

Synthesis and Study of some Amino Derivatives of Triazinyl Stilbene Series as Fluorescent Whitening agents

M. A. AHMED*, A. ALEEM, M. Q. SIDDIQUI AND J. MUGHAL
PCSIR Laboratories, Karachi, Pakistan

(Received 25th August, 2005, revised 25th January, 2006)

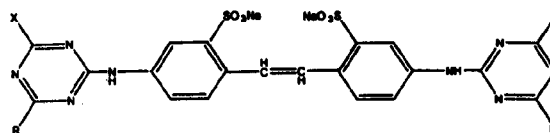
Summary: A range of Fluorescent Whitening Agents of triazinyl stilbene series were synthesized using different amino derivatives. Investigation on the adsorption of these FWA on woven fabric have been carried out. It has been found that these agents exhibit good level of whiteness. Their absorption behaviour was studied in terms of CIE LAB colour space.

Introduction

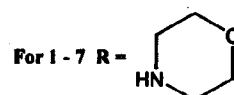
The action of sunlight on wet fabrics and the use of chemical bleaches to reduce the yellowish tinge of natural textile fabrics have known for thousands of years. Initially blue pigment was used in very small quantities for this purpose. Today whiteness is achieved by fluorescent brightening (or whitening) agents which are applied as colourless fluorescent dyes. In 1929, Kraus [1] used the naturally occurring glycoside aesculin to brighten viscose and flax. In 1934 Plain and Radley [2] patented the use of 4,4' bis benzoylaminostilbene 2,2'-disulphonic acid and in 1940 Bayer introduced Blankophore B as brightener for cotton. After the second world war development of FBAs was very rapid. Several hundred commercial products, representing a wide variety of chemical types have now been discovered [3-7]. The physical characteristics of fluorescent whitening agents are such that special illumination (standard illuminant D-65) resembling average daylight is necessary for colorimetric determination. The term whiteness measurement is often given to those colorimetric methods which are used in connection with white samples. White is basically a colour like blue, green or red and can be determined precisely by colorimetric methods. The characteristic which distinguishes white samples from those we call coloured is their high lightness combined with very low colour saturation. In common all other colours, white can be clearly defined by just three parameters of a colour system or in other words in a three dimensional colour space [8].

The present work deals with the preparation of some amino derivatives of triazinyl stilbene series as fluorescent whitening agents. The main objective of this work is to study the interaction of chlorine atoms of 4, 4'-bis (2, 4-dichloro-1, 3, 5 triazinyl) amino

stilbene 2, 2'-disulfonic acid with amino compounds in aqueous medium and absorption behaviour by means of CIE L*a*b* colorimetric system, dyeing and fastness properties.



Scheme-1



For 1a - 7g R = NH(C₂H₅)₂

1-1a: X = Aniline

2-2b: X = 1-Aminobenzene 3-sulfonic acid

3-3c: X = 1-Aminobenzene 4-Sulfonic acid

4-4d: X = 1-Aminobenzene 2-Sulfonic acid

5-5e: X = 1-Amino-8-naphthol 4,6-disulfonic acid

6-6f: X = 2-Naphthylamine-1-Sulfonic acid

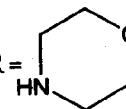
7-7g: X = 1-Naphthylamine-6-Sulfonic acid

Results and Discussion

Optical brighteners having the power of absorbing radiation of wavelength lying between 330 and 380 nm and of re-emitting light within the range 430-490 nm i.e. in the blue region of the visible spectrum. For high fluorescent activity and cotton substantivity the molecule must possess a conjugated system, it must be planar and must contain electron donating groups such as -OH and -NH₂. A range of

*To whom all correspondence should be addressed.

Table-1: Data on characterization of FW as prepared from triazinyl stilbene series where R =



Sample Code	X	R	Molecular Formula	λ_{max}	Absorbance	Log C
1	Aniline	Morpholine	C ₄₀ H ₃₂ N ₁₂ O ₆ S ₂ Na ₂	350	1.528	4.485
2	1-Aminobenzene 3-sulfonic acid	Morpholine	C ₄₀ H ₃₂ N ₁₂ O ₁₄ Na ₂ S ₄	364	1.747	4.543
3	1-Aminobenzene 4-Sulfonic acid	Morpholine	C ₄₀ H ₃₂ N ₁₂ O ₁₄ Na ₂ S ₄	354	1.239	4.394
4	1-Aminobenzene 2-Sulfonic acid	Morpholine	C ₄₀ H ₃₂ N ₁₂ O ₁₄ Na ₂ S ₄	353	1.434	4.457
5	1-Amino-8-naphthol 4,6-disulfonic acid	Morpholine	C ₄₈ H ₄₂ N ₁₂ S ₆ O ₂₂ Na ₂	349	1.433	4.457
6	2-Naphthylamine- 1-Sulfonic acid	Morpholine	C ₄₈ H ₄₂ N ₁₂ S ₄ O ₁₄ Na ₂	350	1.528	4.485
7	1-Naphthylamine-6-Sulfonic acid	Morpholine	C ₄₈ H ₄₂ N ₁₂ S ₄ O ₁₄ Na ₂	344	1.192	4.377

Table – 2 Data on characterization of FWAs prepared from triazinyl stilbene series. Where R=HN (C₂H₅)₂

Sample Code	X	R	Molecular Formula	λ_{max}	Absorbance	Log C
1a	Aniline	Diethyl amine	C ₄₀ H ₄₂ S ₂ O ₆ Na ₂ N ₁₂	348	1.307	4.417
2b	1-Aminobenzene 3-sulfonic acid	Diethyl amine	C ₄₀ H ₄₄ S ₄ O ₁₂ Na ₂ N ₁₂	363	1.535	4.487
3c	1-Aminobenzene 4-Sulfonic acid	Diethyl amine	C ₄₀ H ₄₄ S ₄ O ₁₂ Na ₂ N ₁₂	344	1.192	4.377
4d	1-Aminobenzene 2-Sulfonic acid	Diethyl amine	C ₄₀ H ₄₄ S ₄ O ₁₂ Na ₂ N ₁₂	349	1.189	4.376
5e	1-Amino-8-naphthol 4,6-disulfonic acid	Diethyl amine	C ₄₈ H ₄₆ S ₆ O ₂₀ Na ₂ N ₁₂	343	1.549	4.491
6f	2-Naphthylamine-1-Sulfonic acid	Diethyl amine	C ₄₈ H ₄₆ S ₄ O ₁₂ Na ₂ N ₁₂	350	1.528	4.485
7g	1-Naphthylamine-6-Sulfonic acid	Diethyl amine	C ₄₈ H ₄₆ S ₄ O ₁₂ Na ₂ N ₁₂	351	1.452	4.462

FWAs were synthesized by using different amino derivatives. Their structural formula, maximum absorption with substitution pattern is given in Table - 1 and 2.

The whiteness of fabrics are shown in Table-3 and 4 in terms of CIE L*a*b*. It has been found that fluorescent intensity depends on FWA content to some extent. The changes in substituents have relatively minor influence on the intensity of fluorescence, while the main effect is in altering physical properties, in particular solubility and substantivity. All the listed FWAs exhibit good whitening effect, and adequate light fastness. It can also be seen from these results that adsorption of FWA on cellulosic fibre has little effect on values of L* but has a slight effect on a* and b*.

The assessment of colour was made by calculating the values of X, Y and Z (tristimulus values) and CIE L*, a* and b* (Cartesian coordinates), x and y (chromaticity coordinates) and Munsell coordinates in terms of hue and chroma. The data presented in Table-3 and 4 indicates that for FWAs 1-7 and 1a-7g series the CIE coordinates a* have +ve value and b* have -ve value which proves that the colour of these agents are along the red and blue axis in CIE colour space. Most of the developed FWAs were found to possess better whiteness but appreciably less than the commercial brand. It is also observed that as the amount of FWA on a substrate

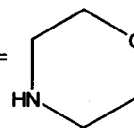
increases, whiteness increases until a maximum value is reached. Further application of FWA results in a reduction in whiteness. In general the main cause of the fall in whiteness with increasing concentration of FWA is an increase in the aggregation of the FWA on the substrate, resulting in a shift in fluorescence hue.

Experimental

All the FWAs were prepared by the conventional method of cyanuration of 4,4'-diamino stilbene-2, 2'-disulphonic acid and substitution reaction of chlorotriazine [9]. The amines used in the synthesis of FWAs are aniline, 1-aminobenzene 3-sulfonic acid, 1-aminobenzene 4-sulfonic acid, 1-aminobenzene 2-sulfonic acid, 1-amino-8-naphthol 4,6-disulfonic acid, 2-naphthylamine-1-sulfonic acid, 1-naphthylamine-6-sulfonic acid. The general structural formula of FWA is given in Scheme-1.

The FWA thus obtained are numbered as 1-7 and 1a-7g. All the amines were dissolved in a minimum quantity of sodium carbonate and then gradually added to a well stirred cyanurated solution of 4,4'-diamino stilbene-2,2'-disulphonic acid in weakly acidic system. The mixture was then slowly refluxed on a water bath at 70°C – 80°C with continuous stirring and then the reaction was allowed to proceed for 60 minutes. During the reaction, aqueous solution of 1N sodium hydroxide was

Table- 3: The colorimetric properties of FA as where R =



Sample code	Berger Whiteness %	Tristimulus value			CIE LAB			Chromaticity Coordinates		Munsell renotation	
		X	Y	Z	L*	a*	b*	x	y	Chroma	Hue
UnTreated Fabric	70.01	83.41	88.11	89.67	95.21	-0.26	3.35	0.31930	0.3374	3.37	94.44
Leucophore	144.64	89.77	93.01	116.57	97.23	2.92	-10.38	0.2999	0.3107	10.78	285.72
1	126.19	88.83	92.65	110.34	97.08	1.82	-6.89	0.3044	0.3175	7.13	284.79
2	93.37	84.38	88.88	97.55	95.53	0.22	-1.46	0.3116	0.3282	1.47	278.49
3	92.51	85.47	90.16	96.94	95.83	0.21	-0.55	0.3131	0.3298	0.59	290.71
4	102.09	84.93	89.17	99.26	95.65	0.72	-2.37	0.3107	0.3262	2.48	286.94
5	91.21	85.42	90.24	96.96	96.10	-0.27	-0.08	0.3133	0.3310	0.28	196.70
6	123.06	87.35	91.85	109.01	96.39	1.79	-6.72	0.3034	0.3165	7.05	282.36
7	104.38	85.31	89.85	100.10	95.91	0.85	-2.89	0.3132	0.3285	2.53	287.31

Table – 4 The colorimetric properties of FWAs where R=HN (C₂H₅)₂

Sample code	Berger Whiteness %	Tristimulus value			CIE LAB			Chromaticity Coordinates		Munsell renotation	
		X	Y	Z	L*	a*	b*	x	y	Chroma	Hue
UnTreated Fabric	70.01	83.41	88.11	89.67	95.21	-0.26	3.35	0.31930	0.3374	3.37	94.44
Leucophore	144.64	88.83	92.65	116.57	97.23	2.92	-10.38	0.2999	0.3107	10.78	285.72
1a	119.89	88.15	91.80	107.91	96.74	2.06	-6.00	0.3062	0.3189	6.34	288.96
2b	102.65	86.30	90.90	101.08	96.37	0.21	-2.31	0.3101	0.3267	2.32	275.15
3c	86.25	83.68	88.38	93.14	95.32	-0.22	1.15	0.3155	0.3333	1.17	100.82
4d	93.85	84.56	89.01	97.68	95.65	0.31	-1.51	0.3120	0.3291	1.51	279.31
5e	102.98	85.93	90.36	97.28	96.15	0.54	-0.25	0.3152	0.3312	0.61	335.15
6f	106.98	85.42	89.73	100.09	95.89	0.65	-2.51	0.3103	0.3260	2.59	284.59
7g	99.43	85.10	90.11	96.59	96.83	0.46	-0.66	0.3315	0.3131	1.73	281.36

gradually added at such a rate that the pH of the reaction mixture remained either neutral or slightly alkaline. After this period, the reaction mixture was allowed to cool and then the product was filtered. The product obtained was washed free of chloride ion and then dried.

Material and Equipments:

Experiment of whitening was carried on 100 % cotton fabric. Dyeings were carried out on Vertical Lab Padder. The colorimetric properties of the dyeings (D-65 illumination 10 ° observer) were determined by means of a spectra flash 650X spectrophotometer.

Method of Application:

Whitening of 0.004–0.00688% depth was carried out by dissolving 0.04–0.0688g/L FWA at 40 – 45°C. The fabric was padded by the above mentioned liquid through a padder with 75% to 85 % pick up with a speed of 40 m/min. After that, the specimen was removed, rinsed with cold water and dried.

Measurement of whiteness

After the application of FWA the whiteness was determined according to AATCC test method [10]. The test specimen was conditioned for 4 hour in an atmosphere of $21 \pm 1^\circ\text{C}$ and $65 \pm 2\%$ relative humidity. The relative efficiency of the sample was determined by using a spectrophotometer, having an insertion of ultraviolet cut off filter into the incident light beam. The difference between the measurement, taken before and after the insertion of U.V cut off filter can provide an indication of the enhancement of the apparent whiteness due to the addition of FWA.

Conclusions

The effect of different amino derivatives of stilbene series of type 1-7 and 1a – 7g on cellulosic fabric have been investigated by means of CIE Lab colorimetric system. All the FWAs were obtained in good yield. Most of the derivatives had excellent fluorescence and dyeing behaviour. The influence on fluorescent intensity of fabrics adsorbed with FWA was determined as a function of FWA content. Their maximum absorption lies between 340 – 364 nm

which shows good co relationship between CIE LAB coordinates and λ_{\max} determined.

References

1. P. Kraus, *Melliand Textilber*, **10**, 468 (1929).
2. C. Paine and J.A. Reedley (ICI), BP 442530 (1934)
3. A. Landholt, *Amer. Dyestuff Rep.* **38**, 353 (1949)
4. D. Barton and H. Davidsan, *Rev. Prog. Coloration*, **53** (1974)
5. Fluorescent whitening agents, Ed. R. Anliker and G. Muller (Stuttgart, Thieme, 1975).
6. H. Gold The Chemistry of Synthetic dyes, **5**, Ed. K. Venkataraman (New York Academic Press, (1971).
7. R. D. Dalal, S.K.Parikh, *J.Inst.Chem. India*, **60** (4), 145 (1998)
8. Roderick Mc Donald, Colorimetry and the CIE system, 2nd edition (Society of Dyers and Colourists (1977.)
9. Colorants and Auxiliaries Organic Chemistry and Application properties by John Shore (1990) Society of Dyers and Colourists.
10. AATCC technical manual, **79** (2004).