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# Preparation of Cationic Azo Dyes Derived from 2-Amino-6-(2-chloroethoxy)benzothiazole and 2-Amino-4-(2-hydroxyethoxy)benzothiazole

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## ABSTRACT

*Azo dyes derived from 2-amino-6-(2-chloroethoxy)benzothiazole and 2-amino 4-(2-hydroxyethoxy)-benzothiazole were prepared by diazotization and coupling with different* N,N-*disubstituted anilines. The dyes were then quaternized with various alkylating agents, re. dimethyl sulphate, benzene-sulfonic acid methyl ester, acrylamides and epoxy compounds. Some parameters of the quaternization reaction are critically evaluated. The new benzothiazolic cationic dyes absorb in the region of 606–636 nm and have molar absorptivity of 40 000–80 000 Lmol$^{-1}$ cm$^{-1}$. © 1998 Elsevier Science Ltd. All rights reserved*

*Keywords*: azo dyes, benzothiazolic, cationic, preparation, quaternization, spectra.

## INTRODUCTION

Benzothiazolic azo dyes are well established as disperse and cationic dyes. The disperse dyes are prepared by diazotization of 2-aminobenzothiazoles followed by coupling with *N,N*-dialkylanilines [1–3] and the cationic dyes are synthesized by quaternization of such disperse dyes [4, 5]. The most commonly used blue cationic dye in the coloration of acrylic fibres is the benzothiazole based azo dye C.I. Basic Blue 41 [6]. Interest to this important class of colorants is still strong. Improvement of the process of diazotization of 2-aminobenzothiazoles in an environmentally friendly reaction media or diazotization of 2-amino-6-methoxy-benzothiazole at room temperature [7]

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has been reported. Some 'high-tech' applications of benzothiazolic dyes are in radiation sensitive compositions [8] or as amphiphilic azo dyes for the preparation of Langmuir–Blodgett films [9]. The typical benzothiazolic cationic dye C.I. Basic Blue 41 has been also used as a panoptic stain for all types of blood cells, and for demonstration of basophils based on intense metachromatic staining of granules [10].

In the present paper we describe the preparation and some spectral properties of newly synthesized benzothiazolic cationic azo dyes derived from 2-amino-6-(2-chloroethoxy)benzothiazole and 2-amino-4-(2-hydroxyethoxy) benzothiazole.

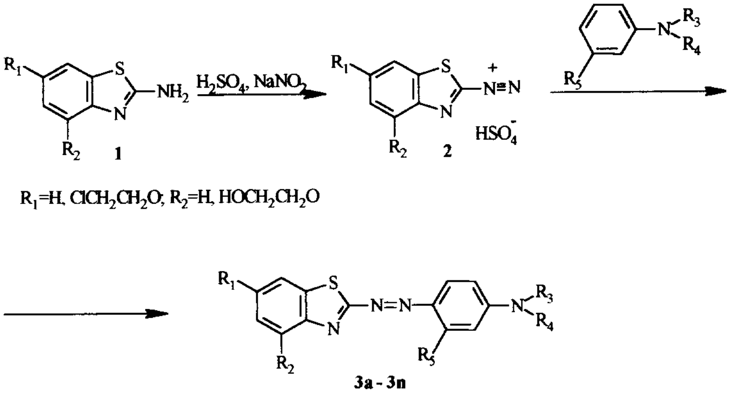
## RESULTS AND DISCUSSION

We have previously reported the preparation of benzothiazolic cationic dyes derived from 2-amino-6-(2-hydroxyethoxy)benzothiazole [4] and the preparation of the starting intermediates 2-amino-6-(2-hydroxyethoxy) benzothiazole, 2-amino-6-(2chloroethoxy)benzothiazole and 2-amino-4-(2-hydroxyethoxy)benzothiazole [11]. It is well established that modification of the structure of these dyes by appropriate substituents has little impact on the spectral properties, but considerable influence on the hydrophilic/hydrophobic properties and consequently on some important parameters of the dyeing process, such as adsorption rate, diffusion rate, K value (compatibility), hydrolytic stability, hue of the colour, etc. It was therefore of interest to synthesize some new benzothiazolic cationic azo dyes (reported herein) and to study the influence of the combination of different substituents on the dyeing properties (these results will be reported later).

The synthesis of the benzothiazolic disperse dyes was effected by diazotization of 2-amino-6-(2-chloroethoxy)benzothiazole and 2-amino-4-(2-hydroxyethoxy)benzothiazole followed by coupling with different *N,N*-disubstituted anilines (Scheme 1, Table 1). Diazotization was carried out in 50% sulphuric acid in the temperature region of 0–5°C; acetic acid can also be used. The coupling process was carried out in strongly acid media ($pH < 1$), because the diazonium salts of 2-aminobenzothiazoles are very active. For some coupling components such as diphenylamine and *N*-methydiphenylamine, acetic acid as solvent was used in the coupling carried at 5–10°C for *ca* 1 h.

Some physical characteristics of the dyes **3a**–**3n** are given in Table 2.

The synthesized disperse dyes were quaternized either in organic solvents (chlorobenzene, dichloroethane, DMF, acetic acid) or in water. Dimethylsulphate, methyl esters of arylsulfonic acids, acrylamides and epoxy compounds were utilized as alkylating agents (Scheme 2).



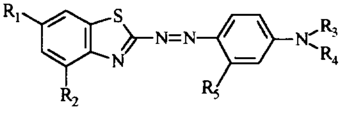
$R_1$=H, $ClCH_2CH_2O$; $R_2$=H, $HOCH_2CH_2O$

$R_3$, $R_4$ = $CH_3$, $C_2H_5$, $CH_2CH_2Cl$, $CH_2CH_2OH$, $C_2H_4OC_2H_4CN$, $CH_2CH_2CN$, $C_6H_5$, $CH_2C_6H_5$, $CH_2CH_2C_6H_5$; $R_5$ = H, Cl.

**Scheme 1.**

The quaternization reaction in chlorobenzene was performed with dimethylsulphate at the most favourable temperature of about 70°C for 2–3 h (Tables 3, 4). Increase of the reaction temperature increases the rate of quaternization, but gives rise to some side reactions which lower the purity of the cationic product. Lower temperatures decrease the rate of the quaternization

TABLE 1
Substituents in Dyes **3a–3n**



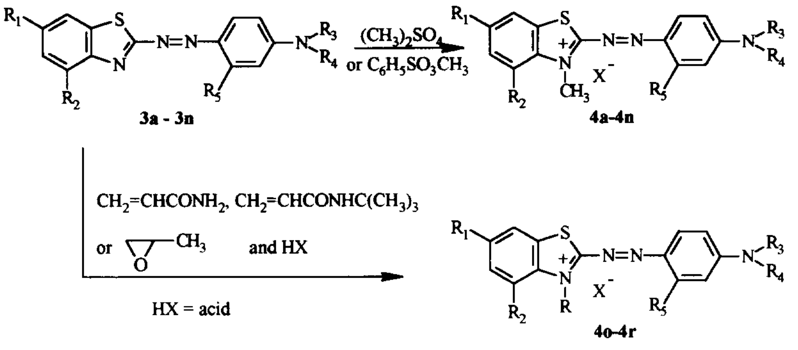
| *Dye* | $R_1$ | $R_2$ | $R_3$ | $R_4$ | $R_5$ |
|---|---|---|---|---|---|
| **3a** | $ClC_2H_4O$ | H | $CH_3$ | $CH_3$ | H |
| **3b** | $ClC_2H_4O$ | H | $CH_3$ | $C_2H_4CN$ | H |
| **3c** | $ClC_2H_4O$ | H | $CH_3$ | $CH_2C_6H_5$ | H |
| **3d** | $ClC_2H_4O$ | H | $CH_3$ | $C_2H_4C_6H_5$ | H |
| **3e** | $ClC_2H_4O$ | H | $C_2H_5$ | $C_2H_5$ | H |
| **3f** | $ClC_2H_4O$ | H | $C_2H_5$ | $C_2H_4OH$ | H |
| **3g** | $ClC_2H_4O$ | H | $C_2H_5$ | $C_2H_4Cl$ | H |
| **3h** | $ClC_2H_4O$ | H | $C_2H_5$ | $C_2H_4OC_2H_4CN$ | H |
| **3i** | $ClC_2H_4O$ | H | $C_2H_5$ | $C_2H_5$ | Cl |
| **3j** | $ClC_2H_4O$ | H | H | $C_6H_5$ | H |
| **3k** | $ClC_2H_4O$ | H | $CH_3$ | $C_6H_5$ | H |
| **3l** | H | $HOC_2H_4O$ | $CH_3$ | $CH_3$ | H |
| **3m** | H | $HOC_2H_4O$ | $CH_3$ | $C_2H_4CN$ | H |
| **3n** | H | $HOC_2H_4O$ | $C_2H_5$ | $C_2H_4OC_2H_4CN$ | H |

TABLE 2
Yield, Melting Points, $\lambda_{max}$, Molar Absorptivity ($\varepsilon$), $R_f$ Values and Elemental Analysis of Dyes **3a–3n**

| *Dye* | *Yield (%)* | *m.p. (°C)* | $\lambda_{max}$ *nm* $C_2H_5OH$ | $\varepsilon$ *(Lmol$^{-1}$cm$^{-1}$)* | $R_f$ *value* | *Molecular formulae* | *Analysis found/calc.* | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | *C%* | *H%* | *N%* |
| **3a** | 83 | 195–197 | 519 | 50400 | 0.80 | $C_{17}H_{17}ClN_4OS$ | 56.8 | 5.1 | 15.9 |
| | | | | | | (360.5) | 56.6 | 4.7 | 15.5 |
| **3b** | 75 | 219–221 | 507 | 49400 | 0.67 | $C_{19}H_{18}ClN_5OS$ | 57.3 | 4.4 | 17.4 |
| | | | | | | (399.5) | 57.1 | 4.5 | 17.6 |
| **3c** | 87 | 150–151 | 518 | 51300 | 0.89 | $C_{23}H_{21}ClN_4OS$ | 63.2 | 5.0 | 13.0 |
| | | | | | | (436.5) | 63.2 | 4.8 | 12.9 |
| **3d** | 86 | 179–180 | 523 | 53500 | 0.82 | $C_{24}H_{23}ClN_4OS$ | 63.6 | 5.3 | 12.4 |
| | | | | | | (450.5) | 63.9 | 5.1 | 12.4 |
| **3e** | 79 | 149–150 | 525 | 53300 | 0.88 | $C_{19}H_{21}ClN_4OS$ | 58.7 | 5.7 | 14.4 |
| | | | | | | (388.5) | 58.7 | 5.4 | 14.4 |
| **3f** | 82 | 161–162 | 525 | 59600 | 0.57 | $C_{19}H_{21}ClN_4O_2S$ | 56.5 | 5.4 | 13.8 |
| | | | | | | (404.5) | 56.4 | 5.2 | 13.8 |
| **3g** | 87 | 134–135 | 513 | 49000 | 0.91 | $C_{19}H_{20}Cl_2N_4OS$ | 54.3 | 4.8 | 13.2 |
| | | | | | | (423) | 53.9 | 4.7 | 13.2 |
| **3h** | 83 | 101–102 | 519 | 50800 | 0.62 | $C_{22}H_{24}ClN_5O_2S$ | 58.0 | 4.9 | 14.9 |
| | | | | | | (457.5) | 57.7 | 5.2 | 15.3 |
| **3i** | 78 | 159–160 | 527 | 46800 | 0.78 | $C_{19}H_{20}Cl_2N_4OS$ | 53.9 | 5.1 | 13.0 |
| | | | | | | (423) | 53.9 | 4.7 | 13.2 |
| **3j** | 80 | 191–193 | 521 | 49400 | 0.71 | $C_{21}H_{17}ClN_4OS$ | 61.5 | 4.2 | 13.8 |
| | | | | | | (408.5) | 61.7 | 4.2 | 13.7 |
| **3k** | 79 | 128–130 | 517 | 50000 | 0.85 | $C_{22}H_{19}ClN_4OS$ | 62.7 | 4.6 | 13.1 |
| | | | | | | (422.5) | 62.5 | 4.5 | 13.2 |
| **3l** | 81 | 251–252 | 519 | 47800 | 0.73 | $C_{17}H_{18}N_4O_2S$ | 60.0 | 5.6 | 16.5 |
| | | | | | | (342) | 59.7 | 5.3 | 16.4 |
| **3m** | 81 | 226–227 | 506 | 46000 | 0.56 | $C_{19}H_{19}N_5O_2S$ | 59.8 | 5.6 | 18.0 |
| | | | | | | (381) | 59.8 | 4.9 | 18.4 |
| **3n** | 88 | 79–80 | 521 | 44400 | 0.73 | $C_{22}H_{25}N_5O_3S$ | 60.4 | 5.8 | 15.9 |
| | | | | | | (439) | 60.1 | 5.7 | 15.9 |

The dyes were recrystallized from $C_2H_5OH$ (**3e, 3g, 3n**); DMF:$C_2H_5OH$:$H_2O$ 1:4:1 (**3a, 3b, 3d, 3i**); $C_2H_5OH$:$CHCl_3$ 1:1 (**3c**); $C_2H_5OH$:$H_2O$ 3:1 (**3f, 3h, 3k**); $C_2H_5OH$:$C_6H_5$ 1:1 (**3j**); $C_2H_5OH$:DMSO:$H_2O$ 4:1:1 (**3l**); $C_2H_5OH$:DMF 3:1 (**3m**).

process. The same observations were valid when the methyl ester of benzenesulfonic acid was used as alkylating agent. The product prepared in chlorobenzene was precipitated and was easily filtered. When the reaction was carried out in dichloroethane, DMF or acetic acid, due to the higher polarity of these solvents, the cationic dye did not precipitate, and some solvent needed to be distilled off. A basic agent (MgO) was needed when the reaction was performed in acetic acid. The most suitable temperatures for the quaternization in dichloroethane, DMF and acetic acid are, respectively, 70, 80, and 90°C. A common drawback of the quaternization in organic solvents is that the process cannot be completed and there is always 5–6% unquaternized



R = $CH_2CH_2CONH_2$, $CH_2CH_2CONHC(CH_3)_3$
$CH_2CH(OH)CH_3$

Scheme 2.

dye. We have recently reported a novel method of quaternization which overcomes this drawback [4].

Another method by which the process can be completed is quaternization with dimethyl sulphate in aqueous media [12], in the presence of a basic reagent binding the sulphuric acid. The process is faster than quaternization in organic solvents and can be carried out at 20–60°C; its duration is 20 h at 20°C, and up to 2 h at 60°C but at temperature higher than 65°C, dimethylsulphate rapidly decomposes.

Quaternization in organic solvents with acrylamide, *N*-*tert*-butylacrylamide and propylene oxide has drawbacks in that its duration is too long (5–10 h) and that quaternization is not completed (about 5% unreacted product). Its main advantage is that the dye molecule is directly modified, thus revealing some new dyeing properties (Tables 3, 4).

IR spectra of new dyes were taken in nujol. Benzene out-of-plane bendings of the dye molecule appear at about 820 and 885 cm$^{-1}$ for 1,2,4-, at 840 cm-$^{-1}$ for 1,4- at 740 and 760 cm$^{-1}$ for 1,2,3-substituted and at 690 and 750 cm$^{-1}$ for the monosubsituted benzene nucleus. Antisymmetric stretching vibrations for the ether bond of type R–O–Ar (R is alkyl) are in the range of 1275–1260 cm$^{-1}$, but symmetric stretching vibration are in the region of 1075–1050 cm$^{-1}$. For the ether bond R–O–R the asymmetric stretching vibrations are at about 1150 cm$^{-1}$. A strong band is observed at about 1600 cm$^{-1}$, which can be assigned to in-plane skeletal vibrations of the benzene ring. In the dyes with a hydroxyl group (from the 2-hydroxyethoxy substituent), the hydroxyl group gives rise to a broad band covering the region of 3200–3500 cm$^{-1}$, which indicates the presence of intermolecular hydrogen bonds. The dyes with a 2-carbamoylethyl substituent are characterized by a strong absorbance at 1720 cm$^{-1}$ due to C=O stretching vibrations (amide I). The bands at about 3400 cm$^{-1}$ and about 3160 cm$^{-1}$ probably originate from antisymmetric and symmetric stretching N–H vibrations of the hydrogen bonded amide groups. A different case is observed in the dyes with *N*-*tert*-butylcarbamoyl substituent. The carbonyl group absorbs at about 1655 cm$^{-1}$ (amide I) and the bands in the range of 3400–3100 cm$^{-1}$ are due to associated amide groups. The dyes with cyano group exhibit a low intensity band at about 2240 cm$^{-1}$.

## EXPERIMENTAL

Melting points were determined on a Kofler apparatus and are uncorrected. $^1$H NMR spectra were recorded on a Tesla BS-487 80 MHz instrument in DMSO-$d_6$ with TMS as internal standard. Visible spectra were recorded on a Carl Zeiss Jena Specord UV-VIS spectrophotometer. IR spectra were recorded in nujol on a Specord 71 IR spectrophotometer, TLC and $R_f$ values were taken on aluminium sheets coated with silicagel (Silufol) and developed with benzene–ethanol (3:1) for disperse dyes (**3a–3n**) and chloroform-pyridine-propanol-2-acetic acid-water (6:3:8:1:2) for cationic dyes (**4a–4r**).

### Preparation of dyes 3a–3n. General procedure

*Diazotization of 2-amino-6-(2-chloroethoxy)benzothiazole and 2-amino-4-(2-hydroxyethoxy)benzothiazole*

When 0.02 moles of the appropriate heterocyclic amine were dissolved in 25 ml 50% sulphuric acid with stirring, the temperature was kept below 25°C. After dissolution of the heterocyclic amine, the liquor was cooled externally in an ice-salt bath to 0°C. The reaction mixture (in the case of 2-amino-6-(2chloroethoxy)benzothiazole it is a suspension) was stirred continuously and 1.4 g. (0.02 moles) sodium nitrite dissolved in 5 ml water was dropped slowly over 30 min, keeping the temperature at 0–5°C. The diazo solution was stirred for a further hour at 0–5°C and then used for coupling.

*Coupling with* N,N-*dialkylanilines*

When 0.02 moles of the appropriate dialkylaniline were dissolved in 200 ml 1% hydrochloric acid, crushed ice was added to the solution to chill below 5°C. The diazo liquor of the appropriate heterocyclic amine was added slowly to the stirred solution of the *N*,*N*-dialkylaniline at such a rate that the temperature was maintained at 5–10°C. Since the viscosity of the mixture increased rapidly, the total volume was made up to 400–500 ml by adding water. The reaction mixture was stirred for 1 h at 10°C and the pH of the suspension then adjusted to about 1–2 with ammonia. The precipitated acid salt of the dye was filtered, resuspended in 200 ml water and made alkaline with ammonia. The precipitate was filtered, washed several times with water and air dried.

### *Coupling with diphenylamine and* N-*methyldiphenylamine*

When 0.02 moles of the appropriate diphenylamine was dissolved in 60 ml acetic acid, the solution was cooled externally in an ice-salt bath to 5°C. To the cooled solution of the diphenylamine, the diazo liquor of 2-amino-6-(2-chloroethoxy)benzothiazole was slowly added and the temperature kept between 5–10°C. The dye liquor was stirred for 1 h at 15°C and then poured into 1000 ml ice water. The suspension was kept overnight and then filtered and the product washed several times with water and air dried.

## Preparation of cationic benzothiazolic azo dyes. General procedures

### *Quaternization in chlorobenzene with dimethylsulphate or methyl ester of benzenesulfonic acid*

To a mixture of 0.01 mole disperse azo dye and 50 ml chlorobenzene, a solution of 2.8 g (0.022 mole) dimethylsulphate or 4.6 g (0.02 mole) methyl ester of benzenesulfonic acid in 5 ml chlorobenzene was dropped in at 70°C with stirring over a period of 30 min. The reaction mixture was stirred and heated at 75–80°C for 2–3 h until completion of the reaction (TLC control). After cooling the precipitated cationic dye was filtered, washed with ether and dried.

### *Quaternization in dichloroethane or DMF with dimethylsulphate*

The procedure used was the same as in the previous process except that the solvent used was dichloroethane or DMF. After completion of the reaction (TLC control) most of the solvent was distilled off under vacuum and the residue liquor was diluted with 100 ml diethylether and the precipitate filtered and dried.

### *Quaternization in acetic acid with dimethylsulphate*

To a suspension of 50 ml acetic acid, 2 g (0.05 mole) magnesium oxide and 0.01 mole of the pertinent dye, 3.8 g (0.03 mole) dimethylsulphate was dropped in at 70°C with stirring over a period of 30 min. The reaction mixture was heated at 90°C until completion of the reaction (TLC control). Most of the solvent was distilled off under vacuum and then 15 ml ethanol was added, followed by 100 ml diethyl ether. The precipitate was then filtered and dried.

*Quaternization in water media with dimethylsulphate*

To a well homogenized dispersion of 0.01 mole of the appropriate dye, 1.7 g (0.02 mole) sodium bicarbonate and 9 ml water, 4.4 g (0.036 mole) dimethylsulphate were slowly dropped in with stirring. The reaction mixture was heated and stirred at 60°C for 2 h until completion of the reaction (TLC control). Then pH was adjusted to about 4 with dilute hydrochloric acid. The dye could be isolated in two ways, viz: (a) if the dye precipitated after cooling, it was filtered and dried; (b) if the dye was oily, it was dissolved in boiling water, the solution filtered hot and saturated hot aq. solution of 4.1 g (0.04 mole) sodium perchlorate added to the dye solution. After cooling reaction mixture to room temperature, the precipitated dye was filtered and dried.

*Quaternization in chlorobenzene with acrylamide and* N-tert-*butylacrylamide*

A mixture of 50 ml chlorobenzene, 0.01 mole of the appropriate dye, 0.025 mole organic or inorganic acid and 0.05 mole of the corresponding acrylamide was heated at 75–80°C with stirring for 5 hours until completion of the reaction (TLC control). After cooling the reaction mixture, the precipitate was filtered, washed with ether and dried.

*Quaternization in chlorobenzene with epoxy compounds*

To a mixture of 50 ml chlorobenzene, 0.01 mole of the appropriate dye and 0.025 mole organic or inorganic acid, 0.05 mole propylene oxide was slowly dropped in. The reaction mixture was heated at 70°C with stirring for 10 h until completion of the reaction (TLC control). After cooling the reaction mixture 100 ml THF was added and on the next day the dye was filtered and dried.

## IR spectra of the dyes 3a–3n and 4a–4r and some $^1$H NMR spectra data

*IR spectra*

$\nu$ cm$^{-1}$, nujol: **3a**—810, 840, 875, 1075, 1275, 1600; **3b**—820, 840, 875, 1075, 1275, 1600, 2230; **3c**—690, 740, 820, 840, 875, 1075, 1275, 1595; **3d**—690, 740, 815, 840, 890, 1040, 1275, 1600; **3e**—820, 840, 875, 1050, 1275, 1600; **3f**—820, 840, 875, 1075, 1250, 1600, 3350; **3g**—820, 840, 890, 1050, 1275, 1600; **3h**—820, 840, 885, 1050, 1140, 1280, 1600, 2230; **3i**—825, 840, 870, 1040, 1270, 1590; **3j**—690, 750, 810, 840, 880, 1075, 1260, 1600; **3k**—690, 750, 820, 840, 875, 1075, 1260, 1510, 1600; **3l**—740, 760, 820, 840, 875, 1075, 1260, 1520, 1600; **3m**—730, 780, 830, 1075, 1260, 1600, 3350; **3n**—740, 760, 820, 840, 885, 1075, 1150, 1270, 1600, 2240, 3350.

**4a**—820, 840, 1075, 1275, 1600; **4b**—690, 740, 810, 840, 870, 1075, 1270, 1600, 2240; **4c**—690, 740, 820, 840, 870, 1075, 1275, 1600; **4d**—690, 740, 810,

TABLE 3
Substituents in Dyes **4a–4r**

| *Dye* | *R* | $R_1$ | $R_2$ | $R_3$ | $R_4$ | $R_5$ | $X^-$ |
|---|---|---|---|---|---|---|---|
| **4a** | — | $ClC_2H_4O$ | H | $CH_3$ | $CH_3$ | H | $CH_3SO_4$ |
| **4b** | — | $ClC_2H_4O$ | H | $CH_3$ | $C_2H_4CN$ | H | $C_6H_5SO_3$ |
| **4c** | — | $ClC_2H_4O$ | H | $CH_3$ | $CH_2C_6H_5$ | H | $CH_3SO_4$ |
| **4d** | — | $ClC_2H_4O$ | H | $CH_3$ | $C_2H_4C_6H_5$ | H | $CH_3SO_4$ |
| **4e** | — | $ClC_2H_4O$ | H | $C_2H_5$ | $C_2H_5$ | H | $CH_3SO_4$ |
| **4f** | — | $ClC_2H_4O$ | H | $C_2H_5$ | $C_2H_4OH$ | H | $CH_3SO_4$ |
| **4g** | — | $ClC_2H_4O$ | H | $C_2H_5$ | $C_2H_4Cl$ | H | $CH_3SO_4$ |
| **4h** | — | $ClC_2H_4O$ | H | $C_2H_5$ | $C_2H_4OC_2H4CN$ | H | $CH_3SO_4$ |
| **4i** | — | $ClC_2H_4O$ | H | $C_2H_5$ | $C_2H_5$ | Cl | $C_6H_5SO_3$ |
| **4j** | — | $ClC_2H_4O$ | H | H | $C_6H_5$ | H | $CH_3SO_4$ |
| **4k** | — | $ClC_2H_4O$ | H | $CH_3$ | $C_6H_5$ | H | $CH_3SO_4$ |
| **4l** | — | H | $HOC_2H_4O$ | $CH_3$ | $CH_3$ | H | $CH_3SO_4$ |
| **4m** | — | H | $HOC_2H_4O$ | $CH_3$ | $C_2H_4CN$ | H | $CH_3SO_4$ |
| **4n** | — | H | $HOC_2H_4O$ | $C_2H_5$ | $C_2H_4OC_2H_4CN$ | H | $ClO_4$ |
| **4o** | $C_2H_4CONHC(CH_3)_3$ | $ClC_2H_4O$ | H | $CH_3$ | $CH_3$ | H | $C_6H_5SO_3$ |
| **4p** | $CH_2CH(OH)CH_3$ | $ClC_2H_4O$ | H | $C_2H_5$ | $C_2H_5$ | H | Cl |
| **4q** | $C_2H_4CONH_2$ | $ClC_2H_4O$ | H | $C_2H_5$ | $C_2H_5$ | H | $ClO_4$ |
| **4r** | $CH_2CH(OH)CH_3$ | $ClC_2H_4O$ | H | $C_2H_5$ | $C_2H_4Cl$ | H | Cl |

840, 870, 1075, 1270, 1600; **4e**—810, 840, 870, 1975, 1270, 1600; **4f**—810, 830, 870, 1075, 1275, 1600; **4g**— 820, 840, 870, 1075, 1275, 1600; **4h**—820, 840, 870, 1070, 1150, 1270, 1600, 2240; **4i**—690, 730, 820, 870, 1070, 1270, 1600; **4j**—690, 740, 810, 840, 870, 1075, 1275, 1590; **4k**—690, 790, 810, 840, 870, 1075, 1275, 1590,; **4l**—740, 770, 840, 1075, 1275, 1610; **4m**—740, 770, 840, 1075, 1275, 1600, 3400; **4n**—740, 770, 840, 1075, 1160, 1270, 1600, 2240; **4o**—680, 730, 820, 840, 1075, 1270, 1610, 1660, broad 3100–3400; **4p**—810, 840, 870, 1075, 1270, 1590; **4q**—820, 840, 870, 1075, 1275, 1610, 1720, 3150, 3400; **4r**—810, 840, 890, 1075, 1270, 1610.

### *$^1H$ NMR spectra*

$\delta$ ppm (DMSO-$d_6$) **3e**—$\mathrm{CH_2C}H_3$ 1.35, methylene protons 3.47–4.0, $\mathrm{C}H_2\mathrm{Cl}$ 4.25, $\mathrm{C}H_2\mathrm{OC_6H_3}$ 4.59, $\mathrm{C_6}H_3$ + $\mathrm{C_6}H_4$ 6.95–8.22; **3h**—$\mathrm{CH_2C}H_3$ 1.40, $\mathrm{C}H_2\mathrm{CN}$ 3.02, methylene protons 3.65–4.05, $\mathrm{C}H_2\mathrm{Cl}$ 4.25, $\mathrm{C}H_2\mathrm{OC_6H_3}$ 4.62, $\mathrm{C_6}H_3$ + $\mathrm{C_6}H_4$ 7.00–8.27; **3j**—$\mathrm{C}H_2\mathrm{Cl}$ 4.22, $\mathrm{C}H_2\mathrm{OC_6H_3}$ 4.62, $\mathrm{C_6}H_3$, $\mathrm{C_6}H_4$ and $\mathrm{C_6}H_5$ 7.18–8.35, $\mathrm{N}H$ 9.62; **3n**—$\mathrm{CH_2C}H_3$ 1.33, $\mathrm{C}H_2\mathrm{CN}$ 2.95, methylene protons 3.72–3.98, $\mathrm{C}H_2\mathrm{OH}$ 4.10, $\mathrm{C}H_2\mathrm{OC_6H_3}$ 4.45, $\mathrm{CH_2O}H$ 5.23, $\mathrm{C_6}H_3$ + $\mathrm{C_6}H_4$ 6.92–8.25.

**4e**—$\mathrm{CH_2CH_3}$ 1.47, methylene protons + N–$\mathrm{C}H_3$ + $\mathrm{C}H_3\mathrm{SO_4}$ 3.80–4.75, $\mathrm{C_6}H_3$ + $\mathrm{C_6}H_4$ 7.00–8.37; **4g**—$\mathrm{CH_2C}H_3$ 1.51, methylene protons + N–$\mathrm{C}H_3$ + $\mathrm{C}H_3\mathrm{SO_4}$ 4.12–4.80, $\mathrm{C_6}H_3$ + $\mathrm{C_6}H_4$ 7.18–8.50; **4n**—$\mathrm{CH_2C}H_3$ 1.56, methylene

**TABLE 4**

Yield, Melting Points, $\lambda_{max}$, Molar Absorptivity $\varepsilon$, $R_f$ Value and Elemental Analysis of Dyes **4a–4r**

| *Dye* | *Yield(%) (method)* | *m.p. (°C)* | $\lambda_{max}$ *nm 70% EtOH* | ε *(Lmol$^{-1}$cm$^{-1}$)* | $R_f$ *value* | *Molecular formulae* | *Analysis found/calc. (N %)* |
|---|---|---|---|---|---|---|---|
| **4a** | 87<br>(3.2.1) | 166–167 | 625 | 65 500 | 0.36 | $C_{19}H_{23}ClN_4O_5S_2$<br>(486.5) | 11.2<br>11.5 |
| **4b** | 82<br>(3.2.1) | 192–193 | 628 | 70 900 | 0.38 | $C_{26}H_{26}ClNO_4S_2$<br>(571.5) | 11.9<br>12.2 |
| **4c** | 87<br>(3.2.3 | 158–160 | 630 | 71 800 | 0.81 | $C_{25}H_{27}ClN_4O_5S_2$<br>(562.5) | 10.5<br>9.9 |
| **4d** | 83<br>(3.2.2) | 164–165 | 621 | 67 900 | 0.79 | $C_{26}H_{29}ClN_4O_5S_2$<br>(576.5) | 9.3<br>9.7 |
| **4e** | 90<br>(3.2.1) | 165–166 | 625 | 70 800 | 0.50 | $C_{21}H_{27}ClN_4O_5S_2$<br>(514.5) | 10.5<br>10.8 |
| **4f** | 89<br>(3.2.2) | 146–147 | 621 | 68 100 | 0.51 | $C_{21}H_{27}ClN_4O_6S_2$<br>(530.5) | 10.5<br>10.5 |
| **4g** | 91<br>(3.2.1) | 153–154 | 628 | 75 600 | 0.56 | $C_{21}H_{26}Cl_2N_4O_5S_2$<br>(549) | 10.1<br>10.2 |
| **4h** | 81<br>(3.2.1) | 121–123 | 618 | 75 900 | 0.50 | $C_{24}H_{30}ClN_5O_6S_2$<br>(583.5) | 11.7<br>12.0 |
| **4i** | 82<br>(3.2.1) | 171–173 | 620 | 73 300 | 0.56 | $C_{26}H_{28}Cl_2N_4O_4S_2$<br>(595) | 9.7<br>9.4 |
| **4j** | 81<br>(3.2.1) | 131–133 | 636 | 40 000 | 0.91 | $C_{23}H_{23}ClN_4O_5S_2$<br>(534.5) | 10.2<br>10.5 |
| **4k** | 83<br>(3.2.4) | 118–120 | 628 | 69 100 | 0.78 | $C_{24}H_{25}ClN_4O_5S_2$<br>(548.5) | 10.1<br>10.2 |
| **4l** | 83<br>(3.2.4) | 185–186 | 609 | 66 000 | 0.61 | $C_{19}H_{24}N_4O_6S_2$<br>(468) | 11.5<br>11.9 |
| **4m** | 79<br>(3.2.4) | 181–182 | 614 | 82 500 | 0.34 | $C_{21}H_{25}N_5O_6S_2$<br>(507) | 14.0<br>13.8 |
| **4n** | 90<br>(3.2.4) | 167–168 | 617 | 83 600 | 0.74 | $C_{23}H_{28}ClN_5O_7S$<br>(553.5) | 12.3<br>12.6 |
| **4o** | 87<br>(3.2.5) | 135–136 | 628 | 68 800 | 0.47 | $C_{30}H_{36}ClN_5O_5S_2$<br>(645.5) | 10.5<br>10.8 |
| **4p** | 82<br>(3.2.6) | 133–134 | 626 | 80 400 | 0.6 | $C_{22}H_{28}Cl_2N_4O_6S$<br>(547) | 10.4<br>10.2 |
| **4q** | 82<br>(3.2.5) | 153–154 | 625 | 74 100 | 0.41 | $C_{22}H_{27}Cl_2N_5O_6S$<br>(560) | 12.5<br>12.5 |
| **4r** | 83<br>(3.2.6) | 172–173 | 606 | 82 300 | 0.78 | $C_{22}H_{27}Cl_3N_4O_2S$<br>(517.5) | 11.0<br>10.8 |

The dyes were recrystallized from $C_2H_5OH:C_2H_5OC_2H_5$ (**4a–4e**, **4g–4r**) and $C_2H_5OH$ (**4f**).

protons + N–$C\mathit{H}_3$ + $C\mathit{H}_3SO_4$ 4.25–4.65, $CH_2O\mathit{H}$ 5.29, $C_6\mathit{H}_3$ + $C_6\mathit{H}_4$ 7.07–8.25; **4p**—$CH_2C\mathit{H}_3$ 1.50, methylene protons 3.80–5.00, CH–O$\mathit{H}$ 5.38, $C_6\mathit{H}_3$ + $C_6\mathit{H}_4$ 7.12–8.42.

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