Available online at www.sciencedirect.com
SCIENCE DIRECT®
Dyes and Pigments 70 (2006) 143–148
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

Synthesis and investigations of the absorption spectra of hetarylazo disperse dyes derived from 2,4-quinolinediol

İzzet Şener [a], Fikret Karcı [a], Nermin Ertan [b], Emine Kılıç [c,*]

[a] Department of Chemistry, Pamukkale University, Kınıklı, 20017 Denizli, Turkey
[b] Department of Chemistry, Gazi University, Teknikokullar, 06500 Ankara, Turkey
[c] Department of Chemistry, Faculty of Science, Ankara University, Tandoğan, 06100 Ankara, Turkey

Received 1 April 2005; received in revised form 6 May 2005; accepted 12 May 2005

Abstract

Synthesis of some novel hetarylazoquinoline dyes was achieved by diazotisation of nine heterocyclic amines using nitrosyl sulphuric acid, coupling with 2,4-quinolinediol. These dyes were characterized by UV–vis, FT-IR and ^{1}H NMR spectroscopic techniques and elemental analysis. Visible absorption spectra of the dyes are discussed, both the effects of varying pH and solvent upon the absorption ability of azoquinolines. The colour of the dyes was discussed with respect to the nature of the heterocyclic ring and to the substituents therein. Temperature and concentration effects on the visible absorption maxima of the dyes are also reported.

Keywords: Azoquinoline dyes; Heterocyclic disperse dyes; Thiazolylazo dyes; Benzothiazolylazo dyes; Solvent effect; Substituent effect

1. Introduction

It has been known for many years that the azo compounds are the most widely used class of dyes due to their versatile application in various fields such as the dyeing of textile fibers, the colouring of different materials, coloured plastics, biological–medical studies and advanced applications in organic synthesis. Many patents and papers describe the synthesis and dyeing properties of azo compounds [1–6]. Especially, azo dyes based on heterocyclic amines have been developed, and the resultant dyes have been higher tinctorial strength and give brighter dyeing than those derived from aniline-based diazo components. For instance, amino-substituted thiazole, isothiazole, thiophene compounds afford very electronegative diazo components and consequently, provide a pronounced bathochromic effect compared to the corresponding benzenoid compounds [7–13].

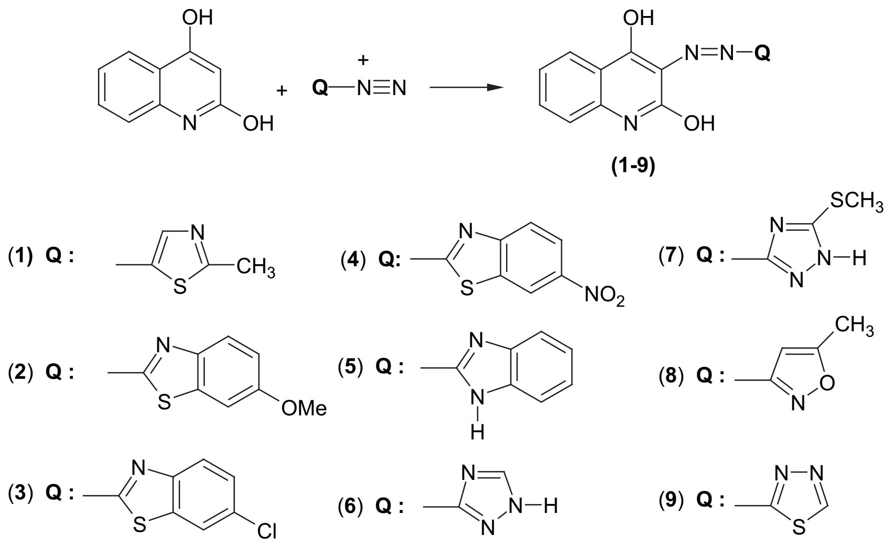
In contrast to the large number of investigations of the reactivity of carbocyclic diazonium ions, in general, and of the mechanism of their azo coupling reactions, limited number of comparable investigations has been made with heteroaromatic diazonium ions. There exist an extensive patent literature on azo dyes synthesized with heteroaromatic diazonium ions since Dickey and Towne [14] recognized in the early 1950s, that industrially interesting disperse dyes could be obtained on this basis.

In a continuation of our work, we report here the synthesis of some hetarylazoquinoline dyes **1–9** resulting from the use of 2,4-quinolinediol as coupling

---

* Corresponding author. Tel.: +90 312 212 6720/1033; fax: +90 312 2232 395.
E-mail address: kilic@science.ankara.edu.tr (E. Kılıç).

doi:10.1016/j.dyepig.2005.05.003



Scheme 1.

component and an evaluation of their visible absorption spectra with respect to the influences of solvent. The colour of the dyes is discussed with respect to the nature of the heterocyclic ring and substituents therein. The effects of temperature, concentration as well as acid and base on the visible absorption maxima of the dyes are also reported. The dye structures are depicted in Scheme 1.

2. Experimental

2.1. General

The chemicals used in the synthesis of all dyes were obtained from Aldrich Chemical Company or Sigma Chemical Company and were used as supplied. The solvents used were of spectroscopic grade.

IR spectra were recorded on a Mattson 1000 FT-IR spectrophotometer in KBr. ^{1}H NMR spectra were recorded on a Bruker 400 MHz spectrometer in DMSO$-d_6$ with TMS as internal reference. Absorption spectra were recorded on a Schimadzu 160A spectrophotometer in various solvents.

2.2. Preparations of hetarylazoquinoline dyes (**1–9**)

The heterocyclic amines were diazotised with nitrosylsulphuric acid. A typical procedure used for 2-methyl-5-aminothiazole is described below; all other dyes were prepared in a similar manner. The yields of the dyes are in the range of 61–87%. ^{1}H NMR and selected FT-IR and elemental analysis are listed in Tables 1 and 2, respectively.

Table 1
Spectral data for dyes **1–9**

Dye no.	FT-IR (cm^{-1}) in KBr					^{1}H NMR (δ, ppm)		
	ν_{O-H}	$\nu_{C-H\ (arom.)}$	$\nu_{C-H\ (alip.)}$	$\nu_{C=C}$	ν_{C-O}	Aromatic-H	Aliphatic-H	X-H
1	3447	3105, 3026	2903	1605	1122	6.65–7.76 (5H, m)	2.37 (3H, s)	10.57 (OH, b)
2	3404	3035, 3000	2912	1597	1114	7.15–7.74 (7H, m)	3.74 (3H, s)	10.93 (OH, b)
3	3439	3123, 3044	–	1588	1108	7.15–8.00 (7H, m)	–	10.37 (OH, b)
4	3456	3105, 3061	–	1588	1132	7.15–9.01 (7H, m)	–	10.56 (OH, b)
5	3439	3061	–	1590	1105	7.38–7.76 (8H, m)	–	13.98 (NH, b) 10.41 (OH, b)
6	3404	3105, 3044	–	1597	1097	7.15–8.40 (5H, m)	–	13.85 (NH, b) 10.97 (OH, b)
7	3370	3123, 3070	2939	1605	1105	7.17–7.74 (4H, m)	3.85 (3H, s)	13.91 (NH, b) 10.97 (OH, b)
8	3456	3105, 3061	2930	1614	1123	6.58–7.97 (5H, m)	2.45 (3H, s)	10.84 (OH, b)
9	3386	3105, 3018	–	1597	1105	7.18–8.96 (5H, m)	–	14.67 (NH, b) 10.53 (OH, b)

X: O, N s: singlet, m: multiplet, b: broad.

Table 2
Element analysis of dyes **1–9**

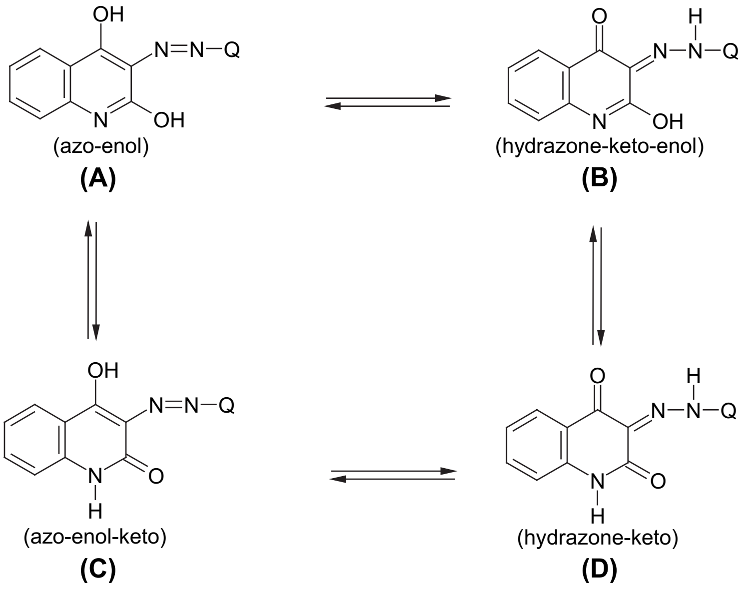
Dye no.	Molecular formula	Molecular mass	Yield %	Elemental analyses, calcd (found) %				Melting point °C
				C %	H %	N %	S %	
1	$C_{13}H_{10}O_2N_4S$	286	62	54.54 (55.10)	3.49 (3.61)	19.58 (20.10)	11.19 (11.45)	271–272
2	$C_{17}H_{12}N_4O_3S$	352	66	57.95 (58.45)	3.41 (3.48)	15.91 (16.35)	9.10 (9.22)	290–291
3	$C_{16}H_9N_4ClO_2S$	356.5	68	48.98 (49.30)	2.30 (2.37)	14.29 (14.51)	8.16 (8.33)	Dec. > 200
4	$C_{16}H_9N_5O_4S$	367	61	52.31 (52.93)	2.45 (2.57)	19.07 (19.28)	8.71 (9.23)	241–242
5	$C_{16}H_{11}N_5O_2$	305	87	62.95 (63.25)	3.60 (3.72)	22.95 (23.50)	–	295–296
6	$C_{11}H_8N_6O_2$	256	70	51.56 (52.05)	3.10 (3.27)	32.81 (33.20)	–	Dec. > 250
7	$C_{12}H_{10}N_6O_2S$	302	72	47.68 (48.02)	3.31 (3.55)	27.81 (28.24)	10.6 (11.02)	320–321
8	$C_{13}H_{10}N_4O_3$	270	84	57.80 (58.10)	3.70 (3.80)	20.74 (21.20)	–	300–301
9	$C_{11}H_7N_5S$	241	69	54.80 (55.15)	2.90 (3.07)	29.00 (29.54)	13.27 (13.53)	340–341

*2.2.1. Preparation of 3-(2′-methyl-5′-thiazolylazo)-2,4-quinolinediol (**1**)*

2-Methyl-5-aminothiazole (0.23 g, 2.0 mmol) was dissolved in glacial acetic acid (2.5 mL) and was rapidly cooled in an ice-salt bath at −5 °C. The liquor was then added in portions during 30 min to a cold solution of nitrosyl sulphuric acid prepared from sodium nitrite (0.14 g, 2.0 mmol) and concentrated sulphuric acid (7 mL) at 70 °C. The mixture was stirred for an additional 1 h at 0 °C. After diazotisation was complete the azo liquor was slowly added to a vigorously stirred solution of 2,4-quinolinediol (0.32 g, 2.0 mmol) in sodium carbonate (0.21 g, 2.0 mmol) and water (2 mL). The pH of the reaction mixture was maintained at 7–8 by simultaneous addition of solid sodium carbonate in portions. The mixture was then stirred for 1 h at 0–5 °C. The progress of the reaction was followed by TLC using a DMF–water mixture (5:2). The resulting solid was filtered, washed with cold water and dried. Recrystallization from DMF–H_2O mixture (1:1) gave dark red dye (**1**); (yield, 62%; m.p 272 °C).

3. Result and discussion

The hetarylazoquinoline dyes **1–9** were prepared by coupling 2,4-quinolinediol with diazotised heterocyclic amines in nitrosylsulphuric acid (Scheme 1). In solutions, the dyes may exist in four possible tautomeric forms, namely the azo-enol forms A and C, and the hydrazone-keto forms B and D as depicted in Scheme 2. The deprotonation of the two tautomers leads to a common anion.



Scheme 2.

The infrared spectra of all the compounds (in KBr) showed broad band within the range 3456–3370 cm^{-1} corresponding to ν_{OH} (Table 1). The FT-IR spectra also show a weak band or shoulder located at 3123–3000 cm^{-1} which was assigned to aromatic C–H. The other ν_{max} values at 2903 cm^{-1} (aliphatic C–H, dye **1**), 2912 cm^{-1} (aliphatic C–H, dye **2**), 2939 cm^{-1} (aliphatic C–H, dye **7**), 2930 cm^{-1} (aliphatic C–H, dye **8**), 1614–1588 cm^{-1} (C=C), 1123–1097 cm^{-1} (C–O) were recorded. It can be suggested that these compounds do not exist as the keto forms in B, C and D in the solid state, because there is no band in $\upsilon_{C=O}$ stretching region.

The ^{1}H NMR spectrum measured in DMSO–d_6 at 25 °C is given in Table 1. These findings show that the dyes are predominantly in the single tautomeric form in DMSO except for the dye **9**. The broad peaks at 14.67 and 10.53 ppm indicate that the dye **9** may exist as mixture of the tautomeric forms in DMSO.

3.1. Solvent effects

Absorption spectra of hetarylazoquinoline dyes **1–9** were recorded in various solvents at a concentration of ~10^{-6}–10^{-8} M and these are all run at different concentrations. The results are summarized in Table 3. The pH value of all solutions used was in the range between acidic and basic. The visible absorption spectra of the dyes did not show regular variation with the polarity of solvents.

The dyes showed single absorbance in DMSO, DMF, acetonitrile, methanol, acetic acid and chloroform, with the exception of the dyes **2**, **5** and **9**. It can be suggested that the dyes are predominantly in the single tautomeric form in used solvents. But, the dyes **2**, **5** and **9** are in the tautomeric forms in various solvents.

It was also observed that the absorption spectra of the dyes in various solvents did not significantly change with the exceptions of dyes **4** and **5** (Fig. 1). The λ_{max} of the dyes **4** and **5** shifted considerably in DMSO and DMF with respect to the λ_{max} in the other solvents; for dye **4**, λ_{max} is 342 nm in CHCl$_3$, 369 nm in DMF and 371 nm in DMSO; for dye **5** it is 418 nm in methanol, 462 nm in DMF and 469 nm in DMSO. Strong evidence that the dyes **4** and **5** exist in equilibrium is provided by the isosbestic points in the visible spectra of, for example, dye **4** in different solvents (Fig. 2). This equilibrium may exist between tautomeric forms and anionic form.

The λ_{max} of the dyes did not change significantly when a small amount of piperidine was added to each of

Table 3
Influence of solvent on λ_{max}(nm) of dyes **1–9**

Dye no.	DMSO	DMF	Acetonitrile	Methanol	Acetic acid	Chloroform
1	444	440	438	439	445	449
2	454	452	452	452, 368 s	466	470, 371 s
3	420	414	412	415	422	424
4	371	369	350	350	338	342
5	469	462	–	418, 464 s	410, 459 s	–
6	395	385	378	380	373	388
7	399	402	390	395	388	418
8	375	369	366	369	369	371
9	322, 335 s	322, 330 s	320	314, 320 s	313, 320 s	–

s: Shoulder.

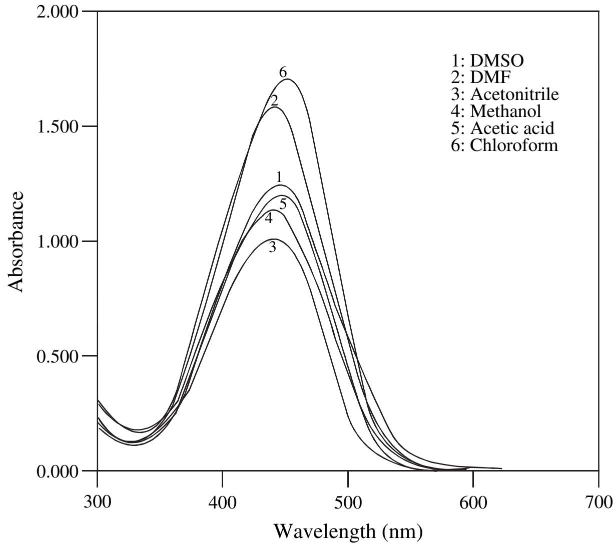


Fig. 1. Absorption spectra of dye **1** in various solvents.

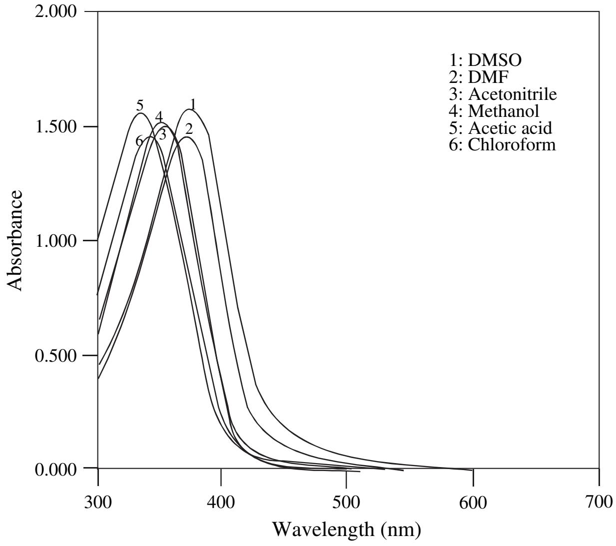


Fig. 2. Absorption spectra of dye **4** in various solvents.

Table 4
Absorption maxima of dyes **1**–**9** in acidic and basic solutions (λ, nm)

Dye no.	DMSO	DMSO + piperidine	DMF	DMF + piperidine	Methanol	Methanol + KOH	Methanol + HCl	Acetic acid	Chloroform	Chloroform + piperidine
1	442	437, 501 s	440	435, 497 s	439	425, 485 s	442	445	445	438, 500 s
2	454	452, 515 s	452	451, 512 s	453, 369 s	443, 510 s	461, 368 s	465	470, 373 s	454, 520 s
3	420	415, 475 s	414	410, 470 s	415	400, 460 s	415	422	422	420, 480 s
4	371	374	370	370	350	351	350	338	342	350
5	469	471	462	468	422, 465 s	420, 470 s	411	411, 459 s	–	432
6	393	400, 450 s	385	395, 440 s	381	389, 443 s	382	375	389	394, 435 s
7	400	406, 450 s	370	387, 475 s	397	395, 445 s	395	391	420	407, 452 s
8	375	387, 500 s	370	387, 475 s	369	374, 475 s	367	366	371	377, 400 s
9	323, 335 s	315	322, 330 s	319	314, 320 s	300	314, 320 s	311, 320 s	–	302

s: Shoulder.

the dye solutions in chloroform, DMSO and DMF (Table 4). But, it was also observed shoulder at the longest wavelength. This indicates that the dyes exist in a partly dissociated state in chloroform + piperidine, DMSO + piperidine and DMF + piperidine except for the dyes **4**, **5** and **9** (Fig. 3). The absorption spectrum of dye **9** partly changed when a small amount of piperidine was added to each of dye **9** solutions in DMSO and DMF. The shoulder at the longest wavelength was disappeared when piperidine was added. Similar effects were observed when a small amount of 0.1 M KOH was added to each of the dye solutions in methanol. The absorption spectra of the dyes in methanol did not change significantly when 0.1 M HCl was added.

The effects of dye concentration and temperature on absorption maxima were examined (Table 5). The λ_{max} of all dyes did not change with dye concentration and temperature. This also indicates that the hetarylazoquinoline in the tautomeric form in used solvents, in a partly dissociated state in chloroform + piperidine, DMSO + piperidine, DMF + piperidine and methanol + KOH except for the dyes **4**, **5** and **9**.

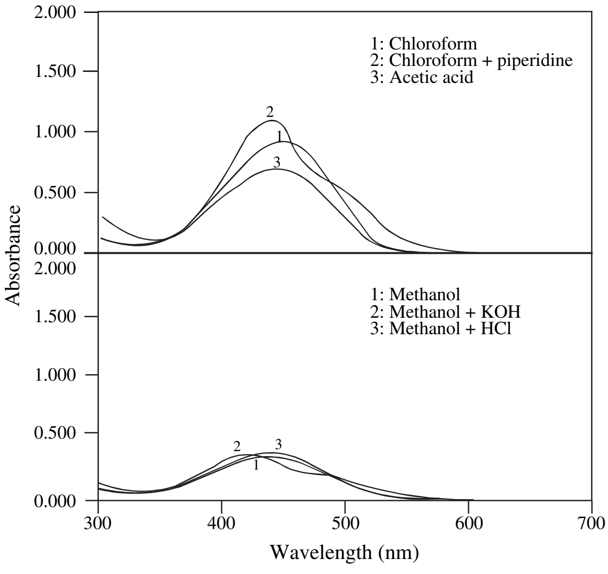


Fig. 3. Absorption spectra of dye **1** in acidic and basic solutions.

3.2. Substituent effects

As is apparent in Table 3, the introduction of electron-donating methoxy group into the benzothiazole ring results in bathochromic shift in all solvents with respect to electron-accepting nitro and chloro groups (for dye **2** $\Delta\lambda = 34$ nm relative to dye **3**; $\Delta\lambda = 83$ nm relative to dye **4** for spectra in DMSO). When compared to the strong electron-accepting nitro group to the slightly electron-accepting chloro group, it gave a large hypsochromic shift. The introduction of electron-accepting nitro and chloro groups into the benzothiazole ring stabilized the excited state one of the tautomeric forms, whereas dye **2** may exist between tautomeric forms in methanol and chloroform.

The introduction of electron-donating methylmercapto group into the 1,2,4-triazole ring results in bathochromic shift in all solvents (for dye **7** $\Delta\lambda = 17$ nm relative to dye **6** for spectra in DMF).

4. Conclusions

In summary, the synthesis, characterization and absorption ability of nine novel hetarylazoquinoline based dyes (**1**–**9**) were studied. The absorption data dyes (**1**–**9**) revealed that these compounds do exist in equilibrium of the tautomeric species (Scheme 2).

Acknowledgements

We gratefully acknowledge the financial support of Ankara University Research Fund. (Project Number 20030705084).

Table 5
Influence of temperature and sample concentration on absorption maxima of dyes **1–9** (λ_{max}, nm)

Dye no.	DMSO conc. 25 °C	DMSO dil. 25 °C	DMSO 70 °C	DMF conc. 25 °C	DMF dil. 25 °C	DMF 70 °C	MeCN conc. 25 °C	MeCN dil. 25 °C	MeOH conc. 25 °C	MeOH dil. 25 °C	AcOH conc. 25 °C	AcOH dil. 25 °C	$CHCl_3$ conc. 25 °C	$CHCl_3$ dil. 25 °C
1	444	442	442	440	440	441	438	438	439	439	445	445	449	445
2	454	454	453	452	452	452	452	450	452, 368 s	453, 369 s	466	465	470, 371 s	470, 373 s
3	420	419	420	414	413	415	412	412	415	416	422	422	424	422
4	371	375	373	369	370	370	350	352	350	350	338	338	342	342
5	469	469	468	462	462	463	–	–	418, 464 s	422, 465 s	410, 459 s	411, 459 s	–	–
6	395	393	393	385	385	386	378	378	380	381	373	375	388	389
7	399	400	400	402	402	402	390	390	395	397	388	391	418	420
8	375	375	375	369	370	371	366	366	369	369	369	366	371	371
9	322, 335 s	323, 335 s	323, 334 s	322, 330 s	322, 330 s	323, 331 s	320	320	314, 320 s	314, 320 s	313, 320 s	311, 320 s	–	–

s: Shoulder; ACOH: acetic acid; $CHCl_3$: chloroform; MeOH: methanol; MeCN: acetonitrile; conc.: concentrated; dil.: diluted.

References

[1] Catino SC, Farris RE. Azo dyes. In: Grayson M, editor. Concise encyclopedia of chemical technology. New York: John Wiley and Sons; 1985. p. 142–4.

[2] Tanaka K, Matsuo K, Nakanishi A, Jo M, Shiota H, Yamaguchi M, et al. Chem Pharm Bull 1984;32:391–8.

[3] Fadda AA, Etmen HA, Amer FA, Barghout M, Mohammed Kh S. J Chem Tech Biotechnol 1994;61:343–51.

[4] Karcı F, Şener İ, Deligöz H. Dyes Pigments 2003;59:53–61.

[5] Karcı F, Şener İ, Deligöz H. Dyes Pigments 2004;62:133–42.

[6] El-Sonbati AZ, Belal AAM, El-Wakeel SI, Hussien MA. Spectrochim Acta A 2004;60:965–72.

[7] Steal CV. Rev Prog Color 1970;1:23–30.

[8] Hallas GJ. J Soc Dyers Col 1979;95:285–94.

[9] Griffiths G. Rev Prog Color 1981;11:37–57.

[10] Towns AD. Dyes Pigments 1999;42:3–28.

[11] Karcı F, Ertan N. Dyes Pigments 2002;55:99–108.

[12] Şener İ, Karcı F, Kılıç E, Deligöz H. Dyes Pigments 2004;62: 143–50.

[13] Şener İ, Karcı F, Kılıç E, Deligöz H. Dyes Pigments 2004;62: 151–9.

[14] Dickey JB, Towne EB. US Patent 2,659,719; 1953.