

Synthesis, Characterisation and Dyeing Properties of New bifunctional Dichloro-s-triazinyl (DCT) Azo Reactive Dyes based on 4,4'-diaminodiphenylsulphone on Wool Fabric

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ABSTRACT

The present research work was carried out due to the problem of hydrolysis associated with monoazo reactive dyes. In the study a series of bifunctional azo reactive dyes based on aromatic diamine moiety were synthesized via cyanuration of various acid (H-acid, J-acid, Laurent acid, Tobias acid and Gamma acid and Condensing them with 4-nitroaniline acids, then coupling with tetrazotized solution of 4,4-diaminodiphenyl sulphone to obtain a series of bifunctional Dichloro-s-triazinyl (DCT) azo reactive dyes. The synthesised dyes were applied on wool fabric under typical exhaustion process and their dyeing properties were evaluated. The structures of the synthesised dyes were characterised and confirmed by melting point, UV-visible spectroscopy, FT-IR spectroscopy, ¹HNMR, MS. The percentage exhaustion and percentage fixation of the synthesised dyes on wool fabric was very good, which is an indication of proper diffusion and fixation onto the fabric. All the synthesised dyes gave well to excellent properties to washing, light and perspiration respectively.

Keywords: Bifunctional azo reactive dyes; Wool fabrics; Exhaustion dyeing; Reactive dyes.

1.0. Introduction

Oforghor *et al.* (2020b), Ibrahim (2011) and Zollinger (2003) reported that the introduction of fibre-reactive colourants onto the marketplace some fifty years ago and this research is still continuing. Many novel functional and reactive groups having different positions with diverse characteristics, particularly forming a stable permanent dye-fibre covalent bond, have been synthesized. The incorporation of two reactive groups into a single dye molecule is a well established route to increased fixation efficiency: all of the leading ranges of dyes for the batch wise dyeing of textiles with reactive dyes now incorporate two or more such groups. Amongst the earliest examples to be exploited commercially were the Procion H-E dyes, which possess two similar monochlorotriazine groups. Novel bis-sulphatoethylsulphone, which incorporates two ureido groups, has been claimed by DyStar to fix and build-up in the presence of reduced concentrations of salt. In this case the ureido groups might be expected to increase substantivity, resulting in a lower salt requirement (Taylor, 2000). A series of bisulphatoethylsulphone reactive dyes have been synthesized and their application properties studied (Limin and Zhenghua, 1998) and (Zhenghua and Limin, 1998). Many such derivatives have been described: the most commonly encountered combinations include vinylsulphone with monofluorotriazine (Ciba-Geigy, 1996); (Hoechst, 1997); (Bayer, 1995), vinylsulphone with 2, 4-difluoropyrimidine (Bayer, 1995), vinylsulphone with 2, 4-difluoro-5-chloropyrimidine (Bayer, 1995), 2,4-difluoropyrimidine with monofluorotriazin (Bayer, 1994) and 4-fluoro-5chloropyrimidine with monohalotriazine (Bayer, 1993, 1994).

The aim of the present work is to synthesize a series of bifunctional azo reactive dyes based on aromatic diamine moiety via cyanuration of various acid (H-acid, J-acid, Laurent acid, Tobias acid and Gamma acid and Condensing them with 4-nitroaniline acids, then coupling with tetrazotized solution of 4, 4'-diaminodiphenylsulphone to

obtain a series of bifunctional Dichloro-s-triazinyl (DCT) azo reactive dyes and investigate their dyeing properties on wool fabric.

2.0. Experimental

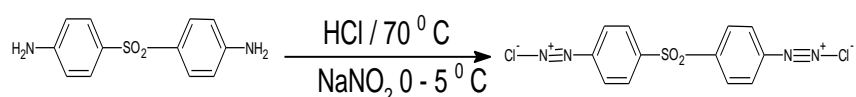
2.1. Materials

All other chemicals and solvent used in this study were of laboratory reagent grade and applied without further purification. 4,4'-diaminodiphenylsulphone, Cyanuric chloride, H-acid, J-acid, Laurent acids, Tobias acid, Gamma acid were purchased from Weifang Senya Chemical Company Limited, China. The melting points were determined by open capillary method. The UV-visible absorption spectra were recorded using Perkin-Elmer Lambda 25 UV-visible spectrophotometer (at the wavelength of maximum absorption (λ_{max})). The FT-IR were recorded using (Perkin-Elmer Spectrum RXIFT-IR Spectrometer, ^1H NMR spectra were recorded using (varian 300 MHz Bruker Instrument) and Mass Spectrometer were recorded using Agilent Technologies 5975C VL MSD Mass Spectrometer at the Kharazmi University, Bureau of International Scientific Cooperation, Department of Organic Chemistry, Tehran, Iran. The already degummed and bleached wool fabric, 80 g/m² was obtained from Chemical Processing laboratory, Department of Polymer and Textile Engineering at the Ahmadu Bello University, Zaria. Before application, the wool fabric was treated in an aqueous solution containing 2% stock concentration of detergent for 1 h at 80 °C and a 50:1 liquor ratio (LR), then washed thoroughly in water and air dried at room temperature. Applications and evaluation of fastness properties were carried out according to the standard methods in Chemical Processing laboratory, Department of Polymer and Textile Engineering at the Ahmadu Bello University, Zaria.

2.2. Methods

2.2.1. General Procedure for Tetrazotization of Intermediates

4,4'-diaminodiphenylsulphone (1.24 g, 0.005 mol) was suspended in distilled water (60 ml) and hydrochloric acid (0.36 g) was added dropwise to the well-stirred suspension. The mixture was gradually heated up to 70 °C, till clear solution was obtained. The formed solution was gradually cooled to below 5 °C in an iced bath, then already cooled (0 - 5 °C) NaNO₂ (0.6 g in 4 mole H₂O) was added over a period of 30 mins with continuous stirring. The stirring was continued for one (1) hour, maintaining the temperature of 0-5 °C with positive test for nitrous acid with starch iodide paper. After completely destroying the excess of nitrous acid with the required amount of sulphamic acid, the clear tetrazonium solution at 0 - 5 °C obtained was used for next coupling reaction as shown in scheme 1 below:

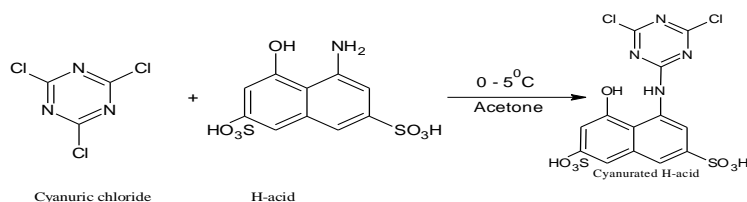


Scheme 1. Tetrazotization of 4,4'-diaminodiphenylsulphone

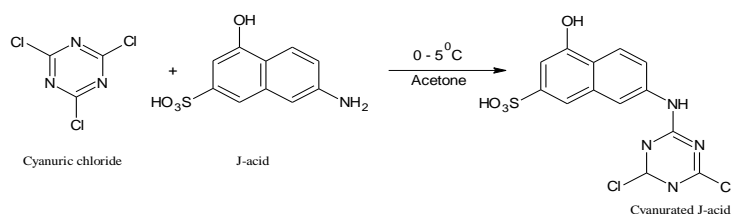
2.2.2. General procedure for cyanuration

Cyanuric chloride (1.85 g, 0.01 mol) was stirred in acetone (25 ml) at a temperature below 5 °C for a period of an hour. A neutral solution of coupling component (3.19 g, 0.01 mole) in aqueous sodium carbonate solution (10%

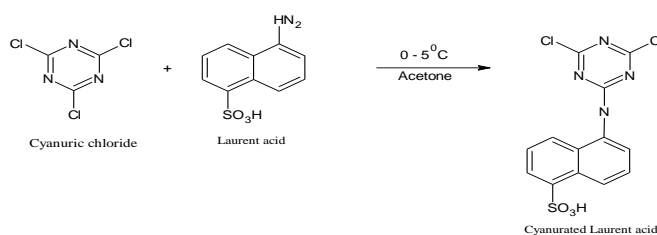
w/v) was then added in small lots for an hour. The pH was maintained neutral by simultaneous addition of sodium carbonate solution (1% w/v). The reaction mass was then stirred at 0-5°C for further 4 hours. The cyanurated coupling component solution was used for subsequent coupling reaction as shown in scheme 2. The same procedure (method) was followed to cyanurate scheme 2b (J-acid), 2c(Laurent acid), 2d (Tobias acid) and 2e (Gamma acid) respectively.



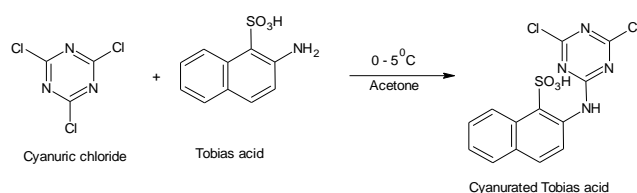
Scheme 2a. Cyanuration of H-acid



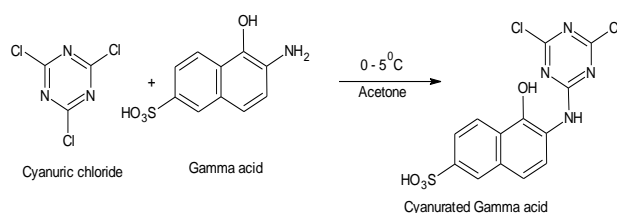
Scheme 2b. Cyanuration of J-acid



Scheme 2c. Cyanuration of Laurent acid



Scheme 2d. Cyanuration of Tobias acid

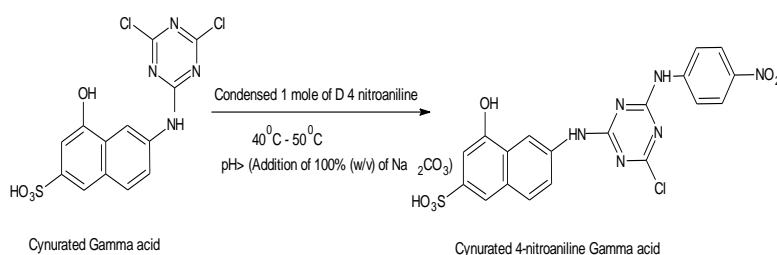
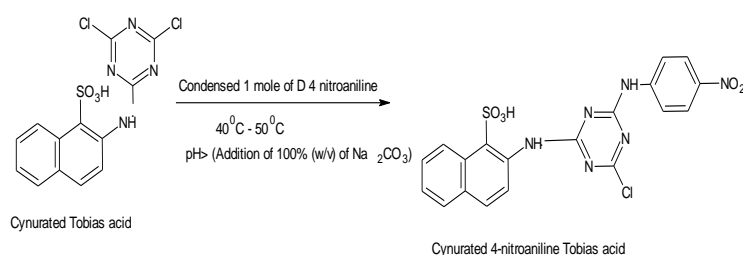
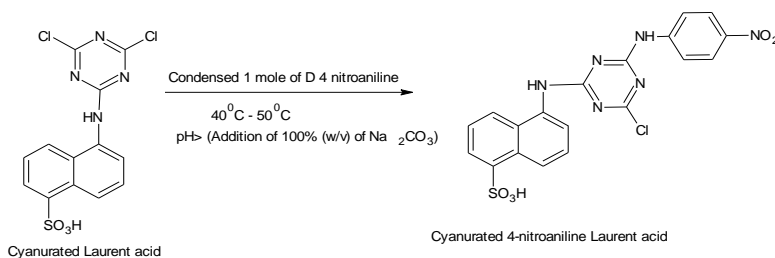
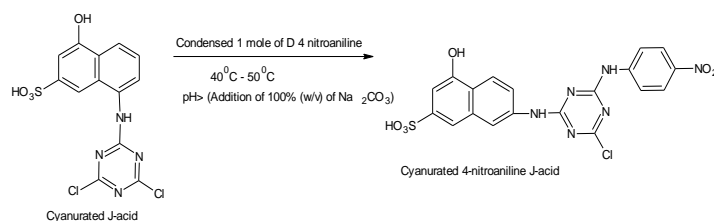
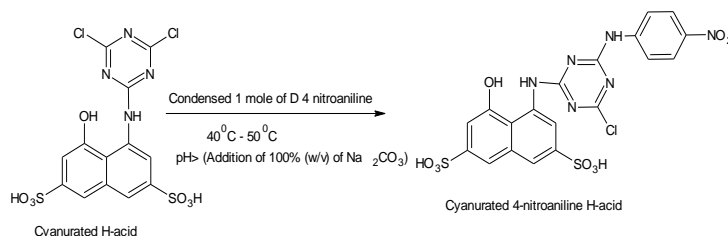


Scheme 2e. Cyanuration of Gamma-acid

2.2.3. General procedure for condensation of the cyanurated acids with aromatic amine

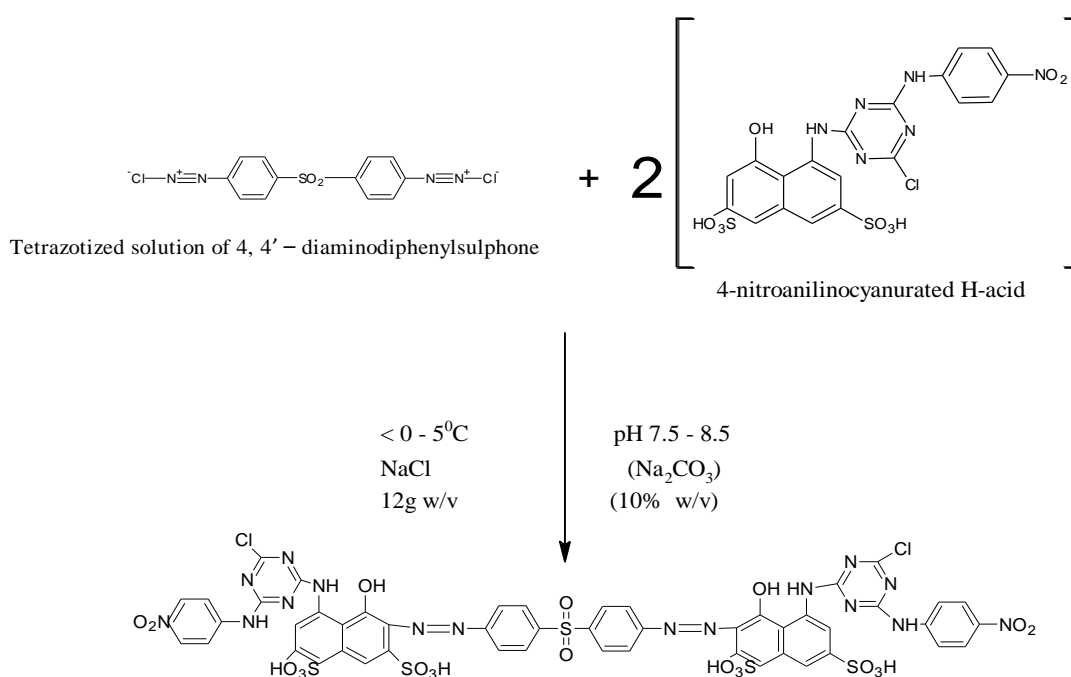
The temperature of ice-cooled well-stirred solution of cyanurated H-acid, (4.67 g, 0.01 moles) was gradually raised to 45-50°C for half an hour. To this cyanurated H-acid, 4-nitro aniline (1.39 g, 0.01 moles) was added slowly

at same temperature, during a period of 30 min, maintaining the pH neutral by simultaneous addition of sodium bicarbonate solution (1% w/v). After the addition was completed, stirring was continued for further 3 hours. The cyanurated 4- nitro anilino H-acid solution thus obtained was subsequently used for further coupling reaction as shown in scheme 3a. The same procedure (method) was followed for the condensation of cyanurated acids as shown in scheme 3b (J-acid), 3c (Laurent-acid), 3d (Tobias-acid) and 3e (Gamma-acid) respectively.



2.2.4. General procedures for synthesis of bi-functional dichlorotriazine azo reactive dyes

The synthesis of DX1 was done by adding a freshly prepared solution of tetrazotized solution of 4,4'-Diamino diphenylsulphone dropwise over a period of 10–20 minutes to the ice-cold and well stirred solution of 4-nitroanilino cyanurated H-acid. The pH 7.5–8.5 was maintained by simultaneous addition of sodium carbonate solutions (Na_2CO_3) (10% w/v) where a purple solution was obtained. The stirring was continued for 4hrs at a constant temperature below $0-5^\circ\text{C}$ for another 1 hr. The solid dye precipitates out and was filtered, washed with little amount of acetone and dried at room temperature as shown in scheme 4a below: The same procedure (method) was followed to synthesize DX2 (J-acid), DX3 (Laurent acid), DX4 (Tobias acid) and DX5 (Gamma acid) in scheme 4b, 4c, 4d, and 4e respectively as shown in the structural formula in Table 1.



Scheme 4a. Synthesis of dye DX1

3.0. Dyeing Procedure

3.1. Dyeing of fibres

All the bifunctional dichloro-s- triazinyl (DCT) azo reactive dyes were applied on wool fabrics in 2% shade according to the usual procedure (Oforghor *et al.*, 2020). After dyeing, all dyed samples were rinsed with water and air-dried.

3.2. Dye exhaustion

The percentage dye exhaustion of the dyed fabrics was evaluated spectrophotometrically using Eqn.1 below. The variation in the hues of the dyed fabric results from both the nature and position of the substituent present on the coupler ring. The remarkable degree of levelness after washing indicates good penetration and affinity of these dyes to the fabric.

$$\% E = \left[\left(\frac{C_1 - C_2}{C_1} \right) \right] \times \frac{100}{1} \quad (1)$$

3.3. Dye fixation

The percentage of exhausted dye chemically bound on the fibre, also called total dye fixation ratio (%*F*), was measured by refluxing the dyed samples in 50% aqueous DMF (liquor ratio 20:1) for 10-15 min to extract the unfixed dye. This procedure was repeated until the extract was clear of the dye solution.

The concentration of the extract was then measured spectrophotometrically at λ_{\max} and the dye fixation ratio was calculated using Eqn. 2

$$\% F = \left[\left(\frac{C_1 - C_2 - C_3}{C_1 - C_2} \right) \right] \times \frac{100}{1} \quad (2)$$

3.4. Fastness properties test

3.4.1. Wash fastness test

The dyed samples were subjected to ISO 3 wash fastness test previously described Oforghor *et al.*, (2020). The change in colour of samples and the staining of the adjacent un-dyed fabric were assessed with an appropriate grey scale.

3.4.2. Light fastness test

This was carried out using a Microsal Tester Xenon arc lamp. The dyed samples were cut into 10 cm by 4 cm, placed in the machine and exposed for 48 hrs after which they were removed and the change in colour was assessed using the blue wool scale.

3.4.3. Fastness to perspiration test

The perspiration fastness of the synthesised dyes were assessed according to the conditions of ISO 105- E04 (2013) previously described Oforghor *et al.*, (2020) for both acidic Perspiration test and alkaline Perspiration test

4.0. Results and Discussion

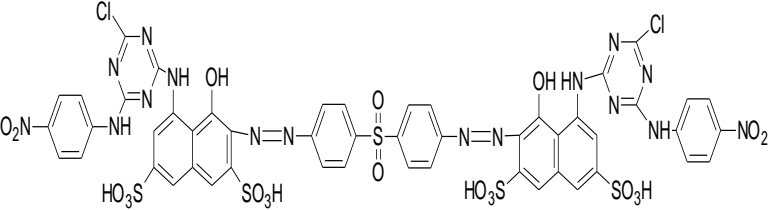
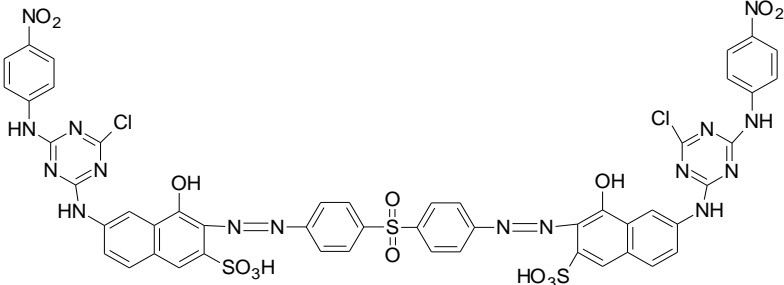
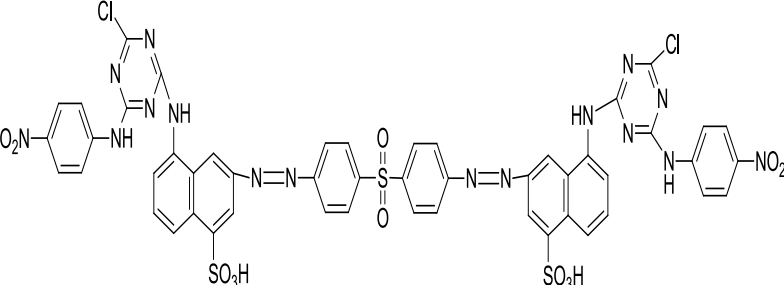
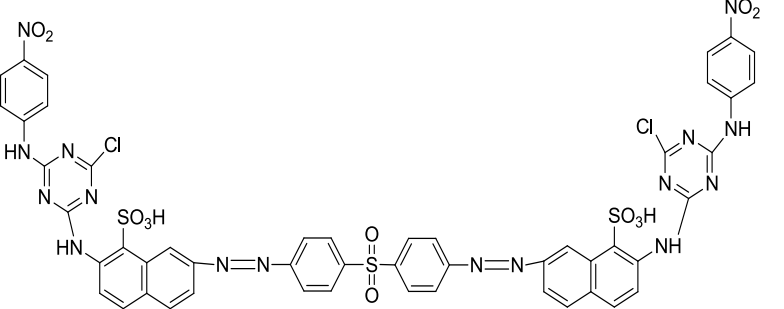
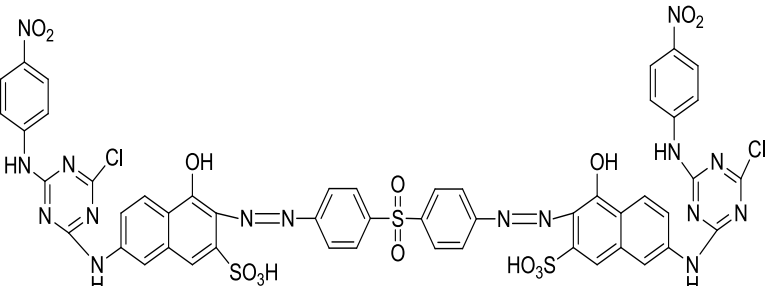
Synthesis of bifunctional azo reactive dye

The synthesis of dye DX1 is shown in scheme 4a the reaction involves four (4) steps. In step one (1) 4,4'-diaminodiphenylsulphone (1.24 g, 0.005 mol) was tetrazotised using nitrosyl hydrochloric acid (NaNO₂/HCl) method to give 4,4'-diaminodiphenylsulphone tetrazonium solution by the method previously described Oforghor *et al.*, (2020), then in step two (2) H acid reacts with cyanuric chloride in the presence of acetone to give cyanurated H-acid.

In step three (3) the cyanurated H-acid was condensed with 4-nitroaniline to give cyanurated 4-nitroanilino H-acid and this was followed by step four (4) with the coupling of cyanurated 4-nitroanilino H-acid with the 4,4'-diamino diphenylsulphone tetrazonium solution to give dye DX1.

The same procedure was followed as showed in scheme 4b (J-acid), scheme 4c (Laurent acid), scheme 4d (Tobias acid) and 4e (Gamma acid) to synthesised DX2- DX5 as shown in Table 1.

Table 1. Structures with IUPAC names of synthesized bifunctional dichloro-s-triazinyl (DCT) azo reactive Dyes

Dye No.	IUPAC Name	Structures of the Synthesised Bi-functional azo reactive Dyes
DX1	3,3'-(sulfonylbis(4,1-phenylene))bis(diazene-2,1-diyl)bis(5-((4-chloro-6-((4-nitrophenyl)amino)-1,3,5-triazin-2-yl)amino)-4-hydroxynaphthelene-2,7-disulfonic acid)	
DX2	3,3'-(sulfonylbis(4,1-phenylene))bis(diazene-2,1-diyl)bis(6-((4-chloro-6-((4-nitrophenyl)amino)-1,3,5-triazin-2-yl)amino)-4-hydroxynaphthelene-2-sulfonic acid)	
DX3	3,3'-(sulfonylbis(4,1-phenylene))bis(diazene-2,1-diyl)bis(5-((4-chloro-6-((4-nitrophenyl)amino)-1,3,5-triazin-2-yl)amino)naphthelene-1-sulfonic acid)	
DX4	7,7'-(sulfonylbis(4,1-phenylene))bis(diazene-2,1-diyl)bis(2-((4-chloro-6-((4-nitrophenyl)amino)-1,3,5-triazin-2-yl)amino)naphthelene-1-sulfonic acid)	
DX5	3,3'-(sulfonylbis(4,1-phenylene))bis(diazene-2,1-diyl)bis(5-((4-chloro-6-((4-nitrophenyl)amino)-1,3,5-triazin-2-yl)amino)-4-hydroxynaphthelene-2-sulfonic acid)	

The physical characteristics of the synthesised dyes are shown in Table 2a and from the table, it can be seen that the molecular weight of all the synthesized dyes are on the high side. Oforghor *et al.* (2020B) and Patel *et al.* (2014) reported that high molecular weight dyes exhibit high melting points. From Table 2, it agrees with the literature since most of the synthesized dyes have very high melting point. The synthesised dyes exhibit excellent solubility characteristics which agree with Oforghor *et al.* (2020b) that highly branched molecular structure are highly soluble.

Table 2. Physical and spectroscopic characteristics of the synthesized bifunctional dichloro-s-triazinyl (DCT) azo reactive Dyes

Dye No.	Mol. Wt (g/mol)	Mt. Pt (°C)	Yield (%)	DMF (λ_{max})	Water (λ_{max})	ϵ_{max} in DMF $\times 10^4 \text{ l Mol}^{-1} \text{ cm}^{-1}$
DX ₁	1405.11	320-322	59	537	527	6.61
DX ₂	1246.08	305-308	97	510	503	3.95
DX ₃	1214.09	330-332	45	458	458	1.81
DX ₄	1214.09	310-312	79	540	403	2.09
DX ₅	1246.08	320-322	65	513	510	3.73

The visible absorption spectroscopic properties of dyes were recorded in water (Table 2). The colour of the dye is affected by substituents in the coupling constituent. The visible absorption maxima of the synthesised bifunctional azo-reactive dyes as recorded in Table 2 fell within the visible region (400-700 nm) of the electromagnetic spectrum. The values of the molar extinction coefficient (ϵ) that were determined by Beer-Lambert's law are in the range of 14324 - 85316.0 $\text{L mol}^{-1} \text{ cm}^{-1}$ which is an indication of high absorption intensity of the synthesised bifunctional azo reactive dyes in DMF respectively. However, the synthesised bifunctional azo reactive dyes have different chromophoric functionalities, but same bridging groups and it is also apparent that the value of λ_{max} depends on the coupling components used. The presence of electron-donating or electron-attracting (withdrawing) groups at the suitable position of the coupler ring affects the absorption characteristics of the synthesised bifunctional azo-reactive dyes (Patel *et al.*, 2014). Comparing the λ_{max} of the dyes DX₁, DX₂, DX₃, DX₄, and DX₅ in DMF showed that the variation in hue is due to the nature of the intermediates employed and positions of the substituent's on the coupler ring (Patel *et al.*; 2014). Dye DX₁ was synthesised by tetrazitising 4,4-diaminediphenylsulphone using NaNO_2/HCl method and coupling with 4-nitroaniline cyanurated H-acid which absorbed at 537 nm in DMF, but when 4-nitroaniline cyanurated H-acid was replaced with 4-notrianiline cyanurated J-acid, dye DX₂ was synthesised which absorbed at 510 nm, hence, there was hypsochromic shift of 27 nm when compared to dye DX₁. Using 4-notrianiline cyanurated Laurent-acid as coupling component result in the synthesis of dye DX₃ and absorbed at 458 nm in DMF and gives a hypsochromic shift of 79 nm when compared to dye DX₁ and hypsochromic shift of 42 nm when compared to dye DX₂. Meanwhile, replacing 4-nitroaniline cyanurated Laurent acid with Tobias acid gives dye DX₄ which absorbed at 540 nm in DMF with a bathochromic

shift of 3nm when compared to DX1, bathochromic shift of 30nm when compared to DX2, bathochromic shift of 82 nm when compared to DX3 respectively. Dye DX5 was by tetrazotising 4,4- diaminediphenylsulphone and coupling with 4-nitroaniline cyanurated Gamma acid and absorbed at 510 nm in DMF which sifted hypsochromically with 27 nm when compared to DX1, 0 nm when compared to DX2, bathochromic shift of 42 nm when compared to DX3 and hypsochromic shift of 30nm when compared with DX4 respectively.

Solvatochromic characteristics of the synthesised bifunctional azo reactive dyes

Also of fundamental interest is the effect of polarity on the wavelength of maxima absorption of the dyes is the solvatochromism. From Table 2, it can be seen that the shift in λ_{max} of the synthesised bifunctional azo reactive dyes in different solvents (solvatochromism) is as a result of the solvatochromic effects emanating from changes in dielectric constant of the solvent. The measurement of λ_{max} in DMF and water indicated that λ_{max} of the intermolecular charge transfer bonds exhibit a remarkable red shift on transfer from non-polar to polar solvent. This behaviour can be attributed to the polar excited states of the synthesised bifunctional azo reactive dyes are stabilized by polarization interactions forces as the polarisability of the solvent increases (Abd El-Aal and Koraiem, 2002).

Oforghor *et al.*, (2020B) reported that solvatochromism is as a result of solute-solvent interactions at both the ground state and excited state. However, from Table 2, the red shift (bathochromic) on changing from lower polar solvent to stronger polar solvent indicates that the dye molecule has a more polar excited state than the ground state. Light absorption causes the π -electron to migrate from the amino donor group to the various electron acceptor residues, hence, making the excited state to become more polar (dipole moment) than the ground state (Oforghor *et al.*, 2011).

Table 3. FT-IR Spectroscopy of the bifunctional dichloro-s-triazinyl (DCT) Azo reactive dyes

Dye no.	Empirical formula	Mol. Wt	Yield (%)	Melting point (°C)	FT-IR (KBR): ν (cm ⁻¹)
DX1	C ₅₀ H ₃₂ Cl ₂ N ₁₆ O ₂₀ S ₅	1405	59	320-322	3441 (O-H str vibr.), 3413 (N-H str vibr.), 3014(C-H str vibr.), 1711 (N=N str vibr.), 1326 (C-N str vibr), 1622 (N-H bend vibr.), 1047 (S=O str vibr.), 1326 (N=O), 730 (C-Cl str vibr.), 845 (SO ₃ H str vibr.)
DX2	C ₅₀ H ₃₂ Cl ₂ N ₁₆ O ₁₄ S ₃	1246	97	305-308	3449 (O-H str vibr.), 3429 (N-H str vibr.), 3055-2995 (C-H str vibr.), 1597 (N=N str vibr.), 1377 (C-N str vibr.), 1651 (N-H bend vibr.), 1045 (S=O str vibr.), 1377 (N=O str vibr.), 779 (C-Cl str vibr.), 828 (SO ₃ H str vibr.)

DX3	$C_{50}H_{32}Cl_2N_{16}O_{12}S_3$	1214	45	330-332	3415 (O-H str vibr.), 3404 (N- H str vibr.), 3000 (C-Hstr vibr.), 1596 (N=N str vibr.), 1408 (C- N str vibr.), 1663 (N-H bend vibr.), 1066-1150 (S=O str vibr.), 1329 (N=O str vibr.), 767 -752 (C-Cl str vibr.), 853 (SO ₃ H str vibr.)
DX4	$C_{50}H_{32}Cl_2N_{16}O_{14}S_3$	1214	79	310-312	3489 (O-H str vibr.), 3413 (N-H str vibr.), 2985 (C-H str vibr.), 1598 (N=N str vibr.), 1598-1411 (C-N str vibr.), 1662 (N- H bend vibr.), 1053 (S=O str vibr.), 1336(N=O str vibr.), 769-751 (C-Cl str vibr.), 854-824 (SO ₃ H str vibr.)
DX5	$C_{50}H_{32}Cl_2N_{16}O_{14}S_3$	1246	65	320-322	3446 (O-H str vibr.), 3416 (N-H str vibr.), 2995 (C-H str vibr.), 1600-1656 (N=N str vibr.), 1436 (C-N str vibr.), 1654 (N-H bend vibr.), 1050 (S=O str vibr.), 1365 (N=O str vibr.), 782-758(C-Cl str vibr.), 831(SO ₃ H str vibr.)

FT-IR spectra of all the dyes from Table 3 generally showed O-H and N-H stretching vibrations in the region 3470-3588 cm⁻¹, 3401-3418 cm⁻¹ respectively, C-H stretching vibration at 3270-3288 cm⁻¹, N=N stretching vibration at 1610-1629 cm⁻¹, C-N stretching vibration at 1507-1548 cm⁻¹, S=O stretching vibration at 1033-1168 cm⁻¹, C-Cl stretching vibration at 709-724 cm⁻¹, NO₂ stretching vibration at 1521-1529 cm⁻¹.

Table 4. Mass Spectroscopy data for bifunctional triazine azo reactive dyes

Dye No.	Empirical formula	Experimental values of m/z fragment	Corresponding positive charge fragment	Theoretical value
DX1	$C_{50}H_{32}Cl_2N_{16}O_{20}S_5$	46.0, 76.0, 114.1, 248.2, 318.1, 1405.1	NO ₂ ⁺ , C ₆ H ₄ ⁺ , C ₃ CIN ₃ ⁺ , C ₁₂ H ₁₂ N ₂ O ₂ S ⁺ , C ₁₀ H ₈ NO ₇ S ₂ ⁺ , M	1405
DX2	$C_{50}H_{32}Cl_2N_{16}O_{14}S_3$	46.0, 76.0, 114.1, 248.1, 239.2, 1246.2	NO ₂ ⁺ , C ₆ H ₄ ⁺ , C ₃ CIN ₃ ⁺ , C ₁₂ H ₁₂ N ₂ O ₂ S ⁺ , C ₁₀ H ₉ NO ₄ S ⁺ , M	1246
DX3	$C_{50}H_{32}Cl_2N_{16}O_{12}S_3$	46.0, 76.0, 114.1, 223.1, 248.1, 1214.3	NO ₂ ⁺ , C ₆ H ₄ ⁺ , C ₃ CIN ₃ ⁺ , C ₁₂ H ₁₂ N ₂ O ₂ S ⁺ , C ₁₀ H ₉ NO ₃ S ⁺ , M	1214

DX4	$C_{50}H_{32}Cl_2N_{16}O_{14}S_3$	46.0, 76.0, 114.1, 223.1, 248.1, 1214.3	NO_2^+ , $C_6H_4^+$, $C_3ClN_3^+$, $C_{12}H_{12}N_2O_2S^+$, $C_{10}H_9NO_3S^+$, M	1214
DX5	$C_{50}H_{32}Cl_2N_{16}O_{14}S_3$	46.0, 76.0, 114.1, 248.1, 239.1, 1246.2	NO_2^+ , $C_6H_4^+$, $C_3ClN_3^+$, $C_{12}H_{12}N_2O_2S^+$, $C_{10}H_9NO_4S^+$, M	1246

The mass spectrum MS for dye DX1 analysis revealed a fragmentation pattern of NO_2^+ , $C_6H_4^+$, $C_3ClN_3^+$, $C_{12}H_{12}N_2O_2S^+$, $C_{10}H_8NO_7S_2^+$, which indicates molar masses of 46.0, 76.0, 114.1, 248.2, 318.1 g/mol respectively. The mass spectrum showed a molecular ion (M^+) at m/z 1405.1 g/mol and this is in agreement with the molecular mass 1405.2 g/mol of the synthesised dye DX1. The mass spectrum MS for dye DX2 analysis revealed a fragmentation pattern of NO_2^+ , $C_6H_4^+$, $C_3ClN_3^+$, $C_{12}H_{12}N_2O_2S^+$, $C_{10}H_9NO_4S^+$, which indicates molar masses of 46.0, 76.0, 114.1, 248.1, 239.2 g/mol respectively. The mass spectrum showed a molecular ion (M^+) at m/z 1246.2 g/mol and this is in agreement with the molecular mass 1246.1 g/mol of the synthesised dye DX2. The mass spectral MS for dye DX3 analysis revealed a fragmentation pattern of NO_2^+ , $C_6H_4^+$, $C_3ClN_3^+$, $C_{12}H_{12}N_2O_2S^+$, $C_{10}H_9NO_3S^+$, which indicates molar masses of 46.0, 76.0, 114.1, 223.1, 248.1 g/mol respectively. The mass spectrum showed a molecular ion (M^+) at m/z 1214.3 g/mol and this is in agreement with the molecular mass 1214.1 g/mol of the synthesised dye DX3. The mass spectrum MS for dye DX4 analysis revealed a fragmentation pattern of NO_2^+ , $C_6H_4^+$, $C_3ClN_3^+$, $C_{12}H_{12}N_2O_2S^+$, $C_{10}H_9NO_3S^+$, which indicates molar masses of 46.0, 76.0, 114.1, 223.1, 248.1 g/mol respectively. The mass spectrum showed a molecular ion (M^+) at m/z 1214.2 g/mol and this is in agreement with the molecular mass 1214.1 g/mol of the synthesised dye DX4. The mass spectrum MS for dye DX5 analysis revealed a fragmentation pattern of NO_2^+ , $C_6H_4^+$, $C_3ClN_3^+$, $C_{12}H_{12}N_2O_2S^+$, $C_{10}H_9NO_4S^+$, which indicates molar masses of 46.0, 76.0, 114.1, 248.1, 239.1 g/mol respectively. The mass spectrum showed a molecular ion (M^+) at m/z 1246.1 g/mol and this is in agreement with the molecular mass 1246.1 g/mol of the synthesised dye DX5. Oforghor et al.; 2020 reported that all these differences may arise due to bridging groups, chromophores, coupling components and reactive systems.

Table 5. Exhaustion and fixation study of the dichloro-s-triazinyl DCT reactive dyes on wool fabric

Dye No.	Shade on wool	Exhaustion (%)		Fixation (%)	
		Wool	Wool	Wool	Wool
DX1	Light yellow	70	90		
DX2	Orange	75	92		
DX3	Yellow	69	85		
DX4	Light yellow	72	92		
DX5	Light orange	68	87		

The percentage exhaustion of 2% dyeing for dye DX1 on wool fabric showed 70% while the percentage fixation of 2% dyeing on wool fabric for dye DX1 is at 90%. The percentage exhaustion of 2% dyeing for dye DX2 on wool

fabric showed 75% while the percentage fixation of 2% dyeing on wool fabric for dye DX2 is at 92%. The percentage exhaustion of 2% dyeing for dye DX3 on wool fabric showed at 69% while the percentage fixation of 2% dyeing on wool fabric for dye DX3 is at 85%. The percentage exhaustion of 2% dyeing for dye DX4 on wool fabric showed at 72% while the percentage fixation of 2% dyeing on wool fabric for dye DX4 is at 92%. The percentage exhaustion of 2% dyeing for dye DX5 on wool fabric showed at 68% while the percentage fixation of 2% dyeing on wool fabric for dye DX5 is at 87% respectively.

Table 6. Fastness performance properties of the bifunctional dichloro-s-triazinyl (DCT) Azo Reactive dyes on wool fabric

Dye No	Wash fastness Wool	Light fastness Wool	Perspiration fastness	
			Alkaline Wool	Acidic Wool
	cc	cc	cc	cc
DX1	4-5	5	3-4	4
DX2	4	5	5	5
DX3	4	4	4	4
DX4	4-5	4	5	5
DX5	4	6	5	5

cc = colour change

1=poor, 2=fair, 3=fairly good, 4=good, 5=excellent –wash fastness;

1=poor, 2=slight, 3=moderate, 4=fair, 5=good, 6=very good, 7=excellent, 8=outstanding light fastness;

1=much change (poor) 2=considerable change (fair), 3=noticeable change (fairly good), 4=slight change (good), 5=negligible (excellent) –Perspiration fastness.

The wash fastness, light fastness and perspiration fastness were studied according to Oforghor *et al.*, 2020. The wash fastness of all the dyes showed good to excellent on wool fabrics. The light fastness of all the dyes showed moderate to good on wool fabrics and the perspiration fastness (acidic and alkaline) of all the dyes showed good to excellent perspiration fastness on wool fabrics (Table 6).

5.0. Conclusion

New bifunctional dichloro-s-triazinyl (DCT) azo reactive dyes based on 4, 4-diaminodiphenylsulphone have been successfully synthesised. 4,4-diaminodiphenylsulphone was tetrazotized and coupled with cyanurated 4-nitro anilino R' acids (H-acid, J-acid, Laurent acid, Tobias acid and Gamma acid) coupling components to give the corresponding bifunctional dichloro-s-triazinyl (DCT) azo reactive dyes (DX1-DX5). These dyes gave pink, orange, brown and yellow shades on wool fabrics. The dyes gave better light fastness and seem to have good dyeing performance on wool fabrics. The exhaustion and fixation performance of these dyes are very satisfactory.

The remarkable degree of levelness after washing indicates the good penetration and affinity of the dyes to wool fabrics.

Recommendations

From the results, it can be recommended as follows;

- the intermediate can be used to synthesize a novel bi-functional azo-reactive dyes;
- the aromatic bridged amines are very suitable for synthesizing novel bi-functional azo-reactive dyes with commercial integrity;
- the synthesized dyes can also be tried on cotton, nylon 6, nylon 6,6.

Declarations

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Competing Interests Statement

Authors have declared no competing interests.

Consent for Publication

The authors declare that they consented to the publication of this study.

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