New Luminophore Dyes

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This study presents synthesis and characteristics of new luminophore dyes starting from naphthalic anhydride reacting with substituted amines. The compounds have been characterized through spectral analysis, with estimation yields for each reaction.

Keywords: *naphthalic anhydride*, *coupling, luminophore dyes*

From structural point of view, luminophore dyes obtained from naphthalic anhydride have a large variety of structures and are classified in naphthalimide dyes, azo dyes, xanthene dyes etc [1]. Other compounds from intermediates of the type anhidride with polyphenolic compound were studied in [2].

These compounds exhibit excitation and emission maxima in the range of 400 and 585 nm, depending upon the groupes contained in their structures [3].

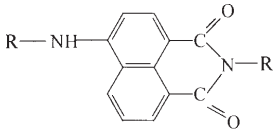
Luminofore dyes are used in dying polyesteric fibres, synthetic and plastic materials and in modern, non-conventional applications such as liquid crystals, laser, fluorescent markers and photochromic materials [4-6].

The aim of this paper is to obtain new luminophore dyes starting from naphthalic anhydride.

Experimental part

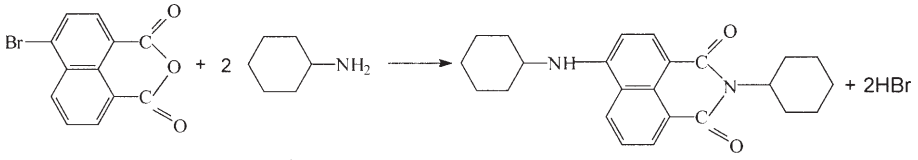
The fluorescent compounds of the present invention can be conveniently prepared by a one-step condensation between naphthalic anhydride or its derivatives possesing the desired functionalities and the appropriately substituted amines.

There were obtained new dyes with the general structure (1) using synthesis methods known in the literature.



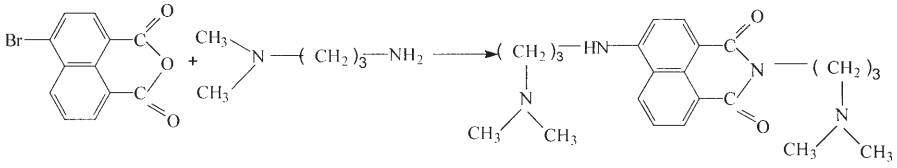
1

Synthesis of 4-ciclohexylamino-N-cyclohexyl-1,8naphthalimide



D1

Synthesis of 4n,N-dimethilpropylendiamine-n,N- dimethilpropylendiamine-1,8 naphthalimide



D2

The obtaining method for the first four dyes is the same, the only difference are the amines that undergo the condensation process: ciclohexylamine: N,N-dimethil-propylen-diamine, 3-amine-1-propanol, toluidine, clorophenylendiamine.

In a three-necked flask, equipped with agitator and thermometer, 4-bromenaphthalic anhydride is dissolved in N-methylpyrolidone under heating; the mixture is heated at 135°C and the neccesar quantity of amine is added in two steps at different temperatures. The amine is added in excess against the anhydride. The mixture is kept for perfecting the reaction for 24h at high temperature.

Excess of amine and N-methylpyrolidone is eliminated by washing with diluted HCl.

The reaction mass is dissolved in chloroform, washed with water and the two obtained phases, organic and aqueous, are separated through separation funnel.

For a higher purity the obtained compound is re-crystallised from ethanol.

For D_5 naphthalic anhydride was added in excess against the necessary quantity.

Due to the fact that this dye presented no visible fluorescence, the sequence of operations was continued with bromination in ethanol medium. Bromination process was conducted at 50°C for 24h.

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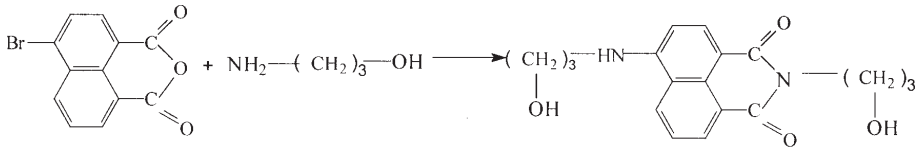
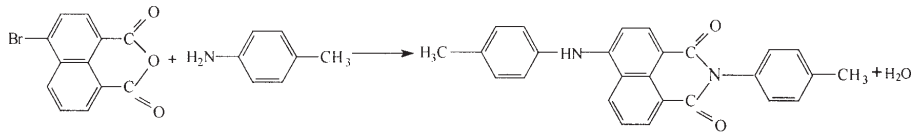
Synthesis of 4-amine-1-prophanol-N-amine-1-prophanol-1,8 naphthalimide



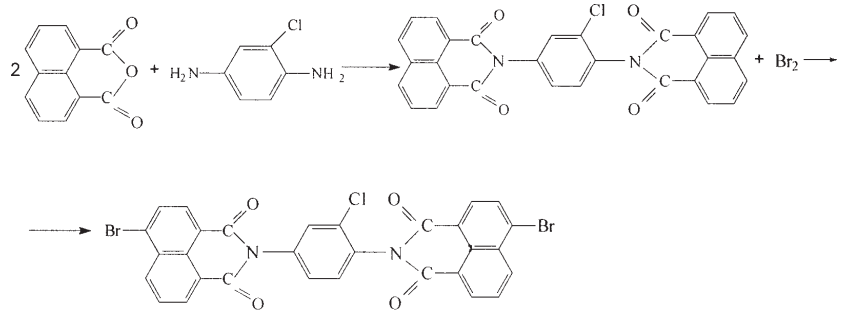
D_3

Synthesis of 4-toluidine-N-toluidine-1,8 naphthalimide



D_4

Synthesis of p,p'-chlorophenylendiimine-bis(3-bromine-4-naphthalic) anhydride



D_5

Results and discussion

The main physico-chemical characteristics were determined for the compounds prepared, in order to support the structures and reactions proposed and also to achieve a quantitative and qualitative assesment of the processes. Both the raw materials and the new naphthalene structures obtained were subjected to analysis.

The reaction parameters values are presented in the table 1.

Melting points were determined using the Boetius apparatus. The new obtained dyes have the melting points values in a narrow range, which denote an advanced degree of purity.

The analysis carried out confirmed the proposed structures, the actual percentage composition being comparable to the one estimated theoretically as shown in table 2.

IR Spectrum Analysis

IR spectra allow the identification of functional groups or chemical bonds and can provide information regarding details of the structure. IR spectra were recorded in KBr disks, and spectra were assigned and interpreted on the basis of the data in the literature. The spectra were recorded on JASCO FT/IR-410 spectrophotometer.

UV-VIS Spectrum Analysis

The visible spectra were recorded in an alkaline alcoholic solution on a SPECORC 75 R Carl Zeiss Jena spectrophotometer. The compounds obtained were characterized by the wavelenght of their absorbtion maximum.

Thin Layer Chromatography

Thin layer chromatography was performed on silica gel G plates, using ethanol-acetic acid-dioxane as an eluent. The chromatograms obtained in the system show

Table 1

REACTION PARAMETERS VALUES

Dye	Amine	Quantity (g)	Temperature(°C)/ Time		Eluent	Fluorescence	η(%)
			Step1	Step 2			
D_1	Ciclohexylamine	5.4	135/10min	66/24h	etanol	yellow	75
D_2	N,Ndimethil-propylen-diamine	5	115/10min	64/24h	etanol	Yellow-green	85
D_3	3-amine-1-propanol	4.4 ml	115/14min	60/24h	etanol	yellow	80
D_4	toluidine	7.6	120/10min	65/24h	etanol	green	78
D_5	Clorphenylendiamine	8.2	150/10h		etanol	-	65

Table 2
ELEMENTAL ANALYSIS AND MELTING POINTS

Dye	Molecular Formula	$M_{calc/det}$	C%		H%		N%		M.P. (°C)
			1)	2)	1)	2)	1)	2)	
D_1	C24H28N2O2	376/367	76.59	76.48	7.44	7.39	7.44	7.38	170-172
D_2	C22H30N4O2	382/373	69.1	68.3	7.85	7.72	14.65	14.52	-
D_3	C18H20N2O4	328/320	65.85	65.74	6.09	6.02	8.53	8.39	160-165
D_4	C26H20N2O2	392/385	79.59	79.43	5.10	5.05	7.14	7.08	140-142
D_5	C30H13O4N2Br2Cl	660.5/657	54.5	54.47	1.96	1.91	4.23	4.17	160-163

1) Calculated; 2) Determined

Table 3
IR AND UV SPECTRA

Dye	$\gamma_{C=Carom}$ cm^{-1}	$\gamma_{C=O}$ cm^{-1}	γ_{C-N} cm^{-1}	γ_{Cl} cm^{-1}	λ nm
D_1	1580.05	1724.12	1235.29	-	496
D_2	1619.32	1722.51	1376.19	-	490
D_3	1600.57	1710.12	1285.23	-	493
D_4	1597.21	1709.54	1290.65	-	500
D_5	1603.63	1718.62	1354.44	668.53	497

nonhomogenous spots, which is indicative of impurities. For purification the compounds were subjected to recrystallizations from ethanol. After 2-3 succesive recrystallizations, thin layer chromatography on silica gel plates in the visible spectrum indicate pure compounds.

Conclusions

There were synthetised five new dyes starting from naphthalic anhydride by coupling with substituted amines: ciclohexyl-amine, N,Ndimethil-propylen-diamine, 3-amine-1-propanol, toluidine, clorphenylendiamine.

The new dyes present yellow-green fluorescence. They were obtained through relatively simple synthesis methods, with high reaction yields.

The new structures proposed are confirmed by the spectral analyses performed (UV-VIS, IR) and the elemental analysis.

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