BROMAMINE ACID DERIVATED DYES

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*În această lucrare este prezentată obţinerea unor noi coloranţi antrachinonici derivaţi de la acidul bromaminic (**1**) prin condensarea acestuia cu diverse amine aromatice. Aceşti coloranţi au fost testaţi prin analiză elementală si metode cromatografice şi spectrale (IR, UV-VIS) pentru confirmarea structurilor propuse.*

*Anthraquinone dyes(**D1-D6**) derived from bromamine acid (**1**) were obtained by condensing bromamine acid with various aromatic amines. These compounds were analysed by elemental analysis, spectral and chromatographic methods in order to confirm the proposed structures.*

Keywords: bromamine acid, anthraquinone, reactive dyes.

1. Introduction

Anthraquinone dyes are very well known in the literature, being the second largest class of textile dyes after azo dyes [1]. They are distinguished by their brilliance, good light-fastness and stability of the chromophore under both acid and alkaline conditions [2, 3].

The color of anthraquinone dyes is partially associated with the anthraquinone nucleus and modified by the type, number, and position of substituents [4]. Unsubstituted anthraquinone is pale yellow and has a weak band at ca. 405 nm, which is due to an $n \rightarrow \pi^*$ transition. Anthraquinone dyes give a wide range of colors in almost the whole visible spectrum, but they are most commonly used for green, blue or violet hues [4].

Some of the very important blue dyes are derivates of the natrium salt of 1-amine-4-bromo-anthraquinone-2-sulphonic acid (bromamine acid). This is usually reacted with a fiber-reactive amine component making possible for the

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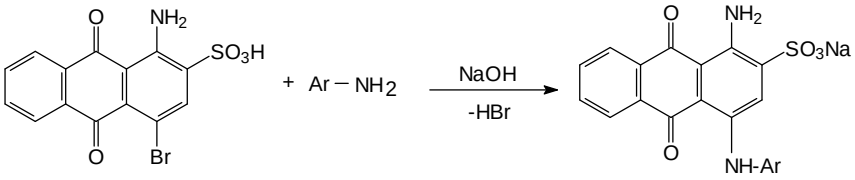
fiber-reactive group to be linked to the amino group via aliphatic or more often via aromatic bridge members. The advantage of utilizing this acid is its water solubility and the easiness in labilization of Br atom (due to carbonylic group and sulphonic group), in reaction with various amines.

Anthraquinone dyes derived from bromamine acid were obtained by condensing bromamine
acid with various amines: p-toluidine, ciclohexylamine, 3-nitro-p-toluidine, 3-nitro-4-N-hydroxiethylamine, 4-amine-benzoethylamide, 1-amino-4,8-naphthaline sulphonyc acid. New dyes have been obtained and tested.

2. Experimental

The synthesis path for six anthraquinone dyes **D1-D6** was realized starting from bromamine acid by condensing with several amine compounds (*Scheme 1*):



D1-D6 **1**

Scheme 1

Ar-NH_2:	**Dyes**
p-toluidine	**D1**
ciclohexyl amine	**D2**
3-nitro-p-toluidine	**D3**
3-nitro-4-N-hydroxyethylamine	**D4**
4-amine-benzoethylamide	**D5**
1-amino-4,8-naphthaline sulphonic acid	**D6**

The condensation was performed in a three-necked glass reactor, where 2 g of bromamine acid was dissolved in 200 mL hot water, stirring continuously. Then were added 0.7 g of $CuSO_4$ as catalyst and a stoechiometric

amount of amine (in three portions). The mixture was maintained at 100°C until the bromamine acid was consumed (between 2-6 hours).

The evolution of the reaction was followed by TLC (Silica Gel F_{254}) using DMF as eluent.

After the reaction was finished, the obtained precipitate was dissolved in 2L H_2O at 60-100°C and the warm mixture was filtered. By cooling the filtrate at 0°C, the dye was precipitated. The precipitate was purified by recristallisation. Suitable crystals were grown by slow evaporation from either chloroform/methanol (1:1) or water. These new dyes were analyzed by elemental analysis, UV-VIS and IR spectroscopy, as well as thin layer chromatography (TLC).

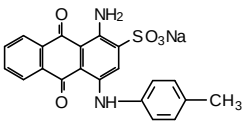
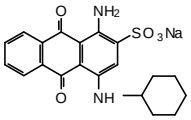
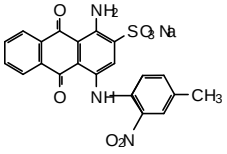
The elemental analyses were recorded by combustion method (Liebig device) with an microcombustion instrument. UV–VIS absorption measurements were performed with a Perkin–Elmer 900 spectrophotometer. IR spectra were recorded on Specord 71 spectrometer in KBr.

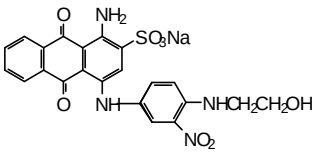
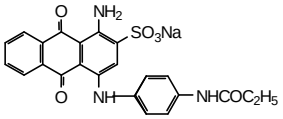
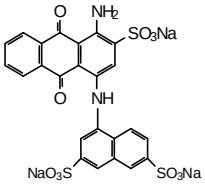
3. Results and discussions

The reaction conditions for the synthesis of the dyes **D1-D6** are presented in the Table 1. The elemental analyses of the dyes are presented in Table 2. The IR, UV-VIS spectral data as well as chromatographic data are shown in Table 3.

Table 1

Reaction conditions for the synthesis of D1-D6

Dye	Structure	Reaction time (hours)	Reaction temperature (°C)	η (%)
D1		2	80-100	80
D2*		2	80-100	90
D3		4	80-100	87

D4		4	80-100	82
D5		4	80-100	79
D6		6	80-100	85

***** Dye **D2** is known as Acid Blue 62 [5]; synthesis conditions in the present paper differs from those met in literature.

Table2

Elemental analyses of the new dyes (D1-D6)

D	**Molecular weight**	**Elemental Analysis(%)**							
		C		**H**		**N**		**S**	
		calculate	found	calculate	found	calculate	found	calculate	found
D	430	58.60	57.84	3.48	2.83	6.51	7.14	7.44	7.76
D	422	56.87	56.23	4.50	3.97	6.63	7.26	7.58	7.83
D	475	53.05	52.03	2.94	2.76	8.84	9.64	6.73	7.10
D	506	52.17	51.96	3.35	3.03	8.30	9.18	6.32	6.71
D	425	64.94	64.14	4.23	3.92	6.58	7.24	7.52	7.84
D	670	42.98	42.27	1.94	1.65	4.17	4.87	14.32	14.65

High extinction coefficients for the synthesized compounds are in agreement with the dark colors and are connected to the nature of the substituents.

The analysis proved that the proposed structures for obtained dyes were correct.

The maximum of UV-VIS absorption were at λ = 590-595 nm.

Table 3

Spectral and chromatographic data, and color of dyes D1-D6

Dye	Functional group	IR	UV-VIS		R_f	Color
		Frequency (cm^{-1})	λ_{max} (nm)	lgε		
D1	p-disubstituted aromatic ring >C=O $ArNH_2$ -NH	840i 1690v.i 3400m 1260m	600	4.91	0.32	Blue
D2	>C=O  $-SO_3H$ Alkyl-NH-aryl	1710v.i 1430m 1051 3500m	590	4.91	0.27	Blue
D3	>C=O $-SO_3H$ 1,2,4-trisubstituted aromatic ring	1700v.i 1045 860m	598	4.91	0.15	Blue
D4	$>CH_2$ C-OH $-NO_2$ Aromatic ring 1,2,4-trisubstituted	1450m 1075i 1340 870m	593	5.14	0.18	Violet
D5	>C=O (amide band 1) >C=O	1680v.i 1723v.i	595	4.90	0.23	Blue
D6	 >C=O	1450m 1689	590	4.91	0.29	Blue

The color of synthesized dyes is blue, similar with other anthraquinone derivated dyes mentioned in literature [6,7]. The purity of these new synthesized dyes was checked by TLC and the estimated Rf values were reported.

The obtained products present a high solubility in water. They can be recommended for testing in unconventional fields, like coloring the liquid crystals, due to the resemblance of these compounds with other known anthraquinone derivated dyes already used in this domain.

4. Conclusions

A classical synthesis method was tested for the synthesis of 6 new dyes starting from bromamine acid and some aromatic and aliphatic amines. The new dyes have been characterized by elemental analysis, IR and UV-VIS spectroscopy, as well as TLC. They present a high solubility in water and good color performances.

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