ChemSearch Journal 5(1): 21 – 26, June, 2014
Publication of Chemical Society of Nigeria, Kano Chapter

Received: 11/02/2014 Accepted: 28/05/2014

Synthesis and Characterization of Some Mono Chloro-S- Triazine Vinyl Sulphone Reactive Dyes

Nadabo, N. A.
Department of Chemistry, Federal College of Education, Kano.
Email: nuradeennadabo@yahoo.com

ABSTRACT

A series of ten bifunctional mono-chloro-s-triazine vinyl sulphone reactive dyes were synthesized based on H-acid with varied substituents coded as (BRD). These dyes were characterized by IR spectroscopy. The results revealed an incorporation of various substituents. The visible absorption spectra of these dyes were examined in various solvents and results shows positive and negative salvatochromism as the solvent polarity; changes, melting point, percentage yield and molar extinction co-efficient of these dyes were also evaluated and the results obtained are within a reasonable range acceptable for commercial dyeing.

Keywords: Bifunctional Reactive Dyes, Characterization, Synthesis

INTRODUCTION

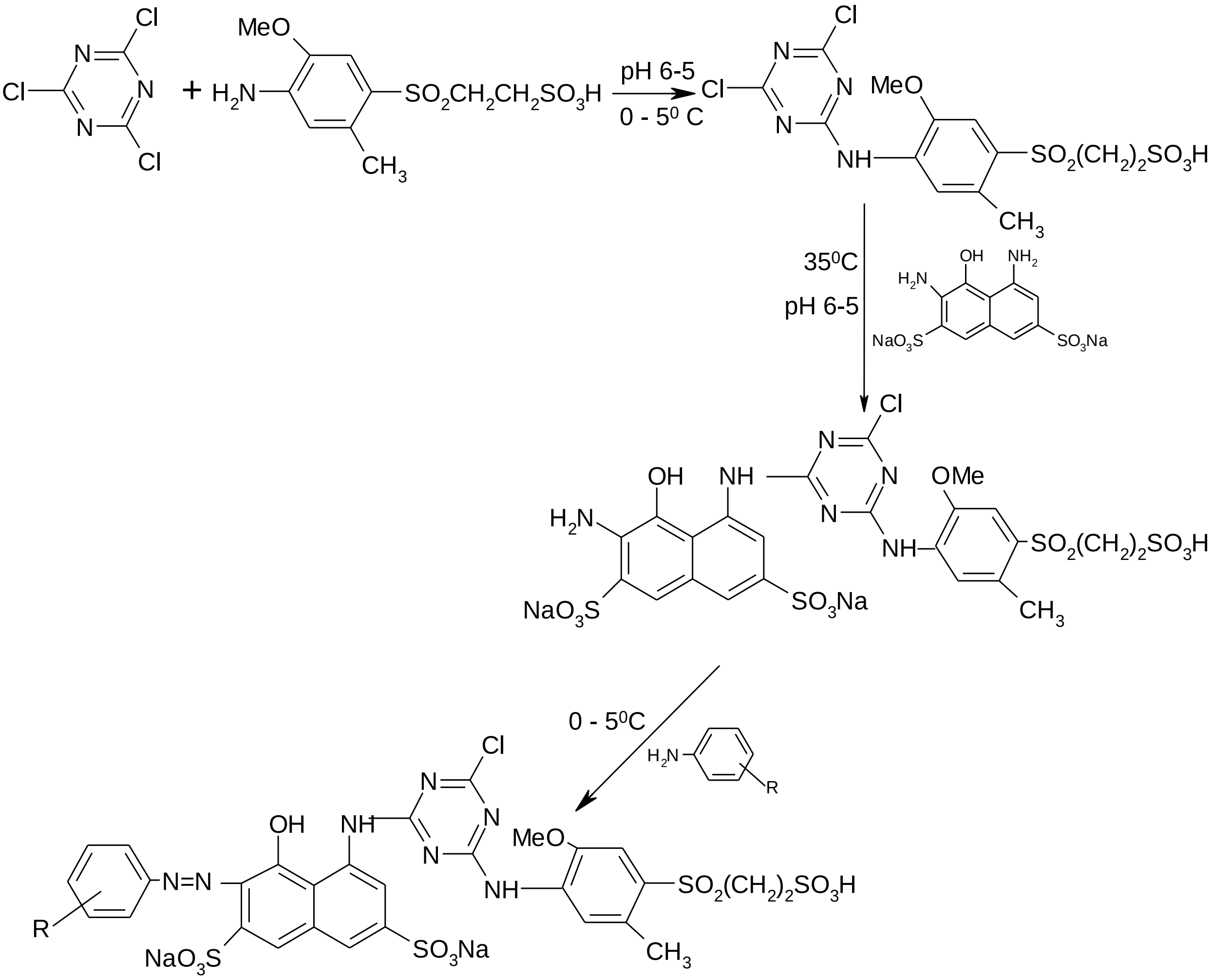
The vinyl sulphone bifunctional reactive dyes that carry two reactive groups are known for their excellent dyeing efficiency and overall fastness properties (Dalai and Desai, 1996). An essential condition for the utilization of these azo dyes is that they are very stable during washing and in light. They are also very resistant to |the microbial attack since these colorants are bonded covalently with textile fiber. A large number of reactive dyes are azo compounds that are linked by an azo bridge (Chatwal, 1990; Venkataraman, 1974).

Moreover, the use of bifunctional reactive dyes (BRD) is rapidly growing because of their improved physicochemical properties during usage. In recent years reactive dyes have been most commonly used due to their advantages such as better dyeing processing conditions, bright colours and superior fastness properties (Warring and Hallas, 1990; Zollinger and Rys, 1981).

The aim of this research work is to synthesize new bifunctional reactive dyes that carry monochloro-s-triazine and sulphato ethyl reactive system based on H-acid with systematically varied substituents and also to examine their possible application to cellulose or polyamide fabrics.

MATERIALS AND METHODS

All the reagents and solvents used were of analytical grade, hence used as supplied. Cyanuric chloride (1.9504g, 0.0106M) was stirred with acetone (40cm^3) and water (10cm^3) for 1hr to form a fine suspension at the temperature of (0° - 2°C) and a neutral solution of H-acid was added (3.18g, 0.01 mole) along with 20cm^3 concentrated sodium bicarbonate solution (10% w/v) in such a way that the temperature did not exceed a level above 5°C. To the above mixture, a solution of 2-methoxy -5-methyl- 4- (β-sulphato ethyl) sulphonyl aniline (3.18g, 0.098M) in (10cm^3) water was added. The mixture was stirred for 30min at 0 -5°C. The temperature of the mixture was gradually raised to 35°C, adjusting the pH to 7.5. The mixture was stirred for 3 hrs, filtered, washed with cold water. The resultant product was coupled with the diazotized substituted anilines (Dalai and Desai, 1996). Dyes containing sulphonic acid groups were salted out by adding 20% NaCl solution and then dried at 60°C in an oven overnight (Scheme 1).



Where:

R = COOH	R = SH	R = CL	R = CH_3
R = H	R = OH	R = SO_3H.	R = OCH_3

Scheme 1: Synthetic Route for the Intermediates and Dyes

i) Determination of molecular weight of the dyes

The molecular weight of the dyes synthesized were calculated from the structure of the dyes obtained.

ii) Determination of mass of dyes and percentage yield of dyes.

Each of the dyes produced was weighed using a weighing balance and the mass of each of the dye obtained.

$$\%\ \text{yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$$

iii) Melting points of the synthesized dyes were carried out using Galenkam melting point apparatus. A small quantity of each of the dye was put in a capillary tube and inserted into the melting point apparatus and the temperature at which the dye melted was recorded.

iv) Measurement of absorption spectra of the dyes.

The peaks of maximum absorption wavelength (λ_{max}) were determined using a digital Jenway U.V. spectrophotometer. The lambda $_{max}$ of the dyes was measured in distilled water a known quantity of the dye samples was dissolved in known volume of water. The solution was then scanned from 400-

800nm. Beer's - Lambert law was used to determine the molar absorptivity coefficient.

v) Determination of extinction coefficient; The molar extinction coefficient of each dye was calculated at each dye absorption maximum (λ_{max}) as well as their concentration at these points was observed by using the formular below

$\varepsilon = A/C\,L$

Where ε = Molar extinction coefficient ($dm^3\ mol^{-1}\ cm^{-1}$)

A = Absorption at λ_{max}

C = concentration in mol/dm

L = path length of cell (1cm)

vi) I.R. spectra measurements of each of the synthesized dyes were carried out on Shimadzu I. R prestige 21FTIR 84005 models at NARICT Zaria

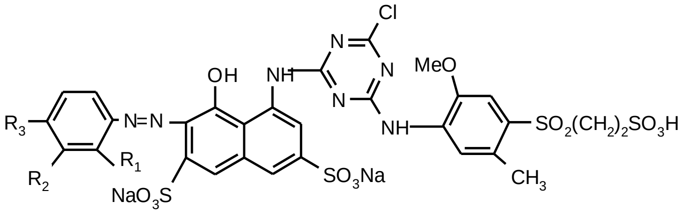
vi) The principal method of forming azo dyes; involves diazotization of primary amines, followed by coupling with hydroxyl or amino derivatives of aromatic hydrocarbons (Abrahat, 1977).

vii) Diazotization; Diazotization simply means formation of diazonium salts Primary aromatic amine on reaction with nitrous acid (HONO) in the presence of hydrochloric acid (or other mineral acid) at 0 – 5°C yields diazonium salts as discrete intermediate (Vishnoi,1979).

$$Ar\text{—}NH_2 + NaNO_2 + 2HCl \rightarrow Ar\text{—}N{\equiv}NCl + NaCl + H_2O$$

RESULTS AND DISCUSSION

Table 1: Structures of the Dyes Synthesized

Basic Structures	Dye no	RR_1	R_2	R_3
	1	H	H	H
	2	Cl	H	H
	3	H	H	CL
	4	H	H	OH
	5	H	COOH	H
	6	H	H	SO_3H
	7	H	CH_3	H
	8	H	H	CH_3
	9	COOH	H	H
	10	H	H	OCH_3

Physical Characteristic of the Dyes

Table 2 summarizes, the physical properties of the dyes synthesized in BRD series. It was observed that the physical appearances of the dyes in these series are red, orange, purple and violet respectively. The percentage yield obtained ranged between 32 to 70% which is satisfactory. The melting point of the synthesized dyes is within a reasonable range.

Table 2: Molar mass and Physical Characteristics of the Dye in BRD Series

Dye No.	Dye structures	Molar Mass	M.Pt °C	%Yield	Colour of Crystals
1		887	300	45	Orange
2		922	290	32	Purple
3		903	293	70	Purple
4		922	295	43	Violet
5		931	300	50	Purple
6		967	305	60	Red
7		901	295	45	Red
8		901	299	50	Violet
9		931	300	62	Red
10		978	298	63	Violet

The Molar Extinction Coefficient of the Dyes

Generally dyes in the BRD series their molar extinction coefficient rages between 5.305 x 10^4 to 7.950 x 10^4 which is satisfactory and within the range acceptable for commercial dyes ($\geq 1 \times 10^4$). The extinction coefficients of these dyes are higher which may be due to higher probability of the transition taking place in the azo chromophore (Bello and Ajayi 1997). The results are shown in Table 3.

Table 3: Molar Extinction Coefficient of the Dyes in BRD Series

Dye	Dye structures	λ_{Max} (nm) In water	Absorbance (Optical density)	Extinction coefficient $dm^3 mol^{-1} cm^{-1}$
	1	506	1.423	7.11 *x* 10^4
	2	499	1.499	7.495 *x* 10^4
	3	510	1.306	6.530 *x* 10^4
	4	400	1.082	5.410 *x* 10^4
	5	540	1.061	5.305 *x* 10^4
	6	494	1.590	7.950 *x* 10^4
	7	490	1.635	8.175 *x* 10^4
	8	594	1.125	5.625 *x* 10^4
	9	500	1.298	6.490 *x* 10^4
	10	510	1.285	6.425 *x* 10^4

The UV Visible spectroscopic Properties of the Dyes

A number of literature citation are available for the studies of simple organic molecules with regard to their interaction in different solvents (Reichardt, 1991). Dye molecules on the other hand are complex organic molecules which might carry charge as an integral part of their structures and are then prone to absorption changes in various solvents (Bevilaqua, et al 2006). visible absorption spectra of the dyes were found to exhibit a strong solvent dependence which did not show a regular variation with dia-electric constant of the solvent. Dye BRD_1absorbed at 500nm in acetone and when chloro group was introduced into diazo component (aniline) the resulting dye BRD_2 absorbed at 550nm in the same solvent and thus there is a red shift of about 50nm because CL group is an electron withdrawing substituents which gives better conjugation of the π electron system, electron withdrawing substituents destabilizes the cation and then decreases the basicity on the nitrogen atom (Griffiths,1976).Hence dye BRD_2 was hypsochromic by 50nm when compared with dye BRD_1.Introduction of chloro group in the para to the azo group into diazo component in the case of dye BRD_3 gave absorption at 557nm red shift of 7nm compared to dye BRD_2 which contains chloro group at meta position.Bathochromic shift is usually achieved by placing the substituents in the position ortho or para to the azo group for effective conjugation (Mishra, et al 2001).When hydroxyl group an electron donating substituents is introduced into aniline diazo coupling component dye BRD_4 absorbed at 570nm,but when the hydroxyl group was replaced by a carboxyl acid group at meta position dye BRD_5 absorbed at 540nm a hypsochromic shift of 30nm when campared with dye BRD_4. This gives a blue shift of 30nm, this could be due to steric hindrance caused by newly introduced carboxylic acid group on the existing chromophore because electron system conjugate best when the molecules is planar in configuration. Therefore prevention of planarity in configuration of the dye molecules by the auxochrome group altered the visible absorption band and could be responsible for the hypsochromic shift. Dye BRD_6 which contains sulphonic acid group an electron withdrawing substituent absorbed at 495nm but when the sulphonic group was replaced by a methyl group an electron donating substituent dye BRD_7 absorbed at 490 this indicated ahypsochromic shift of 4nm. Similarly dye BRD_{10} with a methoxy at para position absorbed at 570nm a bathochromic shift of 80nm was observed compared to dye BRD_7 in the same solvent. Para substituents gives effective conjugation hence leads to the bathochromic shift.

The effect of solvent polarity on the visible absorption spectra was also studied and from the results summarized in Table 4, there is small increased in λ max as the solvent is changed to a more polar solvent e.g. dye BRD_1 absorbed at 505nm in D.M.F. and gave a λ max of 500nm in acetone which is bathochromic shift by 5nm similarly dye BRD$_2$ absorbed at 550nm in acetone and gave a λ max of 560nm in D.M.F. which is also a red shift by 10nm. The interaction of solvent with a solvent with a dye molecules is greater in polar solvents.Generally in many dye molecules, the ground state is less polar than the excited state so that polar solvents will tend to stabilize the excited state more than the ground state leading to a bathochromic shift in absorption maximum(Griffiths, 1976).Acetone which is less polar, can interact with the dye molecules in terms of dipole-dipole interactions there by resulting in a net stabilization of the ground state of the dye molecules and hence one sees a hypsochromic shift in the spectrum in this solvent.

Most of the dyes showed positive and negative salvatochromism when the solvent was changed to a more polar one. Similarly, the effect of addition of few drops of HC1 on the ethanolic solution of dyes showed positive and negative halocromism as can be seen in the results in Table 4.

Table 4: The UV Spectroscopic Properties of Dyes in BRD, Series.

Dye No	Dye structures	Acetone λ_{Max} (nm)	DMF λ_{Max} (nm)	Ethanol λ_{Max} (nm) a	Ethanol + Conc HCl b	Change in λ_{Max} (nm) (b – a)
1		500	505	510	506	- 4
2		550	560	568	570	+2
3		557	559	564	569	+5
4		570	577	580	560	- 20
5		540	549	555	562	+7
6		495	500	520	517	-3
7		490	499	509	518	+9
8		494	505	520	523	+3
9		500	505	515	521	+6
10		570	580	590	582	-8

Infra-red Spectra of the Dyes

As can be seen from the infra-red spectra results in Table 5 all the dyes absorption peaks due to Azo group, N=N Stretching vibration at 1362-1493cm^{-1}. Aromatic C-H Stretching vibration bands appeared in the region 2924-3085cm^{-1}. Aromatic C-H bending vibration bands appeared in the region of 731-876cm^{-1}. C=C Stretching vibration bands appeared in the region 1526-1656cm-^{1} C-N Stretching vibration bands appeared in the region 1738-1773cm-^{1} N-H Stretching vibration also appeared in the region 3284-3286cm-^{1} and N-H bending vibration appeared in the region 1400-1592cm-^{1}. Carboxylic group stretching vibration appeared in the region 3072- 3254cm^{1}. C-CL Stretching vibration appeared in the region 631-682cm-^{1}. C-S0$_3$H vibration appeared in the region 1193-1220cm^{-1}. O-H Stretching vibration bands appeared on the region between 3362-3490cm-^{1} while the C-O bending vibration bands appeared in the region 1035-1048cm-^{1}.

Table 5: Infra-red Spectra for the Dyes in BRD series

Function Group	Azo	N=N	Aromatic C-H	Aromatic C-H	C=C	C=N	N-H	N-H	COOH	C-CL	$C\text{-}SO_3H$	O-H	O-H
Types of vibration Dye No.	Str		Str	bend	Str	Str	Str	bend	Str	bend	Str	Str	bend
1	1362	2987	761	1627	1784	3248	1562	-	662	1193	3423	1362	1046
2	1409	2958	762	1606	1744	3286	1489	-	651	1202	3426	1318	1035
3	1493	2957	749	1567	1738	3262	1567	-	631	1215	3455	1392	1037
4	1479	-	769	1592	-	3184	1592	-	628	1220	-	1313	1037
5	1397	3072	754	1546	1763	3272	1546	-	678	1220	3362	1362	1036
6	1411	3065	731	1656	1773	3392	1594	3254	-	1213	3490	-	1048
7	1391	3053	874	1546	1763	3053	-	-	664	1218	3386	1391	1037
8	1424	2930	753	1656	1765	3255	1424	-	-	1226	3394	1424	1037
9	1400	2940	749	1666	1757	3234	1400	3070	673	2550	3380	-	1035
10	1401	2924	755	1656	1773	3247	1560	-	664	2553	3387	1401	1046

CONCLUSION

Ten mono azo bifunctional reactive dyes were synthesized. The dyes show bright intensive colours and their structures were confirmed by UV-visible and FT-IR spectroscopy. The melting point, percentage yield and molar extinction coefficient of these dyes are within a reasonable range acceptable for commercial dyes. It is recommended that the dyeing performance of these dyes should be investigated on cellulose and polyamide fabrics.

REFERENCES

Abrahat, E.N. (1977). *Dyes and their Intermediate.* Edward Arnold Publishers Ltd.,. Pp 48-60.

Bello K.A and Ajayi, J.O (1997). Fixation characteristics of carboxylated dyes on Polyamide. *Journal of Society of Dyers and Colourist*. 113:131-135.

Bevilaqua,T., Goncalves,T.F.,Venturi,C.G.,Machado,V. G.,(2006);Solute-solvent and London Solvent-Solute Interactions in the Preferential Salvation of 4-(4-dimethyl amino styrl)-1-methyl Pyridinium Iodide in 24 Binary Solvent Mixture. *Spectochim Acta Part A*.65:535-542.

Chatwal, G.R. (1990). *Synthetic Dyes*. Himalaya Publishing House Bombay India. Pp. 34 – 38.

Dalal, M.M. and Desai, K.R. (1996). Dyeing effect of Bifunctional Reactive Dyes on Knitted cotton fabrics. *Journal American Dye Stuff Reporter*. 22 – 24.

Griffiths, J. (1976); *Colour and Constitution of Organic Molecules.* London Academic press pp,172.

Mishra, A .Behera, R.K. Behera, P.K. Mishra, B.K. Behera, G.B. (2001); Cyanines During The 1990s. *Areview Chem. Rev*, 100.

Reichard, C. (1991);Solvent and solvents effect on Si-H stretching bonds of substituted silanes.*Spectochim Acta Part A.*65:542-565.

Venkataraman, K. (1974). *The Chemistry of Synthetic Dyes.* Academic Press, New York Pp. 120 – 130.

Vishnoi, N.K. (1979). *Advanced Practical Chemistry*. Vikas Publishing House Ltd. Pp. 341 – 343.

Warring, D.R. and Hallas, G. (1990). *Chemistry and Application of Dyes*, Plenum Press. New York Pp. 61, 107.

Zollinger, H. and Rys, P. (1981). *Fundamental of the Chemistry and Application of Dyes.* 124 – 140.