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SYNTHESIS, CHARACTERISATION AND DYEING PROPERTIES OF NEW BIFUNCTIONAL SULPHATOETHYLSULPHONE (SES) AZO REACTIVE DYES BASED ON 1, 4'-BENZENEDIAMINE. PART:1: ON NYLON 6 FABRIC

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Abstract: A series bifunctional azo reactive dyes containing two anionic sulphatoethylsulphone (SES) derived from 1,4'-benzenediamine as a tetrazotised solution were prepared by coupling to 4-nitroanilino cyanurated acids (H-acid, J-acid, Laurent acid, Tobias acid and Gamma acid).The synthesised dyes were applied on nylon 6 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, and MS. The percentage exhaustion and percentage fixation of the synthesised dyes on nylon 6 fabric was very good. All the synthesised dyes gave well to excellent properties to washing, light and perspiration respectively.

Key words: Reactive dyes, nylon 6 fabrics, exhaustion dyeing, Reactive dyes, tetrazotisation

INTRODUCTION

Oforghor et al; (2023B), Oforghor et al; (2020B), Gamit et al; (2017), Farha et al; (2010) and Blanco et al; (2016) reported that reactive dyes are textile organic colourants having one or two reactive groups capable of reacting covalently between carbon and phosphorus atom of the dyes and oxygen, nitrogen or sulphur atoms of the fibre. Alan et al; (200), Patel et al; (2010) and Almasian et al; (2015) opined that reactive dyeing systems have become the most important discovery in the colouration industry in the last century. Ever since there were discovered, diminishing era for the demand of other dye class set in (Al-Degs et al; 2008, Christie, 2001, Bravo-Diaz, 2010). Reactive dyes constitute a very important class for dyeing cellulosic and polyamide fibres and a very high rate of growth is predicted in future (Gao, et al; 2023, Patel and Kesshav, 2012. Clark, 2011, Broadbent, 2001)

The earlier dyes synthesised were however, fixed onto the cellulose by an alkaline treatment at times at a higher temperatures. Hence, as a result of this the earlier dyes form esters and ethers with cellulose (Hung and Wu, 2021, Khatri, et al; 2015 and Clark, 2002). These dyes were found to have the following setbacks-lots of dyes wasted due to hydrolysis, could not be applied to cotton/polyester blends as the disperse dye meant for the polyester component decomposes at high temperature of application and due to the high alkalinity required some of the dyes could not be applied onto the substrate (Patel et al; 2002, Khosravi et al; 2005, Konstantinova and Petrova, 2002, Patel et al; 2011)

Oforghor et al; (2023B), Oforghor et al; (2020B), Patel, et al; (2011) and Patel, et al; (2013) reported that it is necessary to increase the fixation properties of the reactive dyes by building bifunctionality into the dye as an efficient method of improving the application properties of the dye. Klaus et al; (2005), Clark, (2011) opined that it is implicit that dyes with two reactive groups provides a higher fixation yield than dyes with one reactive group because if one of the two dye-fibre bonds is hydrolysed, one reactive group is still left for fixation (Patel, et al; (2013). The bifunctional azo reactive dyes are more valuable than the mono azo reactive dyes, as they are more tinctorally stable and potentially more economic than mono azo reactive dyes (Patel, et al; 2011).

Oforghor et al; (2023B), Oforghor et al; (2020B) and Patel, et al; (2014) reported that most interest has recently shored up in the dyes containing DCT reactive groups, which give deep colours on various textile fabrics than the dyes containing only one reactive group. The curiosity implicit in this approach was to synthesised a range of high temperature dyes for exhaust dyeing with substantially improved dyeability, high exhaustion and high fixation in comparison with the conresponding conventional monofunctional azo reactive dyes-this is the most important characteristics of bifunctional azo reactive dyes (Khazaei et al; 2013)

However, the present investigation is to the Synthesis, Characterisation and dyeing properties of five new novel homo bifunctional dichloro-s-triazinyl (DCT) azo reactive dyes containing 1,4-benzenediamine as a tetrazotized component prepared by coupling to 4-nitroanilino cyanurated acids (H-acid, J-acid, Laurent acid, Tobias acid and Gamma acid). The synthesised dyes were characterised using FT-IR, UV-visible absorption spectra, and the percentage exhaustion, percentage fixation and the fastness properties (washing, light and perspiration) were assessed.

2.0 Experimental:

2.1 Materials

2.1.1 Fabric

The nylon 6 fabric was obtained from Chemical Processing laboratory, Department of Polymer and Textile Engineering at the Ahmadu Bello University, Zaria. Before application, the 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.

2.1.2 Chemicals

All other chemicals and solvent used in this study were of laboratory reagent grade and applied without further purification. 1,4- benzenediamine, Cyanuric chloride, H-acid, J-acid, Laurent acids, Tobias acid, Gamma acid were purchased from Weifang Senya Chemical Company Limited, China and sulphatoethylsulphone was obtained from BASF Germany.

2.1.3 Equipment

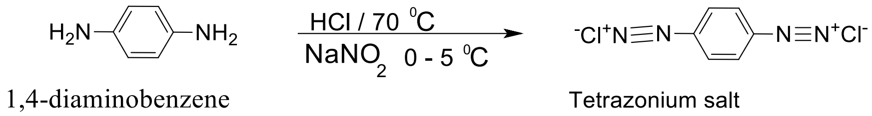
The melting points were determined by open capillary method. The IR and UV-visible absorption spectra were recorded using FT-IR (Perkin-Elmer Spectrum RXIFT-IR Spectrometer and Perkin-Elmer Lambda 25 UV-visible spectrophotometer (at the wavelength of maximum absorption (λ_{max}) at the Kharazmi University, Bureau of International Scientific Cooperation, Department of Organic Chemistry, Tehran, Iran.

2.2 Methods

The synthesis of the bifunctional azo reactive dyes involves four (5) steps which are cyanuration of the acids, condensation of the cyanurated acids, tetrazotisation of the intermadiates, coupling of the tetrazotised intermediates with the condensed cyanurated acids and refluxing with sulphatoethylsulphone (Oforghor et al; 2020)

2.2.1 General procedure for Tetrazotization of Intermediates

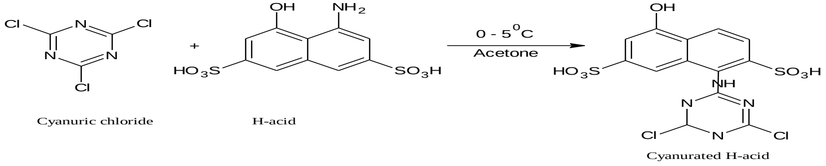
1, 4-benzenediamine (0.54g, 0.005mol) was suspended in distilled water (60ml) and hydrochloric acid (0.36g) was added dropwise to the well stirred suspension. The mixture was gradually heated up to 70°C, till clear solution was obtained. The formed solution was gradually cooled to below 5°C in an iced bath, then already cooled (0-5°C) $NaNO_2$ (0.6g in 4ml H_2O) was added over a period of 30mins with continuous stirring. The stirring was continued for one (1) hour, maintaining the temperature of 0°C-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°C-5°C obtained was used for next coupling reaction. The reaction as shown in the reaction scheme 1 below:



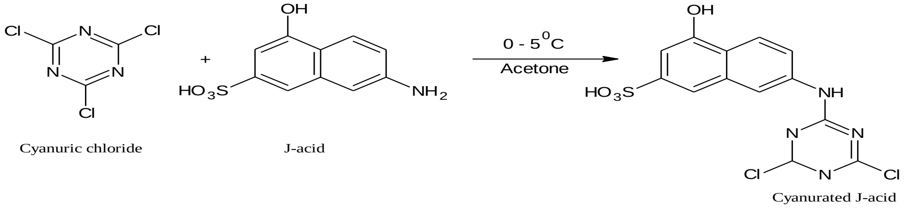
Scheme 1: Tetrazotization of 1, 4’-diaminobenzene

2.2.2 General procedure for cyanuration of the acids

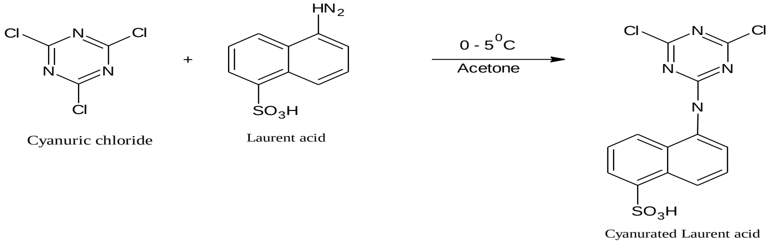
Cyanuric chloride (1.85g, 0.01 mole) was stirred in acetone (25 ml) at a temperature below 5°C for a period of an hour. A neutral solution of H-acid (3.19g, 0.01mole) in aqueous sodium carbonate solution (10% w/v) was then added in small lots about an hour. The pH was maintained neutral by simultaneous addition of sodium carbonate solution (1% w/v). The reaction mass was then stirred at 0-5°C for further 4 hours. The cyanurated H-acid solution was used for subsequent coupling reaction as shown in scheme 2a below. The same procedure (method) was followed to cyanurate J-acid, Laurent-acid, Tobias-acid and Gamma-acid in scheme 2b, 2c, 2d and 2e respectively as shown below.



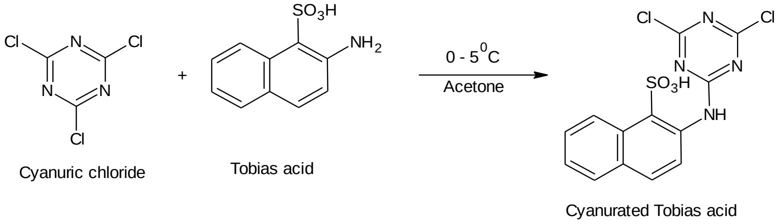
Scheme 2a: Cyanuration of H-acid



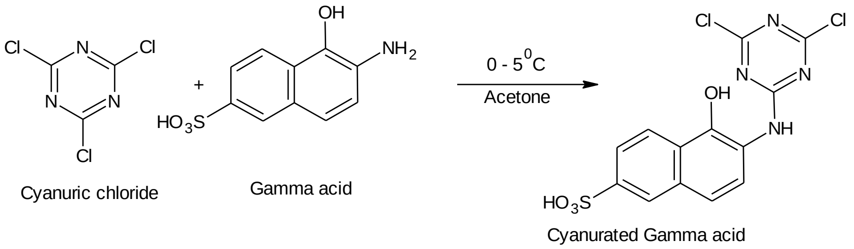
Scheme 2b: Cyanuration of J-acid



Scheme 2c: Cyanuration of Laurent acids



Scheme 2d: Cyanuration of Tobias acid



Scheme 2e: Cyanuration of Gamma-acid

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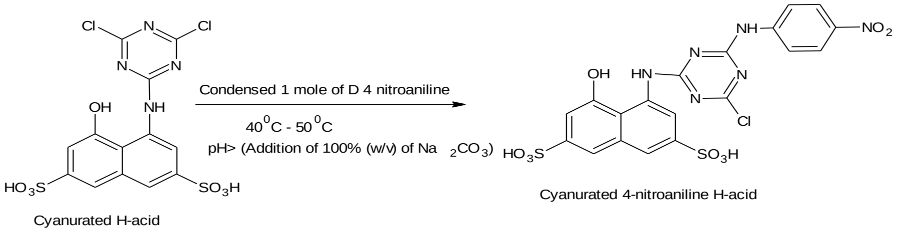
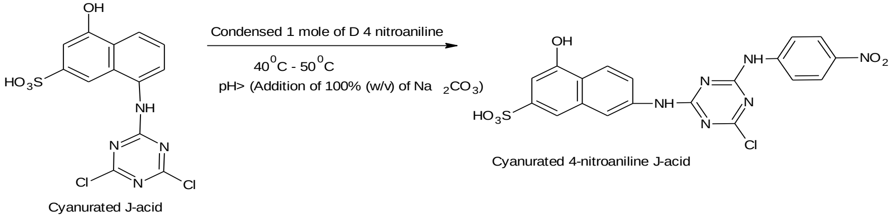
.2.3 General procedure for condensation of the cyanurated acids

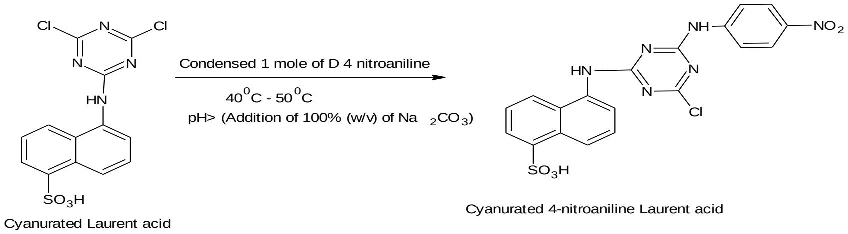
The temperature of ice-cooled well stirred solution of cyanurated H-acid, (4.67 g, 0.01 moles) was gradually raised to 45°C for half an hour. To this cyanurated H-acid, the 4-nitro aniline (1.39 g, 0.01 moles) was added slowly at same temperature, during a period of 30 min, maintaining the pH neutral 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- nitroanilino 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 in scheme 3b (J-acid), 3c (Laurent-acid), 3d (Tobias-acid) and 3e (Gamma-acid) respectively as shown below.



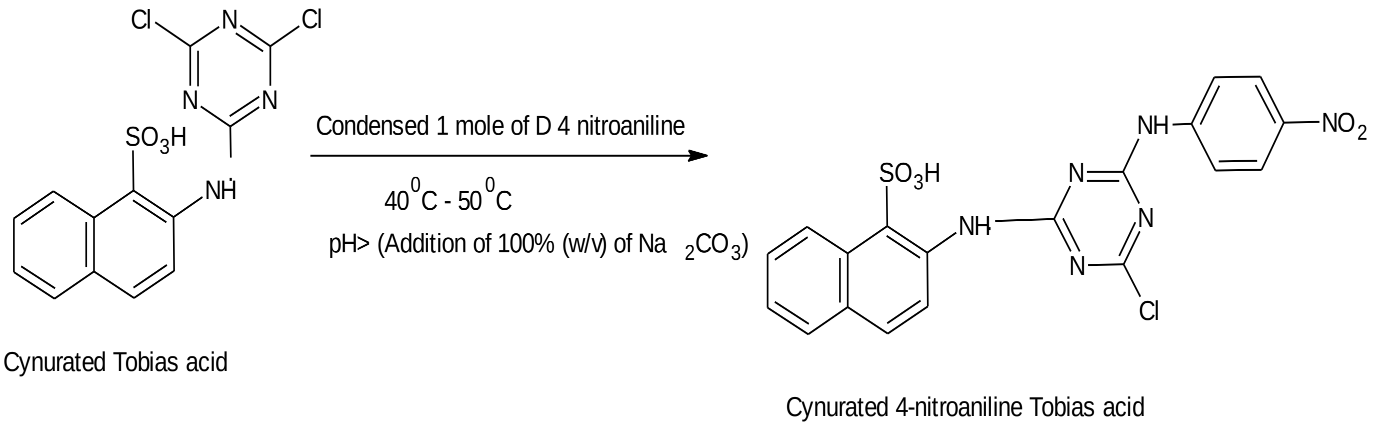
Scheme 3a: Condensation of cyanurated H-acid



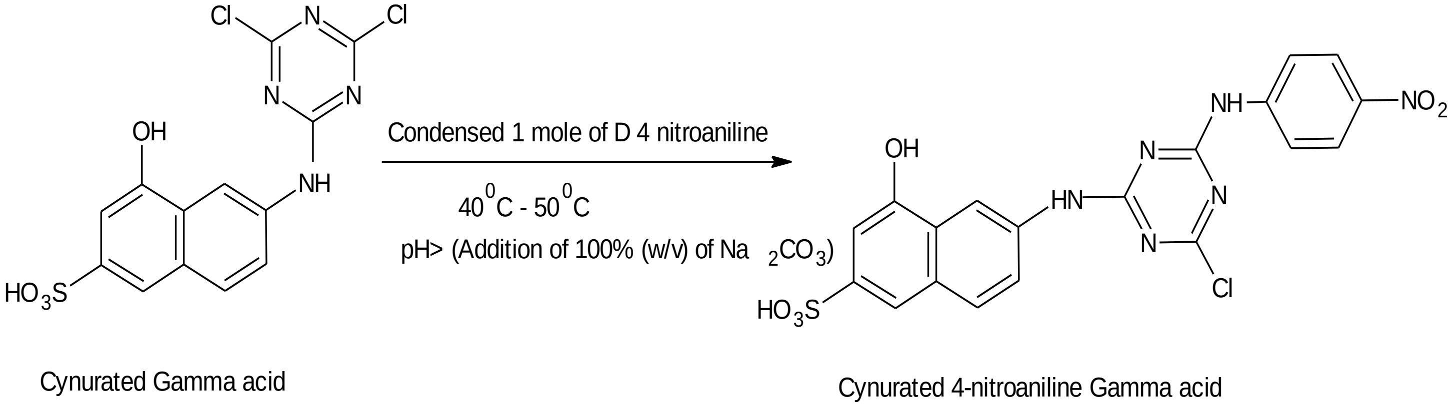
Scheme 3b: Condensation of cyanurated J-acid



Scheme 3c: Condensation of cyanurated Laurent-acid



Scheme 3d: Condensation of cyanurated Tobias-acid

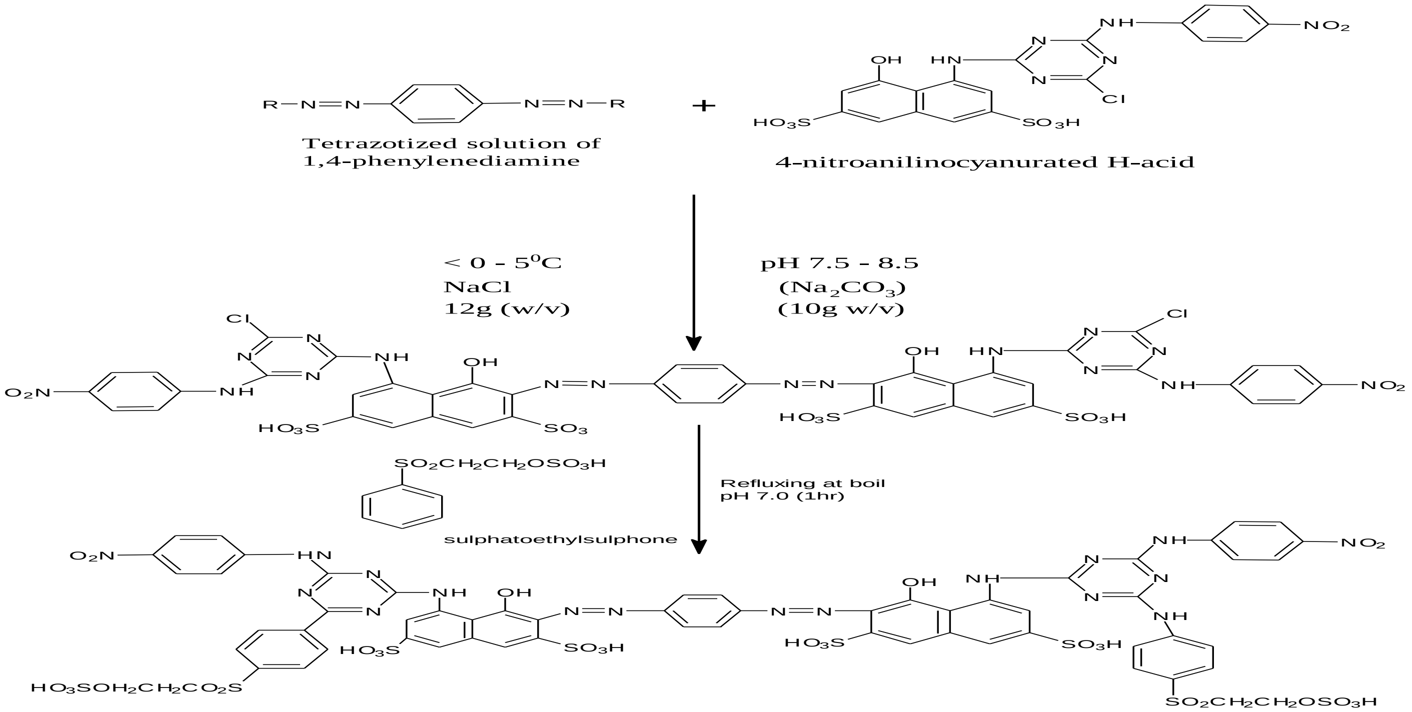


Scheme 3e: Condensation of cyanurated Gamma-acid

2.2.4 Procedure for synthesis of dyes Q1

Dye Q1 was synthesised by addition of the previously prepared fresh tetrazotized solution of 1,4-phenylenediamine dropwise over a period of 10 – 20 minutes to the well stirred ice-cold 4-nitroanilino cyanurated H-acid solution. There was the simultaneous addition of sodium carbonate solutions (Na_2SO_3) (10% w/v) to maintained pH 7.5 – 8.5 and stirring was continued for 3 – 4h at a constant temperature below 0 – 5^0C, then sulphatoethylsulphone (2.86g, 0.01mol) was added dropwise over 15minutes with continuous stirring and reflux at boil for 1h, then salted and stirred for further 1h. The solid precipitate was filtered, washed with little amount of acetone and dried at room temperature to give dye Q1 as shown in scheme 4a.

Following the procedure above the other bifunctional sulphatoethylsulphone (SES) azo reactive dyes Q2 (J-acid, 3b), Q3 (Laurent acid, 3c), Q4 (Tobias acid, 3d) and Q5 (Gamma acid, 3e) as shown in Table 1.



Scheme 4a: Synthesis of dye Q1

3.0 Dyeing of fibres

The synthesized dyes Q1, Q2, Q3, Q4 and Q5 were applied onnylon 6 fabrics using exhaustion method and depth of shade, 2% (Oforghor et al, 2020). A mild alkaline conditions, pH 8.0-9.0 (Na_2CO_3, 0.4ml of 10%w/v) was used for the dyeing ofnylon 6 fabrics while a weakly acidic conditions [(acetic acid-1,5ml of 10%w/v, NaCl-4ml of 10%w/v, distilled water-14.4ml)] was used for the dyeing ofnylon 6 fabrics at 1:50 liquor-ratio for the dyeing of both fabrics

3.1 Dye Exhaustion:

For all dyeing, the dye exhaustion was measured by sampling the dyebath before and after dyeing. The dye concentration (g/l) of the dyebath was measured on Shimadzu UV-2401PC UV/Vis spectrophotometer at □max of the dye. The percentage of dye exhaustion (%E) was calculated using Eqn (1):

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

……………………………….. (1)

where C_1 is the concentration of the dyebath before and C_2 is the concentration of the dyebath after dyeing (Oforghor *et al*., 2020, Burkinshaw *et al*., 2001 and Lewis *et al*., 2000).

3.2 Dye Fixation:

The dye fixation (%F), the percentage of the exhausted dye chemically bound on thenylon 6 fabric, was measured by refluxing thenylon 6 dyed samples in 50% aqueous DMF (20:1 LR) for 15 min to extract the unfixed dye (Burkinshaw, et al., 2001). This procedure was repeated until the extract was colorless. The concentration of the extract was then measured spectrophoto-metrically at the λmax value of each dye and the dye fixation ratio calculated using Eq. 2.

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

……………………………….. (2)

where C_3 is the concentration of extracted dye

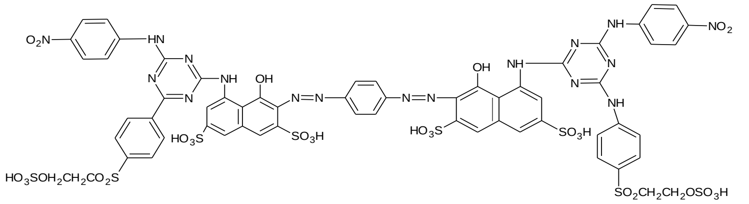
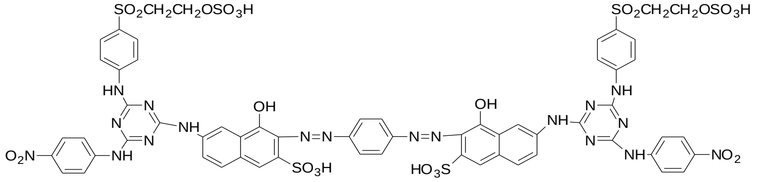
4.0 RESULTS AND DISSCUSSION

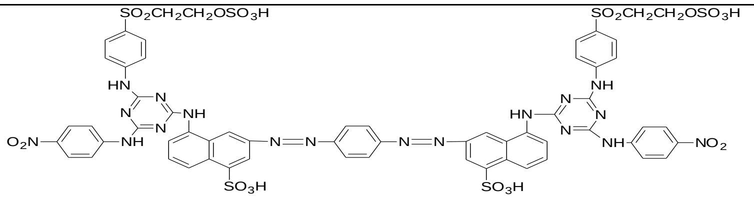
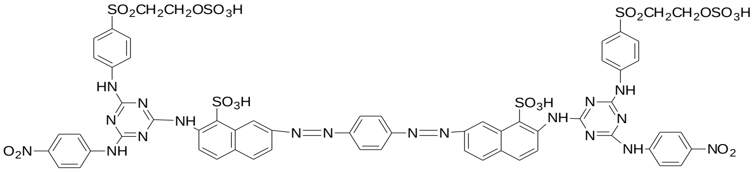
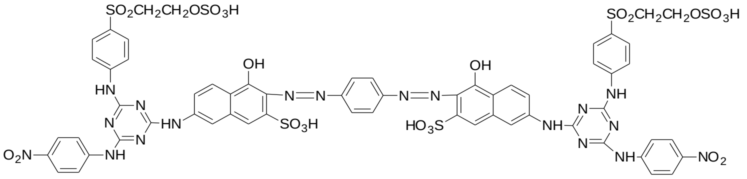
4.1 Dye synthesis

Preparation of Tetrazotised solution of 1, 4-benzenediamine was done by suspending 1, 4-benzenediamine and adding Hcl (0.36g) dropwise with continuous stirring and the temperature raised to 70^{o}C till a clear solution is achieved. The temperature lowed to below O^{o}C-5^{o}C and a solution of already ice cold $NaNO_2$ was added in small lots over 5 minutes with continuous stirring for 1h maintaining same temperature until a clear solution is achieved as shown in scheme 1. Cyanuration of the acids as shown in Schemes 2a-2e was carried out by stirring cyanuric chloride in acetone at a temperature below 0^{o}C-5^{o}C for an hr, then a neutral solution of H-acid [in aqueous solution of $NaCO_3$ (10% w/v)} added in small lots over an hr while maintaining a constant pH by adding 1% w/v $NaCO_3$ at a temperature below 0^{o}C-5^{o}C with continuous stirring for 4h until a clear solution was obtained. In schemes 3a-3e the condensation of the cyanurated acids was carried out by raising the temperature of the ice-cold well stirred cyanurated acids [(H-acid(3a), J-acid(3b), Laurent acid(3c), Tobias acid(3d) and Gamma acid(3e)] gradually to 50^{o}C over 30 minutes, 4-nitroaniline was added in small lots over 30 minutes while maintaining a constant pH by adding 1% w/v $NaHCO_3$ with continuous stirring for 5h to obtain the 4-nitroanilino cyanurated acids.

The dye Q1(3a) was synthesised according the route shown in scheme 4a by adding freshly prepared solution of tetrazotised solution of 1,4-benzenediamine dropwise to an ice-cold well stirred of 4-nitroanilino cyanurated H-acid over a period of 10-15 minutes by maintaining pH at 7.5-8.5 by adding $NaCO_3$ (10%w/v) solution at the same time with continuous stirring for 3-4h at a temperature below 0^{o}C-5^{o}C, then sulphatoethylsulphone (2.81g, 0.01mol) was added dropwise over 15minutes with continuous stirring and reflux at boil for 1h, then salted and stirred for further 1h. The solid violet precipitate was filtered, washed with little amount of acetone and dried at room temperature to give dye Q1. Following the procedure above the other bifunctional sulphatoethylsulphone (SES) azo reactive dyes Q2 (3b), Q3 (3c), Q4 (3d) and Q5 (3e) were synthesised using the various cyanurated coupling components such as J-acid, Laurent acid, Tobias acid and Gamma acid respectively as shown in Table 1.

Table1: Physical characteristics, structures and IUPAC names of the synthesized bifunctional Sulphatoethylsulphone (SES) Azo Reactive dyes

Dye No.	**IUPAC Name**	**Structures of the Synthesized Bi- functional azo reactive Dyes**
Q1	3,3ˈ-(1,4-phenylenebis(diazene-2-1-diyl)bis(4-hydroxy-5-((4-nitrophenyl)amino)-6-((4-((2-(sulfooxy)ethyl)sulfonyl)phenyl)amino)-1,3,5-triazin-2-yl)amino)naphthalene-2,7disulfonic acid)	
Q2	3,3'-(1,4-phenylenebis(diazene-2,1-diyl))bis(4-hydroxy-6-((4-((4-nitrophenyl)amino)-6-((4-((2-(sulfooxy)ethyl)sulfonyl)phenyl)amino)-1,3,5-triazin-2-yl)amino)naphthalene-2-sulfonic acid)	

Q3	3,3'-(1,4-phenylenebis(diazene-2,1-diyl))bis(5-((4-((4-nitrophenyl)amino)-6-((4-((2 (sulfooxy)ethyl)sulfonyl)phenyl)amino)-1,3,5-triazin-2-yl)amino)naphthalene-1-sulfonic acid)	
Q4	7,7'-(1,4-phenylenebis(diazene-2,1-diyl))bis(2-((4-((4-nitrophenyl)amino)-6-((4-((2 (sulfooxy)ethyl)sulfonyl)phenyl)amino)-1,3,5-triazin-2-yl)amino)naphthalene-1-sulfonic acid)	
Q5	3,3'-(1,4-phenylenebis(diazene-2,1-diyl))bis(4-hydroxy-7-((4-((4-nitrophenyl)amino)-6-((4-((2-(sulfooxy)ethyl)sulfonyl)phenyl)amino)-1,3,5-triazin-2-yl)amino)naphthalene-2-sulfonic acid)	

The physical characteristics of the synthesized dyes are shown in Table 2, which indicated that the molecular weight of all the synthesized dyes is on the high side. Oforghor et al.; (2020) reported that high molecular weight dyes generally exhibit high melting points and this agrees with the findings since most of the synthesized dyes have high melting points. From the Table 1, the synthesized dyes recorded high percentage yields which are an indication of careful control of the experimental conditions (Mousa et al., 2014). The the synthesized dyes also exhibit very high solubility which is an indication that the dyes are highly branched and the position of the functional groups in the carbon chains (Oforghor et al., 2023 and Oforghor et al., 2020). The colour and/or hue of the synthesized dyes range from purple, red, pink, due to the nature and presence of functional groups such as -NH_2 and -OH on the dye moiety.

Table 2: Visible Absorption Maxima of the bifunctional Sulphatoethylsulphone (SES) Azo Reactive dyes

Dye No.	**Mol.Wt (g/mol)**	**Mt.Pt (°C)**	**Yield (%)**	**DMF (λmax)**	**Water (λmax)**	**ε_{max}inDMF x$10^4$1Mol^{-1}cm^{-1}**
Q1	1756.05	347-348	56	495	452	6.59
Q2	1596.14	335-337	82	480	480	1.47
Q3	1564.15	325-327	69	461	461	3.27
Q4	1564.15	315-318	74	495	495	1.82
Q5	1596.14	320-322	78	526	526	9.47

The visible absorption spectroscopic properties of the dyes were recorded in DMF and water. From the data reported in Table 2, it is apparent that the λ_{max} value depends on the coupling components used. The colour change observed for each dye is due to the oscillation of electrons and the presence of additional substituent. The shift in λ_{max} of the synthesized 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 (Oforghor et al., 2023). The measuremrnt 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 (Oforghor et al., 2023 and Oforghor et al; 2020). The visible absorption maxima of the synthesised bifunctional azo reactive dyes fall within the visible region (400-700nm) of the electromagnetic spectrum which showed that the synthesised bifunctional azo reactive dyes are colourants with high commercial integrity. The values of the molar extinction coefficient (ε) that were determined by Beer-Lambert's law are in the range of 14705.12-94704.13mol^{-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 Q1, Q2, Q3, Q4 and Q5 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; 2012). However, dye Q1 was obtained by tetrazotising 1,4 benzenediamine and coupling with cyanurated 4-nitroanilino H-acid and refluxing with sulphatoethylsulphone which absorbed at 495nm while Q2 which is obtained by tetrazotising 1,4 benzenediamine and coupling with cyanurated 4-nitroanilino J-acid and refluxing with sulphatoethylsulphone which absorbed at 480nm, in the same solvent hence there was a hypsochromic shift of 15nm. This is attributed to the introduction of additional donor groups onto the coupling component. Dye Q3 was obtained by tetrazotising 1,4-benzenediamine and coupling with cyanurated 4-nitroanilino Laurent acid and refluxing with sulphatoethylsulphone which absorbed at 461nm, dye Q3 shifted hypsochromically by 34nm and 24nm when compared with Q1 and Q2 respectively. When cyanurated 4-nitroanilino Tobias acid was employed as the coupling component and couple with a solution of tetrazotising 1,4 benzenediamine and refluxing with sulphatoethylsulphone, dye Q4 which absorbed at 495nm. Comparing dye Q4 with dye Q1, Q2 and Q3, there was 0nm shift for Q1, 15nm bathochromic shift for Q2 and 34nm bathochromic shift for Q3 respectively. Dye Q5 was obtained by tetrazotising 1,4 benzenediamine and coupling with cyanurated 4-nitroanilino Gamma acid and refluxing with sulphatoethylsulphone which absorbed at 526nm, comparing dye Q5 with dye Q1, Q2 , Q3, and Q4, all the dyes shifted bathochromically 31nm for Q1, 40nm for Q2, 45nm for Q3 and 31nm for Q4 respectively. All the shifts experienced are as a result of introduction of electron donating groups or electron withdrawing groups in the dye moiety.

Table 3: FT- IR of the bifunctional Sulphatoethylsulphone (SES) Azo Reactive dyes

Dye No.	Mol. Formular	Mol. Wt	Yield (%)	Melting Point	FT-IR cm^{-1}
Q1	$C_{60}H_{49}N_{18}O_{30}S_8$	1756	56	347-348	3501 (O-H str. vibr.), 3441 (N-H str vibr.), 3070 (C-H str vibr.), 1550 (N=N str vibr.), 1420 (C-N str vibr.), 1650 (N-H bend. vibr.), 1021 (S=O str vibr.), 1325 (N=O str vibr.), 841 (SO_3H str vibr.)
Q2	$C_{60}H_{48}N_{18}O_{24}S_6$	1596	82	335-337	3439 (O-H str vibr.), 3371 (N-H str vibr.),

					3073 (C-H str vibr.), 1597 (N=N str vibr.), 1366 (C-N str vibr.), 1600 (N-H bend. vibr.), 1046 (S=O str vibr.), 1301 (N=O str vibr.), 835 (SO_3H str vibr.)
Q3	$C_{60}H_{48}N_{18}O_{22}S_6$	1564	69	325-327	3398 (O-H/N-H str vibr.), 2955(C-H str vibr.), 1597(N=N str vibr.), 1498 (C-N str vibr.), 1650 (N-H bend. vibr.), 1229 (S=O str vibr.), 1329 (N=O str vibr.), 851 (SO_3H str vibr.)
Q4	$C_{60}H_{48}N_{18}O_{22}S_6$	1564	74	316-318	3442 (O-H/N-H str vibr.), 2919 (C-H str vibr.), 1329 (N=N str vibr.), 1460 (C-N str vibr.), 1597 (N-H bend. vibr.), 1134 (S=O str vibr.), 1304 (N=O str vibr.), 828 (SO_3H str vibr.)
Q5	$C_{60}H_{48}N_{18}O_{24}S_6$	1596	78	320-322	3395 (O-H str vibr.), 3325 (N-H str vibr.), 3026-2990 (C-H str vibr.), 1595 (N=N str vibr.), 1420 (C-N str vibr.), 1605 (N-H bend. vibr.), 1025 (S=O str vibr.), 1335 (N=O str vibr.), 848-840 (SO_3H str vibr.)

The Infra-red Spectral of all the dyes Q1, - Q5 revealed that O-H and N-H showed stretching vibration at 3561cm-^{1}-3371 cm-^{1}, C=H showed stretching vibration at 2955cm-^{1}, C-N showed stretching vibration at 1574cm-^{1}, 1305cm-^{1}, 1464cm-^{1}, N=N showed stretching vibration at 1597cm-^{1}, S=O showed stretching vibration at 1150cm-^{1}, 1060cm-^{1} (asym. And sym), N=O showed stretching vibration at 1495cm-^{1}, 1411cm-^{1}, 1335cm-^{1}, C-Cl showed stretching vibration at 784cm-^{1} and SO_3H showed stretching vibration at 841cm-^{1} respectively as showed in Table 3.

Table 4: **^{1}HNMR** of the bifunctional Sulphatoethylsulphone (SES) Azo Reactive dyes

Dye No.	**^{1}HNMR**
Q1	3.64 (2H, S, α –CH_2), 3.81 (4H, S, –NH), 3.92 – 3.94 (2H, S, β –CH_2), 4.64 (2H, S, –OH), 7.06 – 8.34 (38H, m, Ar –H), 8.60 (1H, S, SO_3H)
Q2	3.63 (2H, S, α –CH_2), 3.81 (4H, S, –NH), 3.92 – 3.94 (2H, S, β –CH_2), 4.64 (2H, S, –OH), 7.06 – 8.34 (37H, m, Ar –H), 8.60 (1H, S, SO_3H)
Q3	3.63 (2H, S, α –CH_2), 3.66 (4H, S, –NH), 3.91 – 3.93 (2H, S, β –CH_2), 7.06 – 8.34 (39H, m, Ar –H), 8.60 (1H, S, SO_3H)
Q4	3.63 (2H, S, α –CH_2), 3.65 (4H, S, –NH), 3.91 – 3.93 (2H, S, β –CH_2), 7.06 – 8.34 (39H, m, Ar –H), 8.60 (1H, S, SO_3H)
Q5	3.63 (2H, S, α –CH_2), 3.66 (4H, S, –NH), 3.92 – 3.94 (2H, S, β –CH_2), 4.84 (2H, S, –OH), 7.06 – 8.34 (37H, m, Ar –H), 8.60 (1H, S, SO_3H)

The ^{1}H-NMR spectral for dyes showed signals (singlet) at 3.64 δ ppm which confirmed the presence of methylene (–CH) protons, 4.84 δ ppm due to the presence of hydroxyl groups (–OH), 3.92-3.94 δ ppm confirmed the presence of methylene (-CH_2) protons, 3.64 δ ppm which confirmed the presence of amino (-NH_2) protons, 7.06-8.34 δ ppm due to the presence of aromatic (Ar-H) protons, 8.60 δ ppm because of the presence of sulphonate (-SO_3H) groups.

Table 5: Mass Spectroscopy data for bifunctional sulpathoethylsulphone azo reactive dyes Q1 – $Q2_0$

Dye No.	**Empirical formular**	**Experimental values of m/z fragment**	**Corresponding positive charge fragment**	**Theoretical value**
Q1	$C_{60}H_{49}N_{18}O_{30}S_8$	46.0, 76.0, 107.2, 318.1, 374.0, 1757.2	NO_2^+, $C_6H_4^+$, $C_6H_8N_2^+$, $C_7H_6N_3O_2S_2^+$, M	1757
Q2	$C_{60}H_{48}N_{18}O_{24}S_6$	46.0, 76.0, 108.1, 239.1, 373.0, 1596.1	NO_2^+, $C_6H_4^+$, $C_7H_6N_3O_2S^+$, $C_6H_8N_2^+$, $C_{10}H_9NO_4S^+$, M	1596
Q3	$C_{60}H_{48}N_{18}O_{22}S_6$	46.0, 76.0, 108.2, 222.1, 374.1, 1564.3	NO_2^+, $C_6H_4^+$, $C_7H_6N_3O_2S^+$, $C_6H_8N_2^+$, $C_{10}H_4NO_3S^+$, M	1564
Q4	$C_{60}H_{48}N_{18}O_{22}S_6$	46.0, 76.0, 107.1, 223.2, 374.3, 1564.2	NO_2^+, $C_6H_4^+$, $C_7H_6N_3O_2S^+$, $C_6H_8N_2^+$, $C_{10}H_9NO_3S^+$, M	1564
Q5	$C_{60}H_{48}N_{18}O_{24}S_6$	46.0, 76.0, 107.3, 240.2, 374.1, 1596.2	NO_2, C_6H_4, $C_7H_6N_3O_2S^+$, $C_6H_8N_2^+$, $C_{10}H_9NO_4S^+$, M	1596

The mass spectrum MS for dye Q1 analysis revealed a fragmentation pattern of NO_2^+, $C_6H_4^+$, $C_7H_6N_3O_2S_2^+$, $C_6H_8N_2^+$, $C_{10}H_8NO_7S_2^+$, which indicates molar masses of 46.0, 76.0, 107.2, 318.1, 374.0 g/mol respectively. The mass spectrum showed a molecular ion (M^+) at m/z 1757.2 g/mol and this is in agreement with the molecular mass 1756.1 g/mol of the synthesised dye Q1. All these differences arise due to bridging groups, chromophores, coupling components and reactive systems. The mass spectrum MS for dye Q2 analysis revealed a fragmentation pattern of NO_2^+, $C_6H_4^+$, $C_7H_6N_3O_2S^+$, $C_6H_8N_2^+$, $C_{10}H_9NO_4S^+$, which indicates molar masses of 46.0, 76.0, 108.1, 239.1, 373.0 g/mol respectively. The mass spectrum showed a molecular ion (M^+) at m/z 1596.1 g/mol and this is in agreement with the molecular mass 1596.1 g/mol of the synthesised dye Q2. All these differences arise due to bridging groups, chromophores, coupling components and reactive systems. The mass spectrum MS for dye Q3 analysis revealed a fragmentation pattern of NO_2^+, $C_6H_4^+$, $C_7H_6N_3O_2S^+$, $C_6H_8N_2^+$, $C_{10}H_4NO_3S^+$, which indicates molar masses of 46.0, 76.0, 108.2, 222.1, 374.1 g/mol respectively. The mass spectrum showed a molecular ion (M+) at m/z 1564.3 g/mol and this is in agreement with the molecular mass 1564.2 g/mol of the synthesised dye Q3. All these differences arise due to bridging groups, chromophores, coupling components and reactive systems. The mass spectrum MS for dye Q5 analysis revealed a fragmentation pattern of NO_2, C_6H_4, $C_7H_6N_3O_2S^+$, $C_6H_8N_2^+$, $C_{10}H_9NO_4S^+$, which indicates molar masses of 46.0, 76.0, 107.3, 240.2, 374.1 g/mol respectively. The mass spectrum showed a molecular ion (M+) at m/z 1596.2 g/mol^{-}and this is in agreement with the molecular mass 1596.1 g/mol of the synthesised dye Q5. All these differences arise due to bridging groups, chromophores, coupling components and reactive systems.

Table 6: Exhaustion and fixation study of the bifunctional Sulphatoethylsulphone (SES) Azo
Reactive dyes onnylon 6 fabric

		Exhaustion (%)	**Fixation (%)**
Dye No	**Shade onnylon 6 fabric**	**wool fabric**	**Wool fabric**

Q1	Brown	85	72
Q2	Orange	65	70
Q3	Yellow	72	85
Q4	Orange	65	65
Q5	Yellow	62	72

The percentage exhaustion of 2% dyeing on nylon 6 fabric give maximum exhaustion of 85% and minimum exhaustion of 62%,. The percentage fixation of 2% dyeing on nylon 6 fabric give a maximum fixation of 85% and minimum fixation of 65% as showed in Table: 6.

Table 7: Fastness performance properties of the bifunctional Sulphatoethylsulphone (SES)
Azo Reactive dyes on nylon 6 fabrics

			Perspiration fastness	
Dye No	**Wash fastness nylon 6**	**Light fastness nylon 6**	**Alkaline nylon 6**	**Acidic nylon 6**
	cc	Cc	Cc	Cc
Q1	4	5-6	3-4	4
Q2	4-5	5-6	3-4	3-4
Q3	4-5	4	3-4	4
Q4	4	4-4	3-4	4
Q5	4-5	5	3-4	3-4

cc=colour change

Fastness properties to washing: 1-poor, 2-moderate, 3-fair, 4-very good, 5-excellent

Fastness properties to light: 1-poor, 2-slight, 3- moderate, 4- fair, 5- good, 6- very good,

Fastness properties to perspiration – alkaline and acidic: 1-poor, 2-fair 3-good, 4-very good

The light fastness was study according to the procedure of Oforghor et al., (2023) and Oforghor et al; (2020). The wash fastness test in accordance with IS: 765-1979. The wash fastness of all the dyes showed good to excellent on nylon 6 fabrics. The light fastness of all the dyes showed moderate to good on nylon 6 fabrics and the perspiration fastness (acidic and alkaline) of all the dyes showed good to excellent perspiration fastness on nylon 6 fabrics.

CONCLUSION

Bifunctional Sulphatoethylsulphone (SES) azo reactive dyes were synthesised with 4- nitroanilino cyanurated acids- (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) as coupling components and reacting with tetrazotised solutiuon of 1,4-benzenediamine. However, the visible absorption spectra of the dyes showed maximum absorption (λ_{max}) in the range of 400-700nm. The dyes recorded brown. Purple, orange and yellow colours onnylon 6 fabrics. The difference in colour of the dyes may be attributed to both the nature and position of the substituent. The dyes gave a satisfactory performance of exhaustion and fixation efficiency onnylon 6 fabrics. The fastness properties to washing, fastness properties to light and fastness properties to perspiration – alkaline and acidic of the dyes onnylon 6 fabrics showed good to excellent performance.

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