New Azo-Coumarin Compounds

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This paper presents the synthesis and characterization of new azoic dyes derived from coumarin obtained by coupling some diazotated aromatic amines to unsubstituted coumarin. The spectral analysis of the resulted compounds are confirming the proposed structures.

Keywords: coumarin derivatives, diazotation, aromatic amines, coupling, fluorescence

Coumarin is an aromatic compound found throughout the vegetal reign and in some essential oils. Due to of its sweet flagrance, coumarin is used in perfumes, toiletries, tobacco products and previously as a food flavoring additive [1]. Coumarin was first isolated by Vogel in 1820 by extraction from tonka beans (*Dipteryx odorata*). It was subsequently identified in a large number of plants belonging to many different families [2]. Coumarin is currently being evaluated for the treatment of some types of cancer [3, 4] and is used in the treatment of lymphedema [5]. Its use as a food additive was banned in the United States in 1954 because it was shown to be hepatotoxic in rats and dogs [6, 7]. The coumarin compounds have an absorption and a luminous maxima in a visible region and have a satisfactory thermo stability; they have various usages as light absorbing agents or luminous agents in the fields of photochemical polymerization, solar cells, optical filters, dying, dye lasers, analysis etc. [8].

The purpose of the present paper is to synthesize 4 new azo-coumarin dyes obtained by diazotation of 5 aromatic amines and coupling them with unsubstituted coumarin [9].

The use of unsubstituted coumarin as a coupling component has not yet been reported. Until now, the literature mentioned that only substituted coumarin was used in the coupling reactions with diazotized amines.

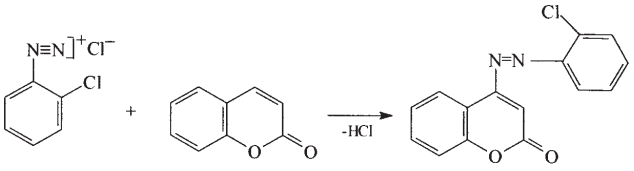
Experimental Part

Synthesis of dye ***1*** *(**D**$_1$)*

1.28g (0.01moles) 2-Chloroaniline was dissolved under stirring in 30mL water and 5mL concentrated HCl. The solution was cooled at 0-5^{0}C and to it, a solution of 0.72g $NaNO_2$ in 10mL water was added drop wise over a period of 15 min. The resulting solution was stirred for additional 15min. and then a small amount of urea was added to remove the slight excess of nitrous acid. The solution was added slowly at 0-7^{0}C to a solution of 1.6g (0.01 moles) coumarin dissolved in a solution of 0.44g NaOH, 3g sodium carbonate and 120mL water. The resulted solution was stirred for 30 min. and the precipitated dye was filtered.

Synthesis of dye **2** *(**D**$_2$)*

1.62g (0.01 moles) 2,5-Dichloroaniline was mixed with 6.6g (5.73 mL; 0.05 moles) HCl 30% and with 20mL H_2O and boiled to form the chlorohidrate of the amine and then cooled. About 250 g crushed ice and 6.90g (6.48 mL; 0.01 moles) $NaNO_2$ 10% solution were added at 0^{0}C. Reaction mass was stirred for 1 hour. The resulted solution was added slowly at 0-7^{0}C to a solution of 1.6 g coumarin (0,01 moles) dissolved in a solution of 0.44 g NaOH, 3 g sodium carbonate and 120 mL water. The solution was stirred for 30 min. and the precipitated dye was filtered.



***D*$_1$**

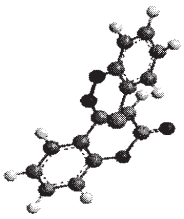
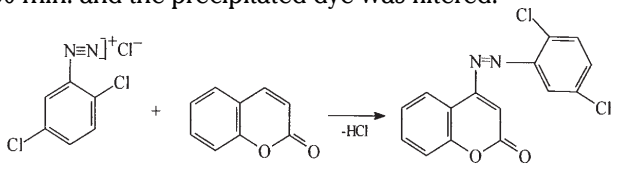


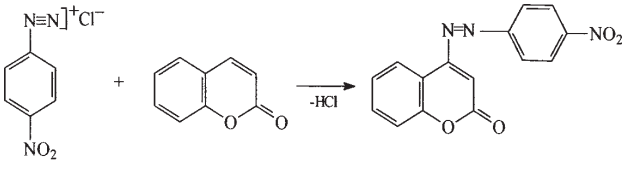
Fig. 1. Space configuration of the D_1 molecules



***D*$_2$**

Synthesis of dye **3** **(D$_3$)**

1.38 g (0.01 mol) 4-Nitroaniline was stirred at 80-90^{0}C with a solution prepared from 3.5 g (3.03 mL; 0.02 moles) HCl 30% and 30 mL H_2O till complete solubilization. The above solution was dropped over one mixture made of 125 mL H_2O and 500 g crushed ice. Temperature mass must not be over 8^{0}C. A solution of 3.5 g (3.10 mL; 0.01 moles) $NaNO_2$ 20%, was added under a continuous stirring. The resulting solution was added slowly at 0-7^{0}C to a solution of 1.6 g coumarin (0.01moles) dissolved in a solution of 0.44 g NaOH, 3 g sodium carbonate and 120 mL water. The resulted solution was stirred for 30 min. and the precipitated dye was filtered.



***D*$_3$**

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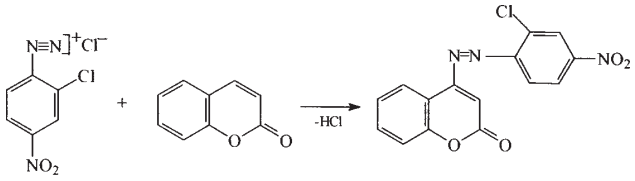
Synthesis of dye ***4*** *(**D**$_4$)*

1.72 g (0.01 moles) 2-Chloro-4-nitroaniline were added to a solution of 4.86 g (4.22 mL; 0.04 moles) HCl 30% and 90 mL H_2O and was stirred for 2 h. The solution was cooled externally at -5^{0}C and to it 1.75 g (1.34 mL; 0.01 moles) $NaNO_2$ as a 40% solution were added. After stirring for 15 min. the resulting solution was added slowly, at 0-7^{0}C to a solution of 1.6 g (0.01moles) coumarin dissolved in a solution of 0.44 g NaOH , 3 g sodium carbonate and 120 mL water . The resulting solution was stirred for 30 min and the precipitated dye was filtered.



D $_4$

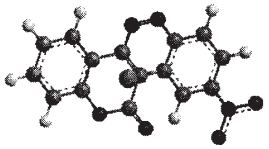


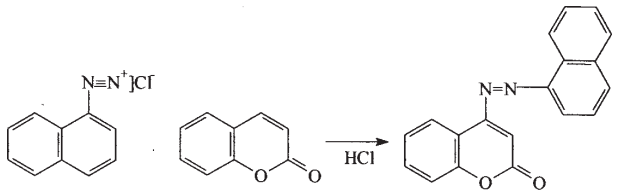
Fig. 2. Space configuration of the D_4 molecules

Synthesis of dye ***5*** *(**D**$_5$)*

1.43 g (0.01 mol) 1-naftilamine was mixed with 1.22 g (1,05 mL, 0.01 moles) HCl 30% and 14 mL H_2O and boiled to form the chlorohidrate of the amine and then cooled. 4g crushed ice were added, then 11 mL H_2O and 2.2 g (1.91 mL, 0.01 moles) HCl 30%. 2.3 g (1.89 mL, 0.01 moles) $NaNO_2$ 30% solution were added drop wise and the resulting solution was stirred for additional 1h. The solution containing the diazonium salt was added slowly at 0-7^{0}C to a solution of 1.6 g (0.01 moles) coumarin dissolved in a solution of 0.44 g NaOH, 3 g sodium carbonate and 120 mL water . The resulting solution was stirred for 30 min and the precipitated dye was filtrered.

Results and discussion

In order to confirm the proposed structures the main physical and chemical characteristics were determined for the prepared compounds.



D $_5$

The purity of the obtained products was tested by TLC using Silica Gel F_{254} plates and dioxane : methanol (1:1) as a mobile phase. For purification the compounds were recrystallization from water acidulated with HCl. All compounds were pure after 2-3 recrystallizations as confirmed by TLC.

The elemental analysis was done by the combustion method. The results are given in tabel 1. The obtained percentages are comparable with the calculated ones.

The UV-VIS spectroscopic measurements were performed with a SPECORD 40 apparatus in the range of 200-600 nm in dioxane solutions. The new compounds were characterized by the wavelength of their absorption maximum that was found in the range of 340-350 nm.

The characteristic maximum of coumarin from 274 nm is also present in the synthesized compounds showing that the core of the coumarin structure was not modified. Results of UV-VIS spectroscopy are given in table 2.

The IR absorption spectra were recorded on a BRUKER apparatus in KBr pellets in the range of 500-3500 cm^{-1}. The results of the IR spectroscopy are presented in table 2.

The ^{1}H-NMR measurements were performed on a VARIAN EM-360L apparatus at 60 MHz.

The ^{1}H-NMR spectra of D1 in D_2O reveals the appearance of 8 characteristic signals in a range of δ = 7.4 – 7.8 ppm.

The ^{1}H-NMR spectra of D4 in D_2O reveals the appearance of 7 characteristic signals in a range of δ = 7.4 – 8.3 ppm

The ^{1}H-NMR spectra of D5 in D_2O shows 10 characteristic signals in a range of δ = 7.4 – 8.9 ppm.

The ^{1}H-NMR spectra of coumarin in D_2O shows 6 signals in a range of δ= 6.4 - 7.8 ppm.

Fluorescent spectra was recorded using a CARY 10 (VARIAN) apparatus in the range λ=190-1000 nm. The recorded absorbtion maxima (in dioxane) for the studied compounds were in the range of 345-354nm. The tests were performed at *p*H = 9 and at *p*H = 12.

Table 1
ELEMENTAL ANALYSIS

Comp	Mp (oC)	Molecular Formula	%C		%H		%N		%Cl	
			Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
D_1	247.3-249	$C_{15}H_9O_2N_2Cl$	63.26	63.25	3.16	3.15	9.84	9.82	12.47	12.42
D_2	158	$C_{15}H_8O_2N_2Cl_2$	57.17	57.13	2.85	2.84	8.88	8.84	22.53	22.51
D_3	245.7-247.3	$C_{15}H_9O_4N_3$	61.01	59.08	3.05	3.01	14.23	14.21	-	-
D_4	178	$C_{15}H_8O_4N_3Cl$	54.6	54.3	2.42	2.4	12.74	12.71	10.77	10.76
D_5	175	$C_{19}H_{12}O_2N_2$	76	75.97	4	3.96	9.33	9.31	-	-

Table 2
PHYSICO-CHEMICAL PARAMETERS OF THE SYNTHESIZED DYES

Compound	λ (nm)	Type of bond	Frequency (cm^{-1})	R_f
D_1	241,4 349,8	$C=C_{arom}$ ›C=O -N=N- Ar-Cl -C-O-C-sim -C-O-C-asim	1454,39 1716,49 3308,49 679,37i 1068,47 1233,64	0,53
D_2	289,9 348	$C=C_{arom}$ ›C=O -N=N- Ar-Cl -C-O-C-sim -C-O-C-asim	1527,8 1722,58 3310,74 694,23i 1082,24 1278,18	0,57
D_3	260,8 340,1	$C=C_{arom}$ ›C=O -N=N- $-NO_{2as}$ $-NO_{2sim}$ -C-O-C-sim -C-O-C-asim	1487,89 1717,25 3307,46 1570fi 1369,35fi 1054,56 1264,32	0,64
D_4	278,6 347,8	$C=C_{arom}$ ›C=O -N=N- Ar-Cl $-NO_{2as}$ $-NO_{2sim}$ -C-O-C-sim -C-O-C-asim	1514,21 3307,87 1584,73 687.43i 1572fi 1364,86fi 1102,56 1325,86	0,67
D_5	213,2 273,1 399,1	-N=N- $-C=C_{-antr}$ >CO $-CH_3$ -C-O-C-as -C-O-C-sim	3308,58 1453 1738,47 1540 1114,26 1287,68	0,63

Conclusions

Five new azo-coumarin compounds were obtained by coupling coumarin with various diazotized aromatic amines.

The use of coumarin as a coupling component is new; until now, the literature data mention that only the substituted coumarin derivatives were used in coupling reactions with diazotized amines.

Structures of the synthesized dyes were confirmed by IR, UV-VIS spectra. The UV-VIS spectra show a maximum absorption at 340-350 nm, which is characteristic for the azo group.

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