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SYNTHESIS AND CHARACTERIZATION OF NEW AZO COUMARIN DYES

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În această lucrare sunt prezentate sinteza şi caracterizarea unei serii de 9 noi coloranţi azocoumarinici. Aceşti coloranţi au fost obţinuţi prin cuplarea cu cumarină a sărurilor de diazoniu ale unor amine aromatice: 3,4-dinitroanilină, 4-clor-2,5-dinitroanilină, 2-amino-4-nitronafthalin, 2-methoxyaniline, 4-metilanilină , 2-hidroxianilină, 2-metil-1-aminoantrachinona, 2 - aminoantrachinona şi 2-amino-3-metilantrachinona. Randamentele reacţie au fost cuprinse între 64% şi 79%. Structurile propuse pentru aceşti coloranţi au fost confirmate şi caracterizate prin cromatografie, analiza elementală şi din spectrele UV-Vis, de fluorescenţă şi ^{1}H *-RMN. Coloranţii obţinuţi au prezentat culoarea galben-portocalie şi sunt solubili în apă şi solvenţi organici.*

Synthesis and characterization of a series of 9 new azocoumarin dyes were presented in this paper. These dyes were obtained by the coupling of coumarin with the diazotized aromatic amines: 3,4-dinitroaniline, 4-chlor-2,5-dinitroaniline, 2-amino-4-nitronafthaline,2-methoxyaniline, 4-methylaniline, 2-methyl-1-amino-anthraquinone, 2-hdroxyanthraquinon, and 2-amino-3-methylanthraquinone. The reaction yields were between 64%-79%. The proposed structures of the dyes were confirmed and characterized by using chromatography, elemental analysis, and UV-Vis, fluorescence and ^{1}H *-NMR spectra. The obtained dyes showed a yellow–orange color and they are soluble in water and organic solvents.*

Keywords: Benzene derived amines, Anthraquinone derived amines, Diazotization, Coupling, Azocoumarin dyes

1. Introduction

Coumarins are the simplest heterocyclic compounds that naturally occur. A lot of coumarins and their derivatives have been identified from natural sources, especially in the green plants. They are used as additives in foods, perfumes, cigarettes, cosmetics, pharmaceuticals, for optical brighteners, in fluorescent and laser dyes [1, 2].

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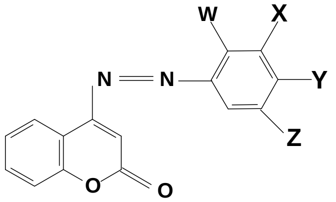
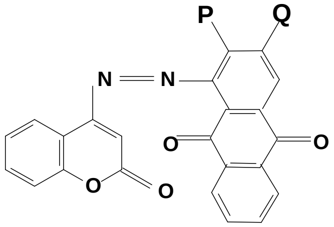


Dye Number	W	X	Y	Z
Ia	H	NO_2	NO_2	H
Ib	NO_2	H	Cl	NO_2
Ic	NH_2	H	NO_2	H
Id	OCH_3	H	H	H
Ie	H	H	CH_3	H
If	OH	H	H	H

Fig. 1. Formula of the new synthesized azocoumarin dyes of type I



Dye Number	P	Q
IIa	CH_3	H
IIb	NH_2	H
IIc	NH_2	CH_3

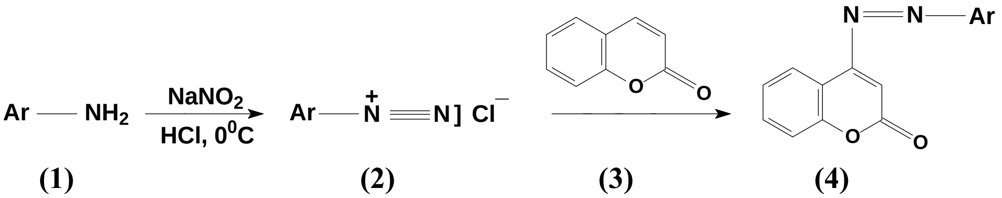
Fig. 2. Formula of the new synthesized azocoumarin dyes of type II

The synthesis of coumarin dyes has attracted the attention of chemists for many years, as a large number of natural products contain this heterocyclic nucleus. These dyes are also exploited in chemical, biochemical, physical and pharmaceutical applications. The coumarin is not fluorescent, but the introduction of an electron-withdrawing group such as a diazotized aromatic amine or an acetyl group makes it highly fluorescent. The coumarins are generally very convenient compounds for chemical modification due to the ease of synthesis [3].

The goal of this study was to use unsubstituted coumarin as a coupling component and electron donor to synthesize new azocoumrin dyes by coupling it with different diazotized aromatic amines, derived from benzene or anthraquinone. The structures for the new dyes are shown in Figs. 1 and 2, respectively.

2. Experimental

Azocoumarin dyes were synthesized in two-step procedure, formation of diazonium salt, then coupling reaction with coumarin [4], as shown in Scheme 1, where Ar = substituted phenyl ring, to synthesize dyes type I, or substituted anthraquinone to synthesize dyes type II.



Scheme 1

2.1. Diazonium salt formation

To a suspension prepared from: 1.38 g (0.01mole) 3,4-dinitroaniline**(1)**, 12 mL water and 12g ice, 6mL (0.052 mole) 32% hydrochloric acid was added under stirring at 8 ^{o}C, a solution of 3.5g (0.01 mole) 20% $NaNO_2$. The reaction mass was stirred during 1 h at 0-7 ^{o}C with 10 mL concentrated sulfuric acid, till the end of the diazotization reaction. The solution of the obtained diazonium salt (**2**) was used in the coupling reaction.

2.2. Coupling reaction

0.01mole of the coupling component, coumarin, was dissolved in a sodium hydroxide solution (10 g NaOH in 100mL water) and then it was cooled up to 5-9^{o}C. The previously prepared diazonium salt solution was dropwisely added to a basic solution of unsubstituted coumarin (**3**) during 15-30 minutes at 0-7 ^{o}C, under a stirring and by adjusting of the pH (8.5-9) with 15% Na_2CO_3 solution. Then the obtained reaction mass was filtered.The precipitate was washed with 20% HCl solution to remove the traces of unreacted amines and then with water up to neutral pH. Then the precipitate was dried and recrystallized from ethanol: water (1:10).

2.3. Purification

The melting point of the synthesized dyes was recorded with a Boetius micro apparatus [5, 6]. The purity of the obtained dyes were verified by TLC using Silica Gel F_{254} plates and dioxane:methanol (1:1) as mobile phase.

For purification the compounds were recrystallized from their diluted HCl solutions [4].

2.4. Characterization

The purified dyes were checked by elemental analysis. The IR spectra in KBr pellets were recorded using a VERTEX spectrophotometer, and their UV-Vis spectra in dioxane were recorded on a SPECORD 40 spectrometer according to the procedure already described [9-11]. The fluorescent spectra were recorded using a CARY 10 Varian spectrometer.

The ^{1}H - NMR measurements are performed with VARIAN EM-360L, apparatus at 60 MHz.

3. Results and discussion

The 9 new azocoumarin dyes were synthesized by diazotization of different aromatic amines: 3,4-dinitroaniline, 4-chlor-2,5-dinitroaniline, 2-amino-4-nitronafthalin, 2-methoxyaniline, 2-methylanaline, 2-hydroxylanaline, 2-methyl-1-aminoanthraquinone, 2-aminoanthraquinone and 2-amino-3-methylanthraquinone with the formation of diazonium salts, followed by coupling with the unsubstituted coumarin according to Scheme 1. In this scheme Ar is a substituted phenyl ring, to synthesize azocoumarin dyes of type **I** (**Ia**-**If**), or substituted anthraquinone to synthesize dyes of type **II** (**IIa**-**IIc**).

The dyes of type **I** and **II** were obtained according to the procedure described in the experimental part with the reaction conditions given in Table 1, for an amount of (0.01mole) coumarin as coupling agent . The coupling reaction temperature was between 5-9°C. The yield, the color and the coupling time are also shown in Table 1.

The main physical and chemical data were determined and they are shown in Table 2 and 3. They confirmed the structures of the new synthesized dyes according to the standard procedures.

Table 1

Reaction conditions in the dyes synthesis

Dye	Amount of diazotizing components g (moles) for 0.01mole of coumarin	Coupling time (min)	Yield (%)	Dye color
Ia	1.38 (0.01)	30	79	Orange-Yellow
Ib	5.15 (0.05)	15	74	Orange-Brown
Ic	1.38 (0.01)	30	64	Orange-Yellow
Id	1.23 (0.01)	20	70	Orange-Yellow
Ie	2.23 (0.01)	15	70	Orange-Red
If	2.37 (0.01)	20	74	Orange-Yellow
IIa	2.37 (0.01)	15	68	Yellow
IIb	2.33 (0.01)	15	71	Orange-Yellow
IIc	2.33 (0.01)	18	68	Orange-Yellow

Table 2

Physical data of the new synthesized dyes

Dye Number	Chemical Formula	M.P. (^{o}C)	R_f	Elemental Analysis (%) Calculated /Found			
				C	H	N	Cl
Ia	$C_{15}H_8O_6N_4$	220-222	0.53	52.95/52.9	2.35/2.29	16.46/16.1	-
Ib	$C_{15}H_7O_6N_4CI$	156-158	0.57	48.14/48.01	1.87/1.81	14.97/14.9	9.3/9.1
Ic	$C_{15}H_9O_4N_4$	188-190	0.58	58.26/58.01	2.91/2.86	18.18/18.1	-
Id	$C_{16}H_{12}O_3N_2$	182-184	0.55	68.58/68.1	4.28/4.18	17.13/17.1	-
Ie	$C_{16}H_{12}O_2N_2$	206-208	0.63	72.74/72.06	4.57/4.61	10.6/10.5	-
If	$C_{15}H_{10}O_3N_2$	166-168	0.67	67.68/67.2	3.75/3.68	10.52/10.5	-
IIa	$C_{24}H_{14}O_4N_2$	210-212	0.69	73.0/72.89	3.55/3.48	7.1/7.01	-
IIb	$C_{23}H_{13}O_4N_3$	268-270	0.61	69.88/69.73	3.79/3.68	10.63/10.5	-
IIc	$C_{23}H_{15}O_4N_2$	230-232	0.51	72.0/71.88	3.91/3.84	7.3/7.27	-

Table 3

Spectroscopic data for the new synthesized dyes

Dye Number	UV -Visible Absorption		Fluorescence λ max (nm)		IR ν (cm^{-1})
	λ max (nm)	ε ($dm^3mol^{-1}cm^{-1}$)	Excitation	Emission	
Ia	246	11680	356	442	1364 , 1570 , 3462
Ib	354	13450	378	466	1370 , 1572 , 3450
Ic	366	11458	366	432	1368 , 1570 , 3452
Id	350	11700	388	432	1370 , 1586 ,3466
Ie	348	11210	374	488	1364 , 1580 , 3450
If	256	13858	328	478	1365 , 1582 , 3450
IIa	396	13800	450	490	1366 , 1586 , 3456
IIb	410	14260	476	510	1364 , 1576 , 3480
IIc	406	13900	446	580	1364 , 1572 , 3478

The elemental analysis results are comparable with the calculated values [7, 8]. The ^1H – NMR spectra of the dyes **Ia-If** in D_2O revels the appearance of 6-8 characteristics signals in the range between δ = 7.4 - 8.9 ppm (as it can be seen in Table 4).

The ^1H – NMR spectra of the dyes **IIa-IIc** in D_2O revels the appearance of 9-10 characteristics signals in the range between δ = 7.4 – 8.3 ppm.

The ^1H – NMR spectra of both dyes (type **I** and type **II**) contains also the coumarin signals 6 signals in the range of δ = 6.4–7.8 ppm.

The fluorescence spectra were also recorded in the range λ =190-1000nm. The results are shown in Table 3 for excitation and emission wave lengths.

The UV-Vis spectroscopic measurements for the new dyes in dioxane solutions showed characteristic absorption maxima in the range of 340-375 nm while coumarin bands was detected at 274 nm.

The IR absorption spectra were measured in the 500-3500 cm^{-1} region. Their characteristic signals are shown in Table 3.

Table 4

^{1}H-NMR characteristic signals for the synthesized dyes

Dye Number	**δ (ppm)**
Ia	8.62 (s, 1H, NH); 8.55 (d,1H, H-1,6.9); 7.4 (m, 4H, H-arom); 7.32 (dd,1H,H-3,2.3); 7.15 (dd,1H, H-4); 6.73 (d,1H, H-4); 6.4 (s, 2H, H-6)
Ib	8.95(s,1H,NH,1.4);8.6(m,1H,H-arom);7.41(m,4H,H-arom); 7.25(dd,1H,H-4,1.7); 7.02(d, 1H, H-3, 8.0); 6.80 (dd, 1H,H-4, 2.4); 6.4(d,1H, H-4, 8.3)
Ic	8.78 (s, 1H, NH, 1.8); 7.95 (m, 2H, H-arom); 7.80 (d,1H, H-1,2); 7.6(m, 3H, H-4, 3.6); 7.4 (m, 6H, H-arom); 7.29 (dd, 1H, H-3); 6.8 (d , 1H, H-4, 8.4).
Id	8.79 (s, 1H, NH, 8.3); 8.49 (d, 1H, H-1, 6.4); 7.75 (d, 2H, H-3, 5.1) 7.43 (m, 4H, H-7, 3.2); 7.29(dd, 1H, H-3, 7.3); 6.85 (d,1H, H-4 , 8.4).
Ie	8.72 (s, 1H, NH); 8.65 (d, 1H, H-1, 5.6); 8.25(dd, 1H, H-3, 2.8); 7.95(d,1H, H4); 7.4 (dd,1H, H-6); 6.7 (m,4H,H-arom).
If	8.86 (s,1H, NH, 1.9); 8.4 (dd, 1H-H-8, 1.9); 8.1 (d, 1H, H-1, 2.6); 7.84 (dd, 1H, H-4, 1.6); 7.41 (m, 6H, H-arom); 6.9 (dd, 1H, H-3, 8.4).
IIa	8.26 (s, 1H, NH, 2.1); 8.12 (dd, 1H, H-2, 4.5); 8.02 (d, 1H, H-1, 2.8); 7.9 (DD, 1H, H-6);7.82(dd, 1H, H-3,2.8); 7.66(dd,1H, H-4, 8.4);7.82(dd,1H, H-3, 2.4); 7.4(m, 4H, H-arom); 6.8(d, 1H, H-4, 3.4).
IIb	8.3 (s, 1H, NH, 1.6); 8.18 (d, 1H, H-1, 8.6); 8.02(d, 2H, H-8, 2.8); 7.9(d, 1H, H-4, 4.6) ;7.6 (dd, 1H , H-3, 4.8); 7.41(m,4H, H-arom); 6.6 (dd,1H, H-2, 3.6).
IIc	8.38 (s, 1H, NH, 1.1);8.3 (d, 1H, H-4, 8.1);7.96 (dd,1H,H-3, 2.8); 7.68 (d, 2H, H-1 ,8.2); 7.42 (m,4H,H-arom); 7.25 (dd,1H, H-7, 7.8);6.8 (d, 1H, H-4, 2.2); 6.4 (d, 1H, H-1, 3.2) ..

4. Conclusions

9 new azocoumarin dyes were prepared by the coupling reaction of coumarin as electron-donor with various diazotized aromatic amines derived from benzene or anthraquinone. The dyes were obtained by relatively simple synthesis methods with high and good reaction yields (64-79%).

The proposed structures of the new dyes were confirmed by spectral analysis performed by IR, UV-Vis, ^{1}H-NMR and elemental analysis. They also were characterized as dyes by colour and R_f.

It was shown that coumarin is a good coupling agent for these various diazotized aromatic amine derivatives. The new dyes showed light orange-yellow fluorescence, more intense then that of coumarin. That is why these are promising dyes which could be recommended for new applications.

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