ACID AZO DYES AND PIGMENTS DERIVED FROM 2-AMINO-4-NITRODIPHENYLAMINE

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S-a realizat sinteza de 2-amino-4-nitrodifenilamină prin diazotare şi a fost utilizată pentru cuplare cu acid H în mediu acid şi bazic (i), cu acid I în mediu acid (ii) şi cu sare R în mediu alcalin (iii) (pentru a obţine coloranţi bazici) şi cu azonaftol A (iv), azonaftol OT (v), naftol ASSW (vi), azonaftol derivat de la 2- metil -6- aminobenzimidazol (vii) şi 2-naftoI (viii) (pentru a se obţine pigmenţi). Coloranţii au fost analizaţi prin cromatografie, spectre VIS şi aplicare pe lână şi alte fibre. S-a determinat rezistenţa lor la apă rece, spălare la 40° şi transpiraţie alcalină.

The synthesis of 2-amino-4-nitrodiphenylamine was realized by diazotation and it has been used for coupling with H acid in acid and alkaline medium (i), I acid in acid medium (ii) and R salt in alkaline medium (iii) (to get acid azo dyes) and with azonaphthol A (iv), azonaphthol OT (v), naphthol ASSW (vi), azonaphthol derived from 2- methyl -6- aminobenzimidazol (vii) and 2-naphthoI (viii) (to get pigments). The dyes were analyzed by chromatography, VIS spectra and application on wool and other fibers. Their fastness to cold water, washing at 40° and alkaline sweat was determined.

Keywords: azo dyes, coupling, 2-amino-4-nitrodiphenylamine, 2-naphthol, Naphtol A, Naphthol OT, Naphthol ASSW, 3-hydroxy-N-(2-methyl-3H-benzimidazol-5-yl) naphthalene-2-carboxamide, color fastness

1. Introduction

The acid azo dyes are characterized by the presence of the acid -SO_3H groups in the molecule and, more rarely of -COOH groups [1]. They are obtained and used exclusively as water- soluble sodium salts. In a weakly acid aqueous solution, they can dye supports with basic groups and form salts with them. The acid dyes are applied on wool, silk [2, 3], acid-modified polyacrylic (polyamidic) fibers, leather, paper, food and cosmetic products.

In most cases, the acid dyes are mono — [1] and diazo compounds [4]. The chromophore system of the primary diazo dyes of the type $D_1 \rightarrow C \leftarrow D_2$

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(where D_1, D_2 are the diazotation components and C the coupling component) is interrupted, there for the range of colors is restricted. In the naphthalene series are very commonly used H and Chicago SS acids.

The azo pigments are insoluble, a consequence of their chemical structure and of the substituents nature grafted on the azo dye molecules which reduce their solubility [5]. These dyes are used in different types of liquid binders, in manufacturing finishing varnishes, printing inks, resin- based enamels, alkydals for dyeing car bodies.

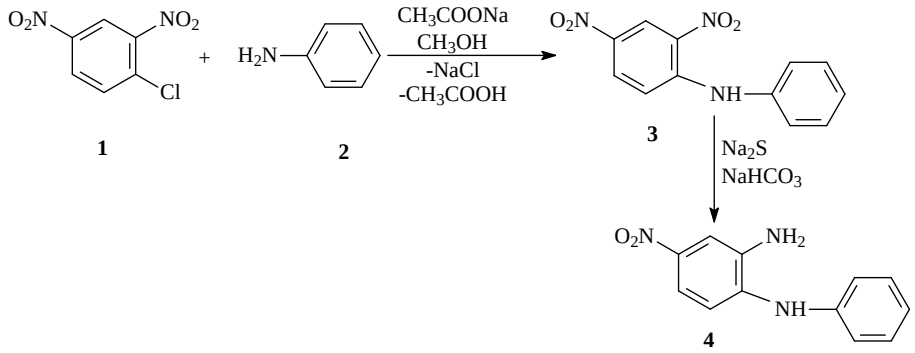
The pigments, which are intensely coloured products, could be incorporated into different materials, like plastics, rubber, linoleum, in a finely powdered state. Another method is to bring them on the surface of the support from a suspension, by applying them with a brush, sprinkling, sinking-or imprinting.

In order to extend the range of dyes, new acid azo dyes (3) and organic pigments (5) were obtained, using 2-amino 4- nitrodiphenylamine. This intermediate results from the arylamination of 2,4 dinitrochlorobenzene, reduction of the 2,4-dinitrodiphenylamine which was formed with Na_2S solution, in CH_3OH medium in the presence of $NaHCO_3$ [8].

The resulted amine is diazotated [9] with nitrosylsulphuric acid and then coupled with various components (azonaphthols A, OT, ASSW, the naphthol resulted from condensating acid BON chloride with 6- amino-2-methylbenzimidazole, 1-phenyl - 3- methyl - 5 - pyrazolone, R salt (7), H acid (6), the results being azo dyes.

2. Experimental

The synthesis of 2-amino-4-nitrodiphenylamine was performed according to Scheme 1:

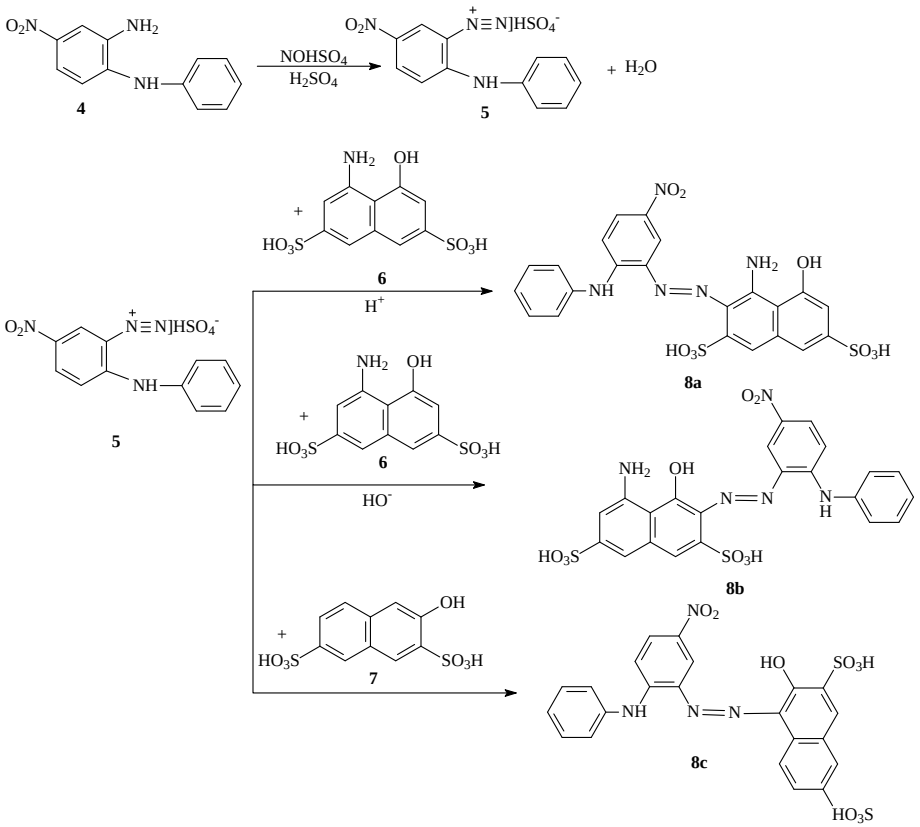


1 **2** **3** **4**

Scheme 1

An amount of 7.55 g (0.037 moles) of 2,4 - dichlorobenzene and 5.9 g (0.071 moles) CH_3COONa was introduced into a 500 mL flask, fitted with stirrer reflux cooler and $CaCl_2$ tube. The content was heated in 50 mL(1.234 moles) CH_3OH, stirred until it started boiling and then it was mixed with 16.8 mL (17.3 g, 0.184 moles) aniline poured in drops in the next 30 minutes [8].

After being refluxed for 3 hours, the reaction mass was cooled and the resulted precipitate was filtered and dried. The result was 7.5 g of 2,4 - dinitrophenylamine orange crystals with a boiling point of 148^0 C. For reduction, 5 g (0.019 moles) of 2,4 - dinitrodiphenylamine were introduced into a 500 mL flask fitted with stirrer and reflux cooler. 4.2g (0.050 moles) $NaHCO_3$, previously dissolved into 95 mL CH_3OH at high temperature are added in the flask. Then 26.2 mL Na_2S solution 33 % (0,1 moles - Solid Na_2S) were dripped for 1 hour while stirring. The whole mixture was refluxed for 4 hours. At the end of this period the reaction mass was poured on 600 mL water. After 24 hours, the formed precipitate was filtered and dried. The result was 3 g of 2 -amino 4- nitrodiphenylamine as red crystals (m.p. 124°, 68 % yield).



Scheme 2

2-amino 4-nitrodiphenylamine is diazotated in a similar manner to the data in the literature [9]. Then, it was coupled with different coupling agents to get the new dyes. The coupling with H acid (6 in Scheme 2) in basic medium involves its dissolution into 10 mL NaOH solution 5 % (0.0125 moles solid NaOH) at 20° C. The solution was cooled at 0°. In the next 3 hours, at 0^0 C the diazonium salt solution was dripped over the suspension. Stirring continued four hours after coupling, the product being then filtered and washed until its acidity disappeared. The dye resulted after drying at 60° C, the reaction yield being 95%.

The coupling with H acid (6) in acidic medium involved its dissolution into 10 mL NaOH solution 5 % (0.0125 moles solid NaOH) at 20° C. The solution was cooled at 0° C and H_2SO_4 20% was dripped over it until it gets acid on Congo red. In the next 3 hours, at 0^0 C the diazonium salt solution is dripped over the suspension. Stirring continued four hours after coupling, the product being then filtered and washed until its acidity disappeared. The dye resulted after drying at 60° C, the reaction yield being 90%.

The spectrophotometric analysis of the dyes in order to determine λ_{max} was performed on a PVE UNICAM spectrophotometer. Synthesized dyes were analyzed in terms of purity by thin layer chromatography using pyridine as eluent. Electronic spectra were measured with a PVE UNICAM spectrophotometer. The dyes were used to dye fibers and the pigments were applied on plastics [13].

The new dyes and pigments were obtained according to Scheme 2 and 3, respectively.

The coupling with R acid (7 in Scheme 2) involves its dissolution into 10 mL NaOH solution 5 % (0.0125 moles solid NaOH) at 20° C. The solution was cooled at 0° C and the diazonium salt solution was dripped over the suspension in the next 4 hours. Stirring continued four hours after coupling, the product being then filtered and washed until its acidity disappeared. The dye resulted after drying at 60° C, the reaction yield being 96%.

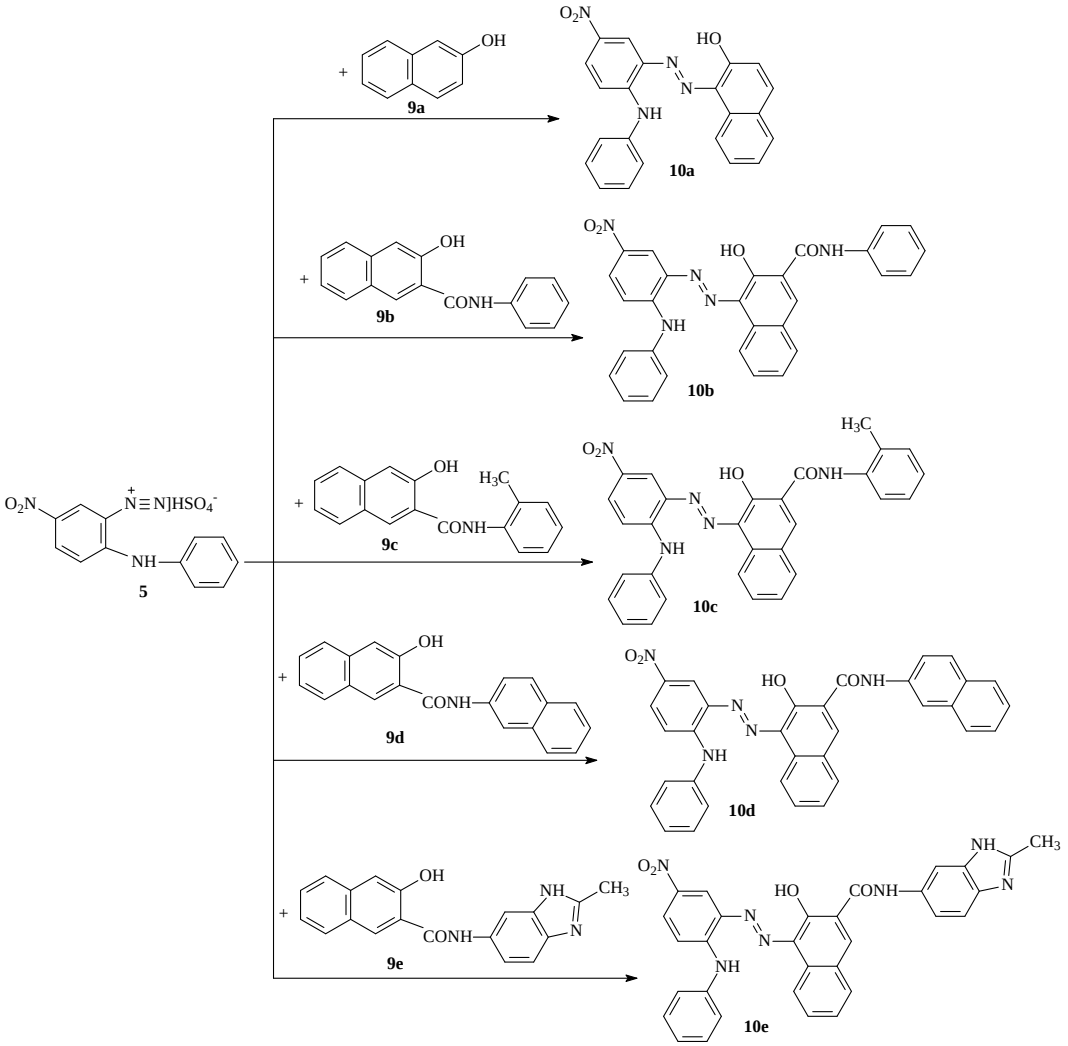
Table 1 gives the reaction conditions for coupling reactions.

Table 1

Reaction conditions for the synthesis of acid monoazo dyes 8a-8c starting from 3g (0.04 moles) 2-amino-4-nitrodiphenylamine

Dyes nr.	Coupling component		pH	Reaction time (h)	Yield (%)
	g	moles			
8a	**6**		5	3	90
	12.8	0.04			
8b	**6**		8	3	95
	12.8	0.04			
8c	**7**		8	4	96
	12.2	0.04			

The azo pigments resulted from the coupling of 2-amino-4-nitrodiphenylamine previously diazotated with: 2- naphthol (9a), Naphthol A (3-hydroxy-N-phenyl-naphthalene-2-carboxamide, 9b), Naphthol OT (3-hydroxy-N-(o-tolyl) naphthalene-2-carboxamide, 9c), Naphthol ASSW (3-hydroxy-N-(2-naphthyl) naphthalene-2-carboxamide, 9d) and 3-hydroxy-N-(2-methyl-3H-benzimidazol-5-yl) naphthalene-2-carboxamide (9e). The reactions are shown in Scheme 3:



Scheme 3

The 2-amino-4- nitrodiphenylamine diazoderivative (5) was coupled with 2- naphthol in the following way. 0,62g(0,0043 moles) 2-naphthol were dissolved

into 10 mL NaOH solution 5% at 60^0. Then the solution was cooled to 0^0 C and the diazonium salt solution was dripped for 3 hours, at 0° C. Stirring continued for one more hour after coupling terminated. It was then filtered and washed to remove the acid. The reaction yield was 82%.

Table 2 gives the reaction conditions for the new pigments which resulted from coupling 2-amino-4-diphenylamine as diazotation component with **9a-9e**.

Table 2

Reaction conditions and results in the preparation of pigments 10 from 3g 4 as diazotation component at 0º C

Pigment no.	Coupling component		pH	Reaction time (h)	Yield (%)
	Type	(g)			
10a	**9a**	1.9	8	3	82
10b	**9b**	3.5	8	3	80
10c	**9c**	3.7	8.5	3.5	85
10d	**9d**	4.2	9	3	96
10e	**9e**	4.2	8.5	3	93

3. Results and discussions

The reduction reaction which occurred to prepare the intermediate (2-amino-4-nitrodiphenylamine) was performed at different molar ratios, with the following results:

Table 3

Variation of the reduction yield for different amounts of Na_2S for 1 mole of 2,4-dinitrodyphenylamine

No.	Na_2S (mole)	Yield (%)
1	1.5	59.4
2	2	64
3	2.5	68.2
4	3	68.3

The optimum result was considered for the molar ratio Na_2S - 2,4-dinitrodyphenylamine of 2.5:1.

Table 4 gives the spectrophotometric characterizations of the dyes and pigments 8 and 10.

Table 4

Experimental data on electronic absorption spectra

Dye	λ_{max} (nm)	lgε	Rf (pyridine eluent)
8a	550	3.014	0.63
8b	410	1.141	0.32
8c	440	2.947	0.77

10a	590	1.129	0.75
10b	575	2.051	0.22
10c	600	2.714	0.41
10d	580	3.578	0.52
10e	606	1.634	0.12

The acid dyes **8a**, **8b**, **8c** were used to dye wool fibres, while azo pigments **10a-10d** were applied on plastics [13].

8a, 8b and **8c** were applied on wool and other natural (silk) and synthetic (Relon) fibers. The application of dyes were performed at identical parameters: dye bath composition (bath ratio 1:3), 10% dye (with respect to the material), softening agent (1-2g/l), 20% electrolyte acid medium (CH_3COOH-1-3%), sulphonated fatty alcohol (1-2g/l) as leveling agent solution. Wool is dyed in acid medium, at a pH 4.5.

Dye **8a** gives a slightly dull shade of pink, with good fastness properties. When washed several times in alkaline medium the colour changes (slight discolouring). The fastness properties of the dyeing process are good to washings, wet treatments, alkaline sweat, etc, in general of 4-5.

Dyes **8b** and **8c** gave a light yellowish-brown color, with medium fastness properties. They are not recommended for fibres which are later washed in alkaline medium, because the colour changes significantly. Wool is dyed in acid medium at a pH 4.5.

The fastness properties for dyes **8a - 8c** (cold water, washing at 40° C, alkaline sweat) are good.

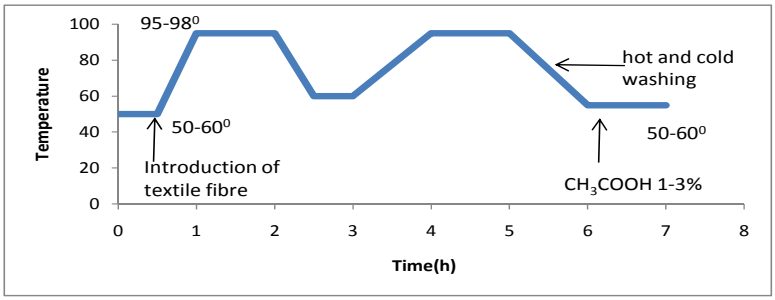


Fig.1. Dying diagram for dyes **8a-8c**

Hot and cold washings with softened water for exhaustion do not change the colours.

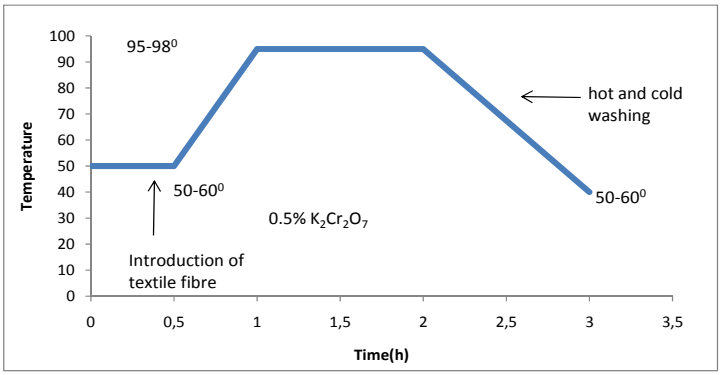


Fig. 2. Dying diagram for dyes **10a-10e**

4. Conclusions

The synthesis of 2-amino-4-nitrodiphenylamine was done by condensation of 2,4- dinitrochlorobenzene CH_3COONa (in methanol) followed by reduction of 2,4 dinitrophenylamine with Na_2S solution in a CH_3OH medium and in presence of $NaHCO_3$. The azo dyes resulted from the diazotation of the newly formed amine with nitrosylsulphuric acid followed by coupling with different coupling components (2- naphthol, Naphthols A, OT, ASSW and 3-hydroxy-N-(2-methyl-3H-benzimidazol-5-yl) naphthalene-2-carboxamide) are new compounds with good fastness properties.

R E F E R E N C E S

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