Synthesis and Characterization of Some New Azo Dyes for Synthetic and Artificial Fibres

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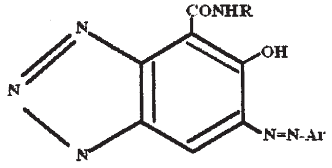
This paper presents the synthesis of direct azo dyes derived from benzotriazole, according to the following succession of reactions diazotisation of 4-amino-3-nitrotoluene, coupling with cresidine, m-toluidine, m-xylidine and 1-aminonaphthalene reduction and cyclisation leading to a triazolic heterocycle, sulphonation and oxidization. All the stages followed the synthesis procedures found in the literature. The dyes were obtained in high yields, in different shades of yellow. They have variable tinctorial properties, are resistant to lacquers, to dry friction and less resistant to humid friction. The dyes which can be applied on wool have a red colour. They are not soluble in water, but, at high temperatures, become soluble in alkaline medium. At a low temperature, the dyes are soluble in methanol-ethanol solutions and they can be used to dye cotton – like cellulose fibres and previously bleached woollen fibres. In order to validate the azoic structure of the synthesized dyes, we have studied their suspension in neutral and alkaline medium at high temperatures, when they were reduced with sodium hydrosulphite and reoxidized with $K_2S_2O_6$. The dyes absorb in UV-Vis at wavelengths ranging from 430 to 500 nm. After being applied on the fibres, we tested their reaction to wet treatments via reapplication with potassium dichromate and aniofix. If the suspension is reduced with sodium hydrosulphite and is exposed to air, the colour fades. This behaviour is specific to azo dyes which are not soluble in water in a neutral medium.

Keywords: direct azo dyes, benzotriazole, cresidine, 4-amino-3- nitrotoluene, m- toluidine, m- xylidine, 1- aminonaphthalene

Azo compounds being intensely coloured have a widespread use as pigments and dyes in a variety of applications including textile colouring [7].

The direct azo dyes which are used especially for dyeing cellulose materials must have a specific molecular configuration in order to have substantivity to the fibre during the dyeing process [1]. The structures which favour this substantivity are: polyazoic, benzidinic, stilbenic, triazinic chains and benzotriazole remains in the molecule [8-10].

The dyes belonging to this category must have groups which should help them become water soluble as sodium.The researchers [2] prepared a series of benzotriazolic acid azo dyes with the general formula:



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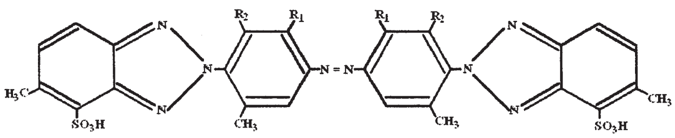
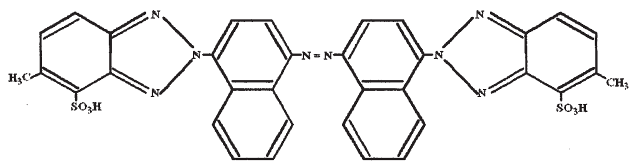
where R and Ar are aromatic radicals and –CONHR is in ortho position to the hydroxyl group [2]. The dyes which correspond to the general formula I were obtained via coupling with the benzotriazolic derivative corresponding to an amine diazonium salt. In general, these dyes with shades of yellow, orange or red have variable fastness properties, are resistant to lacquers, dry friction and less resistant to humid friction [3]. These dyes can be applied on woollen fibres, giving a red colour [4].

The present paper describes direct azo dyes which were derived from benzotriazole corresponding to formulae 2 and 3.



2a-c

2a $R_1 = R_2 = H$;
2b $R_1 = OCH_3$, $R_2 = H$
2c $R_1 = H$, $R_2 = CH_3$



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Experimental part

The synthesis has the following stages: diazotisation of 4-amino-3- nitrotoluene, coupling of 4-amino-3- nitro-toluene diazonium salt with m-toluidine, cresidine, m-xylidine and 1-aminonaphthalene, reduction and cyclisation resulting in the triazolic heterocycle, its sulphonation and oxidization. These reactions proceeded in similar conditions to those mentioned in the literature [5]. The reaction conditions and the experimental results are listed in table 1. The cotton – type cellulose fibres and the previously bleached woollen fibres were dyed with the new dyes and the results are listed in table 2.

The cotton fibres were dyed using the exhaustion procedure at 100°. For dye 2c, the dyeing bath contains 2g/L EDTA, 2g/L ACVAFIL, 3% dye, neutral medium and 100 mL water.

As far as dyes 2a, 2b and 3 are concerned, the bath contains 2g/L EDTA, 2g/L ACVAFIL, 3% dye, alkaline medium (pH=12), 100 mL water. The water does not

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Table 1
THE REACTION CONDITIONS IN THE SYNTHESIS OF DYES 2a-2c AND 3

Dye	Amount of diazotizing component (moles)	Amount of coupling component (moles)	Reaction temperature °C	Reaction period (h)	Yield %	Colour
2a	0.01	0.05	5-10°	0.5	85	orange yellow
2b	0.01	0.05	5-10°	0.5	90	orange red
2c	0.01	0.05	5-10°	0.5	92	orange
3	0.01	0.05	5-10°	0.5	98	red

Table 2
REACTION CONDITIONS IN THE REDUCTION, CYCLISATION, SULPHONATION AND OXIDIZATION STAGES OF OBTAINING DYES 2a-2c AND 3

Dye	Reduction and cyclisation				Sulphonation				Oxidization			
	Mass (g)	Moles	Colour	Yield	Mass (g)	Moles	Colour	Yield	Mass (g)	Moles	Colour	Yield
2_a	6	0.025	yellowish	66	8	0.023	pinkish	96	8.5	0.015	yellow	80
2_b	9	0.03	dingy green	75	9.3	0.026	green	90	12	0.018	yellow	70
2_c	7.5	0.03	yellow brown	76	8.5	0.027	brown	90	11	0.02	yellow	75
3	8	0.03	olive green	70	9.79	0.027	olive green	80	12	0.019	orange yellow	69

become clear enough after 4 washings in water with EDTA. The wool fibres are dyed using the exhaustion method at 100°. For 2c the dyeing bath has 2g/L EDTA, 2g/L ACVAFIL, 0,5g/L glycerine, neutral medium and 100 mL water.

In the case of dyes 2a, 2b and 3 the bath contains: 2g/L EDTA, 2g/L ACVAFIL, 1% N – propylic alcohol, 0.5g/L glycerine, 3% dye, alkaline medium (*p*H = 9 not 12 as it was in the case of cotton, to protect the wool).

Retreatments – to increase fastness to wet treatments:

a)the woollen fibres are treated again with $K_2Cr_2O_7$ – after being dyed and washed, the wool is treated for 20-30 minutes at 80-90° in a bath with contains 2g/L EDTA, 2% $K_2Cr_2O_7$, 1% technical CH_3COOH, 2% CH_3COOH 30%. When this process is completed, it is washed in water with EDTA.

b)further treatment with aniofix D of cotton fibres – cotton is washed after being dyed, then it is kept for 20-30 minutes at 25-35° in the bath with 2g/L EDTA and 3% aniofix.

In order to determine the chemical class to which the resulted dyes belong, according to the data in the literature [6], we have studied the aqueous suspension of the dyes after treatment at high temperature with NaOH solution and sodium hydrosulphite.

The effect which was noticed after dioxidization with $Na_2S_2O_8$:

-in neutral medium → loss of colour,

-in alkaline medium → loss of colour.

After the suspension is reduced with sodium hydrosulphite and is exposed to the air, the colour fades. According to [6] this reaction is specific to azo dyes which are insoluble in water in neutral medium.

Results and discussions

The synthesis of dyes 2a-2c proceeded in this succession: diazotisation of 4-amino-3- nitrotoluene coupling with cresidine (2a, 2b), m-toluidine (2a), m-xylidine (2c) and 1-aminonaphtalene (2c), reduction and cyclisation the triazolic heterocycle being formed, sulphonation and oxidization. All the stages were similar to the data in the literature [5]. The raw material which is used in the specialised literature [5] is also 4-amino-3-nitrotoluene, but only the anilinemethylenesulphonic acid is used as coupling component. The result is a yellow dye with 30% yield.

The present paper tried replacing this coupling component with other 4 substances. An increase in the yield was noticed, each dye having a different percentage. All of them have different shades of yellow.

Table 1 presents the reaction conditions and yields for dyes 2a-2c and 3 – while table 2 lists the reaction conditions in the reduction, cyclisation, sulphonation and oxidization stages in the process of obtaining dyes 2a-2c and 3.

Dyes 2a-2c and 3 are not water soluble. They become water soluble at high temperature in alkaline medium and soluble in methanol – ethanol solutions (table 3) at low temperature.

In order to be able to validate the azoic structure of the resulted dyes their suspension in neutral and alkaline medium at high temperature was tested during the reduction with sodium hydrosulphite and the reoxidization with $K_2S_2O_6$ [5].

The dyes absorb in UV-Vis at wavelengths ranging from 430 to 500 nm. When the dyeing process was completed we studied their response to wet treatments by treating once again with potassium dichromate and aniofix.

Dyes 2a-2c and 3 were applied on cotton – type cellulose fibres and on previously bleached wool.

Table 3 lists solubilities in the types of solutions which were indicated.

The dyeing process was done on cotton fibres using the standard dyeing procedure, the procedure via exhaustion at 100° for dye 2c. The dyeing bath contained 2g/L EDTA, 2g/L ACVAFIL, 3 % dye, neutral medium (100 mL water). For dyes 2a, 2b and 3 we used a bath with 2g/L EDTA, 2g/ L ACVAFIL, 3% dye, alkaline medium (*p*H = 12), 100 mL water.

The dyeing diagram is illustrated in figure 1.

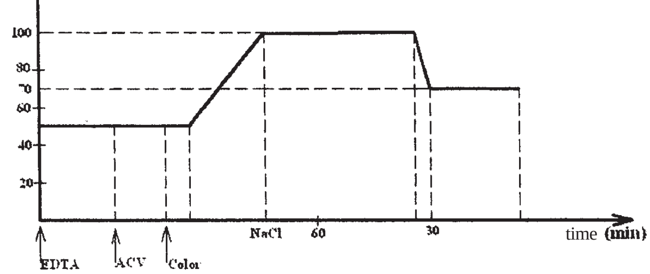

Fig.1 Dyeing diagram

Table 3
SOLUBILITY OF DYES 2a-2c, 3

Dye	Water EDTA Acvafil pH-neutral		Water EDTA Acvafil pH=9.5-10		Water EDTA Acvafil pH=12		Water EDTA Acvafil Propylic alcohol pH=4-4.5		Water EDTA Acvafil Propylic alcohol pH=3-3.5
	Cold	Hot	Cold	Hot	Cold	Hot	Cold	Hot	Cold | Hot
2a	It does not solubilize	It does not solubilize	Hardly soluble	Relative change to heat	Similar aspect to pH=10	Ochre yellow clear solution	It does not solubilize	It does not solubilize	Flocculated ↔ solubilization with sediments of impurities
2b	It does not solubilize	It does not solubilize	Slightly soluble	Relative change	Similar situation to pH=10, hot	Clear solution with undissolved particles (impurities)	It has solubilized verry little	It has solubilized yellow with impurities	Similar to pH= 4 - 4.5
2c	Good solubilization	Soluble	Soluble	Soluble	Soluble	Soluble	Insoluble	Insoluble	Relative solubilization with sediments of impurities
3	It does not solubilize	It does not solubilize	Slightly soluble	Relative change	Clear solution with possible impurities	Clear solution with the same impurities	Insoluble	Insoluble	Flocculated ↔ solubilization with sediments of impurities

In order to dye woollen fibres with the synthesized dyes, the exhaustion procedure at 100^0 is applied.

For dye 2c, the dyeing bath contains 2g/L EDTA, 2g/L ACVAFIL, 2-3 % dye, neutral medium and 100 mL water.

When dyes 2a, 2b and 3 are used, the dyeing bath contains 2g/L EDTA, 2g/L ACVAFIL, 1% propylic alcohol, 0.5g/L glycerine, 3% dye, alkaline medium (*p*H = 9).

The dyed woollen fibres are re-treated with $K_2Cr_2O_7$ to increase dyeing fastness to wet treatments. After being dyed and washed, the fibres are treated for 20-30 min, at 80-90° in bath with 2g/L EDTA, 2% $K_2Cr_2O_7$, 1% technical CH_3COOH, 2% CH_3COOH 30%. The dyed cotton fibres are re-treated with aniofix – after being dyed and washed they are kept for 20-30 min, at 25-35° in bath with 2g/L EDTA, 3 % aniofix. Washing is not necessary.

Application of dyes 2-3 does not present any uniformization difficulties.

The dyes are sensitive to salt, which increases the exhaustion speed of the dye bath. After retreatment the fastness to wet treatments is considerably higher, but the colour changes after the use of $K_2Cr_2O_7$.

As in the literature [5], we have studied the reaction to heat with NaOH solution and sodium hydrosulphite. The effect which was noticed at reduction with $Na_2S_2O_8$ in neutral medium leads to colour fading as in alkaline medium.

By using sodium hydrosulphite, the colour does not come back. According to data in the literature [5], this kind of reaction is specific to azo dyes which are water insoluble in neutral medium.

Conclusions

The replacement of the coupling component in the synthesis of dyes 2-3 led to much higher yields than those mentioned in the literature [5].

The resulted dyes absorb in UV-Vis at wavelengths ranging from 430 to 500 nm.

The following steps were followed in the synthesis of the dyes: diazotization of 4-amino-3- nitrotoluene coupling of the mentioned compound diazonium salt with m-toluidine, cresidine, m- xylidine and 1-aminonaphthalene, reduction and cyclisation forming the triazolic heterocycle, its sulphonation and oxidization.

Cotton type cellulose and previously bleached was dyed with the new dyes at yields ranging from 85 to 98 %, higher than in the literature.

In order to determine the chemical class the new dyes belong to, their aqueous suspension resulted from treatment with NaOH solution and sodium hydrosulphite at high temperature was tested. The effect which was noticed after reduction with $Na_2S_2O_8$ in neutral and alkaline medium was colour fading. The colour does not get to its initial form not even after exposure to the air of the suspension reduced with sodium hydrosulphite. This reaction is specific to azo dyes which are not soluble in water in neutral medium.

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