted with several salicylaldehydes to give the corresponding BSPs in good yields. Characterization data of the synthesized BSPs are summarized in Table 1.



1a X = H
1b = NO_2
1c = NH_2



2a n = 3
2b = 5
2c = 7

2.2 Spectroscopic properties of the compounds, 1–3

The IR spectral frequencies of the synthesized BFBs and BSPs are collated in Table 2. They show characteristic carbonyl absorptions at 1651–1655 cm^{-1}, as well as 1607–1609 cm^{-1} in the case of BFBs, and 1612 cm^{-1} in the case of BSPs, indicating that the double bond character of the carbonyl group of BSPs is somewhat greater than that of BFBs. The —NO_2 asymmetric stretching band for the benzopyran group of BSP is observed at 1518–1519 cm^{-1} and the —NO_2 symmetric stretching band at 1337–1339 cm^{-1}. These bands are close to those of *p*-nitroaniline

TABLE 2
IR Spectroscopy Data for BFBs (**2a–c**) and BSPs (**3a–c**)

Compound	*Frequency*^{a} *(cm^{-1})*				
2a	3288(s'),	1651(s),	1608(w),	1553(w),	1501(s),
	1134(w)				
2b	3294(s'),	1655(s),	1609(w),	1549(s),	1501(s),
	1130(w)				
2c	3290(s'),	1653(s),	1607(w),	1551(s),	1501(s),
	1134(w)				
3a	3300(d),	1655(m),	1612(m),	1519(s),	1490(s),
	1339(s),	1273(s),	1090(m),	953(m),	812(m)
3b	3300(d),	1655(m),	1612(m),	1518(s),	1491(s),
	1337(s)	1273(s),	1090(m),	953(m),	812(m)
3c	3300(d),	1655(m),	1612(m),	1518(s),	1491(s),
	1337(s),	1273(s),	1090(m),	953(m),	812(m)

[a] Symbols denote as follows: s' = singlet, d = doublet, s = strong and sharp, m = medium, w = weak.

and *p*-nitrophenol, i.e. 1524, 1346 and 1508, 1340 cm^{-1}, respectively.[20] This may indicate that the extent of conjugation of the nitro group with the attached structure in these BSPs corresponds to that in *p*-nitroaniline and *p*-nitrophenol. The —NH— stretching vibrational bands at 3290 cm^{-1} in the case of BFBs consist of singlets, whereas those of BSPs are found as doublets at 3300, 3400 cm^{-1}. This is interesting since one would expect from this result that the carbonyl groups occur in somewhat different environments. Peak intensity ratios of the doublet band of these dyes are *c.* 1 for the BSP, **3a**, and decrease as the length of the carbon chain becomes longer. This doublet band in a secondary amide may be misleading, since doublet bands in this region are expected from primary amides.

Table 3 summarizes the 400 MHz ^{1}H-NMR chemical shifts for the compounds in the present study. The BFBs and BSPs prepared show *N*-methyl peaks at 3·00–3·01 and 2·69–2·72 ppm for **2** and **3**, respectively. Two geminal methyl groups occur at 1·30–1·32 ppm for **2** and 1·17–1·20 and 1·26–1·29 ppm for the 8- and 9-methyl groups of **3**, respectively. The olefinic protons (H-3' and H-4') for **3** appear at 5·83–5·85 and 6·91–6·93 ppm and have coupling constants $J_{\text{H-3'–H-4'}}$ = 10·3–10·5 Hz. The olefinic proton (H-3') is a highly characteristic signal of spiropyrans, as reported previously.[11] All other protons on SP (Ref. 3) carbons absorb in the region 2·49–1·38 ppm.

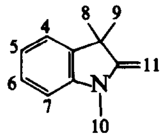
TABLE 3

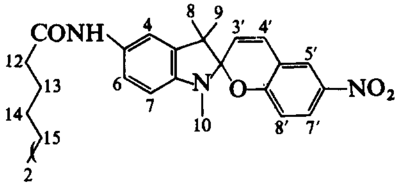
^{1}H-NMR Data[a] for AFB (**1c**), BFBs (**2a–c**) and (**3a–c**)

Proton[b]	*1c*	*2a*	*2b*	*2c*	*3a*	*3b*	*3c*
H-4	6·55	7·31	7·18	7·33	7·38	7·38	7·39
H-6	6·51	7·18	7·10	7·13	7·24	7·16	7·18
H-7	6·33	6·44	6·40	6·42	6·42	6·50	6·45
8—CH_3	1·30	1·32	1·30	1·31	1·29	1·26	1·28
9—CH_3	1·30	1·32	1·30	1·31	1·20	1·17	1·18
10—CH_3	2·96	3·01	3·00	3·00	2·72	2·69	2·71
11=CH_2	3·73	3·82	3·81	—	—	—	—
—NH—	3·32	—	—	—	—	—	—
H-12	—	2·49	2·35	2·31	2·53	2·37	2·35
H-13	—	2·12	1·79	1·72	2·18	1·79	1·75
H-14	—	2·49	1·50	1·38	2·53	1·51	1·41
H-15	—	—	—	1·38	—	1·79	1·41
H-3'	—	—	—	—	5·85	5·83	5·84
H-4'	—	—	—	—	6·93	6·91	6·92
H-5'	—	—	—	—	8·00	7·98	8·00
H-7'	—	—	—	—	8·04	8·01	8·02
H-8'	—	—	—	—	6·76	6·91	6·75
J(H-3',H-4')	—	—	—	—	10·3	10·4	10·5
J(H-5',H-7')	—	—	—	—	2·2	2·5	2·7
J(H-7',H-8')	—	—	—	—	6·6	8·4	7·7
J(H-6,H-7)	8·0	8·2	8·3	8·3	8·5	8·3	8·3
J(H-12,H-13)	—	6·8	7·1	7·4	6·7	7·2	7·2

[a] Data in $CHCl_3$-d.

[b] The numbering systems are shown below:





The UV-VIS spectroscopic data of the opened, merocyanine forms of BSPs, **3a–c**, obtained on UV irradiation in various solvents, are given in Table 4. The BSPs exhibit strong photochromism, with very large molar extinction coefficients for the open chain merocyanines. A negative solvatochromism[9,13,21] is observed, as discussed previously for general indolinospirobenzopyran dyes. As solvent polarity increased from dioxane (E_T = 36·0) to ethyl alcohol (E_T = 51·9), a hypsochromic shift (from 546 to 596 nm) was generally observed for **3a–b** (Table 4).

TABLE 4
UV-Visible Spectroscopic Data (λ_{max}, 1000 × $\bar{\nu}$) of Opened Forms of Bis-indolinobenzopyrans (**3a–c**) in Various Solvents

Solvent	E_T	*3a*	*3b*	*3c*
Dioxane	36·0	596 (16·7)	587 (17·0)	591 (16·9)
CH_2Cl_2	40·7	589 (17·0)	587 (17·0)	588 (17·0)
Acetone	40·2	578 (17·3)	579 (17·3)	579 (17·3)
DMF	43·8	576 (17·4)	577 (17·3)	579 (17·3)
EtOH	51·9	547 (18·3)	546 (18·6)	548 (18·2)

3 EXPERIMENTAL

3.1 General

Melting points were determined using a Fischer–Jones melting point apparatus and are uncorrected. IR spectra were recorded on an Analet Instrument FT-IR (MAP-60) using KBr pellets. Proton NMR spectra were taken with a Bruker CXP-400 FT-NMR spectrophotometer and UV-VIS absorption spectra were determined on a Shimadzu UV-2100 spectrophotometer. Electrospray (ES) mass spectra were recorded on a VG Quattro mass spectrometer.

3.2 Synthesis of Fischer base derivatives

3.2.1 Nitro-Fischer base (*1b*) and amino-Fischer base (*1c*)

5-Nitro(and amino)-1,3,3-trimethyl-2-methyleneindoline (**1b** and **1c**) were obtained from commercially available Fluka grade Fischer base (1,3,3-trimethyl-2-methyleneindoline, **1a**), according to a previously described procedure.[19]

1a was nitrated with H_2SO_4/HNO_3 at 10°C. After the reaction was complete, the solution was neutralized and kept in a refrigerator for 1 day. The solid was then filtered, dissolved in ether, washed with water and dried (anhydrous Na_2SO_4). The crude product was recrystalized from methylene chloride/light petroleum ether to give **1b**, m.p. 88–91°C (Ref. 19, 85–91°C) in 60% yield. The red solid, **1b**, was refluxed with stannous chloride dihydrate and concentrated hydrochloric acid for 2 h. The precipitate obtained cooling was extracted with methylene chloride/light petroleum ether to give colorless **1c**, m.p. 98–100°C (Ref. 19, 98–100°C) in 77% yield.

*3.2.2 Bis-Fischer base, **2a–c***

Glutaryl dichloride ($n = 3$) (4·83 mmole) in methylene chloride (20 ml) and triethylamine (10 ml) was added dropwise to a cold solution of **1c** (10·62 mmole) in methylenechloride (30 ml) and the mixture was stirred for 3 h at room temperature. The reaction mixture was washed with water and brine, dried and evaporated. The white solid which formed was recrystallized from methylene chloride/hexane to give **2a** in 70% yield, m.p. 182–184°C.

For the synthesis of **2b** and **2c**, the same procedure was followed using pimeloyl dichloride ($n = 5$) and azelaoyl dichloride ($n = 7$), except that THF was used as solvent in both cases. Yields and m.p. were 71 and 92%, and 136–138 and 142–143°C, for **2b** and **2c**, respectively.

*3.2.3 Bis-indolinospirobenzopyrans, **3a–c***

The appropriate bis-Fischer base, **2a–c** (0·24 mmole), in ethanol 50 ml was added dropwise to a stirred solution containing 2-hydroxy-5-nitrobenzaldehyde (0·55 mmole) in ethanol (50 ml). The solution was kept at 40°C for one day. The precipitates thus obtained were purified by column chromatography on silica gel (100–200 mesh) using $CHCl_3$/EtOAc 9 : 1 as eluent. Recrystallization from methylene chloride/hexane gave pure **3a–c**. Yields were 70, 88, and 81%, and m.p. were 172–173, 155–158, and 155–156°C, for **3a**, **3b** and **3c**, respectively.

ACKNOWLEDGEMENTS

This work was supported partly by a grant from the Non-Directed Research Fund, Korea Research Foundation, 1992 and partly from the Ministry of Education of the Republic of Korea under the Basic Science Research Program. The authors thank Dr E. Buncel for helpful discussion and Mr Kap-Soo Cheon for recording the ES mass spectra of the synthesized dyes.

REFERENCES

1. Brown, G. H. (ed.), Photochromism. In *Technique of Chemistry, Vol. 3.* John Wiley, New York, 1971.
2. Durr, H. & Bouas-Laurent, H. (eds), *Photochromism: Molecules and Systems*. Elsevier, 1992.
3. Durr, H., *Angew. Chem., International Edition*, **28** (1989) 413.
4. Tamaki, T. & Ichimura, K., *J. Chem. Soc. Chem. Commun.*, (1989) 1477.
5. Inouye, M., Kim, K. & Kitao, T., *J. Am. Chem. Soc.*, **114** (1992) 778.

6. Miyata, A., Unuma, Y. & Higashigaki, Y., *Bull. Chem. Soc. Jpn*, **63** (1993) 993.
7. Williams, D. J., Nonlinear Optical Properties of Organic and Polymeric Materials. ACS Symposium Series 233, 1983, pp. 135–151.
8. Keum, S. R., Hur, M. S. & Lee, K. B., *Indus. Devel. Rev.*, **1** (1989) 117.
9. Keum, S. R., Hur, M. S., Kazmair, P. M. & Buncel, E., *Can. J. Chem.*, **69** (1991) 1940.
10. Keum, S. R., Lee, K. B. & Chi, K. Y., *Indus. Devel. Rev.*, **2** (1992) 209.
11. Keum, S. R., Lee, K. B., Kazmair, P. M. & Buncel, E., *Magn. Reson. Chem.*, **30** (1992) 1128.
12. Keum, S. R., Yun, J. H. & Lee, K. W., *Bull. Kor. Chem. Soc.*, **13** (1992) 351.
13. Keum, S. R. & Lee, K. W., *Bull. Kor. Chem. Soc.*, **14** (1993) 16.
14. Wyn-Jones, E. & Gormally, J., *Aggregation Processes in Solution*. Elsevier, 1983, chap. 10–12.
15. Krongauz, V. A. & Shvartsman, F. P., *J. Phys. Chem.*, **88** (1984) 6448.
16. Miyata, A., Unuma, Y. & Higashigaki, Y., *Bull. Chem. Soc. Jpn*, **66** (1993) 993.
17. Keum, S. R., Kazmaier, P. M., Mandeville, R. & Buncel, E., *J. Chem. Soc. Perkin* I, in press.
18. Shvartsman, F. P. & Krongauz, V. A., *J. Phys. Chem.*, **88** (1984) 6485.
19. Gale, D. J. & Wilshire, J. F., *J. Soc. Dyers Colour*, **90** (1974) 97.
20. Conley, R. T., *Infrared Spectroscopy*. Allyn and Bacon, Boston, 1966, chap. 5, pp. 87–202.
21. Reichardt, C., *Solvents and Solvent Effects in Organic Chemistry* (2nd edn). VCH, Weinheim, 1988, pp. 339–405.