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Dyes and Pigments 43 (1999) 1–6

DYES and PIGMENTS

Synthesis and properties of reactive dyes, derivatives of 3,10-bis(3′-aminopropylamino)-6,13-dichlorotriphenodioxazin-4,11-disulphonic acid

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Received 9 November 1998; accepted 14 January 1999

Abstract

2-Chloro-5-nitrobenzenesulphonic-1 acid, 1,3-propylenediamine, chloranil and cyanuric chloride were used as raw materials to synthesise several reactive dyes, derivatives of 6,13-dichlorotriphenodioxazine. Spectroscopic and application properties of the dyes were determined. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: 3,10-bis(3′-aminopropylamino)-6,13-dichlorotriphenodioxazine-4,11-disulphonic acid; 6,13-dichlorotriphenodioxazine; triphenodioxazine dyes; reactive dyes

1. Introduction

6,13-Dichlorotriphenodioxazine is a structural element of a few commercially accessible direct [1] and reactive [2] dyes that are highly valued for their application properties as well as for their excellent blue colour on dyeing; this colour is not easily accessible with other chromophore systems.

Dioxazine reactive dyes became commercially available in the 1970's and they are now considered a suitable alternative for blue dyes derived from bromamine acid. Over several years of application, the dioxazine dyes have proved to have high dyeing efficiency and light-fastness. 3,10-Bis(2′-aminoethylamino)-6,13-dichlorophenodioxazine-4,11 disulphonic acid was the basic compound applied in the synthesis of the dyes. The two aminoethylamino groups at the 3,10-positions in the triphenodioxazine ring are an important structural element, and Renfrew [3] has shown that these groups stabilise the molecule and make it resistant to alkalies. Additionally, the alkylamino groups can easily react with trichloro- or trifluoro-*s*-triazine as well as with their derivatives. Dyes obtained as a result of these reactions contain two reactive groups and exhibit high affinity to cotton. Other aminoalkylamino groups can be of similar importance, as is claimed in an ICI patent [4] concerned only with dye molecules containing an aminoethylamino linkage. Another patent [5] reports the synthesis of reactive dyes containing an aminopropylamino linkage, but these dyes are derivatives of the not readily accessible 2,4,6-trifluoro-*s*-triazine. The practical importance of dioxazine dyes justifies the need for further research concerning methods of their synthesis and application.

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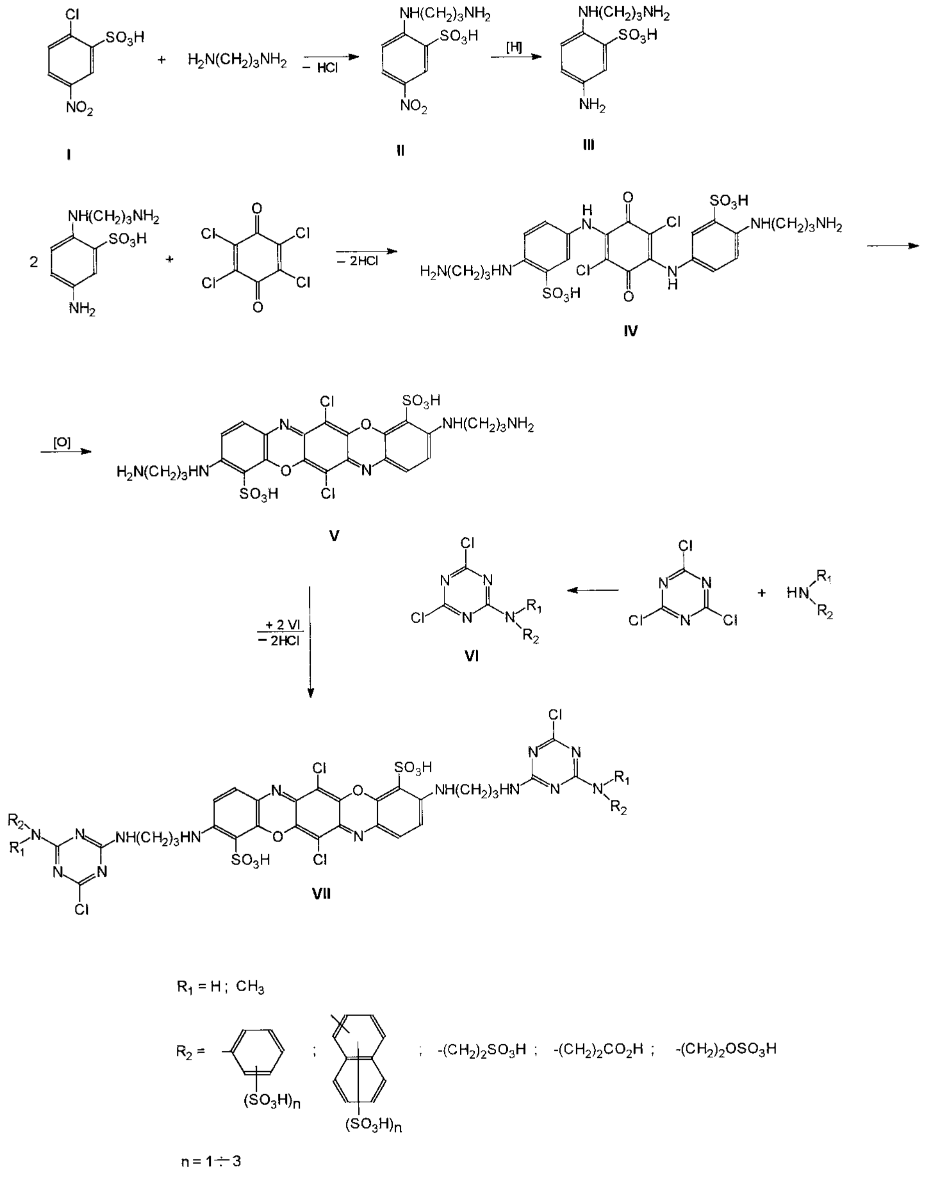
PII: S0143-7208(99)00023-6

The purpose of the present work was to synthesise reactive dyes derived from cyanuric chloride and 3,10-bis(3′-aminopropylamino)-6,13-dichlorotriphenodioxazine-4,11-disulphonic acid and to determine their application properties; an important part of the work consisted in the determination of the effect of the triazine ring substitution on the properties of the dyes.

2. Experimental

The synthesis of the reactive dyes is shown in Scheme 1. The main starting material used in the synthesis, 3,10-bis(3′-aminopropylamino)-6,13-dichlorotriphenodioxazine-4,11-disulphonic acid, was prepared according to the CIBA-GEIGY patent description [5] (except the cyclization process).



Scheme 1.

The following raw materials were used in the synthesis.

—2-Chloro-5-nitrobenzenesulphonic-1 acid, sodium salt, 77% (techn., "Boruta", Poland).
—Propylenediamine-1,3 (pure, Aldrich).
—Chloranil (pure, Fluka).
—$K_2S_2O_8$ (pure, Reachim, Russia).
—10% Oleum (self-made).

A mixture of 2-chloro-5-nitrobenzenesulphonic acid-1 (**I**), 1,3-propylenediamine and water in molar ratio 1:3:22 was heated at 90–95°C for a period of 1 h. The mixture was then diluted with water and acidified with hydrochloric acid to pH 3–3.5. The precipitated solid was filtered and then added in small portions to a mixture of Fe powder, water and acetic acid at 90–95°C. After completion of the reduction, the mixture was basified with NaOH, the precipitated ferric oxides were filtered off and the pH of the filtrate was adjusted to 7–7.3 with hydrochloric acid. The resulting 2-(3′-aminopropylamino)-5-aminobenzenesulphonic-1 acid (**III**) was filtered. In order to determine the content of the amine, a weighed amount of the product was dissolved in dilute hydrochloric acid and titrated with 0.1 M $NaNO_2$ (monitored with iodine-starch indicator paper). Overall yield of the condensation and reduction reactions was 84.6%. The purity of the compounds obtained was monitored by TLC on Kieselgel 60 using the following eluents:

(1) *n*-propanol-ethyl acetate-H_2O (3:1:3);
(1) *n*-propanol-ethyl acetate-H_2O (3:1:3);
(2) butanone-2-diethylamine 25% NH_3 (11:2:2).

The dianilide **IV** was prepared by reacting 2-(3′-aminopropylamino)-5-aminobenzene-sulphonic acid with chloranil in aqueous solution in the presence of sodium acetate and a small amount of dispersing agent. The reaction mixture was stirred at 60–65°C for 8 h while adjusting pH to 6–6.5 with dilute NaOH. The reaction was monitored on Whatman 3 paper using Py–25% NH_3–1% NaCl (1:1:8) as eluent. The precipitated dianilide was filtered and treated with boiling EtOH. The product obtained was practically free of inorganic salts; yield 92%. Cyclization of the dianilide was carried out in 10% oleum at 30–35°C using $K_2S_2O_8$ as an oxidant. The reaction was monitored by chromatography, similar to that used for compound **IV**. After completion of the reaction (about 10 h) the mixture was poured into ice and neutralised with sufficient NaOH to form $NaHSO_4$. The resulting solid was filtered and treated with boiling EtOH in order to purify it. In a dried sample of the product, the two sulphonic groups were determined by means of potentiometric titration with 0.1 M NaOH; yield 90.5%.

The dioxazine derivative obtained as described above was used to synthesise the reactive dyes **VII**. The first stage of the synthesis consisted in condensation of cyanuric chloride with primary or secondary amines, for example 3-aminobenzenesulphonic-1; 3-*N*-methylamino-benzenesulphonic-1; 2-amino-benzenedisulphonic-1,4; 3-aminonaphthalenedisulphonic-1,5; 8-aminonaphthalenetrisulphonic-1,3,6; 2-aminoethanesulphonic; 3-aminopropionic acid; 2hydroxyethane-amine-*O*-sulphonic.

The amine acids were neutralised with dilute NaOH and added to an aqueous suspension of cyanuric chloride at 0–3°C, while stirring intensively and adjusting the pH to 6–6.5 with dilute NaOH. The end point of the reaction was determined by TLC on Kieselgel 60 (Merck) using a mixture of propanol–ethyl acetate–water (3:1:3) as eluent.

The products of the above reactions were then reacted with 3,10-bis(3′-aminopropylamine)-6,13-dichlorotriphenodioxazine-4,11-disulphonic acid. The reactions were carried out at 40–45°C for 8–10 h while adjusting pH to 7.8–8 by adding dilute NaOH. The reactions were monitored chromatographically on Whatman 3 paper using DMF-diethanol-amine-H_2O (18:2:80) as eluent.

The dyes were isolated from the reaction mixtures by adding the appropriate amount of NaCl or KCl and filtering the resulting precipitated solid. The wet press-cakes were mixed with a mixture of NaH_2PO_4 and Na_2HPO_4 and dried at 40–45°C. The content of chlorides was determined in the dry dyes and taken into account together with the content of the phosphates added. Samples of cotton fabric were then dyed using the following parameters:

—liquor ratio 1:20,
—liquor composition: dye 1%, Na_2SO_4 50 g/dcm^3, $Na_3PO_4 \times 12H_2O$ 12.5 g/dcm^3,
—dyeing time: 1 h at 80°C.

After completion of the dyeing process the dyebath was cooled to 40°C and the dyed fabric samples subsequently subjected to:

—rinsing with hot and cold water,
—washing with a hot detergent solution (Rokaphenol N8P14 1% + ABS (Na) 1%),
—rinsing with hot and cold water,
—drying.

The degree of dye exhaustion from the bath (E) was determined colorimetrically on the basis of the determination of its concentration in the bath before dyeing (c_1) and after dyeing (c_2):

$$E(\%) = \frac{c_1 - c_2}{c_1} \cdot 100\%$$

The dyed samples were examined according to Polish Standards. Lightfastness, fastness to washing (60°C) and rubbing (dry and wet), as well as fastness to acid and alkaline perspiration were determined. For spectrophotometric investigation, the dyes samples were freed from inorganic salts as follows: the powdered dyes were treated twice with 50–60% 2-propanol, then stirred intensively for 0.5 h, filtered and the residues dried at 40–50°C to constant weight.

A Perkin–Elmer Lambda 40 spectrometer was used to record absorption spectra of the dye solutions in water as well as in 10% urea, 50% EtOH, 50% acetone and 50% aqueous DMF. Results of the spectrophotometric and application investigations of the dyes are given in Tables 1 and 2.

3. Discussion of the results and conclusion

The synthetic work showed that the synthesis of 3,10-bis(3′-aminopropylamino)-6,13-dichlorotriphenodioxazine-4,11-disulphonic acid **V** could be easily carried out on a technical scale. Additionally the raw materials needed are cheap and easily accessible. The reaction yields for all the stages are high (> 90%) and the products obtained are of acceptable purity. The starting material, 2-chloro-5-nitrobenzenesulphonic acid reacts with an excess of 1,3propylenediamine to give a monocondensed product, which was easily isolable from the reaction mixture, and did not need to be dried before reduction of the nitro group. The aminoalkyl derivative of 1,4-phenylenediamine obtained proved to be very reactive towards chloranil suspended in water, giving a high yield of the dianilide. It was observed that good stirring and addition of detergents improved the yield. Cyclization of the dianilide was carried out in 10% oleum by adding $K_2S_2O_8$ at 30–35°C. This method is more efficient than methods described in some patents that apply 20–25% oleum at 50–80°C. It was also shown that the conditions of the oxidation reaction can exert a significant effect on the tint of the dyes obtained. Low-temperature oxidation leads to dyes tints that are similar to Procion Blue H-EGN (C.I. Reactive Blue 198), whereas the more drastic method gives blue dyes with green tints. It was also found that the synthesis of dyes in the reaction of the acid **V** with derivatives of cyanuric chloride proceeds more easily in slightly basic solutions (pH 7.5–8). This observation may be explained by formation of inner-salts in solutions at lower pH. This problem can be avoided by intensive stirring and adjusting the pH during the reaction progress.

The dioxazine dyes obtained are characterised by very interesting dyeing properties, including a particularly high dyeing efficiency, as well as high lightfastness and fastness to washing. The dyes also have very high molar extinction coefficients (54105–77160 in 50% EtOH), and in terms of dyeing intensity the dyes obtained surpass dyes containing other chromophore groups. The dyes have high lightfastness values (4–5) which fulfil the requirements of most users. Most of the dyes obtained (except B-5) are characterised by exhaustion degree values within the range 73.3–83.5%. The lower value (65%) for dye B-5 may be attributed to a moderating effect of the three sulphonic groups attached to an aromatic ring of the 8-amino-naphthalenetrisulphonic-1,3,6 acid moiety. The moderating effects of alkyl groups are also evident for dyes B-6, B-7 and B-8; these dyes

Table 1
Structure and properties of reactive dyes **VII**, derivatives of 3,10-bis(3-bm5-aminopropylamino)-6,13-dichlorotriphenodioxazine- 4,11-disulphonic acid

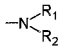
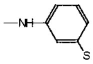
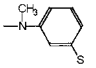
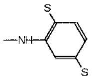
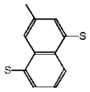
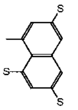
Dye number	Structure	Fastness (1% dyeing, cotton)					
	 S = SO$_3$Na (K)	Exhaustion degree (%)	Light (Xenotest)	Washing (60°C) cotton/change/wool	Rubbing	Perspiration	
						Acid cotton/change/wool	Alkaline cotton/change/wool
B-1		81.9	4÷5	5/4/5	5/5	5/4/5	5/4–3/4
B-2		74.6	4÷5	4/4/5	5/5	5/4–3/5	5/4–3/5
B-3		75.3	4÷5	5/5/5	5/5	5/4/5	5/4/5
B-4		78.7	4÷5	5/5/5	5/5	5/4/5	5/4/5
B-5		63.0	4÷5	5/4/5	5/5	5/4–3/5	5/4–3/5
B-6	$-NH(CH_2)_2SO_3Na$	87.5	4÷5	4/4/4–5	5/5	5/3/4	4/3/4
B-7	$-NH(CH_2)_2CO_2Na$	73.3	4÷5	4/4/4–5	5/5	5/3/4–5	4/3/4–5
B-8	$-NH(CH_2)_2OSO_3Na$	77.4	4÷5	4/4/5	5/5	5/3/5	4/4/5

Table 2
Spectroscopic properties of the reactive dyes $\left(\frac{\lambda_{\max}\ (\mathrm{nm})}{\varepsilon_{\mathrm{mol}}\left[\mathrm{dcm}^3/\mathrm{mol\ cm}\right]}\right)$

Dye	Water	10% Urea	50% Ethanol	50% Acetone	50% DMF
B-1	$\frac{621.1}{48\,915}$	$\frac{624.3}{50\,110}$	$\frac{630.1}{62\,765}$	$\frac{625.9}{65\,300}$	$\frac{633.0}{65\,860}$
B-2	$\frac{591.2}{46\,285}$	$\frac{592.1}{49\,550}$	$\frac{633.2}{54\,670}$	$\frac{629.2}{58\,675}$	$\frac{634.8}{67\,490}$
B-3	$\frac{620.8}{64\,920}$	$\frac{622.1}{65\,810}$	$\frac{630.9}{77\,160}$	$\frac{627.9}{79\,965}$	$\frac{632.8}{82\,480}$
B-4	$\frac{616.9}{58\,195}$	$\frac{618.7}{66\,125}$	$\frac{628.3}{76\,540}$	$\frac{626.6}{78\,460}$	$\frac{631.3}{79\,010}$
B-5	$\frac{615.0}{50\,075}$	$\frac{617.1}{59\,340}$	$\frac{633.4}{62\,970}$	$\frac{630.0}{66\,565}$	$\frac{634.9}{68\,425}$
B-6	$\frac{616.9}{51\,220}$	$\frac{619.2}{56\,730}$	$\frac{627.9}{62\,875}$	$\frac{625.3}{65\,925}$	$\frac{630.1}{71\,765}$
B-7	$\frac{586.9}{50\,465}$	$\frac{588.5}{55\,455}$	$\frac{625.7}{54\,105}$	$\frac{623.2}{58\,685}$	$\frac{629.9}{69\,710}$
B-8	$\frac{594.4}{51\,530}$	$\frac{592.6}{59\,525}$	$\frac{630.1}{59\,525}$	$\frac{628.2}{64\,125}$	$\frac{634.2}{68\,425}$

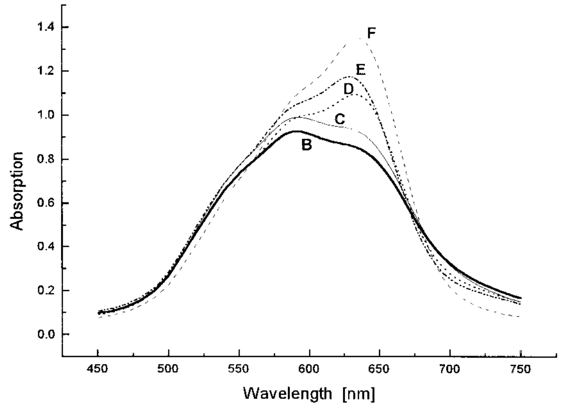


Fig. 1. Absorption spectra of B-2 dye in water (**B**) and in aqueous solutions of: **C**—urea (10%), **D**—EtOH (50%), **E**—acetone (50%), **F**—DMF (50%). Concentration of the dye: $c = 2{\cdot}10^{-4}$ mol/l.

are characterised by low fastness both to washing and to acid or alkaline perspiration.

The properties of these dyes as well as their molar extinction coefficients (Table 2) clearly indicate the influence of substituent groups on the solubility and aggregation of the dyes in the dyebath. Values of $\varepsilon_{\max}$ for spectra recorded in mixtures of water and urea, EtOH, acetone or DMF are greater than those determined in water (Table 2). This can be attributed to the greater intensity of the 620–630 nm band assigned to the monomeric form (for example: values of $\varepsilon_{\max}$ in 50% DMF are 30–40% greater than in water). Spectra of water solutions of the dyes show a broad band with a shoulder at 580–590 nm that can be assigned to the aggregated form. The presence of both forms in the absorption spectrum of dye B-2 is shown in Fig. 1. It was also found that the aggregated forms of the dyes are susceptible to a disaggregating effect by some compounds, for example urea. The possibility of disaggregation is very important, as reaction of monomeric molecules with cellulose fibers is the main role in the dyeing process. Dyes B-3 and B-4 are very interesting because their absorption spectra are characterised by the highest $\varepsilon_{\max}$ values both in water (64920 and 58195) and in mixed solvents. These dyes contain moieties of 2-aminobenzene-1,5-disulphonic and 3-aminonaphthalene-1,5-disulphonic and exhibit the best application properties in the examined group of dyes.

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