# Synthesis and Characterization of Some Coumarin Fluorescent Dyes

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*The synthesis of some fluorescent coumarin dyes derived from coumarin-3-carboxylic acid were described.The new dyes are obtained by condensation of coumarin – 3 - carboxylic acid derivatives with para - substituted ortho - phenylenediamines and cyclisation of the mono condensed ortho - phenylenediamines in an acid medium. The obtained dyes were characterized from their physico-chemical point of view by elemental analysis, UV-VIS, IR ,[1]H - NMR spectra.*

*Keywords: coumarin dyes, coumarin-3-carboxylic acid, fluorescence*

Coumarin derivatives constitute an important class of organic fluorescent dyes with considerable interest for various applications[1].Recent developments on long wavelength fluorescent compounds such as heterocyclic compounds have been reviewed[2] . Coumarin moieties have gained commercial interest as optical brighteners for polyester, polyamide and polyvinyl chloride. Derivatives of coumarin are quite stable to light, which is rather unusual among fluorescent dyes [3].The uses of dyes in laser technique are based on their nonlinear absorption or their fluorescent properties.

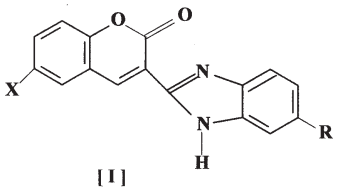
The range in which laser coumarin dyes are used is between 460 and 540 nm, and their solutions make up the active medium in the device. The most important characteristic of the dye laser is its continuous tunability. Dye lasers operate in large range from about 250 nm to 1285 nm. Each individual dye offers the potential of being tuned over 40-50 nm [4].The sensitized fluorescence and laser emissions of dye mixtures, coumarin dye as donor and acridine orange as acceptor, with UV light and laser excitation were measured. The interaction donor-acceptor for studied dyes involves singlet-singlet energy transfer [5]. The performance of energy transfer from coumarin acridine dye lasers are estimated in terms of spectral characteristics of the dyes and their penetration depths [6].

The fluorescent coumarin-xanthene dye mixtures with lasing properties present theoretical and practical interest [7].The total energy transfer involve both radiative and non radiative energy transfer for the coumarin dyes as donors and Rhodamine (640, 6G) as acceptor [8,9].

The presence of the heterocyclic structures induce generally, a spreading of the laser band , as the dyes that consist of fluorescent heterocyclics compounds are of interest to be used, as functional materials and emitters of electroluminescence devices and in laser techniques as in molecular probes used for biochemical techniques , traditional textile and polymer fields [10].

## Experimental part

The main object of our study was presenting an alternative synthesis of benzimidazoly-[2H]-1-benzopyran-2-one dyes, by condensation of coumarin-3-carboxylic acid derivates with para-substituted ortho-phenylendiamines and cyclisation of monocouplated intermediate with the following general structure



[ I ]

R= H, $CH_3$, Cl , $NO_2$ ; X= H ,$NO_2$

$I_a$: R=H , $I_b$: R=$CH_3$ , $I_C$: R=Cl ,$I_d$: R=$NO_2$
X=H, X=H, X=H , X=H

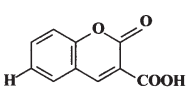
The synthesis of these dyes, as described in the literature, is achieved through a reaction of aldol condensation of salicylic aldehyde with heterocyclic compound with an active methylene group [11].

*Acids synthesis*

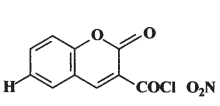
Synthesis of coumarin-3-carboxylic acid (**1a**) was performed by reaction of salicylic aldehyde with methane- carbothiolic acid , in the presence of aniline, at a molar ratio 1:1:1, in ethanol (85% yield) [12].

Synthesis of coumarin-3-carbonyl chloride (**1b**) was performed by the reaction of coumarin-3-carboxylic acid with sulphonyl thionyl, in benzene, at molar ratio 1:2, in the presence of N,N-dimethylformamide (90% yield) [12].

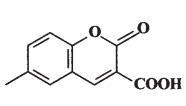
Synthesis of 6- nitrocoumarin-3-carboxylic acid (**1c**) was performed by an original method in a three –necked flask , fitted with agitator, thermometer and dropping funnel where 4.9 gm (0.025 moles) coumarin-3-carboxylic acid, 10.9 mL $HNO_3$ (60%) and 14 mL $H_2SO_4$ (98%) were introduced under energetic stirring, for 2h, at 80 $^oC$,. At the end weeping of sulphonitric mixture, the temperature is increased to 110 $^oC$ and maintained for 4 hrs. Reaction mass is cooled down at 20 $^oC$ , the formed precipitate is filtered under vacuum, washed with water and dried at 80$^oC$ (85.5 % yield) [12].



(1a)



(1 b)



(1c)

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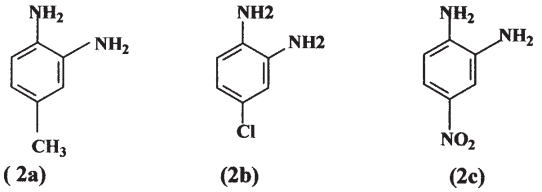
*Amines synthesis for monocondensation*

·4-methyl-o-phenylendiamine (**2a**) was obtained by reducing 2-nitro-p-toluidine with stannous chloride in HCl 36 % at a molar ratio 1:3:6 (87% yield) [12].

- 4-chloro-o-phenylenediamine (**2b** ) was obtained by reduction of 4-chloro-2-nitroanline with small amount of smoothing iron, in xylol and water, in the presence of acetic acid (79% yield) [12].

- 4- nitro-o-phenylendiamine (**2c**) was obtained by reduction of 2,4- dinitroaniline with $Na_2S$ 30% and sodium acid carbonate , in methanol (80 % yield) [13]



( 2a) (2b) (2c)

*Dyes Synthesis*

Four new dyes were obtained by an original method.

Dye $I_a$

In a three- necked flask fitted with agitator, dropping funnel and refrigerator were introduced 2.52 g (0.0235 moles ) ortho-phenylenediamine, 50 mL dioxan and 2.94 g (3mL, 0.037 moles) pyridine than a solution obtained from 4.9 g (0.0235 moles) of coumarin-3-carboxylic chloride were dissolved in 175 mL dioxan and were dripped for one hour, under stirring , in the reaction mass. After dripping ends, the reaction mass is heated up to reflux, under stirring for 4 h.

The precipitate was filtered, washed with water and dried at room temperature 4.4g monoacylated o-phenylendiamine (M.P : 315 - 316 $^oC$ , 71% yield ) was obtained .

In a round –bottom flask, fitted with refrigerator 1 g (2.15 mmoles) monoacylated product and 15 mL $H_2SO_4$ 98% were introduced. The temperature is increased to 150$^oC$ under stirring and maintained for 3 h. The residue was added in water , the formed precipitate was filtered and dried at 80-90$^oC$ , to give the dye $I_a$, as green crystals (M. P.; 238-240$^oC$, 64 % yield ) was obtained .$^1$H-NMR δ 9.28(1H,$S_{br}$,7-H),

8.34-6.09(8H,m,ar-H);IR ν 3448, 3267 ,3067 ,1686 , 1640, 1609,1583, 1488, 1481, 1459, 1382 cm-$^1$; MS m/z :263 (23), 262 ($MH^+$ , 100), 261 (20), 234 (15), 233 (9), 206 (9), 205 (15), 179(9), 39 (9), 28(16).The dye $I_a$ $C_{16}H_{10}N_2O_2$.

Dye $I_b$

It was synthesized similarly with dye $I_a$. 3.05 g ( 0.025 moles ) 4- methyl-o-phenylenediamine were dissolved in 50 mL dioxan , 50 mL benzene and 2.49 g (3 mL , 0.037 moles )pyridine. To this solution 5.21 g (0.025 moles ) coumarin-3- carboxylic chloride dissolved in 125 mL chloroform were added, under stirring. 5.5 gm monoacylated 4- methyl-o-phenylenediamine was obtained (80% yield). It was cyclizated in the acid medium to give the dye $I_b$, M.P.: 243-246$^oC$, (71 % yield). $^1$H –NMR δ 9.32(1H,$S_{br}$,7-H) 8.04-6.87 (8H,m,ar-H),2.25 (3H, s,$CH_3$);IR ν3287,3113,1685, 1638,1605, 1576,1480 ,1364 ,cm$^{-1}$ ,MS m/z : 277 (18) ,276 ($MH^+$, 100) ,275 (16) ,247 (9) ,44(9).The dye $I_b$ $C_{17}H_{12}N_2O_2$.

Dye $I_c$

3.5 g (0.025 moles) 4-chloro-o-phenylenediamine were dissolved in 50 mL dioxan , 50 mL benzene , 2.49 g (3 mL, 0.037 moles )pyridine and to the solution 5.21 g (0.025 moles) coumarin-3-carboxylic chloride dissolved in 125 mL chloroform were added, under stirring for one hour. 4.8 g monoacylated 4-chloro-o-phenylene-diamine was obtained(65% yield).After cyclization the resulted dye $I_c$ has the M.P (201-203$^oC$ (58% yield). $^1$H- NMR (DMSO.400 MHz, δ ppm,J in Hz 011.07 (1H,s,N-H), 11.05 (1H, $S_{br}$,N-H)8.76 (1 H,d.J=8.5 Hz, H-4), 7.65 (1H,d, J= 7.2 Hz ,H-4)7.58 (1H, t,J=7.2Hz,H-6).7.43(1H,d.J=7.2 Hz, H-7), 7.07 (1H,dd,J=8.5,1.7Hz,H-5),7.03( 1H,t, j= 7.2 Hz ,H-5), 6.91(1H,t ,j=1.7 Hz, H-7): CI-MS m/z 297,299 $(M+H)^+$. The dye $C_{16}H_9N_20_2Cl$.

Dye $I_d$

2.5 g ( 0.0163 moles )4-nitro-o-phenylenediamine were dissolved in 75 mL dioxan, 50 mL benzene, 2.49 g (3 mL, 0.037 moles) pyridine. 3.4 g (0.0163 moles) coumarin-3-carboxylic chloride were dissolved in 125 mL chloroform and were dripped to the form solution under stirring for one hour. 2.4 g monoacylated 4- nitro-o-phenylenediamine was obtained (72% yield). By cyclization in acid medium is obtained the dye $I_d$

(M. P. 260-263 $^oC$ , 65% yield) .$^1$H -NMR (400 MHZ ,DMSO-$d_6$) δ ppm 11.48 (s, 1H, NH).11.18 (s,1H ,NH) ,9.68 (s,1H ,H-4), 8.18 (d, 1H ,J=8.4 Hz ,H-6), 7.70 (d,1H, J=8.0 Hz, H-4), 7.61(t ,1H,J=8.0Hz ,H-6), 7.44(D ,1H, J= 8.4 Hz, H-7), 7.05-7.10 (m,2H,H-7,H-5), IR=3314, 3094, 2874, 1687, 1593, 1522 cm$^{-1}$. The dye $C_{16}H_9N_3O_4$.

The reaction intermediates and products were characterized by elemental analysis, $^{13}$C and $^1$H-NMR, IR( in potassium bromide palettes on a SPECORD 75 / R Carl Ziess Jena Spectrometer) and UV ( in dimethylsulphoxyide on SPECORD 40 Analytic Jena Spectroscopy) [13] .

**Results and discussions**

Considering our interest in synthesizing new fluorescent benzimidazol benzopyrans (scheme I), it was decided to prepare compounds of the coumarin type containing benzoimidazole type [14]. For this goal we synthesized some intermediates, as coumarin-3-carboxylic acid, its chloride, and o-phenylendiamines substituted in the 4$^{th}$ position as starting materials from the corresponding p-substituted compounds, similar to the methods described in the literature [15].

By direct nitration of coumarin-3-carboxylic acid the coumpond 6- nitrocoumarin-3 –carboxylic acid was prepared with a very good yield [16].

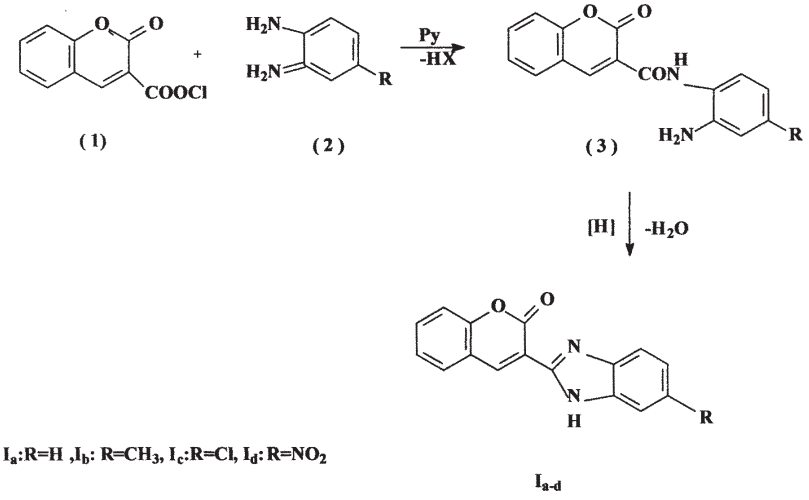
6- nitrocoumarin -3-carboxylic acid is an intermediate for laser dyes prepared by heating coumarin acid with sulfonitric mixture and then characterized physico-chemically , melting point was (230-232$^0$C) , IR and $^1$H-NMR spectroscopy, the experimental data confirming its structure. The presence of the nitro group in the 6$^{th}$ position by the bands in the IR spectrum at the wavelength of 1520 cm$^{-1}$ and 1560 cm$^{-1}$ [16].

The tendency is well-known for orto-phenylene-diamine to react with heterocyclic compounds through a reaction of condensation with carboxylic acids [16].

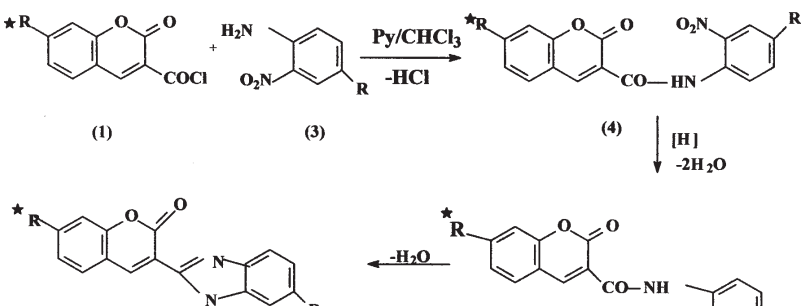
Two synthesis pathways are proposed for coumarin dyes:

**A**-The condensation of coumarin-3-carboxylic acid chloride (1) with para-substituted orthophenylendiamines (2) : followed by cyclisation of monoacylated compound (3) (scheme 2)

**B**-Acylation of p- substituted 2 –nitro-aniline (3) with coumarin acid chloride(1) reduction of acylated product



Scheme 2



Scheme 3

(4) and cyclization of the amino derivative(5) (scheme 3).

By the proposed (B ) method, coumarin dyes with structure II was not obtained, the main product being a nitroamide.Coumarin acid is not active enough to form C-N bonds at temperatures of about 100°C , and at higher temperatures (150°C) its decarboxylation prevails, and as a consequence, it was not possible to close the imidazole cycle. O-phenylenediamines react with the coumarin-3-carboxylic acid, but unexpectedly, at 1:1 molar ratio, in dioxan, under reflux, in the presence or absence of the protophile, monoacylated o-phenylenediamines were isolated with yields over 80%.As secondary products of dyes synthesis oligomers with fluorescent properties, absorbing in the same region as laser dyes was identified. The oligomers having molecular weights of tri-and tetramers are more effective in absorbing laser generated radiation, as described in literature [16].

The dyes structure $I_{a-d}$ was confirmed by UV and IR spectra .The results of the absorption in UV-VIS spectroscopy are given in table 1. The spectra were recorded in DMSO solutions at concentrations of $10^{-M}$ .

The most important functional groups were found in IR spectra according to their vibrations frequency. They are:

·NH- 1260 $cm^{-1}$

·Cyclic ketones 1720 $cm^{-1}$

·Coumarin 1630 $cm^{-1}$ and 1560 $cm^{-1}$ [13]. The UV-VIS spectroscopy absorption results of the dyes are presented in the table 1. The elemental analysis of the dyes is presented in table 2.

**Table 1**
RESULTS FOR ABSORPTION UV-VIS SPECTROSCOPY (DMSO)

| **Coumarin Dye Cx $10^{-20}$ (mol/l)** | **Chemical formula** | **λ Max, nm** | | **∑** | **lg** |
|---|---|---|---|---|---|
| Benzimidazolyl-[2H]-1-benzo-pyran-2-one,$I_a$ | $C_{16}H_{10}N_2O_2$ | 280 | 448 | 449 | 4,04 |
| 4-Methyl-benzimidazolyl-[2H]-1-benzopyran-2-one,$I_b$ | $C_{17}H_{12}N_2O_2$ | 284 | 450 | 471 | 3,99 |
| 4-Chloro-benzimidazolyl-[2H]-1-benzopyran-2-one, $I_c$ | $C_{16}H_9N_2O_2Cl$ | 285 | 460 | 471 | 4,00 |
| 4-Nitro-benzimidazolyl-[2H]-1-benzopyran-2-one,$I_d$ | $C_{16}H_9N_3O_4$ | 289 | 460 | 470 | 4,05 |

**Table 2**
ELEMENTAL ANALYSIS OF COUMARIN DYES

| Coumarin Dye | Molar Weight g/mole | Elemental analysis,% Calculated / Determined | | | |
|---|---|---|---|---|---|
| | | C | H | N | Cl |
| $I_a$ | 262 | 73.28/73.16 | 3.82/3.77 | 10.68/10.63 | - |
| $I_b$ | 276 | 73.91/73.78 | 4.35/4.26 | 10.14/10.01 | - |
| $I_c$ | 296.5 | 68.80/68.62 | 3.05/2.99 | 9.43/9.37 | 11.97/11.86 |
| $I_d$ | 307 | 62.54/62.41 | 2.93/2.84 | 13.68/13.58 | - |

## Conclusions

New fluorescent dyes emitting in the blue-green spectral region were obtained using an original method for the synthesis of benzimidazolyl-coumarin dyes based on the condensation of coumarin-3-carboxylic acid derivates with para-substituted orto-phanylene diamines and cyclisation of mono-acylated compounds. The obtained yields were practically similar to those described in the literature. All the intermediates were characterized by elemental analysis $^1$H -NMR, IR, UV-VIS and MS spectrometry.

The synthesized dyes present the characteristic spectral bands for coumarin derivatives, in the range UV at 280-290 nm , and in the visible range at 440-460 nm.

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