Dyes Derived from Carbazole

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The paper describes the synthesis of some carbazole dyes used as acid or disperse dyes. The disperse dyes have been alkylated and applied on polyacrilonitrile fibers. The dyes were analyzed by TLC, elemental analysis (C, H, N), IR and visible spectra.

Keywords: carbazole dyes, IR and UV-VIS, solubility

Dyes derived from carbazole belong to several structural classes of dyes as azo or anthraquinone and to several tincturial classes as VAT, acid, cationic, disperse etc. dyes [1]. Carbazole dyes can dye natural proteic fibers such as wool, silk or synthetic fibers as polyamides or polyesters [2].

These dyes have good tincturial qualities and a great affinity for the fabrics and superior fastness properties to light, wet and humido-thermal treatments.

Dyes derived from carbazole contain the carbazole residue linked to anthraquinone, azo and polyazo or azomethine residues. They can be used, depending on their structure, as disperse, cationic or direct dys.

The color of the carbazole dyes can range from orange – yellow and red to green, blue, violet and black [4]. Some carbazole derivatives may show fluorescence.

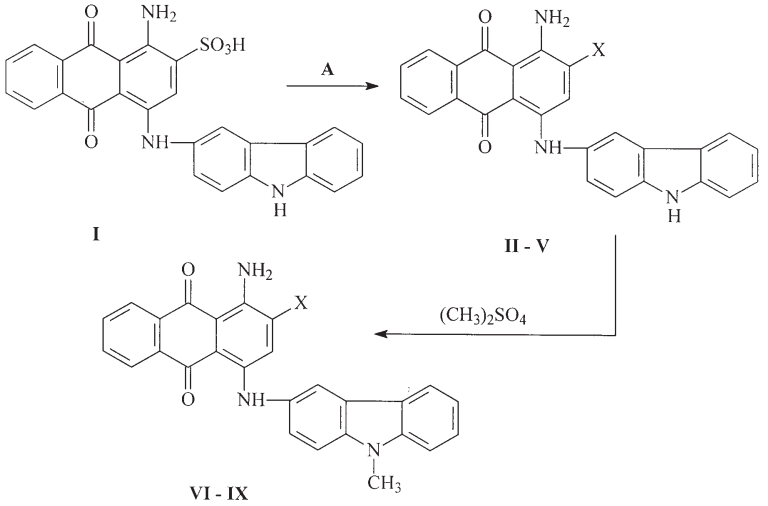
Experimental part

In the present paper disperse dyes derived from carbazole were synthesized and then alkylated using dimethylsulfate, according to the equations (1) – (2):

For the synthesis of dyes **II – V** 3-aminocarbazole obtained by nitration of carbazole and the reduction of the nitro-derivative, according to the following experimental method, was used [6].

8.3 g (0,05moles) carbazole are introduced into a solution prepared by mixing 77.5 mL HNO_3 65% with 450 mL water and mixed for 4h at 75 – 80°C. Then 250 mL of cold water are added and the mixture is filtered. The precipitated is washed with cold water to neutral and dried at 70°C. 10.3 g of a mixture of 3-nitrocarbazole (75%) and 1-nitrocarbazole (25%) in a 90.2% yield are obtained.

For purification, 10.3 g of mixture of isomers are finely grinded, mixed with tetrachloroethane for 5h at 20°C, filtered and the precipitate is washed with the same solvent and then dried. 70 g of 3-nitrocarbazole (yield ~70% towards the bruto product and 68% reported to carbazole) are obtained, yellow crystals from xylene, m.p. = 210°C (206°C).



Scheme 1

Compound	II, VI	III, VII	IV, VIII	V, IX
X	H	OCH_3	OCH_2CH_3	OC_4H_9
A	NaOH + glucose	CH_3OH	$CH_3\,CH_2OH$	C_4H_9OH

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Table 1
PROPERTIES OF THE DYES AND THEIR YIELD

No.	Dye	Aspect	Yield	Solubility
1.	I	Dark blue powder	87,8%	Soluble upon heating in acids and organic solvents
2.	II	Very dark blue powder	99,33%	Ethyl alchol, acid solutions, slightly in water upon heating
3.	III	Black-violet powder	96,1%	Ethyl alchol, concentrated sulfuric acid, xylene, toluene
4.	IV	Black-violet powder	93,4%	Acid acetic, toluen, alcool etilic, H_2SO_4 concentrat
5.	V	Black-violet powder	98,6%	Acetic acid, toluene, ethyl alcohol, concentrated sulfuric acid
6.	VI	Black-blue powder	92,2%	In water upon heating, ethyl alcohol, toluene, xylene
7.	VII	Black-violet powder	87,3%	In water upon heating, ethyl alcohol, hot acetic acid
8.	VIII	Black-violet powder	72,7%	In water upon heating, hot acetic acid
9.	IX	Black-violet powder	77,7%	In water upon heating, ethyl alcohol, hot acetic acid

The reduction of 3-nitrocarbazole is obtained according to the following method:

- in a reaction vessel equipped with a mechanical stirrer, thermometer and reflux condenser 0.5L xylene, 0.5L water, 0.1L acetic acid and cast iron spans are placed and refluxed at 130°C. 3-nitrocarbazole in hot xylene is added in several portions. Additional 10 g of iron are added in 4 portions and the temperature is maintained for 16 h. The reaction mass is filtered hot. The iron turns are washed 3 times with 100 mL of ethyl alcohol, reunited with the main portion of the filtrate, 200 mL water are added and the ethyl alcohol is distilled. The residue is cooled and 3-aminocarbazole precipitates and then filtered. The 3-nitrocarbazole crystals are washed with water and then dried. The white – grey crystals have a m.p. of 250 – 255°C (measured using a Boetius apparatus) in a yield of 85%.

*The synthesis of dye **I***

In a round bottom flask 18.9 (0.02 moles) bromanine acid sodium salt, 180 mL water and 1 g cuprous chloride are placed. The mixture is heated to 60 – 80°C and then a solution of 36.4 g (0.2 moles) 2-amino-carbazole solution in 150mL ethyl alcohol is added in portions. The mixture is refluxed for 7 – 8 h, cooled, filtered and the precipitate is washed with water and then dried. The yield is 87.8%.

*Syntheses of the dyes **II – V***

In a three neck round bottom flask 4.83g (0.01 moles) dye **I** is dissolved in a sodium hydroxide solution made from 1.2 g NaOH in 100mL water. The mixture is heated to 85-90°C, then over 15 min a hot solution of 6.7g (0.037 moles) glucose in 170 mL water and 3.3 g (0.08 moles) potassium hydroxide in 100 mL methyl alcohol (for dye **II**), or ethyl alcohol (for dye **III**) and or butyl alcohol (for dye **IV**) respectively are added. The reaction mixture is maintained at 95°C for 4 – 5 h. The mixture is then cooled at 15-20°C and neutralized with concentrated chlorhydric acid at *p*H 6.5-7, filtered, the precipitate is washed with plenty of water and dried. The yields are given in table 1.

*Alkylation of dyes **II – IV***

In a three neck round bottom flask 60 g (45.1 mL, 0.476 moles) dimethylsulfate and 50 mL water is added, cooled at 15-20°C and over 1h 30.96 g (0.08 moles) of the dye **II** (or 32.7g (0.08 moles) dye **III,** or 34g (0.08 moles) dye **IV** or 36 g (0.08 moles) dye **V** respectively) are added under stirring and cooling. After 1h at 35°C, the temperature is risen at 80°C in 3.5 h and maintained at this temperature for an additional hour, then cooled at 65°C and 30 mL of water and 12 mL acetic acid are added. The mixture is poured over ice-water and the formed suspension is filtered and dried. The yields are given in table 1.

Results and discussions

By nitration of carbazole two isomers of nitro-carbazole were obtained (1-nitrocarbazole and 3-nitrocarbazole). In order to increase the amount of 3-nitrocarbazole a variation on the literature method was performed. Carbazole was nitrated using sodium nitrite, 65% nitric in chlorobenzene. at 60 – 80°C for 8 h. Yellow-brown 3-nitrocarbazole crystals with m.p. = 200-210°C were obtained in a 94% yield.

In the synthesis of dye **I** the molar ratio and the working conditions were modified. 3-aminocarbazole was dissolved in ethanol, the molar ratio was 1 : 1 and the reaction

Table 2

ELEMENTAL ANALYSIS OF **II-V**

Compound.	Molecular formula	Molecular mass	C %		H %		N %		Rf
			Calc.	Found	Calc.	Found	Found	Calc.	
II	$C_{26}H_{17}O_2$	387	77,04	76,8	4,2	10,0	4,1	10,4	0.45
III	$C_{27}H_{19}O_3$	409	72,2	72.4	4,38	9,5	4,4	9,2	0,49
IV	$C_{28}H_{21}O_3$	425	89,1	89,3	4,2	9,5	4,4	9,3	0,50
V	$C_{30}H_{25}O_3$	451	80,0	80,2	5,2	9,2	5,5	8,9	0,55

Table 3

IR SPECTRA OF DYES **I** AND **VI-IX**

Peak \ Dye	I	VI	VII	VIII	IX
νSO_2 as	1160	-	-	-	-
sym	1345	-	-	-	-
νNH_2 as	3505	-	-	-	-
sym	3395	3502	3502	3502	3502
νNH	3452	3452	3452	3452	3452
νCO	1670	1670	1670	1670	1670
νCH_3 as	2960	2960	2960	2960	2960
sym	2870	2870	2870	2870	2870
$\nu N\text{-}CH_3$	-	3495	3495	3495	3495
Ar $\nu C{=}C$	1560	1560	1560	1560	1560
δ	980	980	980	980	980
δ	800	800	800	800	800
ν C-O-C as	-	-	1250	1250	1250
sym	-	-	1065	1065	1065
νCH_2 sym	-	-	-	2850	2850

Table 4

VIS SPECTRA OF DYES **I** AND **VI-IX**

No.	Dye	Wavelength $\lambda_{max.}$[nm]	Color
1	I	590	Deep blue
2	VI	585	Blue
3	VII	580	Dark violet
4	VIII	578	Violet
5	IX	575	Deep mauve

temperature was maintained at 80 – 90°C for 7 – 8 h. The yield was 87,8%.

The alkylation of the dyes **II, III, IV** and **V** leads to more water soluble products that can be used for dyeing polyacrylonitrile fibers. The properties of the dyes and their yield are given in table 1. The chromatographic analysis of the dyes was performed by TLC using a silicagel plastic plates as a stationary phase. The mobile phase was butyl alcohol:ethyl alcohol:25% ammonia = 1:3:5 (v/v). [7]. The Rf values are given in table 2.

The elemental analysis results are given in table 2.

The IR spectra were performed in KBr pellets using a SPECORD 70IR spectrometer and the VIS spectra were performed on a SPECORD M40 spectrometer in order to prove the identity of the dyes and are given in table 3 and 4 [8].

The dyes were used to dye wool, silk and polyamide using a dye-bath ratio of 1,1 : 10, an amount of dye of 1 – 2.5% and a temperature of 30 - 90°C [9].

Conclusions

3-Aminocarbazole was synthesized starting from 3-nitrocarbazole and then used in the synthesis of some carbazole dyes.

3-Aminocarbazole was reacted with bromamine acid to obtain the dye **I** which was then used to obtain 4 disperse dyes by replacing the sulfonic group in position 2 with hydrogen, methoxy, ethoxy, and butoxy groups respectively, in 92 – 98 % yields.

The disperse dyes **II** – **IV** were alkylated using dimethylsulfate leading to the dyes **VI** – **IX**. These dyes have colors from dark blue to light yellow.

The alkylation process was monitorized by TLC and the IR and VIZ spectra were recorded.

The alkytated dyes were used to dye polyacrilonitrile fibers and the optimum dyeing conditions were determined. The dye **I** was used to dye proteic fibers (wool) and polyamide fibres (nylon).

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