

Synthesis of Unsymmetrical Dis-Azo Dyes from 4,4'-Diamino-Diphenylamine-2-sulphonic Acid

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Summary: Some unsymmetrical dis-azo dyes have been synthesised from 4,4'-diamino-diphenylamine-2-sulphonic acid in an attempt to find a suitable substitute for benzidine which is now an established carcinogen. The shade, strength and absorption characteristics in the visible region have been compared with the corresponding dyes derived from benzidine.

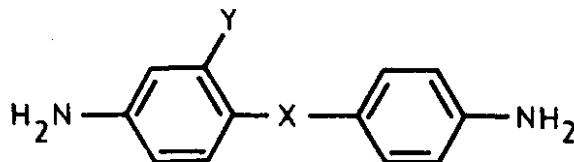
Introduction

Continuing [1] our attempt to replace benzidine which is now an established carcinogen by a suitable non-carcinogenic intermediate for the preparation of direct dyes, we have prepared another series of dis-azo dyes derived from 4,4'-diamino-diphenylamine-2-sulphonic acid.

In spite of its importance for cotton dyes benzidine has been suspected since long as carcinogenic in nature. Now it has been proved beyond any doubt that benzidine and its dyes cause urinary bladder cancer and therefore the production of benzidine and its dyes is completely banned in most of the countries [2-5]. There is quite a good deal of literature on the carcinogenicity of benzidine [6-10]. The risk is not limited to the workers in the dyes industry but also the dyers and other users of these dyes face similar risk [11,12].

It has been reported [13-17] that substitution of benzidine in the nucleus with chloro, sulphonic and even methyl group has been found to remarkably reduce its carcinogenic properties. For example, dichlorobenzidine which is an important intermediate for pigments, is not carcinogenic. Similarly, tetramethylbenzidine has been found non-carcinogenic.

Another approach that has gained an appreciable commercial importance, is to synthesize dyes in which the two rings of benzidine have been separated by a suitable group.



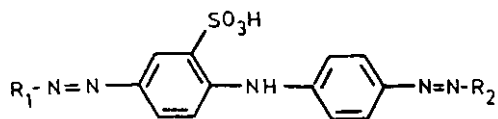
X = NH, O, S, SO₂, N=N, CONH₂, etc.

Y = H, Cl, CH₃, SO₃H, etc.

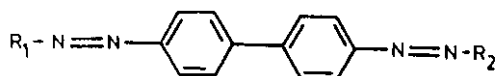
Thus, 4,4'-diamino-diphenylamine-2-sulphonic acid in which X = NH and Y = SO₃H has very often been reported in patent literature as an intermediate for the synthesis of dyes for cotton and leather with properties very close to those of benzidine dyes [18,19].

In the present case, the dyes were prepared by the usual method involving the tetrazotisation of 4,4'-diamino-diphenylamine-2-sulphonic acid and

then coupling it with two different coupling components step-wise at suitable pH, and are represented by the general structure II. The corresponding dyes derived from benzidine are represented by III.

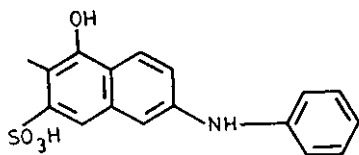
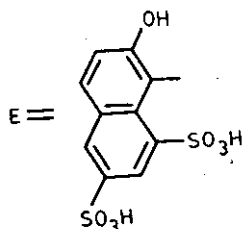
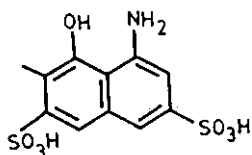
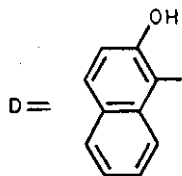
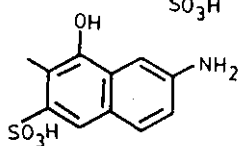
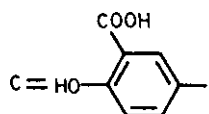
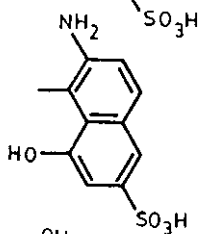
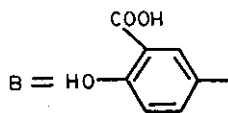
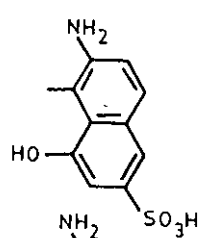
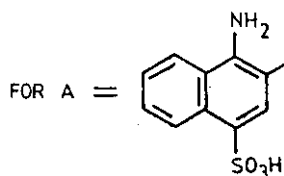


II



III

WHERE

 R_1 R_2 

Experimental

4,4'-diamino-diphenylamine-2-sulphonic acid, benzidine and the coupling reagents, R_1 and R_2 for the dyes A to E were obtained from Farben Fabriken Bayer of West Germany and were used as such without further purification. Sodium nitrite, sodium carbonate, sodium hydroxide and hydrochloric acid were purchased from the local market and were of commercial grade.

Tetrazotized 4,4'-diamino-diphenylamine-2-sulphonic acid was prepared as earlier [1] and used in the solution form.

Visible spectra were recorded on Hitachi double beam spectrometer Model 220, using distilled water as solvent in 1 cm quartz cell.

Synthesis of II (A).

24.5 gm (0.1 mol) of sodium salt of 1-naphthylamine-4-sulphonic acid were dissolved in 200 ml of water by adding 5.5 gm (0.05 mol) of sodium carbonate in a one litre beaker. The solution was cooled to 5°C by immersing the beaker in an ice bath, assisted by the direct addition of crushed ice. Tetrazotized 4,4'-diamino-diphenylamine-2-sulphonic acid solution and a solution of 40 gm of sodium acetate in 100 ml of water were added simultaneously from two separate dropping funnels, with vigorous stirring. Stirring was continued for 2 more hours till the coupling was complete which was checked by H-acid (1-amino-8-naphthol-3,6-disulphonic acid).

To the above reaction mixture was added a solution of 24.0 gm (0.1 mol) of gamma acid (8-hydroxy-2-naphthylamine-6-sulphonic acid) and 5.5 gm (0.05 mol) of sodium carbonate in 200 ml of water, with stirring. The stirring was continued to complete the second coupling. 100 gm of sodium chloride were then added and heated to boiling. It was filtered while still hot and allowed to cool to precipitate the dye stuff which was filtered under suction, washed with water and dried at 80°C.

Synthesis of II (B).

13.8 gm (0.1 mol) of salicylic acid were dissolved in a solution of 8.0 gm of sodium hydroxide

in 100 ml of water in a one litre beaker which was then placed in an ice bath to bring the temperature to 10°C. Tetrazotised 4,4'-diamino-diphenylamine-2-sulphonic acid solution was added gradually from a dropping funnel with stirring. The stirring was continued for one hour to complete the coupling.

24.0 gm (0.1 mol) of gamma acid were dissolved in a 200 ml of 10% solution of sodium carbonate in a one litre beaker and added slowly with stirring to the above reaction mixture obtained after the first coupling reaction and whose pH had been adjusted to 5 by means of glacial acetic acid before addition. The reaction mixture was allowed to stand for about four hours with occasional stirring. 100 gm of sodium chloride was added. The solution was heated to the boiling point and filtered through a heated funnel. The filtrate was allowed to cool to precipitate the dyestuff. It was filtered under suction, washed with water and dried at 80°C.

Synthesis of II(C).

Salicylic acid (13.8 gm, 0.1 mol) was dissolved in 100 ml of 10% solution of sodium hydroxide in a one litre beaker and cooled to 10°C by placing in an ice bath. To this was added the tetrazotised solution of 4,4'-diamino-diphenylamine-2-sulphonic acid slowly with stirring. The contents were stirred for about one hour more to complete the first coupling.

24.0 gm (0.1 mol) of gamma acid were dissolved in 200 ml of 10% solution of sodium carbonate and then added gradually with stirring to the above reaction mixture of the first coupling reaction and kept at a temperature of 10°C. It was then acidified with glacial acetic acid and stirring continued for about one hour, 100 gms of sodium chloride were added to facilitate the precipitation of the dyestuff which was filtered under suction, washed thoroughly with water and dried by heating to 80°C.

The dyes IID and IIE were prepared by the same procedure as used for the preparation of IIC.

The dyes III(A-E) derived from benzidine were prepared by the methods used for the corresponding dyes derived from 4,4'-diamino-diphenylamine-2-sulphonic acid.

Table-1: Comparison of the properties of dyes derived from 4,4'-diamino-diphenylamine-2-sulphonic acid(II) with those from Benzidine (III)

Dyes	Strenght (%)	Shade	Absorption maxima (nm)	Red Shift (nm)
IIA	90	Reddish Violet	515	10
IIIA	100	Bluish Red	505	
IIB	80	Reddish Yellow	340	30
IIIB	100	Red	310	
IIC	90	GreyishBlue	565	5
IIIC	100	Reddish Blue	560	
IID	80	Violet-Blue	550	40
IIID	100	Reddish-Brown	510	
IIE	90	Bluish Violet	560	
IIIE	100	Blue	540	20

Results and Discussion

The dyes prepared from 4,4'-diamino-diphenylamine-2-sulphonic acid and those from benzidine were applied on cotton under similar dyeing conditions. Their strength and shades were compared and the results are shown in Table 1 together with their absorption maxima in the visible region taken from Figure 1.

The comparison of the dyeing results reveals that the shades of the dyes derived from 4,4'-diamino-diphenylamine-2-sulphonic acid (IIA-E) are not very different from those of the corresponding dyes derived from benzidine (III A-E) but generally they are slightly more bluish which is also indicated by the red shift of their visible bands. There is a larger variation in the shifts (ranging from 5 to 40 nm) as compared to the case of symmetrical dis-azo dyes [1].

The strength of the dyes obtained from 4,4'-diamino-diphenylamine-2-sulphonic acid is generally 80-90% of the strength of the benzidine dyes. This small decrease in strength may be due to

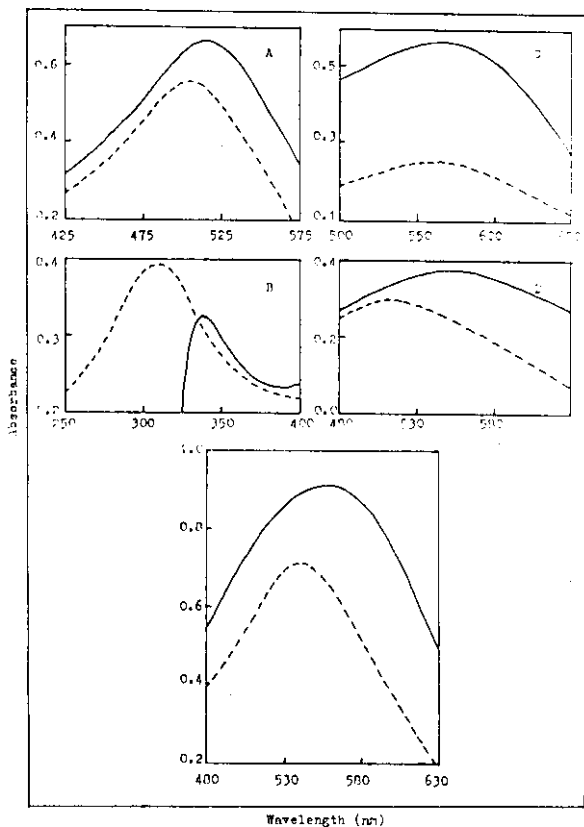


Fig.1: The Visible Spectra of the Dis-azo Dyes (A - E) derived from 4,4'-Diamino-diphenylamine-2-sulphonic acid (—) and benzidine (-----)

interruption in conjugation between the two phenyl rings by the -NH- group. The brightness of the colours is quite satisfactory.

In general, the dyeing properties of the dyes prepared from 4,4'-diamino-diphenylamine-2-sulphonic acid are comparable to those of the benzidine dyes. Therefore, it could reasonably be used as a replacement of benzidine as an intermediate for the preparation of dyes.

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