Synthesis of Symmetrical Azo Dyes from 4,4'-Diamino-Diphenylamine-2-Sulphonic Acid

M.A. SAEED*, BADRUDDIN*, M. FAROOQ*,
M. YOUNAS** AND FAUZIA SHAFI**

*PCSIR Laboratories, Lahore, Pakistan.

**Institute of Chemistry, Punjab University, Lahore, Pakistan.

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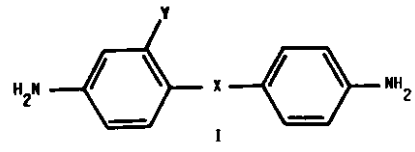
Summary: Synthesis of some bis-azo dyes based on 4,4'-diamino-diphenylamine-2-sulphonic acid has been described. The properties of these dyes have been compared with similar dyes derived from benzidine. Since benzidine is one of the established carcinogens, the possibility to replace it with 4,4'-diamino-diphenylamine-2-sulphonic acid for the production of some direct dyes has been studied.

Introduction

Since long benzidine has been one of the most important intermediates for the synthesis of direct dyes for cotton. These dyes have been in use for more than hundred years. Even today thousands of tonnes of benzidine dyes are manufactured annually, although the public opinion as well as health authorities are against the use of benzidine due to its carcinogenic nature. These dyes have been so popular because they have good substantivity for cotton fibre, the dyeing procedure is simple and these dyes are cheaper as compared to other classes of dyes. The carcinogenic nature of benzidine is known since long as the incidents of urinary cancer were more frequent among the workers involved in the production of benzidine intermediate or the dyes based on it [1-4]. Now the carcinogenic nature of benzidine has been proved beyond any doubt and there is voluminous literature on the possible hazards due to the use of benzidine and other aromatic amines [5-8]. Therefore, the public opinion in Europe and USA has pressurised the dye manufacturers to stop the production of benzidine based dyes.

Due to the importance and commercial value of these dyes, the dye chemists are trying to find out substitutes of these dyes by replacing benzidine with other noncarcinogenic diamines. The diamines of the general formula (I) have been reported in recent literature [9-14].



I

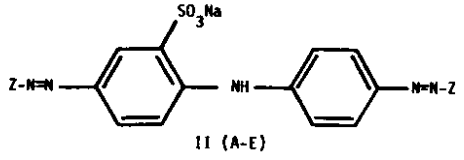
X = NH, S, O, SO_2 or CONH

Y = H or SO_3H

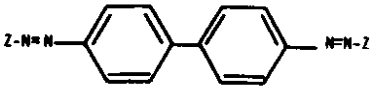
Most of the dyes derived from 4,4'-diamino-diphenylamine-2-sulphonic acid known in the literature are tris-azo or tetrakis-azo dyes and their shades are, black or greenish black [12-14]. Very little is reported in literature about the bis-azo dyes derived from it. Therefore, we have selected 4,4'-diamino-diphenylamine-2-sulphonic acid to prepare bis-azo dyes, which is expected to give yellow, orange, red and blue dyes.

The standard method [15] for the synthesis of such dyes has been followed. 4,4'-Diamino-diphenylamine-2-sulphonic acid was tetrazotised and then one equivalent of the tetrazotised amine was coupled with two equivalents of the desired coupling component to get the bis-azo dyes. The corresponding benzidine dyes were also prepared so that a comparison could be made for their hue, strength and the dyeing behaviour.

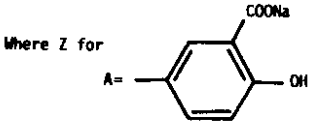
The dyes prepared from 4,4'-diamino-diphenylamine-2-sulphonic acid are represented by the general formula II(A-E) and those from benzidine by III(A-E).

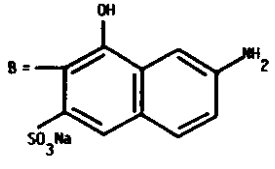


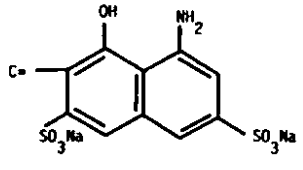
II (A-E)

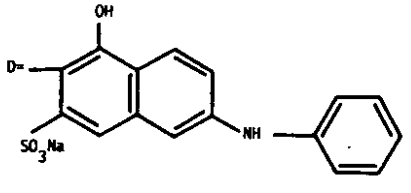


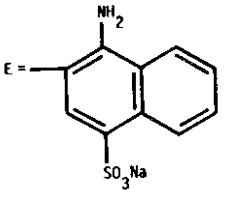
III(A-E)











Experimental

Material:

4,4'-diamino-diphenylamine-2-sulphonic acid and the intermediates for A to E were obtained from Bayer Company of West Germany and were used as such without purification. Sodium nitrite, hydrochloric acid and sodium carbonate etc. were purchased from the local market and were of the commercial grade.

Visible spectra were recorded on Hitachi Double beam Spectrometer Model 220 in distilled water using 1 cm quartz cell.

Synthesis of 4,4'-diamino-diphenylamine-2-sulphonic acid bis-azo salicylic acid (II A):

4,4'-Diamino-diphenylamine-2-sulphonic acid (3.45 gm) was dissolved in a solution of 10 ml 10% sodium carbonate in 50 ml of water contained in a one litre beaker which was immersed in a crushed ice bath. The solution was cooled by adding some ice in the beaker with stirring until its temperature fell to 0°C. 15 ml of 10% sodium nitrite solution was then added in small portions (2-3 ml at a time) with constant stirring. It was followed by the gradual addition of 10 ml of conc. hydrochloric acid. The temperature was kept below 5°C by adding crushed ice into the reaction mixture if necessary. Stirring was continued for about two hours till the presence of nitrous acid was detected by potassium iodide-starch paper. The excess of nitrous acid was removed by sulphamic acid.

30 gm of salicylic acid and 6.0 gm of sodium carbonate were taken in a beaker to which was added 50ml of water and stirred until clear solution was obtained. To this solution was added the above tetrazotised solution gradually from a dropping funnel. The pH of the reaction mixture was adjusted to about 8.5 by adding sodium carbonate. The reaction mixture was stirred overnight at room temperature. 50 gm of sodium chloride was then added to salt out the dyestuff. The product was filtered and the paste of the dye was dried in an oven at 70-80°C. 6.2 gm of the dark brownish yellow powder of the dyestuff (IIA) was obtained. The same procedure was used for the dyes II(B-D).

The procedure for the dye IIE was slightly modified. In this case 1 gm of sodium acetate and 2 gm of sodium chloride were added to sodium naphthionate dissolved in water before coupling and the pH of the reaction mixture was maintained at 6.5 - 6.8.

The corresponding dyes from benzidine were prepared for comparison using the general method described above.

Results and Discussion

The dyes prepared from 4,4'-diamino-diphenylamine-2-sulphonic acid and those from benzidine were applied on cotton fibre under the same conditions. Table I shows a comparison of the strength, shade, and absorption maxima for the two series of dyes.

Figure 1 shows absorption maxima for the dyes which indicate that all the diamino-diphenylamine based dyes show a red shift (displacement of characteristic absorption maxima towards longer wavelength) of about 20 nm. The shades of the diamino-diphenylamine dyes are therefore more bluish (Complimentary of reddish colour) than those of the benzidine dyes which has indeed been confirmed

Table-I: Comparison of the properties of dyes derived from 4,4'-diamino-diphenylamine-2-sulphonic acid with those from benzidine.

Dye	Strength	Shade	λ_{max} (nm)	Red Shifts(nm)
IIA	50 %	Yellow	428	
				24
IIIA	100 %	Reddish Yellow	404	
IIB	80 %	Black	578	
				20
IIIB	100 %	Grey	558	
IIC	75 %	Dark Blue	596	
				20
IIIC	100 %	Light Blue	576	
IID	90 %	Bluish Violet	544	
				18
IIID	100 %	Reddish Violet	526	
IIE	90 %	Bluish Red	502	
				8
IIIE	100 %	Red	494	

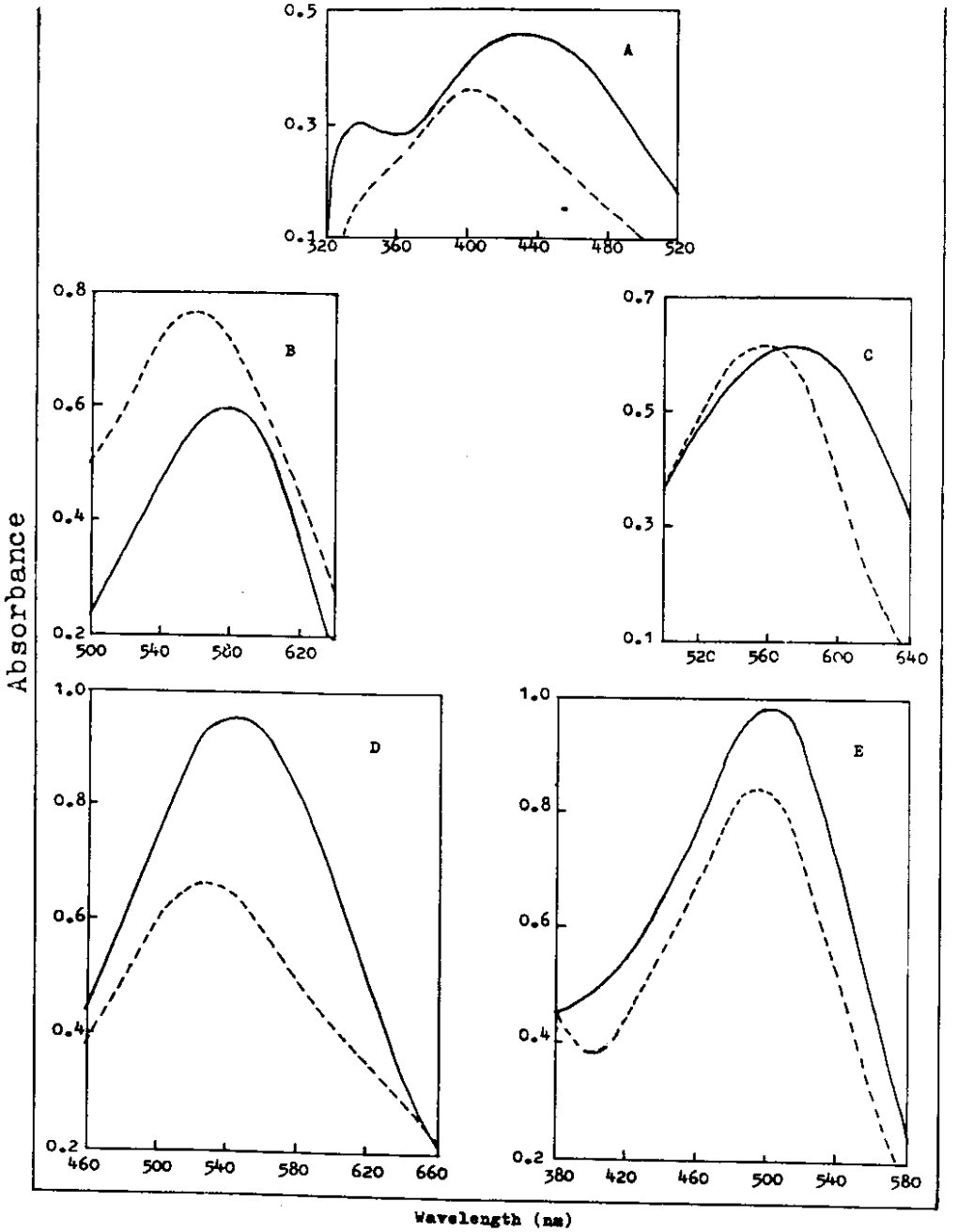


Fig.1: The Visible Spectra of the Dyes (A - E) derived from 4,4'-Diamino-diphenylamine-2-sulphonic acid (——) and Benzidine (- - -).

by the red shifts of the visible spectra. The absorption coefficients were not calculated as the products contained some sodium chloride as innert material.

The comparison of dyeing results of the dyes obtained from 4,4'-diamino-diphenylamine-2-sulphonic acid (IIA-E) with those from benzidine (IIIA-E) showed that the dyes derived from the former are generally 10-25% weaker in strength in the case of B, C, D, and E and 50% weaker in the case of A. (It may be due to low solubility). The shades of the colour are slightly different in the corresponding cases. The slight decrease

in strength is not surprising since in the case of diamino-diphenylamine derivatives the conjugation is broken between the two phenyl rings. Inspite of a slight decrease in strengths the dyeing properties in general are comparable to those of benzidine dyes. Therefore, the 4,4'-diamino-diphenylamine-2-sulphonic acid dyes may be quite a reasonable replacement for the corresponding benzidine dyes.

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