Dyes and Pigments, Vol. 30, No. 3, pp. 225–234, 1996
Copyright © 1996 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0143-7208/96 $15.00 + 0.00

ELSEVIER 0143-7208(95)00078-X

Synthesis and Characterization of Unsymmetrical Bis-indolinospirobenzopyrans, a New Class of Thermo- and Photo-chromic Dyes

Sam-Rok Keum,*[a] Soon-Sung Lim,[b] Byung-Hun Min,[b]
Peter M. Kazmaier[b] & Erwin Buncel[c]*

[a]Department of Chemistry, Graduate Studies of Korea University, Seoul, Korea 136-701
[b]Xerox Research Centre of Canada, Mississauga, Ontario, Canada L5K 2L1
[c]Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6

(Received 24 July 1995; accepted 21 August 1995)

ABSTRACT

A new class of unsymmetrical bis-indolinobenzospiropyran dyes (U-BSP) and their precursors have been synthesized. Unsymmetrical bis-indolinobenzospiropyrans are obtained by condensation of the precursor, Fischer base–spiropyran derivatives (FB–SP^x), with substituted salicylaldehydes. The alternative Fischer base–spiropyran precursor (FB–SP^y), which has an electron-withdrawing substituent, was not found to be suitable for the synthesis of U-BSPs. The synthesized U-BSPs have been characterized by ^{1}H NMR, UV-Vis, and mass spectroscopy; they show abnormal solvatokinetic behavior in nonpolar solvents, suggestive of aggregate formation.

1 INTRODUCTION

Much information has been published[1,2] on the behavior of thermo- and photo-chromic indolinobenzospiropyran dyes. Interest in these compounds arose from their combination of photochemical, thermal and kinetic features which have made them promising with regard to possible practical applications,[3–8] such as in recording, copying, and display materials.

The thermo- and photo-chromic processes of the spiropyran system consist of reversible opening and ring-closure, spiropyran $\rightleftharpoons$ merocyanine (Scheme 1).

---

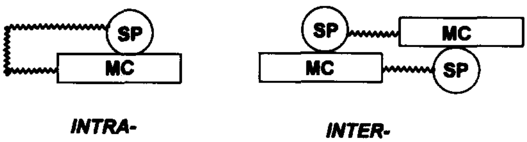
*Corresponding authors.

Scheme 1. SP $\rightleftharpoons$ MC interconversion.

Irradiation of the colorless spiro form results in a photodynamic equilibrium with the colored merocyanine form, MC. The reverse process to the colorless SP form is induced by light, heat, or spontaneously.[8–13]

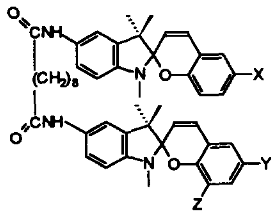
The observed change in the spectra of colored solutions with variation in temperature and concentration are commonly ascribed either to mutual transformations of the merocyanine stereomers, or to formation of MC dimers and higher aggregates.[14] In addition to MC–MC aggregation, the spiropyrans are also believed to take part in SP–MC aggregate formation on UV irradiation in nonpolar solvents (cf. 'quarsicrystals' reported by Krongauz *et al.*[15]).

We have reported[16,17] previously the synthesis of the symmetrical bis-indolinobenzospiropyrans (BSP), with the possibility of influencing aggregation (MC–MC aggregate). However, those bis-spiropyrans being symmetric, could not eliminate the formation of unsymmetrical aggregates, such as SP–MC complexes (Scheme 2).



Scheme 2. Molecular aggregates.

We have thus undertaken synthetic studies aimed at the preparation of unsymmetrical bis-indolinobenzospiropyrans (U-BSP, **1a–d**), which could lead to a novel unsymmetrical dimer (SP–MC complex) on irradiation. One SP unit (SP^{y}, y = activating group such as NO_2) of the U-BSP's is expected to form a ring-opened MC and the other SP unit (SP^{x}, x = non-activating group such as H or CH_3) should remain in the unopened spiro form.

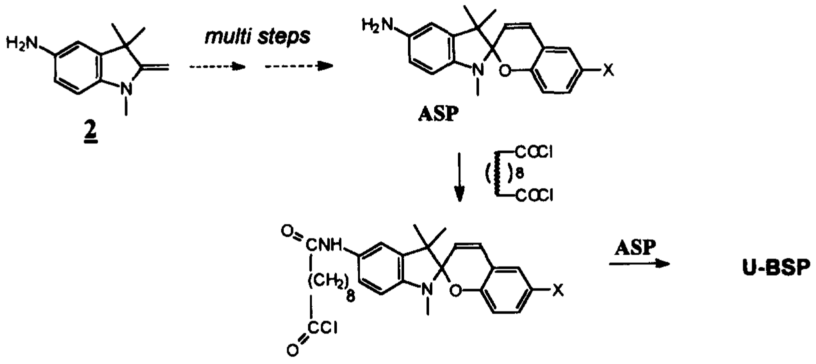


	X	Y	Z
1a	H	NO_2	H
1b	H	I	I
1c	H	NO_2	NO_2
1d	CH_3	NO_2	H

2 RESULTS AND DISCUSSION

2.1 Synthesis

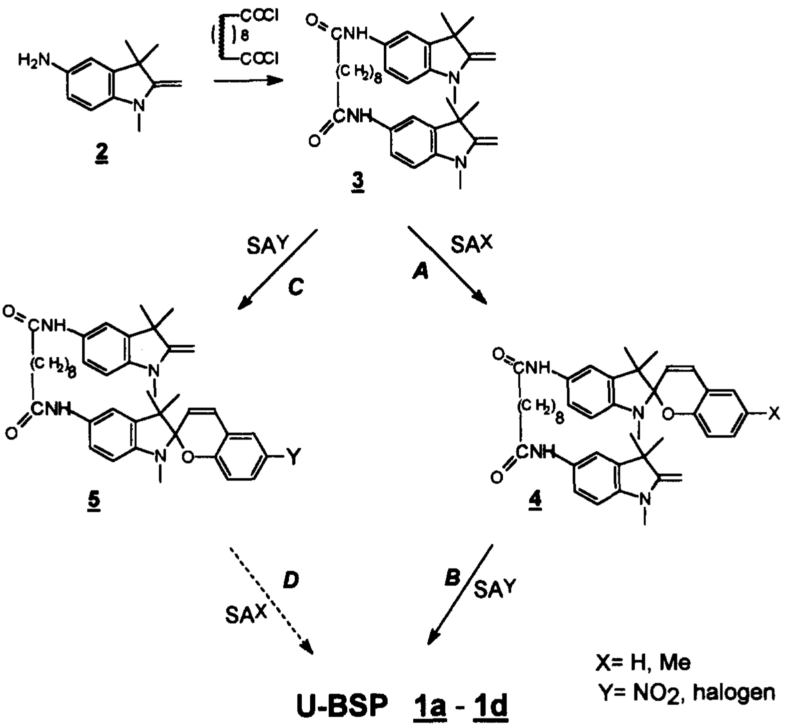
The simplest route to U-BSPs could well be expected to follow that shown in Scheme 3. According to this scheme, sebacoyl chloride would react with 1 mol of 5-amino-1,3,3-trimethylspiro(indolino-2,2'-benzopyran) derivative (ASP) to form an indolinobenzospiropyranyl sebacamide, which would be followed by reaction with another ASP molecule to form the unsymmetrical bis-indolinobenzospiropyran sebacamide. However, formation of the ASP from 5-amino-Fischer base (**2**), requires a multistep synthesis, with several tedious steps for blocking of the amino group and deblocking, in the reaction with salicylaldehydes, since **2** has an extra nucleophilic centre in the amino group. Hence the synthetic route in Scheme 3 is not recommended for the synthesis of U-BSPs.



Scheme 3.

As in our previous work,[16,17] we proposed to use sebacoyl acid halide as both blocking group of the amino function and as carbon chain to make connection between two spiropyranyl groups, as shown in Scheme 4. Of the two possible routes from the bis-Fischer base (BFB), steps A & B vs C & D, the former pathway was successful but not the latter. We have found a great deal of difficulty in separation of the precursor, **5** (FB–SP^y), from the reaction mixture in step C. This may be due to the strong interaction between the MC form of the precursor and the stationary phase of the column used.

In the procedure that was adopted, Fischer base (FB, 1,3,3-trimethyl-2-methyleneindoline) was nitrated and reduced to form 5-amino Fischer base (AFB, **2**, 5-amino-1,3,3-trimethyl-2-methyleneindoline). An excess molar ratio of **2** was then reacted with sebacoyl chloride to form the bis-Fischer base (BSP, **3**, [bis{5-(2-methylene-1,3,3-trimethylindoline)}]-α,ω-sebacamide.



Scheme 4.

The precursor [FB–SP^x, **4a** (x = H), **4b** (x = CH_3)], which is the key intermediate in the unsymmetric bis-indolinospirobenzopyran synthesis, was obtained from the reaction of BFB, **3**, with salicylaldehyde (SA^x) in ethanol. The unsymmetric BSP compounds, **1a–d** were then obtained from the reaction of the key intermediate, **4**, and the corresponding substituted salicylaldehydes (SA^y).

The yields and m.p.s of the synthesized unsymmetrical BSPs (**1a–d**) as well as of their precursors (**3**,**4**) are given in Table 1. Electron spray (ES) mass spectral data of the synthesized U-BSPs are summarized in Table 2. In contrast to the symmetrical bis-spiropyrans, the relative MS intensities of U-BSPs were quite low.

2.2 Structural elucidation of the synthesized U-BSPs and their precursors

Structural elucidation of the precursors, **3** and **4**, and the unsymmetrical BSP, **1a–d**, was achieved mainly with the aid of ^{1}H NMR spectroscopy. The N-Me and 2-methylene peaks of Fischer base units of compounds **3** and **4** are very characteristic, resonating at *ca* 3·80 and 3·00 ppm, respectively

TABLE 1

Characterization of the Synthesized Unsymmetrical BSPs, **1a–d** and Their Precursors, **3** and **4**

Compound	*X*	*Y*	*Z*	*m.p. (°C)*	*Colour*	*Yield (%)*	*T/P*[a]
3				143–145	white	91	
4a	H			154–155	camel	39	T/P
4b	CH_3			144–145	mauve	36	T/P
1a	H	NO_2	H	140–143	blue-green	71	T/P
1b	H	I	I	147–150	jade-green	64	T/P
1c	H	NO_2	NO_2	214–218	violet	61	T/P
1d	CH_3	NO_2	H	187–190	blue-gray	82	T/P

[a] T and P denotes thermo- and photo-chromic behavior, respectively.

TABLE 2

Characteristic ^{1}H NMR Data of U-BSPs, **1a–d** and Their Precursors, **2–4** in the Region of 2·5–6·5 ppm, in $CDCl_3$

Compound	*Methylene (= CH_2)*	*N-Me(FB)*	*N-Me (SP)*[a]		*Vinyl (H-3′)*[a]		*Ratio*[b]
			α	*ω*	*α*	*ω*	
2	3·73	2·96					
3	3·80	2·99					
4a	3·83	3·01		2·69		5·65	
4b	3·82	2·98	2·67		5·62		
1a			2·69	2·70	5·67	5·85	1:1
1b			2·63	2·69	5·66	5·71	1:1
1c			2·70	4·05[c]	5·82	6·54[c]	1:1
1d			2·61	2·64	5·56	5·76	1:1

[a] The α and ω denote the corresponding peak of α- and ω-ring of U-BSPs.

[b] Integration ratios of the corresponding peak of α- and ω-ring.

[c] The values are of the opened MC form of **1c**.

TABLE 3

Electron Spray (ES) Mass Spectral Data of Unsymmetrical BSPs, **1a–d**

Compound	Mw	*Molecular ion*	
		(m/z)	*rel. int. (%)*
1a	795·96	796·24	25
1b	1002·76	1003·40	43
1c	840·96	841·21	32
1d	809·96	810·10	12

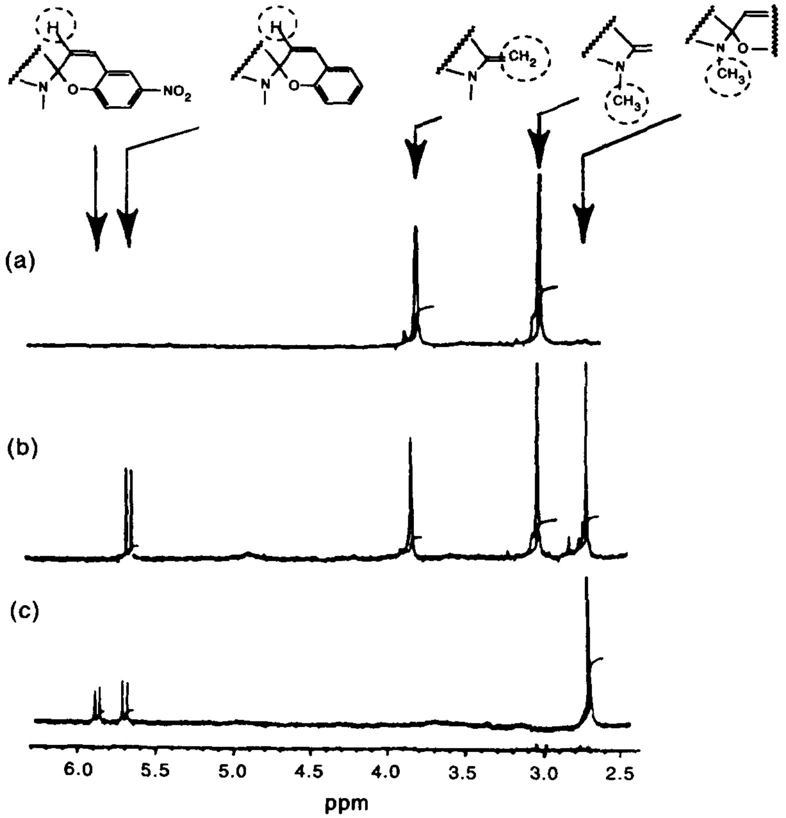


Fig. 1. ^{1}H NMR spectra in the range 2·5–6·0 ppm, showing the progress of reaction between BFB and SA^x indicating: (a) methylene protons of BFB; (b) appearance of H-3 in a 1:1 ratio with methylene and *N*-methyl of one FB unit of precursor, **4**; (c) appearance of two different H-3 protons characteristic of product U-BSP (see Scheme 4).

(Fig. 1). As SP units were formed from the reaction of FBs and SA derivatives, vinyl peaks (H-3') and N-Me peaks of SP units newly appeared at *ca* 5·56–5·85 ppm and 2·61–2·70 ppm, respectively. The N-Me and vinyl (H-3') protons of U-BSPs give an integral ratio of 1:1 between the α and ω rings in their ^{1}H NMR spectra (Table 3). ^{1}H NMR spectral data of the precursors **4a** and **b** and the unsymmetrical BSP's, **1a–d**, are summarized in Tables 4a and 4b, for the α- and ω-rings of those systems, respectively.

UV-Vis spectral data of the opened MC form of U-BSPs are collected in Table 5. The spectral data of the U-BSP's synthesized showed normal thermo- and photo-chromic behavior in various organic solvents examined, as found previously in mono-spiropyrans.[9] In contrast, the reverse photochromic behavior has been found for **1b** in DMSO. Thus **1b** in DMSO

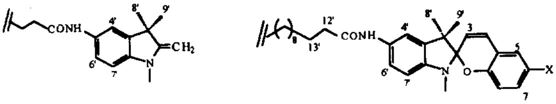
TABLE 4a

^{1}H NMR Spectral Data[a] of the α-Ring in Unsymmetrical Bis-spiropyrans, **1a–d**, and Their Precursors, **4a** and **b**, in $CDCl_3$

Proton[b]	**4a**	**4b**	**1a**	**1b**	**1d**
H-4'	7·34	7·32	7·34	7·35	7·38
H-6'	6·68	6·56	6·68	6·68	6·65
H-7'	6·44	6·42	6·44	6·45	6·52
8'-Me	1·16	1·13	1·16	1·16	1·12
9'-Me	1·28	1·30	1·28	1·27	1·20
N-Me	2·69	2·67	2·63	2·69	2·62
-NH-	7·16	7·15	7·18	7·16	7·12
H-12'	2·33	2·33	2·33	2·35	2·25
H-13'	2·04	1·67	1·74	1·75	1·63
$-(CH_2)_4-$	1·36	1·35	1·37	1·37	1·29
H-3	5·65	5·62	5·66	5·67	5·56
H-4	6·86	6·84	6·69	6·86	6·82
H-5,6,7&8	7·10	7·32	7·08	7·08	7·32
J^c (H3–H4)	10·2	10·39	10·24	10·18	10·32
J^c (H6'–H7')	8·33	8·83	8·25	8·12	8·12
J^c (H12'–H13')	7·49	7·25	7·03	7·05	7·02

[a] In ppm.

[b] The numberings of the α- and ω-ring systems are:



[c] Coupling constants in Hz.

TABLE 4b

^{1}H NMR Spectral Data[a] of the ω-ring in Unsymmetrical Bis-spiropyrans, **1a–d**, and Their Precursors, **4a** and **b**, in $CDCl_3$

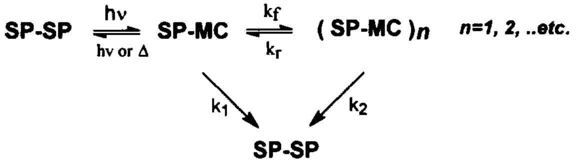
Proton[b]	**4a**	**4b**	**1a**	**1b**	**1d**
H-4'	7·34	7·32	7·37	7·42	7·94
H-6'	7·15	6·56	7·17	7·18	6·75
H-7'	6·44	6·42	6·45	6·48	6·35
8'-Me	1·33	1·30	1·17	1·18	1·12
9'-Me	1·33	1·30	1·28	1·28	1·29
N-Me	3·01	2·98	2·69	2·70	2·64
$=CH_2$	3·83	3·82	—	—	—
-NH-	7·18	7·15	7·21	7·19	7·12
H-3	—	—	5·71	5·85	5·77
H-4	—	—	6·85	6·90	7·28
H-5	—	—	7·31	8·00	7·30
H-7	—	—	7·80	8·03	7·92
H-8	—	—	—	6·74	7·32
J^c (H3–H4)	—	—	10·18	10·42	10·32
J^c (H5–H7)	—	—	2·02	2·59	2·02

[a–c] As in Table 4a.

TABLE 5
UV-Vis Data (λ_{max}) of Unsymmetrical BSPs, **1a–d**, in Various Solvents

Solvent	**1a**	**1b**	**1c**	**1d**
Toluene	657	607	555	606
Diethyl ether	650	570	540	580
1,4-Dioxane	643	597	560	594
Ethylacetate	633	589	556	589
Acetone	623	577	540	576
DMSO	619	573	531	573
Acetonitrile	600	569	529	569

remained as the opened MC form in the absence of light. When **1b** was irradiated with visible light, the colorless closed SP form was found. The opened form of U-BSPs showed negative solvatochromism as in the previous work.[9,12,19–21] However, these compounds exhibited unusual solvatokinetic behavior for the ring-closure reaction in nonpolar solvents, showing two consecutive reaction processes, i.e. a fast reaction followed by a slow process. The fast process (k_1) was solvent dependent and the rates were the same as those of mono-spiropyrans, but the slow process (k_2) turned out to be solvent-independent. This may implicate the formation of dimers and/or higher aggregates, $(SP–MC)_n$, (Scheme 5).



Scheme 5.

Further detailed studies on the aggregation behavior of these bis dyes are in progress and will be reported in due course.

3 EXPERIMENTAL

3.1 General

Melting points were determined using a Fischer–Jones melting point apparatus and are uncorrected. Proton NMR spectra were taken with a Bruker CXP-400 FT-NMR spectrophotometer, while 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 bis-Fischer base derivatives (BFBs)

Commercially available Fluka grade Fischer base (FB, 1,3,3-trimethyl-2-methyleneindoline) was nitrated with H_2SO_4–HNO_3 to form 5-nitro Fischer base (NFB), which was then reduced with stannous chloride dihydrate and concentrated hydrochloric acid to form 5-amino Fischer base (**2**, AFB), according to a previously described procedure.[17]

The bis-Fischer base (**3**, BFB), [bis{5-(2-methylene-1,3,3-trimethyleneindoline)}-α, ω-sebacamide was obtained from the reaction of sebacoyl chloride with excess molar ratio of AFB, adapting Gales' method.[18] A portion (10·6 mmol) of sebacoyl acid in 30 ml methylene chloride and triethylamine (20 ml) was added dropwise to a solution of **2** (4 g, 21·1 mmol) in 50 ml methylene chloride, which was stirred for 3 h at room temperature. The white solid which formed was recrystallized from methylene chloride–hexane to give product **3**, in 91% yield, m.p. 143–145°C.

3.3 Synthesis of the precursors

A portion of BFB (1 g, 1·84 mol) in 50 ml ethanol was added to a solution containing 2·27 mmol salicylaldehyde in 50 ml ethanol and stirred at 60°C for 30 min. After the reaction was complete, 50 ml of water was added, followed by basification with 0·5 g NaOH. The crude material was extracted twice with 50 ml methylene chloride, and the resultant solution was dried with anhydrous magnesium sulfate. Column chromatography was used for separation of the mixture of BSP and the precursor, **4** (FB–SP^x), which were formed simultaneously, using silica gel (100–200 mesh) with $CHCl_3$–EtOAc (9:1) as eluent. The key intermediate [**4a**(x = H), **4b** (x = Me)] in the unsymmetric bis-indolinospirobenzopyran synthesis was obtained after column separation. The yields and m.p.s are recorded in Table 1.

3.4 Synthesis of U-BSPs

Unsymmetrical BSPs, **1a–d** were obtained from the reaction of the key intermediate, **4**, and correspondingly substituted salicylaldehydes. The solution of **4** (0·07 mmol) in 5 ml ethanol was poured slowly into an ethanolic solution (3 ml) of the salicylaldehyde derivative (0·07 mmol) and was then stirred for 30 min at 60°C. After the reaction was complete, 10 ml of water was added, followed by basification with 0·01 g of NaOH. The crude material was extracted twice with 10 ml of methylene chloride and the resultant solution was dried with anhydrous magnesium sulfate. The crude material was recrystallized from methylene chloride–hexane.

ACKNOWLEDGMENTS

This work was supported in part by a research grant from the Korea Science and Engineering Foundation (941-0300-006-2) and from the Korean Ministry of Education under Basic Research Program (BSRI-94-3405) (S.R.K.), and in part by the Natural Sciences and Engineering Research Council of Canada (E.B.).

REFERENCES

1. Brown, G. H., ed., Photochromism, In *Techniques in Chemistry*. Wiley, New York, 1971, Vol. 3.
2. Durr, H. & Bouas-Laurent, H. eds, In *Photochromism, Molecules and Systems*. Elsevier, Amsterdam, 1992.
3. Levy, D. & Avnir, D., *J. Phys. Chem.*, **92** (1988) 4734.
4. Tamaki, T. & Ichimura, K., *J. Chem. Soc. Chem. Commun.*, (1989) 1477.
5. Durr, H., *Angew. Chem., Int. Ed. Engl.*, **28** (1989) 413.
6. Inouye, M., Kim, K. & Kitao, T., *J. Am. Chem. Soc.*, **114** (1992) 778.
7. Miyata, A., Unuma, Y. & Higashigaki, Y., *Bull. Chem. Soc. Jpn.*, **66** (1993) 993.
8. Williams, D. J., In *Nonlinear Optical Properties of Organic and Polymeric Materials*. ACS Symposium Series, 1983, Vol. 233, pp. 135–51.
9. Keum, S. R., Hur, M. S., Kazmaier, P. M. & Buncel, E., *Can. J. Chem.*, **69** (1991) 1940.
10. Keum, S. R., Lee, K. B., Kazmaier, P. M. & Buncel, E., *Magn. Res. Chem.*, **30** (1992) 1128.
11. Keum, S. R., Yun, J. H. & Lee, K. W., *Bull. Kor. Chem. Soc.*, **13**(4) (1992) 351.
12. Keum, S. R. & Lee, K. W., *Bull. Kor. Chem. Soc.*, **14**(1) (1993) 16.
13. Keum, S. R., Lee, K. B., Kazmaier, P. M. & Buncel, E., *Tetrahedron Lett.*, **35** (1994) 1015.
14. Wynne-Jones, E. & Gormally, J., In *Aggregation Processes in Solution*. Elsevier, Amsterdam, 1983, Chap. 10–12.
15. Krongauz, V. A. & Shartsman, F. P., *J. Phys. Chem.*, **88** (1984) 6448.
16. Keum, S. R., Lee, J. H., Seok, M. K. & Yoon, C. M., *Bull. Kor. Chem. Soc.*, **15**(4) (1994) 275.
17. Keum, S. R., Lee, J. H. & Seok, M. K., *Dyes and Pigments*, **25** (1994) 21.
18. Gale, D. J. & Whilshire, J. F., *J. Soc. Dyers Colour.*, **90** (1974) 97.
19. Buncel, E. & Rajagopal, S., *J. Org. Chem.*, **54** (1989) 798.
20. Buncel, E. & Rajagopal, S., *Acc. Chem. Res.*, **23** (1990) 226.
21. Rajagopal, S. & Buncel, E., *Dyes and Pigments*, **17** (1991) 303.