Synthesis of Dyes with Compactly -Condensed Quinolic Structure

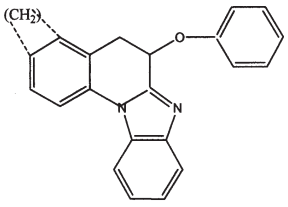
FLORICA ILINA[1], ION SEBE[2]

[1,2] Politehnica University of Bucharest, Faculty of Applied Chemistry and Science of Materials, Department: Technology of Organic Substances and Macromolecular Compounds, 149 Victoria Avenue, 010072, Bucharest, Romania

This present paper describes the synthesis of quinolinic dyes with condensed quinolinic structure similar to those presented in the literature,which have been tested on polyamidic and polyester fibers. Owing to the similarity in structure to those from the literature, they may be used for laser too. The dyes were obtained from the reaction between phenoxybenzimidazolic intermediates (phenoyibenzimidazolil, p-chloro-phenoxybenozibenzimidazolil, p-nitro phfenoxybenzimidazolil) with salicylic aldehyde and naphtholic aldehyde. The dyes were anaysed physico-chemically and spetroscopically in IR and UV-VIZ. The proposed structures confirmed the analogy with those presented in the literature in terms of dyeing textile fibres. They will be applied further.

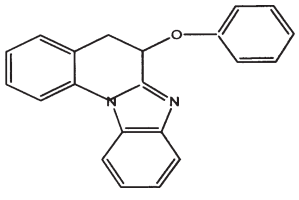
Keywords: *quinoline dyes*, *IR and UV spectra, phenoxybenzimidazolil, salicylic aldehyde, naphtholic aldehyde*

The dyes with general structure 1 are used to dye acrylic and in laser printers. [1-7]. Alkyl groups in positions 2 and 4 of the quinolinic cycle are very reactive and therefore can easily give condensation reactions which often lead to coloured substances .The used of the dyes in dyeing acrylic fibres and in the techniques are based on their fluorescent properties and non –linear absorption [10]. The use of dyes in painting acrylic fibres and in the laser technique is based on linear absorption or fluorescent properties. Chinolic dyes that have properties for laser must contain adequate substitutes which have the above mentioned properties.



1

The present study shows the synthesis of dyes with a similar structure to the one above (1), similar to those of the literature, which have been tested to which properties are specified to be applied on acrylic fibres. Such dyes have been synthesized having the following quinolinic structures:



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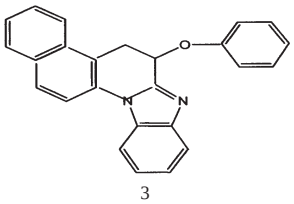

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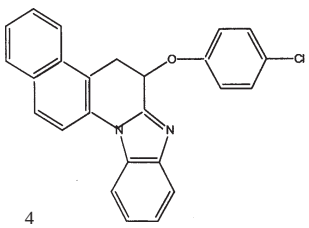

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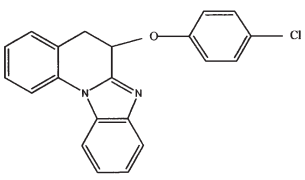

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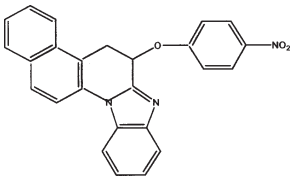

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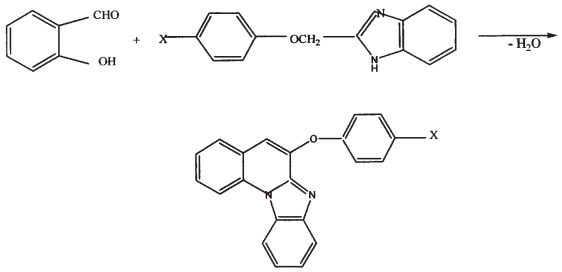
These dyes are obtained from the following reactions:

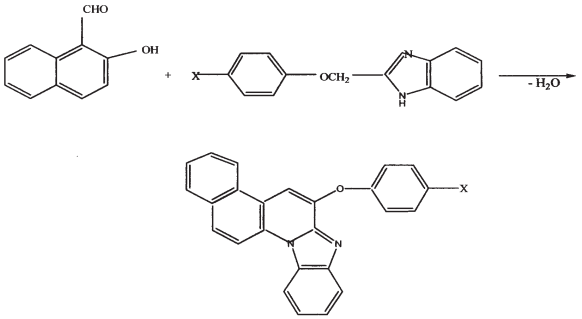
I



2, 3

2) X= H; 3) X= Cl

II.



4, 5, 6

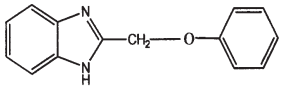
4) X= H; 5) X= Cl; 6) X= NO_2.

The dyes were analysed by chromatography, IR and UV-Vis spectra.

* *ilinaflorica@yahoo.com; Tel.: 0723963064*

Experimental part

The following synthetic intermediates were obtained: phenoxyacetic acid and its derivatives, phenoxy bezimidazolic intermediate structures:



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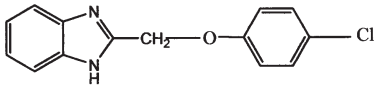

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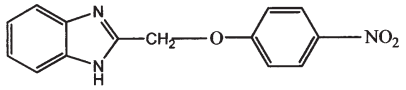

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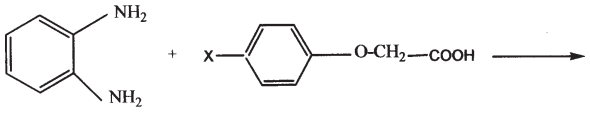
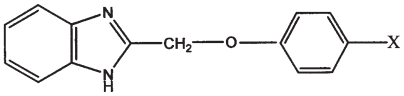
from the reactions:





The synthesis was done by adopting the methods described in the literature [8].

We introduce the phenolate solution into a flask equipped with thermometer and cooler and heat it to 95^0 C. Then the solution of monochloroacetic sodium salts is poured through the dripping funnel for the next three hours. When the process is over, the temperature is risen to 105^0 C and it is finalized at 105-110^{0}C for one more hour. Then, the reaction mass is heated at 40^{0}C , acidified with HCl at *p*H= 1. At 40^{0}C, 100 mL dichloroethane is added and stirred for 1 h. The organic layer is separated from the inorganic one in a funnel. After the precipitation of organic layer , it is filtered. A product with b. t. 97-108^{0}C and 79% yield is thus obtained. In order to get the p- chlorophenoxy acetic acid, a solution of p- chlorophenolate is introduced into a flask equipped with thermometer and cooler and is heated at 96^{0}C. Then, a sodium salt solution of the monochloroacetic acid is poured through a dripping funnel for 3 h. This solution has 24g (25 mL) of monochloracetic acid.

After the addition is over , the temperature is risen to 105^0 C and the reaction is finalized for one more hour at 105-116^{0}C. The reaction mass is then cooled at 40^0 C and acidified with concentrated HCl to a *p*H =1. 100mL dichloroetane are added and the stirring continues for one more hour. The reaction mass is introduced in the funnel and the organic layer is separated from the inorganic one. The organic layer is filtered and washed with a small amount of dichloroetane on the filter. The p-chloro-phenoxyacetic acid is obtained, with a b.p of 157-159^{0}C and 75% yield. The p- nitro- phenoxyacetic acid can be obtained using the same method. The acid b.p. 135^{0}C and 61% yield is obtained.

The phenoxybenzimidazol is obtained as follows.

0.138 moles of o-phenylendiamine (0.14g), 0.078 moles phenoxy-acetic acid (12g) şi 150mL water are introduced into a flask equipped with stirrer, thermometer and cooler. The mixture is heated at 95^{0}C (on reflux)upon stinring where it is kept for 3-4 h. It is cooled afterwards to 25^0 C and NaOH solution (about. 25g; 2.24 mL) is added with stiring, which leads to a weakly alkaline solution identified by a narrow margin with litmus paper.

The raw phenoxybenzimidazole, thus obtained is filtered and washed on the filter with 100 mL cold water(0-2^{0}C), being vigorously treated. It is washed again with 100 mL cold water. The result is 160g of practically impure product at 87% yield. The raw product is purified with bone charcoal in the following way: a saturated solution of phenoxy-benzimidazolil is prepared and the bone charcoal is added (0,4g),it is then heated and stirred with the rod. It is left to settle as sediment for about 15 min, then it is filtered while it is hot. The filtrate is cooled, it christalizes and it is filtered again. We obtain 14g phenoxybenzimidazolil with b.p. 130-135^{0}C. Intermediates 8 and 9 are obtained in a similar manner.

Dye	ortophenylendiamine $C_6H_8N_2$	Acid	Solvent H_2O	Temperature	Yield %
7	14,8 g (0,138 moles)	p-phenoxy-acetic acid: (12g) 0,078 moles	150 mL	95^0 C	87%
8	16 g (0,148 moles)	p-chloro-phenoxy-acetic acid 12 g (0,064 moles)	160mL	97^0 C	87,5%
9	18g (0,166 moles)	p-nitro - phenoxy-acetic acid 14g (0,09 moles)	165mL	98^0 C	88%

Table 1
SYNTHESIS OF INTERMEDIATES 7-9

Preparation of dye 2

An amount of 1.71mL (1 mol) of salicylaldehyde and 4g (1 mol) phenoxybenzimidazole are introduced into a flask equipped with stirren and ascending cooler equipped with AST; oven 200 mL xylene are added. The mixture is heated at reflux , where it is maintained for 6 h. A condensation reaction occurs. The water resulting from the reaction is colleted into the ATSM or it is found as emulsion with the xylene. The resulted product goes through distillation until the xylene is recovered. The dye is treated with H_2SO_4 (2 mL), it is then filtered and the precipitate is washed several times with water (on filter paper) to remove the traces of H_2SO_4. A grey- coloured dye is thus obtained, with m= 32g, b.p. 140^{0}C, and 64% yield. Dyes 3,4,5 and 6 are obtained in similar manner. (table 2). Dyes 2-6 were purified on a column with Silicagel G filling, having 50mm in width and 1m height, using as a mobile phase the mixture acetone-benzene8:2. The sample are solubilised in N, N dimethylformamide.

Results and discussion

The purity of the synthesized dyes has been checked via determination of boiling points. The dyes were purified by repeated recristalization from solvents (until the boiling points of intermediates were unitary). The intermediates and dyes phusical properties are presented in table 3:

The structure of dyes was checked by IR and UV spectroscopy [9, 11]. In the IR spectra of dyes the frequencies corresponding to the mains functional groups are emphasized, as it can be seen in table 4.

The sample were analyzed into a SPECORD 75 IR(Karl Zeiss Jena) spectrum through absorption spectroscopy in IR under tablet form in KBr and the following was established :

- heterocyclic of 5 members present three bands at 1590, 1490 and 1400 cm^{-1}. The electron donor substitutes lead to an increase in the intensity of the 1480cm^{-1} band;
- the bands from spectral region of 1200cm^{-1} belong to the C-O-C link from aromatic ether ;
- the disubstituted aromatic nucleus present an intensive band on 750 cm^{-1};
- the monosubtituted aromatic nucleus is characterized by the bands from 685 and 740 cm^{-1};
- the C-Cl link appears at 700-750 cm^{-1} due to the presence of the absorption bands attributed to the substituted aromatic nuclei in ortho position chlorine can not be identified. Maybe the chlorine atom was introduced in the molecule, in the planned position, due to the increase in the intensity of the absorption bands from 1820 cm^{-1} because of the substitution of the benzene nucleus in position 4,4' para position.

Dye	Molecular formula	Aldehyde	Intermediate	Solvent
2	$C_{21}H_{16}ON_2$	salicylic aldehyde	phenoxybenzimidazole	xylene
3	$C_{25}H_{18}ON_2$	naphtholic aldehyde	phenoxybenzimidazole	xylene
4	$C_{25}H_{17}ON_2Cl$	naphtholic aldehyde	p- chloro-phenoxybenzimidazole	xylene
5	$C_{21}H_{15}ON_2Cl$	salicylic aldehyde	p- chloro-phenoxybenzimidazole	xylene
6	$C_{25}H_{17}O_3N_3$	naphtholic aldehyde	p- nitro-phenoxybenzimidazole	xylene

Table 2
SYNTHESIS OF DYES 2-6

Substance obtained	**b.p^0 C**	**yield%**	**colour**
phenoxybenzimidazole	130-135	76	dark brown
p-chloro-phenoxybenzimidazole	155-157	80	light brown
p-nitro - phenoxybenzimidazole	160	75	brown
dye 2	140	64	grey
dye 3	147	85	red-brown
dye 4	157	58	black
dye 5	167	59	grey-black
dye 6	168	61	green-black

Table 3
PHYSICAL PROPERTIES OF INTERMEDIATES AND DYES

Dyes	benzene	benzene	benzene	benzene	υ_{C-O-C}	υ_{C-O-C}		υ_{NO_2}	υ_{NO_2}				
	υ_{CH}	δ_{CH}	$\upsilon_{C=C}$	δ_{CH}	asim	sim	υ_{C-Cl}	asim	sim	δ_{CH}	υ_{CH}	$\upsilon_{C=C}$	$\gamma_{C=N}$
2	3020	1670	1520	1090	1255	1065				780	3030	1600	1480
3	3020	1670	1520	1090	1255	1065	730			780	3030	1600	1480
4	3020	1670	1520	1090	1255	1065				780	3030	1600	1480
5	3020	1670	1520	1090	1255	1065	730			780	3030	1600	1480
6	3020	1670	1520	1090	1255	1065		1562	1365	780	3030	1600	1480

Table 4
IR SPECTRA OF COMPOUNDS 2-6

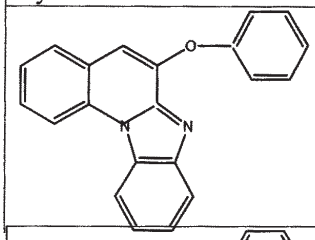
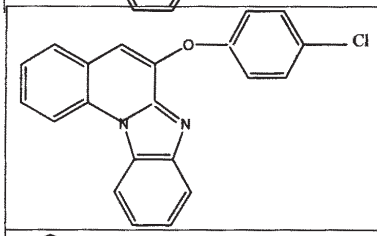
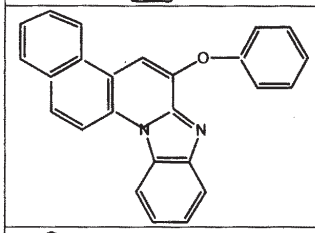
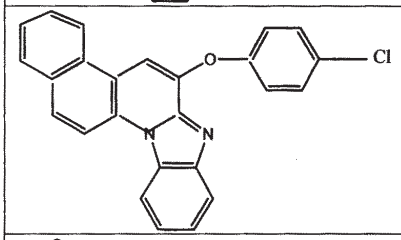
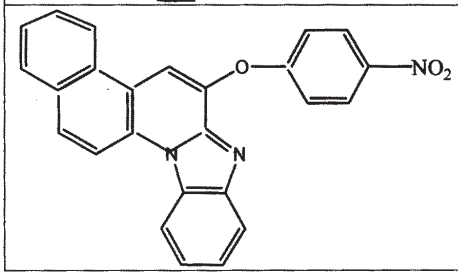
Dye	λ_{max}	ε_{max}
	225	2900
	210	3500
	220	3200
	225	2900
	210	1950

Table 5
THE λ_{max} AND ε_{max} VALUES IN UV-VisSPECTRA OF 2-6 COMPOUNDS

- the NO group (dyes 6) appears ot 1360-1320 cm^{-1}. It is noticed that the resulted frequencies correspond to the dates from the literature,[9] which demonstrates that the proposed structures are correct.

The heterocyclic 2-6 structures present electronic spectra with six atoms whose electronegativity is decreasing. In the UV-Vis spectra of dyes 2-6 λmax values and low ε values of the extraction coefficient are obtained.The spectral data are obtained in n-hexane. The resulted values are listed in table 5. The resistances for polyester and polyamides are ranging from 4 to 5.

Conclusions

The following conclusions can be drawn as a result of the research on quinolinic dyes:

-the reaction conditions are relatively simple and the results were quite satisfactory,.

-the synthesized substances were pure and this could be noticed in the IR spectra, they can be used for laser.

-the purity of products and of intermediates and even dyes was satisfactory.

-the syntheses of intermediates were performed according to the data from the literature.

-taking into consideration the structure and colour of these dyes, they may be used for dyeing polyamidic fibres and in the laser technology..

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