Synthesis of a series of Homo-Bifunctional Azo Reactive dyes and Evaluation of their dyeing properties on Silk fabric

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ABSTRACT

This paper was conceived with the objective of synthesizing and evaluating some novel bifunctional Dichlorotriazine (DCT) azo reactive dyes. They were synthesized via tetrazotization of 1, 4- benzenediamine followed by the coupling with cyanurated 4-nitroanilino acids components (H-acid, J-acid, Laurent acid, Tobias acid and Gamma acid) respectively. The spectra properties (UV-vis spectra, FT-IR, 1H NMR and MS) of the synthesised dyes are reported. The novel bifunctional dichlorotriazine (DCT) azo reactive dyes were applied on silk fabric using the exhaustion techniques. The total exhaustion and fixation values were estimated. The basic fastness properties to washing, light and perspiration of the dyes on silk fabric were discussed in terms of their chemical structure. The dyes showed good build up, levelling and fastness properties on silk fabrics.

Keywords: 1, 4-benzenediamine; Azo dyes; Fastness properties; Reactive dyes; Silk fabric.

1.0. Introduction

Oforghor, et al. (2023C) and Zhangr, et al. (2019) reported that reactive dyes were initially introduced commercially for application to cellulosic fibres, and this is still their most important use. The growth rate of reactive dyes for cellulosic fibres is expected to continue increasing. Souhangir, et al. (2022), Shankarling, et al. (2017), Mortazavi-Derazkola (2017) reported that this is expected because reactive dyes continue to gain market share at the expense of other dye types such as azoic dyes. Mohamed, et al. (2018), Lokhandyala and Kapadiya (2017) stated that reactive dyes have also been developed for application on protein-silk and wool fibres and polyamide - silk fibres respectively. Several heterocyclic compounds are extensively used in dye chemistry for textile or non-textile applications in recent years (Lewis, 2014). These dyes are now marketed to produce a full range of dispersed dyestuffs without the use of colorants based on heteroaromatic diazo components (Mokatari, et al. (2005). Oforghor, et al. (2023C), Shindy (2017), and Shor (2002)) reported that most of the heterocyclic dyes are derived from the diazo components consisting of five-membered rings containing one or more nitrogen heteroatoms, with the rings being fused into another aromatic ring. Lewis (2009), Lewis and Siddique (2008) and Taylor (2000) reported that the dyes with heterocyclic diazo components have been intensively investigated, to produce bright and strong colour shades ranging from red to greenish blue on synthetic fabrics. These results led to commercial products to replace the conventional azobenzene disperse dyes. The nitrosubstituted aminothiophenes, and aminothiazoles are primarily of importance as diazo components (Patel et al., 2013). Recently, Towns has summarized the developments in azo disperse dyes derived from heterocyclic diazo components (Patel et al., 2002). Non-textile uses of heteraylazo disperse dyes have been explored, for example in reprographic technology, functional dye applications, and non-linear optical systems (Patel and Patel, 2012). The monoazo dyes containing heterocyclic rings or carbocyclic rings result in brighter and often deeper shades than their disazo or trisazo analogues. On the other hand, the disazo or trisazo dyes are very important in applications such as disperse dyes for

polyester fibres, and as photoconductors. Dyes of these types are usually produced by careful selection of the diazo and coupling components such as to create room for convenient diazotisation and further coupling. Clearly, the large number of possibilities for disazo structures is very large and the choice is increased further in the trisazo and polyazo series. However, very few trisazo disperse dyes have been reported. Recently, our research has reported the synthesis of a series of monoazo disperse dye derivatives of 2-amino-5-nitrothiazole and their application on polyester fibres (Oforghor et al., 2023 and Patel et al., 2014). The results of this gave well to excellent dyeing properties. In the present study, the synthesis, characterisation and dyeing performances of novel bifunctional Dichlorotriazine (DCT) azo reactive dyes based on 1, 4-benzenediamine on silk fabric are reported. The dyes were characterised by UV-vis, FTIR, 1H NMR and MS analyses. The fastness properties of the bifunctional Dichlorotriazine (DCT) azo reactive dyes silk fabrics were also evaluated.

2.0. Experimental

2.1. Materials

The chemicals used in this research study were of analytical grade procured from Weifang Senya Chemical Company Limited, China. The chemicals include 1, 4-benzenediamine, Cyanuric chloride, H-acid, J-acid, Laurent acids, Tobias acid, and Gamma acid. The fabric use was wool material which was sourced from the Chemical Processing laboratory within the Department of Polymer and Textile Engineering at Ahmadu Bello University, situated in Zaria. Preceding the dyeing process, the fabric underwent treatment with a 2% stock solution of detergent at a temperature of 60 °C for a duration of 30 minutes, followed by thorough rinsing with water and subsequent air drying at ambient room temperature.

The determination of the melting points was accomplished through Gallenkamp melting point apparatus (the open capillary technique.) The FT-IR (Fourier-transform infrared) and UV-visible absorption spectra were captured utilizing the Perkin-Elmer Spectrum RXIFT-IR Spectrometer and the Perkin-Elmer Lambda 25 UV-visible spectrophotometer (at the wavelength of maximum absorption (λmax) at the esteemed Kharazmi University, Bureau of International Scientific Cooperation, specifically within the Department of Organic Chemistry, located in Tehran, Iran.
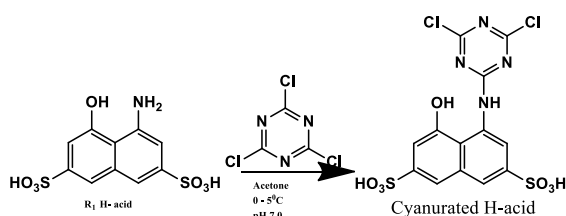
2.2. Methods

2.2.1. Route for the synthesis of the bifunctional azo reactive dyes

2.2.1a. The 1, 4- benzenediamine intermediate (0.54 g, 0.005 mol) was tetrazotised by dispersed in 60 ml of distilled water, followed by the gradual addition of 0.36 g of hydrochloric acid to the vigorously stirred suspension. The temperature was raised incrementally to 70 °C until a transparent solution was achieved. Subsequently, the resulting solution was slowly cooled to a temperature below 5 °C using an iced bath, after which the pre-cooled NaNO$_2$ (0.6 g in 4 moles of water) was introduced over a 30-minute period with continuous agitation. Stirring was sustained for one hour while keeping the temperature between 0-5 °C, indicated by a positive nitrous acid test with starch iodide paper. Following the complete removal of excess nitrous acid through the addition of the necessary amount of sulphamic acid, the clear tetrazonium solution obtained at 0-5 °C was utilized for the subsequent coupling reaction as depicted in Scheme 3.
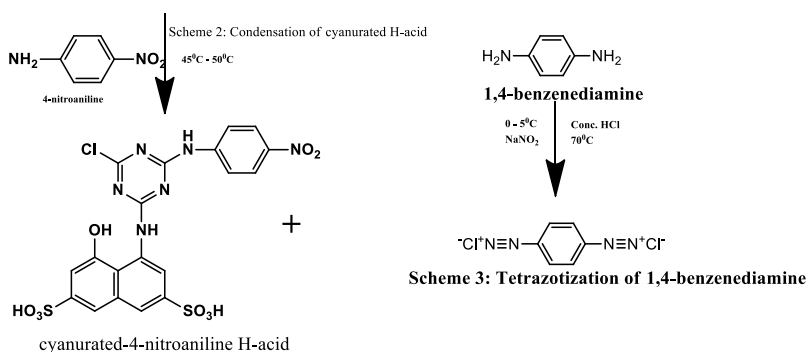
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2.2.1b. Cyanuration of H-Acid

The H-acid was cyanurated by agitating cyanuric chloride (1.85 g, 0.01 mol) in a solution of acetone (25 ml) at a temperature of 5 °C for a duration of 1hr. Following this, a solution of the coupling component (3.19 g, 0.01 mol) in an aqueous solution of sodium carbonate (10 % w/v) was gradually introduced over the course of an hour. The pH level was carefully maintained at a neutral level through the simultaneous addition of a sodium carbonate solution (1 % w/v). Subsequently, the mixture underwent stirring at a temperature range of 0-5 °C for an additional 4 hours. The resulting solution of the cyanurated coupling component was utilized for the subsequent coupling reaction as illustrated in scheme 2. The identical procedure (method) was applied to cyanurate to yield J-acid (cyanurated J-acid), Laurent-acid (cyanurated Laurent acid), Tobias-acid (cyanurated Tobias acid), and Gamma-acid (cyanurated Gamma acid) in scheme 1.
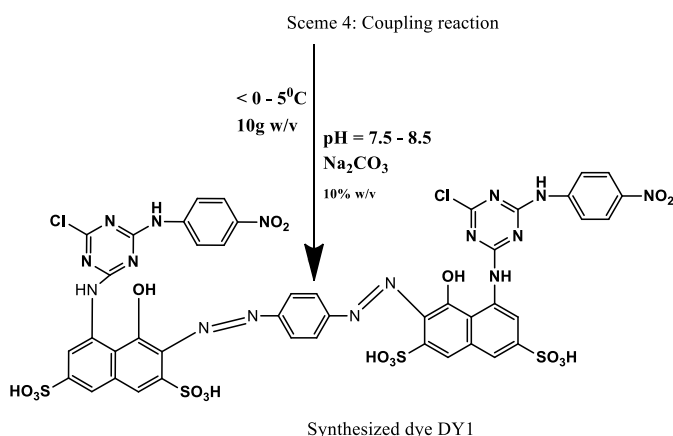

Scheme 1: Cyanuration of H-acid

R$_1$ = H- acid
R$_2$ = J- acid
R$_3$ = Lawrent acid
R$_4$ = Tobias acid
R$_5$ = Gamma acid

Scheme 2: Condensation of cyanurated H-acid

cyanurated-4-nitroaniline H-acid

Scheme 3: Tetrazotization of 1,4-benzenediamine

Sceme 4: Coupling reaction

Synthesized dye DY1

2.2.1c. Condensation of the cyanurated acids with 4-nitroaniline

The ice-cooled well stirred solution of cyanurated H-acid, (4.67 g, 0.01 moles) was condensed by gradually raised to 45-50 °C for 30 min. 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 hr. The

cyanurated 4- nitro anilino H-acid solution thus obtained was subsequently used for further coupling reaction as shown in scheme 3. The same procedure (method) was followed for the condensation of cyanurated J-acid to yield (cyanurated 4- nitro aniline J-acid), Laurent-acid (cyanurated 4- nitro aniline Laurent acid), Tobias-acid (cyanurated 4- nitro aniline Tobias acid) and Gamma-acid (cyanurated 4- nitro aniline Gamma acid) in scheme 3 respectively.

2.2.1d. Synthesis of bi-functional dichlorotriazine azo reactive dyes

The synthesis of DY1 was done by adding a freshly prepared solution of tetrazotized solution of 1, 4-diaminobenzene 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_2SO_3) (10 % w/v) where a purple solution was obtained. The stirring was continued to for 4hrs at a constant temperature below 0–5 $^\circ$C for another 1hr. The solid dye precipitates out and was filtered, washed with little amount of acetone and dried at room temperature as shown in the scheme 4. According to the above procedure; other reactive dyes DY2–DY5 were synthesized using DY2 (J-acid), DY3 (Laurent acid), DY4 (Tobias acid) and DY5 (Gamma acid) in scheme 4 respectively as shown in Scheme 4. All the synthesized dyes as recorded in Table 1.

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 usual procedure (Oforghor et al., 2023 and 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 Equation 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.

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

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 calculated using Equation 2.

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

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*., (2023) and Oforghor *et al., (*2020). The change in colour of samples and the staining of the adjacent un-dyed fabric were assessed with appropriate grey scale.

3.4.2. Light fastness test

Oforghor *et al*., (2023) procedure was adopted. 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 were assessed using the blue wool scale.
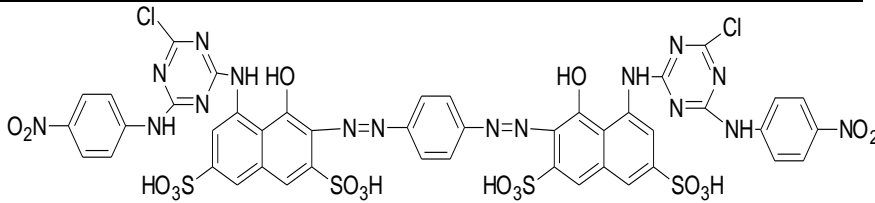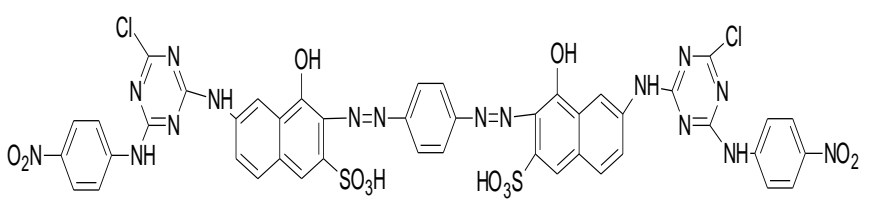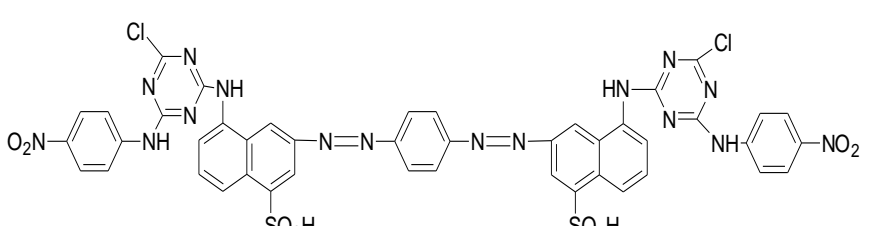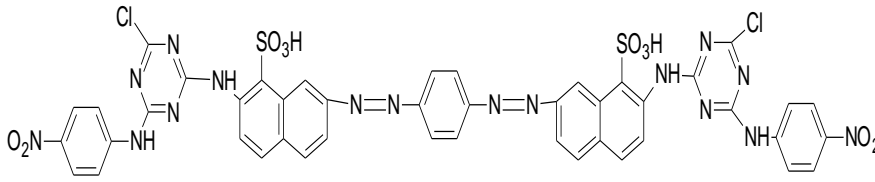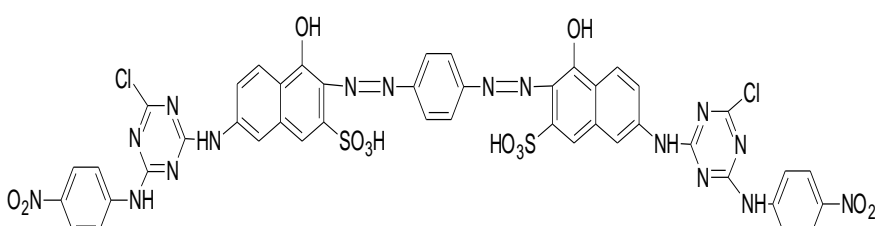
3.4.3. Fastness to perspiration test

The perspiration fastness of the synthesised dyes were assessed according to the conditions of ISO 105- E04 (1989) previously described Oforghor et al., (2023) and Oforghor *et al., (*2020) for both acidic Perspiration Test and alkaline Perspiration Test

4.0. Results and Discussion

4.1. Synthesis of the bifunctional dichloro-s-triazinyl (DCT) Dyes

The preparation of a Tetrazotised solution of 1,4-benzenediamine involved suspending 1,4-benzenediamine and incrementally adding 0.36g of HCl while stirring continuously at a temperature of 70°C until a clear solution was obtained. Subsequently, the temperature was reduced to between 0°C and 5°C, and ice-cold $NaNO_2$ solution was slowly introduced in small portions over a 5-minute period with continuous stirring for 1 hour, maintaining the same temperature until clarity was achieved, as outlined in scheme 1. The cyanuration of the acids depicted in Schemes 2 was executed by agitating cyanuric chloride in acetone at a temperature below 0°C-5°C for an hour. This was followed by the gradual addition of a neutral solution of H-acid (in an aqueous 10% w/v $NaCO_3$ solution) in small increments over an hour, while ensuring a constant pH by introducing 1% w/v $NaCO_3$ at a temperature below 0°C-5°C, and stirring continuously for 4 hours until a clear solution was obtained. In schemes 3, the condensation of the cyanurated acids involved incrementally raising the temperature of the ice-cold well-stirred cyanurated acids (H-acid, J-acid, Laurent acid, Tobias acid, and Gamma acid) to 50°C over 30 minutes. 4-nitroaniline was then added gradually over 30 minutes while maintaining a constant pH by adding 1% w/v $NaHCO_3$ with continuous stirring for 5 hours to obtain the 4-nitroanilino cyanurated acids. The dye DY1 was synthesized following the procedure outlined in scheme 4 by slowly adding a freshly prepared Tetrazotised solution of 1,4-benzenediamine to an ice-cold well-stirred 4-nitroanilino cyanurated H-acid over a 10-15 minute period, while maintaining the pH between 7.5 and 8.5 by adding a 10% w/v $NaCO_3$ solution simultaneously with continuous stirring for 3-4 hours at a temperature below 0°C-5°C. Subsequently, the dye was precipitated by adding 12g NaCl and stirring continuously for an additional hour, followed by filtration, washing, and drying at room temperature.

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

Dye No.	IUPAC Name	Structures of the Synthesised Bi-functional azo reactive Dyes
DY1	3,3'-(1,4-phenylenebis(diazene-2-1-diyl)bis(5-((4-chloro-6-((4-nitrophenyl)amino)-1,3,5-triazin-2-yl)amino)-4hydroxynapthelene-2,7-disulfonic acid)	
DY2	3,3'-(1,4-phenylenebis(diazene-2-1-diyl)bis(5-((4-chloro-6-((4-nitrophenyl)amino)-1,3,5-triazin-2-yl)amino)-4hydroxynapthelene-2-sulfonic acid)	
DY3	3,3'-(1,4-phenylenebis(diazene-2-1-diyl)bis(5-((4-chloro-6-((4-nitrophenyl)amino)-1,3,5-triazin-2-yl)amino)napthelene-1-sulfonic acid)	
DY4	7,7'-(1,4-phenylenebis(diazene-2-1-diyl)bis(2-((4-chloro-6-((4-nitrophenyl)amino)-1,3,5-triazin-2-yl)amino)napthelene-1-sulfonic acid)	
DY5	3,3'-(1,4-phenylenebis(diazene-2-1-diyl)bis(7-((4-chloro-6-((4-nitrophenyl)amino)-1,3,5-triazin-2-yl)amino)-4-hydroxynapthelene-2-sulfonic acid)	

From Table 1 and Table 2, it can be seen that the percentage yield of the synthesized dyes is on the very high side although very few have low percentage yield. The high percentage yield recorded is an indication that there was a control of the experimental conditions (Oforghor *et al.,* 2020 and Mousa *et al.,* 2014). The synthesized dyes were also very soluble in water which is an indication that the structure of the synthesized dyes are highly branched and the position of the functional groups in the carbon chains also favours the solubility of the dyes (OH, SO_3H) (Oforghor *et al.,* 2020 and Divyesh *et al.,* 2009; Lina and Patel, 2014; Patel *et al.,* 2015; Ahmad *et al.,* 2016). The colour or hue of the synthesized dyes ranges from purple, red, pink due to the presence of functional groups such as NH_2 and –OH on the dye structure.

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

Dye No.	Mol.Wt (g/mol)	Mt.Pt (^{o}C)	Yield (%)	DMF (λmax)	Water (λmax)	ε_{max} in DMF x$10^4$1Mol^{-1}cm^{-1}
DY1	1267.00	310-312	51	530	529	2.07
DY2	1106.09	338-340	81	510	510	3.18
DY3	1074.10	320-321	50	415	403	8.53
DY4	1074.10	315-318	70	413	413	1.69
DY5	1106.09	300-302	62	526	516	2.30

It is evident that the coupling components utilised have an impact on the value of λmax. Each dye exhibits a colour shift that is caused by extra substituents and electron oscillation. Water was used to record the dyes' visual absorption spectroscopic characteristics (Table 2). The coupling constituent's substituents have an impact on the dye's hue. The synthesised bifunctional azo reactive dyes' visible absorption maxima, as listed in Table 2, are located in the visible (400–700 nm) region of the electromagnetic spectrum, indicating that they are colourants with excellent commercial integrity. The values of the molar extinction coefficient (ε) that were determined by Beer-Lambert's law are in the range of 16904.14-85316.01mol^{-1}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 the same chromophoric functionalities, but different in the bridging groups. 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. Meanwhile, comparing the λmax of the synthesised bifunctional azo reactive dyes DY1, DY2, DY3, DY4 and DY5 in DMF showed that their nature of their coupling components (cyanurated 4-nitroanilino H-acid, cyanurated 4-nitroanilino J-acid, cyanurated 4-nitroanilino Laurent-acid, cyanurated 4-nitroanilino Tobias-acid and cyanurated 4-nitroanilino Gamma-acid) are very significant in the context of colour change (Patel et al., 2014). Dye DY1 was obtained by tetrazotising 1,4 benzenediamine and coupling with cyanurated 4-nitroanilino H-acid which absorbed at 530nm while DY2 which is obtained by tetrazotising 1,4 benzenediamine and coupling with cyanurated 4-nitroanilino J-acid absorbed at 510nm, hence there was a hypsochromic shift of 20nm. This is attributed to the

introduction of additional donor groups onto the coupling component. The coupling of tetrazotised solution of 1, 4 benzenediamine with cyanurated 4-nitroanilino Laurent acid yield dye DY3 which absorbed at 415nm, and there was hypsochromic shift of 125nm when compared to dye DY1 and hypsochromic shift of 20nm when compared with DY2. Dye DY1 was obtained by tetrazotising 1,4 benzenediamine and coupling with cyanurated 4-nitroanilino Tobias acid which absorbed at 413nm while DY1, DY2, and DY3 absorbed at 530nm, 510nm and 415nm which shifted hypsochromically by 127nm, 107nm and 2nm respectively.

The dye DY1 was created by tetrazotising 1,4 benzenediamine and coupling with cyanurated 4-nitroanilino Gamma acid, which absorbed at 526 nm. As a result, when DY1, DY2, DY3, and DY4 were compared, there was a bathochromic shift of 10, 111, and 113 nm, respectively, and a hypsochromic shift of 4 nm (DY1). These observations may be explained by the fact that, despite having the same groups, the dyes' positions vary. As a result, dyes with a higher bathochromic shift (higher value) have more space for groups like NH and SO_3H, which accelerate electron oscillation and, in turn, accelerate electron neutralisation more quickly than dyes with a lower value hypsochromic shift.

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): v (cm⁻¹)
DY1	$C_{44}H_{28}Cl_2N_{16}O_{18}S_4$	1267	51	310-312	3405 (O-H str. Vibr.), 3365 (N-H str vibr.), 2900 (C-H str vibr.), 1595-1643 (N=N str vibr.), 1505-1429 (C-N str vibr.), 1525 (N-H bend. vibr.), 1032-1165 (S=O str vibr.), 1374 (N=O str vibr.), 664-560 (C-Cl str vibr.), 894 (SO_3H str vibr.)
DY2	$C_{44}H_{28}Cl_2N_{16}O_{12}S_2$	1106	81	338-340	3413 (O-H str vibr.), 3404 (N-H str vibr.), 2917 (C-H str vibr.), 1578 (N=N str vibr.), 1409 (C-N str vibr.), 1491 (N-H bend vibr.), 1025 (S=O str vibr.), 1326 (N=O str vibr.), 703-660 (C-Cl str vibr.), 830 (str vibr.)
DY3	$C_{44}H_{28}Cl_2N_{16}O_{10}S_2$	1074	50	320-321	3451 (O-H str vibr.), 3335 (N-H str vibr.), 2995 (C-H, str vibr.),

Dye	Formula				
					1597 -1650 (N=N str vibr.), 1375 (C-N str vibr.), 1489 (N-H bend vibr.), 1027 -1183 (S=O str vibr.), 1375 (N=O str vibr.), 779 (C-Cl str vibr.) 878 (SO$_3$H str vibr.)
DY4	C$_{44}$H$_{28}$Cl$_2$N$_{16}$O$_{10}$S$_2$	1074	70	315-318	3446 (O-H str vibr.), 3416 (N-H str vibr.), 2996 (C-H str vibr.), 1603 (N=N str vibr.), 1378 (C-N str vibr.), 1651 (N-H bend vibr), 1047 (S=O str vibr.), 1378 (N=O str vibr.), 779-757 (C-Cl str Vibr.), 827 (SO$_3$H str vibr.)
DY5	C$_{44}$H$_{28}$Cl$_2$N$_{16}$O$_{12}$S$_2$	1106	62	300-302	3410 (O-H str vibr.), 3401 (N-H str vibr.), 2918 (C-H str vibr.), 1720 (N=N str vibr.), 1329 (C-N str vibr.), 1619 (N-H bend vibr.), 1041 (S=O str vibr.), 1329 (N=O str vibr.), 768-781 (C-Cl str vibr.), 825(SO$_3$H str vibr.)

In general the infra-red spectral of all the dyes DY1, - DY5 revealed that O-H showed stretching vibration at 3405-3451 cm^{-1}, N-H showed stretching vibration at 3365cm^{-1}, C=H showed stretching vibration at 2915cm^{-1}, C-N showed stretching vibration at 1515cm^{-1}, 1329cm^{-1}, 1464cm^{-1}, N=N showed stretching vibration at 1651cm^{-1}, S=O showed stretching vibration at 11755cm^{-1}, 1153cm^{-1} (asym. And sym), N=O showed stretching vibration at 1515cm^{-1}, 1361cm^{-1}, 1335cm^{-1}, C-Cl showed stretching vibration at 779cm^{-1} and SO$_3$H showed stretching vibration at 956cm^{-1} respectively as showed in Table 3

Table 4. ^{1}H NMR (500 MHz, DMSO): δH (ppm) Data of bifunctional dichloro-s-triazinyl (DCT) Azo Reactive Dyes DY1 – DY5

Dye No.	^{1}H NMR
DY1	1.42(1H, S, CH). 3.66 (4H, S, –NH), 4.80(2H, S, OH), 7.11 – 8.36 (17H, m, Ar–H), 8.60 (1H, S, SO$_3$H)
DY2	1.42(1H, S, CH).3.67 (4H, S, –NH), 4.85(2H, S, OH), 7.06 – 8.41 (19H, m, Ar–H), 8.61 (1H, S, SO$_3$H)

DY3	1.42(1H, S, CH).4.66 (4H, S, –NH), 7.06 – 8.42 (20H, m, Ar–H)
DY4	1.42(1H, S, CH).3.67 (4H, S, –NH), 7.06 – 8.29 (20H, m, Ar–H
DY5	1.42(1H, S, CH).3.64 (4H, S, –NH), 4.81(2H, S, OH), 7.09 – 8.31 (17H, m, Ar–H), 8.60 (1H, S, SO_3H)

The ^{1}H-NMR spectral for dyes DY1-DY5 from Table 4, showed respective signals

Table 5. Mass Spectroscopy data for bifunctional triazine azo reactive dyes DY1 – DY5

Dye No.	Empirical formula	Experimental values of m/z fragment	Corresponding positive charge fragment	Theoretical value
DY1	$C_{44}H_{28}Cl_2N_{16}O_{18}S_4$	46.0, 76.0, 106.1, 114.1, 318.1, 1267.2	NO_2^+, $C_6H_4^+$, $C_3ClN_3^+$, $C_6H_8N_2^+$, $C_{10}H_8NO_7S_2^+$, M	1267
DY2	$C_{44}H_{28}Cl_2N_{16}O_{12}S_2$	46.0, 76.0, 106.2, 114.1, 1107.2	NO_2^+, $C_6H_4^+$, $C_3ClN_3^+$, $C_6H_8N_2^+$, $C_{10}H_9NO_4S^+$, M	1107
DY3	$C_{44}H_{28}Cl_2N_{16}O_{10}S_2$	46.0, 76.0, 106.1, 114.1, 222.1, 1075.1	NO_2^+, $C_6H_4^+$, $C_3ClN_3^+$, $C_6H_8N_2^+$, $C_{10}H_4NO_3S^+$, M	1075
DY4	$C_{44}H_{28}Cl_2N_{16}O_{10}S_2$	46.0, 76.0, 106.1, 114.1, 222.1, 1075.1	NO_2^+, $C_6H_4^+$, $C_3ClN_3^+$, $C_6H_8N_2^+$, $C_{10}H_9NO_3S^+$, M	1074
DY5	$C_{44}H_{28}Cl_2N_{16}O_{12}S_2$	46.0, 76.0, 106.1, 114.1, 241.1, 1107.1	NO_2^+, $C_6H_4^+$, $C_3ClN_3^+$, $C_6H_8N_2^+$, $C_{10}H_9NO_4S^+$, M	1107

The mass spectral as indicated in Table5 above showed the recorded protonated peaks and sodiated peaks which corresponds to the various molecular mass of the synthesized dyes as seen in the calculated peaks and the experimental peaks.

Table 6. Exhaustion and fixation study of the dichloro-s-triazinyl DCT reactive dyes on silk fabric

		Exhaustion (%)	Fixation (%)
Dye No.	Shade on silk	Silk	Silk
DY1	Light brown	69	92
DY2	Light orange	63	87

DY3	Yellow	68	85
DY4	Light orange	78	89
DY5	Yellow	71	79

From the Table 6 above, the percentage exhaustion of 2% dyeing of the synthesized dichloro-s-triazinyl DCT reactive dyes on silk fabric showed percentage exhaustion from 637% to 78%. The percentage fixation of 2% dyeing on silk fabric showed from 87% to 92% respectively.

Table 7. Fastness properties of the bifunctional dichloro-s-triazinyl (DCT) Azo Reactive dyes on silk fabric

Dye No			Perspiration fastness	
	Wash fastness	**Light fastness**	**Alkaline**	**Acidic**
	Silk	**Silk**	**Silk**	**Silk**
DY1	4	6	5	5
DY2	5	5-6	3-4	5
DY3	4-5	4	4-5	4
DY4	4	4	4	4
DY5	4	5	4	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 fatness.

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 silk fabrics (Table 7).

5.0. Conclusions

A range of novel bi-functional azo reactive dyes with two functions were produced using 1, 4-benzenediamine. These artificial dyes give silk fabrics excellent fastness qualities and colours like pink, yellow, orange, and brown. The type and location of the auxochrome on the coupling components are what cause the dyed materials' colours to vary as seen. These dyes have great solubility and affinity with the silk fabric, as seen by their excellent exhaustion and fixing. Excellent substantivity and bonding of the dyes onto the fabric is indicated by the observed extent of uniformity and levelness following washing. On the other hand, the tetrazo structure's intrinsic conjugate produces good colour strength.

Declarations

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Competing Interests Statement

The authors have declared that no competing financial, professional or personal interests exist.

Consent for publication

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

Authors' contributions

All the authors took part in literature review, analysis, and manuscript writing equally.

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