

THE UV-VIS CHARACTERIZATION OF AZO DYE BY IRRADIATION

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Abstract: The stereochemical factor, which play a significant role about colour azo dyes, lead at Z(sin)-E(anti) isomerism. The E(anti) form are much more stable at temperature rooms, while the Z(sin)-isomer can be generated only by photochemical methods.

Keywords: azo dyes, isomerism, photochrom.

1. Introduction

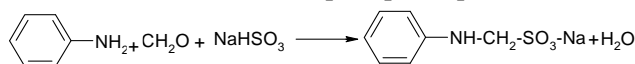
Photoresponsive systems are compounds which respond to light energy beyond only absorbing and releasing it as heat. The storage of the light energy for varying lengths of time, the reappearance of fluorescence and chemical or even mechanical energy are properties of photoresponsive system [1,2].

The absorption spectra of both two isomer form of azo dye are always differed. The detectable quantities of Z(sin)-isomer are obtained at exhibit of dye to light, lead to colour change, which will be reversible to the removal lights [3,4].

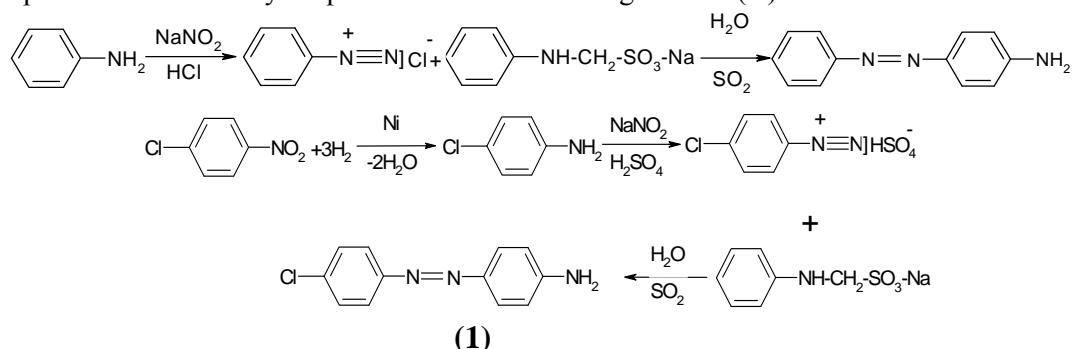
This phenomenon is named as photochromia or phototropy and it isn't wanted in the dyes with commercial applications [5]. The photocromic degree depends decisive of the quantic yield of photoisomerization and of Z(sin) forms thermostability. Fortunately, the strong donor groups from electrons azobenzene system reduce sensible life duration of Z(sin) isomers and thus the photochroma is a grand question for dyes producers [6].

2. Experimental part

In this work synthesis of azo dye is present. This dye a will be polymerization and study photochromic proprieties [1,2]. The synthesis follows two steps: diazotizing of p-aniline and the coupling salt of diazonium with the phenylaminomethylsulphonic acid. A mixture of NaHSO₃ solution and 28% formaldehyde solution for synthesis of phenylaminomethylsulphonic acid is heated at 70°C, where it is maintained for 0,5h. After that the resulted solution is cooled at 25°C, then the aniline is added and the mixture is heated for 3h at 25-30°C and maintained for 1h at 35°C. The mixture was diluted with water, cooled to 20°C and precipitate product is formed [7].



The preparation of the azo dye is presented in the following scheme (A):

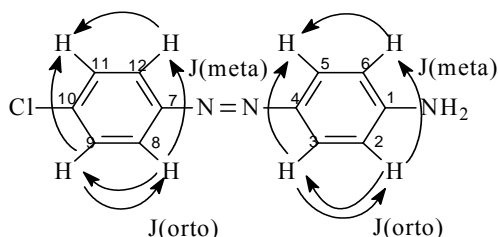


Scheme A. The preparation of azo dye

The purification of azo dye (**1**) through recrystallization from solvents was achieved. The solvents utilized are 1,4 dioxane and N,N dimethylformamide, which are purified by anhydridation procedure. The purity was checked by thin-layer chromatography.

The physico-chemical characterization of the synthesised compound was done by UV, IR and NMR spectroscopy [8]. The spectra UV was recorded on a SECOMAM S750 spectrophotometer, quartz vat used for all solution of concentration $2 \cdot 10^{-5}$ mol/L in DMF (Table 1).

The synthesised compound (**1**) was characterized by ^{13}C -NMR and ^1H -NMR, using deuterated dimethyl-sulfoxide as a solvent.



The ^1H - NMR spectra: (H^6) H^2 split doublet δ_{H} : 7.56 ppm with the coupling constants orto $J(2,3) = 8.64$ Hz; (H^3) H^3 split doublet δ_{H} : 7.80 ppm with the coupling constants orto $J(3,2) = 8.64$ Hz; (H^{12}) H^8 split doublet δ_{H} : 7.67 ppm with the coupling constants orto $J(8,9) = 8.64$ Hz; (H^9) H^{11} split doublet δ_{H} : 6.83 ppm with the coupling constants orto $J(9,8) = 8.64$ Hz

The results of the elemental analysis proved the presence of nitrogen and chloride atoms (Table 2).

Table 2. Elemental analysis of the azo dye

%C calculated	62.20
found	61.52
%H calculated	4.31
found	3.76
%N calculated	18.14
found	17.60
%Cl calculated	15.33
found	14.85
%Br calculated	-
found	-

The irradiation of the azo dye (**1**) was made with a experimental installation with Hg lamp (250 W) [1] to record the UV-VIS spectra before and after irradiation. The intensity of absorption before and after irradiation was measured with the same UV-VIS spectrophotometer (Table 3). The irradiated dye samples were transported immediately in the dark after irradiation. The solutions were exposed to UV light to increase the rate of *Z(sin)*-*E(anti)* isomerization.

Table 1. Results of UV-VIS analysis of azo dye

Compound	Concentration [mol/L]	λ_{max} [nm]	Absorbance $\lg [I_0/I]$
	$2 \cdot 10^{-5}$	271.0	0.817
		370.8	1.401
		420,6	1.901

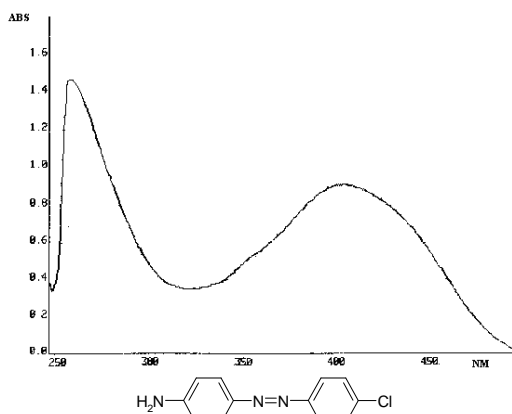


Fig.1. The UV-Vis spectra after 2 h from irradiation

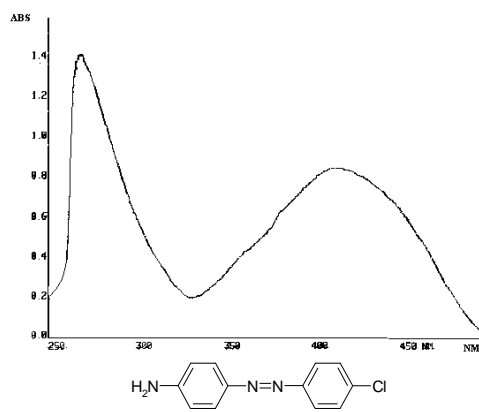
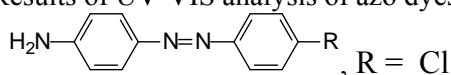


Fig.2. The UV-Vis spectra after 24 h from irradiation

Table 3. Results of UV-VIS analysis of azo dyes solutions



R*		Cl
Conc. 10 ⁻⁴ (mol/L)		3.00
Before irradiation	λ_1	261
	A ₁	1.408 (4693)
	λ_2	405
	A ₂	1.301 (4337)
After 2 h from irradiation	λ_1	261
	A ₁	1.488 (4960)
	λ_2	408
	A ₂	0.910 (3033)
After 24 h from irradiation	λ_1	266
	A ₁	1.382 (4606)
	λ_2	414
	A ₂	0.856 (2853)

*in bracket are the molar extinction coefficient (L/mol·cm).

It has been observed a change in the absorption spectral domain after irradiation (Fig.1, Fig.2) of the chromophor solution with UV radiation for a short time (Table 1). The absorption spectra of both two form isomer of azo dye are differed and thus, if exhibit of a dye to light produce the detectable of Z(sin)-isomer, noticed changed it and colour will be reversible to the removal lights.

3. Conclusions

In all the cases a decrease in optic absorbance is observed, subsequently to the irradiation, with a tendency to come back at initial value (sometimes just outrunning in UV radiation absence, after 24 hours). Similarly to the absorption evolution behavior was molar extinction coefficient, too. The both parameters render default, in the fact, the frequency of Z(sin)-E(anti) transitions concomitantly the concentration of both isomers in system. The irradiation of the chromophor solution

with UV radiation for a short time, it can be observed a change in the spectral absorption domain. The DMF solvent selection solvent was needed for the later utilization in polymer analogue reactions [2]. The preference for DMF is justified because of this is solvent as much for dye and for polymeric substrate. If the intermediaries present two absorption maximums in the UV area which are characterized by order 10^4 molar extinction coefficient, their coupling in azo colour structures determine a movement of second maximum towards bigger wavelengths in visible zone. The bathochrome movement or hypsochromy which appears in the dye case is a direct consequence of azo chromophore which is responsible for the maximum movement in visible area and respectively, the nature and the volume of the substituent produce these phenomena. The spectra analysis show for all dyes the existence of two maximums of absorption on covering curve in visible area. All these prove the existence of two isomeric forms *Z(sin)*-*E(anti)*.

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Manuscript received: 15.03.2009 / accepted: 06.05.2009