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Synthesis of New Fluorescent Whitening Agents.

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SYNTHESIS of NEW FLUORESCENT WHITENING AGENTS

By

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ABSTRACT

New bis-(triazinlamion) - stilbene disulphonic acid was prepared as fluorescent whitening agent by the ternary condensation of the diaminostilbene disulphonic acid with cyanuric chloride, followed by the rection with different amines, and alkoxides.

INTRODUCTION

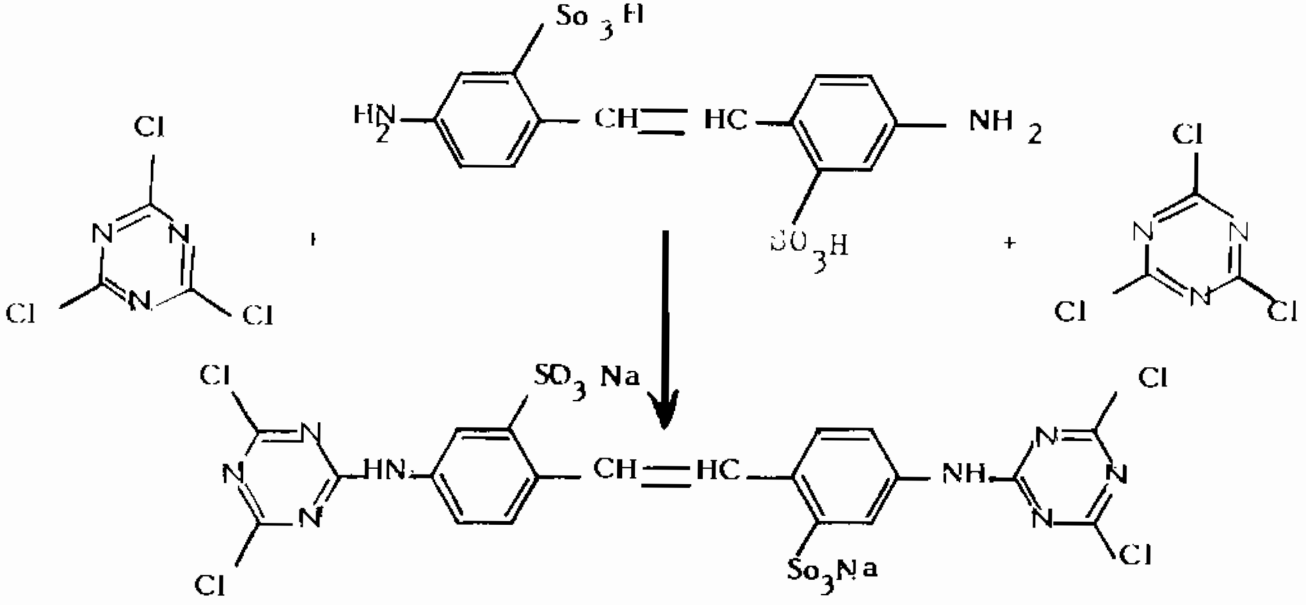
Fluorescent whitening agents are known under various names, e. g. optical whitening agent, optical bleaching agents or optical bleaches, fluorescent bleaching agents, whiteners, brighteners, etc. In the colour index they are listed as fluorescent brighening agents. The ASTM have suggested the term " Fluorescent Whitening Agents " for them, and for the sake of convenience and simplicity it is preposed to refer to them in this paper as FWAS.

FWAS are dyes which absorb UV radiant energy and remit the energy as added to the reflected light from the cloth, there is an overall increase in reflectance. Thus, the FWA eliminates the yellow cast of the original cloth, but it also increase the amount of light emitted.

The flourescence and whitening characteristics of many aromatic and heterocyclic system have been studied in recent years, and the results are to be found in a number of patents and reviews. [1-4] Most FWAS on the market are derivatives of 4,4 - diaminostilbene- 2,2 - disulphonic acid (DAS).

Results and Discussion

In the present part some new bis - (triazinylamino) stilbene FWAs were prepared as sodium salts. They are produced as shown in the following figures.



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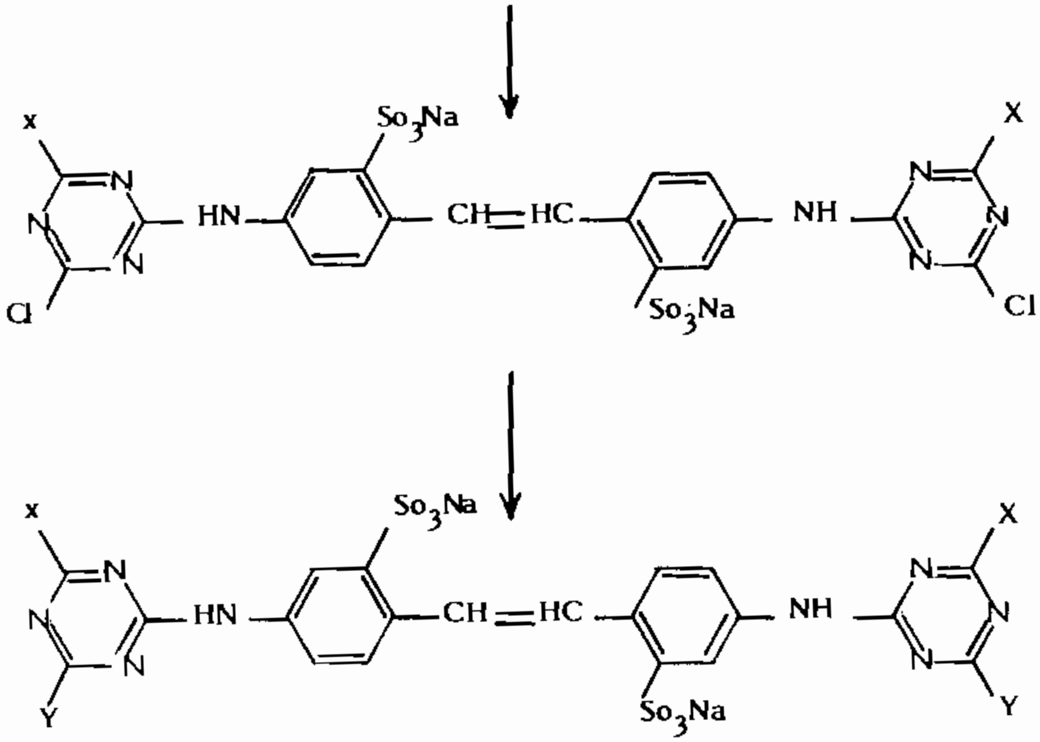
* Correspondence



In the Fig. X and Y are different amines and alkoxides.

The method of preparing these compounds depends on the fact that the three chlorine atoms of cyanuric chloride can be replaced in a step - wise manner by the residue of an amines or alkoxides. In general, the first atom in the ring is replaced at temperatures of 0-10 °C , the second chlorine at 20-50° C and the third at 60-100' °C , The reaction temperature depend upon the nature of the reacting aminess[5] .

The above bis-(triazinylamino) stilbene FWAS were characterised by elemental analysis (See Table 1) and assessment of their spectra in the ultra-violet, visible (See Table 2) and infrared ranges.

The infrared measurements showed stretching frequencies at about 1620 cm^{-1} characteristic for the -C = C- and 3320 cm^{-1} for the NH group .

Most of these FWAS showed main absorption band at approximately 360 + 3 mn. The introduction of amino or alkoxy groups in such compounds have no effect on their max and on their fluorescent intensity[6].

Bis-(triazinylamino)-stilbene disulphonic acid (Table 1) obtained by condensing 4-4 diamino stilbene-2,2-disulphonic acid with 2 moles of cyanuric chloride, yields a tetrafunctional compound which makes a great number of substitution possible. The substitution usually alter decisively those properties of the basic brightener molecule which determine the way the brightener is used. For example,

Table 1: Chemical Analysis of the Newly Synthesized FWAS

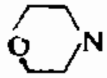
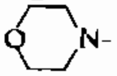
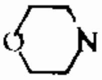
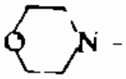
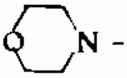
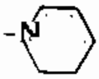
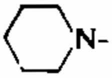
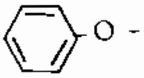
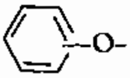
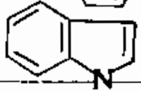
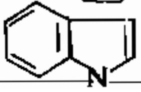
Colour	X	Y	Analysis Calod (Found) C	H	N
Yellow	$(CH_3)_3C-O$	$(CH_3)_3C-O$	50.22 (49.41)	5.38 (5.10)	13.02 (12.82)
Yellow	$CH_3-CH_2)_3-O$	$CH_3(CH_2)_3-O$	50.22 (49.72)	5.38 (5.31)	13.02 (13.00)
Yellow	$(CH_3)_2-CH-O$	$(CH_3)_2-CH-O$	49.03 (48.63)	5.08 (4.77)	13.45 (13.40)
Yellow	$NH-C_6N_4-SO_3H$	$NH<^{CH_2-CH_2OH}_{CH_2CH_2OH}$	45.56 (45.51)	3.61 (2.89)	17.72 (17.51)
Yellow		$NH-C_6H_4-SO_3H$-m	47.99 (47.87)	3.80 (3.80)	16.68 (16.61)
Browinsh		$CH_3CH_2\backslash N-$ $CH_3CH_2/$	48.20 (47.93)	5.39 (4.93)	18.74 (18.71)
Yellow					
Yellow			47.36 (47.12)	4.63 (4.57)	18.41 (18.00)
Yellow	CH_3NH-	CH_3NH-	41.91 (41.82)	3.81 (3.73)	24.44 (24.41)
Yellow			47-36 (47.13)	4.63 (4.56)	18.41 (18.21)
Yellow	CH_3NH-	$CH_3CH_2\backslash N-$ $CH_3CH_2/$	46.62 (46.16)	4.95 (4.91)	21.75 (21.43)
Yellow Brownish	CH_3-NH-	$-HNCH_2CH_2OH$	41.70 (41.10)	4.04 (3.89)	22.45 (22.13)
Yellow	C_2H_5O-	C_2H_5O-	44.91 (44.56)	4.04 (3.92)	14.96 (14.62)
Yellow	CH_3NH-		44.99 (44.91)	4.27 (4.20)	20.99 (20.91)
Yellow	CH_3-NH-	$NH-C_6H_4-SO_3H$-m	44.93 (44.23)	3.32 (3.30)	18.48 (18.31)
Yellow	$NH-C_6H_4-SO_3H-O$	$NH-C_6H_4-SO_3H-O$	42.10 (41.82)	2.73 (2.70)	13.39 (13.13)
Yellow	$NH-C_6H_4-COOH-O$	$NH-C_6H_4-COOH-O$	51.79 (50.93)	3.08 (2.76)	15.10 (14.53)
Yellow	NH_2-	$-N<^{CH_2CH_2OH}_{CH_2CH_2OH}$	39.99 (39.72)	3.63 (3.60)	23.42 (23.00)
Yellow	$CH_3\backslash N-$ $CH_3/$	$CH_3\backslash N-$ $CH_3/$	41.85 (41.71)	3.81 (3.77)	24.40 (24.15)
Yellow	C_2H_5-HN-	C_2H_5-NH-	45.15 (44.83)	4.60 (4.41)	22.57 (22.12)
Yellow	$C_6H_5-N-COCH_3$	$C_6H_5-N-COCH_3$	56.51 (56.17)	3.83 (3.80)	15.21 (14.82)
Yellow	CH_3CONH-	CH_3CONH-	41.99 (56.17)	3.27 (3.80)	20.98 (14.82)

Table 1: Chemical Analysis of the Newly Symthesized FWAS

Colour	X	Y	Analysis Calcd (Found)		
			C	H	N
Yellow	CH_3CONH-	CH_3CONH-	41.99 (41.47)	3.27 (3.21)	20.98 (20.36)
Yellow	$\underset{H}{N}-CH_2COOH$	$-\underset{H}{N}-CH_2COOH$	38.88 (38.56)	3.03 (2.93)	19.44 (19.12)
Yellow			53.08 (52.91)	5.56 (5.52)	18.56 (18.11)
Yellow			56.16 (56.10)	3.21 (3.20)	11.91 (11.23)
Yellow			60.46 (60.12)	3.32 (3.13)	16.27 (16.00)

they influence the solubility, the rate of bsorption and the affinity for different substrates at varing temperature. Moreover, the shade of the brightened fabric is strongly in fluenced?

FWAS in this series, which have amino or alkylamino groups as substituents showed good results with cotton (at low temperature). Also, have good affinity for cellulosic materials. This give the advantage to be used as FWAS in a large scale at different temperatures ?

On the other hand, FWAS (1-25) which have an alkoxy group showed a good stability towards the effect of acids, these stability prompoted us to use these compounds as FWAS for polyamide and in the preparation process of cotton in order to increase its strength ?

The disodium salt of 4,4-bis (dimorpholino-1,3,5-FWAS which have one -NH- group attached to the triazine ring showed low stability towards the hypochlorite compounds ?

It was reported that ethylene derivatives of stilbene exhibit both the cis-trans isomers, and it can be convert one of them to the an, other by the effect of short wave radiation[8] . It was noted that both the cis-and trans forms, can be separated in dark by using the TLC methed, these results with greet agrement with earlier investigated work[9,10] , also it was found that the cis form have no fluorescence.

It was noted that the intensity of λ_{max} at, 365 decreased by increasing the time of exportion to the radiation of short waves and the coffecient at 278 increased ?

The cis-isomer easily dissolved than the trans-form, so it can be obtained in dilute solution, therefore, the dilute solution of bis-(triazinylamino)-stilbene FWAS must be placed (stored) in dark place and far away from the short wave radiations. The concentrated solution of such FWAS showed high stability towards the influence of such waves.

Experimental :

Analysis were carried out in the Microanalytical Unit, Faculty of Science, Mansoura University. Ultra-violet and fisible spectra were performed using a Pye-Unicam SP 1800 spectrophotometer. Infrared were recorded on a Pye-Unicam SP-2000 spectrophotometer using potassium bromide technique.

General Procedure :

1 . Diaminostilbene disulphonic acid (1.5 mole) was dissolved in 5 li. of water contains 75.5 gm. NaOH pure or 170 c.c. of NaON 38 Be at room temp.

2 . Gyanaric chloride power (3 mole) 90% technical grade was suspended in 5 li. of water contains 2 gm/l nonionic dispersing agent at 10-15 °C under continuous stirring .

3 . Sodium salt of diaminostilbene solution prepared in step No. I was added drop-wise to the suspended solution of cyanuric chloride prepared in step No. 2(at 10-15°C) through 30 minutes. At this end, stirring was continued

Table 2: Absorption Maxima of Bis-(triazinylamino)- stilbene FWAS in distilled water.

FWAS No .	Colour in crystal	Colour in water
1	Yellow	Greenish yellow
2	"	Fluorescent
3	"	"
4	"	"
5	"	"
6	Brownish yellow	"
7	Yellow	"
8	"	"
9	"	"
10	Yellow	"
11	"	"
12	Brownish yellow	"
13	Yellow	"
14	"	"
15	"	"
16	Yellow	"
17	"	"
18	"	"
19	"	"
20	"	"
21	"	"
22	"	"
23	"	"
24	"	"
25	"	"

for another 30 minutes.

Note:

PH reaches 0-1 at the end of the reaction of this stage.

4. To theabove prepared bis-triazinyl diamino stilbene, 102 gm. NaOH flakes or 230 c.c. NaOH 38 Be were added continucus stirring until a clear solution was obtained.

Note:

PH reaches 8-9.

5. (4 mole) of amine solution was added to the above clear solution follwed by addition of 66.6 gm NaOH flakes or 150 c.c. of NaOH 38 Be, in 3 portions through 15 minutes, the temp. was raised gradually from 15 to 50 c as a result of adding NaOH.
6. (2 mole) of morpholine or other amine or alkoxide was added to the previous main bulk, follwed by addition of NaOH solution (38 Be) in 3 portions through 15 minutes, the temp. was raised gradually from 50 to 85 C during the time of addition of NaOH.
7. The bulk was maintained for 20 minutes more at 90 C with continuous stirring to complete the reaction.
8. The total bulk of solution was calculated and 150 gm/l NaCL were added for salting out.
9. The product was abtained through filtration and dried at 120 C.
10. The total dried bulk was purified with acetion.

References:

1. Anon., Am. Dyestuff. Reporter, 57 (9), 303 (1968).
2. Fluorescence -Theory and Practice, Ed. G. Guilbault. Edward Arnold (1967).
3. I.G. Forben, D.R.P. 752, 677. D.R.P.731, 558 and Fr. Pat. 874, 939.
4. R. zweidler, H. Hauserman, kirk-Othmer's Ency. Chem. Tech., 3, 737 (1964); H.W. Zusmann, Ency. Polymer Sci. and Tech., 2, 606 (1965); D.A.W. Adams, J. Soc. Dyers and Color., 75, 22 (1959); E. Uhlein, Optischer Aufheller, Mosor Verlag, W. Germany, 1957.
5. S. Horrobin, J. Chem. Soc., 4130 (1963); B. Bitter and H. Zollinger, Helv. C im Acta, 44, 812 (1961).
6. A Yabe, M. Hayashi, Kogyo Kagaku Zasshi, 63, 987 (1960); C.A. 60, 10860d (1964).
7. Venkataraman K., " THe chemistry of Synthetic Dyes" , (Academic press, New York and London) Vol. VI (1972).
8. G.N. Lewis, T.T. Masel, D. Lipkin. J. Am. Chem. Soc., 62; 2973 (1940).
9. H. Theidel. Melliand Textilber., 514 (1964).
10. Y. Soyato. Shokutin Eiseigaku Zasshi, 2, 56 (1961); C.A., 56, 878d (1962).