

Preparation and Spectroscopic Study of Some Mono Azo Dyes Derived from 4-Amino Phenazone and Some phenols

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Abstract

This work involves of the preparation of three mono azo compounds; 4-(4-phenazone azo)- resorcinol (PAR), 2-(4-phenazone azo)- orcinol (PAO), and 2-(4-phenazone azo)-para nitro phenol (PAPNP). The dyes were prepared by using coupling reaction between heterocyclic amine: 4-amino phenazone with the above mentioned phenols.

The UV-visible and fluorescence spectra of the three dyes were recorded. Some physical and chemical properties such as: maximum absorption λ_{max} , molar absorption coefficient ϵ_{max} and yield were concluded. Melting points and flow rates of dyes were reported. The compounds were identified via using FT-IR spectra. The work involved a study of interaction between dyes and TiO_2 surface by X-ray diffraction spectra; It has been found that the rates of photodegradation of three dyes were higher in presence of TiO_2 .

الخلاصة

تتضمن هذه الدراسة تحضير ثلاث اصباغ وهي 4 - (4 - فينازون آزو) - ريزورسينول (PAR) 2-(4-phenazone azo) - اورسينول (PAR) و 2 - (4-فينيازون آزو) - بارانايتروفينول (PAPNP) و 2-(4-phenazone azo)- orcinol (PAO) عن طريق احداث تفاعل الاذواج بين الامين الحلقى غير المتجانس 4-امينوفينازون (4-amino phenazone (AP) مع الفينولات في محيط حامضي .

تمت دراسة الاطياف الالكترونية واطياف الفلورة للاصباغ المحضرة ، كذلك استنتجت بعض الخواص الفيزيائية والكيميائية مثل الامتصاص λ_{max} ومعامل الامتصاص المولاري ϵ_{max} والحصول ، ودرست ايضاً للاصباغ المحضرة بعض الخواص الفيزيائية مثل درجات الانصهار وسرعة الجريان R_f . تم تشخيص المركبات المحضرة بواسطة طيف امتصاص الاشعة تحت الحمراء FT-IR . تضمن البحث دراسة تداخل الاصباغ المحضرة على سطح ثاني اوكسيد التيتانيوم ، كذلك درس تفاعل التحطم الضوئي للاصباغ بوجود وغياب TiO_2 .

Introduction

Beside the main use of azo dyes in field of textile dyeing, many of those dyes have additional uses, such as photometric reagents^(1,2), metal indicators⁽³⁾, in the colouring of gasoline (gasoline dyes)⁽⁴⁾ which add in the ratio 6.7 kg/1x10⁶ galone to characterize the types of gasoline. Some of azo compounds are considered as reactive ligands which coordinate with transition metals in order to prepare the complexes⁽⁵⁾.

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In recent years, some of mono azo dyes are derived from heterocyclic amines such as amino thiozoles^(3,5,6), amino imidazole⁽⁷⁾, 8-hydroxy quinoline⁽⁸⁾, or amino pyrazole⁽⁹⁾.

Some of azo compounds are derived from pyrazole by coupling the diazotized pyrazole, such as common red wool dye 1-(3,5-dimethyl pyrazol azo)-2-naphthol⁽⁹⁾.

The photodegradation of azo dyes has been studied in the absence of TiO₂⁽¹⁰⁻¹³⁾ and in its presence⁽¹³⁻¹⁵⁾. The literatures⁽¹⁻³⁾ indicate that the rate of photodegradation of dyes depends on quantity of TiO₂, concentration of dye, pH and temperature.

The main aim of the present work is to prepare and study three mono azo dyes by coupling reaction between heterocyclic amine: 4-amino phenazone and some phenols.

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Experimental

Materials: 4-amino phenazone and resorcinol were supplied by Riedl De Haen; Orcinol, sodium hydroxide, ethanol (absolute), hydrochloric acid, and acetic acid were obtained from BDH; Sodium nitrite and p-nitrophenol were bought from Fluka, Titanium dioxide was supplied by Degussa. All chemicals were used as received.

Preparation of Dyes

The three dyes were prepared by adding 0.025 mol of amine to 25ml of mixture of distilled water and hydrochloric acid 1:1. 0.025 mol (10ml) of sodium nitrite solution was added dropwise with stirring to above yellow-red solution and by maintaining the temperature at 0 °C.

The diazonium salt resulting above was added dropwise to basic phenol solution which is prepared by dissolving the phenol(0.025 mol) into 40ml of 10% sodium hydroxide. The yielding compound was left at room temperature for 90 min, then it was separated by filtering process and washed with cold water for several times. The dyes were purified by recrystallization from aqueous methanol and dried at 70 °C for three hours.

The purity of prepared dyes was checked via melting point and thin layer chromatography methods. R_f values of dyes were investigated in silica gel plates; The eluent used was (ethanol, acetic acid, distilled water 4: 1: 5).

Spectroscopic Measurements

FT-IR spectra were obtained via using Perkin Elmer FT-IR Spectrophotometer. UV-visible absorption spectra were recorded by using Shemdzu UV-160 Spectrophotometer. Fluorescence spectra were recorded by using Jenwan model 6200 Fluorimeter

Preparation of Samples for -X-rays diffraction spectra

The samples for XRD spectra were prepared by impregnation method mentioned previously⁽¹⁸⁾. The XRD spectra were recorded by using Philips X-rays diffractometer and by using $\text{CuK}\alpha$ radiation at $\lambda=1.541 \text{ \AA}$.

Photodegradation Experiments

The photodegradation of dyes was carried out by irradiating the aqueous solutions of the prepared dyes in quartz cell with light of middle pressure mercury lamp for 90 min at laboratory temperature; Then the quantity of degraded dye was measured in the λ_{max} of dye via using Shimadzu UV-160 Spectrophotometer. Then the same photodegradation experiments were again performed in the presence of TiO_2 suspension (0.4 gm/l) and with continuous stirring of suspension

Results and Discussion

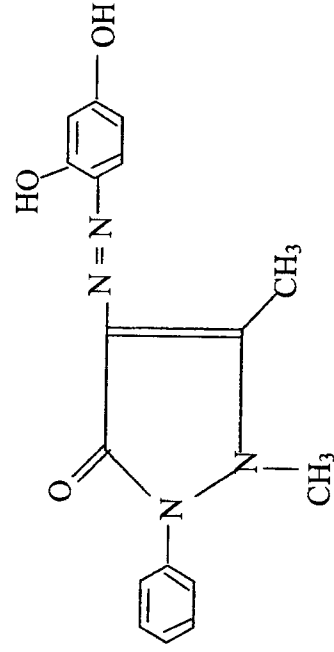
Azo dyes are characterized with special properties as a simple and easy method of preparation in a wide range of disire colors, high solubility into common solvents, and high and stable adsorption on the surfaces of cotton and wool textiles.

The amine used in the present work: 4-amino phenazone is a reagent used in the colometric determination of phenols⁽²⁰⁾ and the synthesis of transition metals and lanthanide⁽²¹⁾. Phenazone is a derivative of pyrazole; The 4-amino phenazone is also called 4-amino antipyrine; The antipyrine is one of the oldest synthesized drugs. It was discovered by Knorr at 1984⁽¹⁰⁾ and used as an anti-pain. Recently time some of drugs and dyes contain its cyclic system⁽¹⁹⁾, Fig.(1) shows the electronic spectra of 4-aminophenazone, and the λ_{max} of it about 300nm.

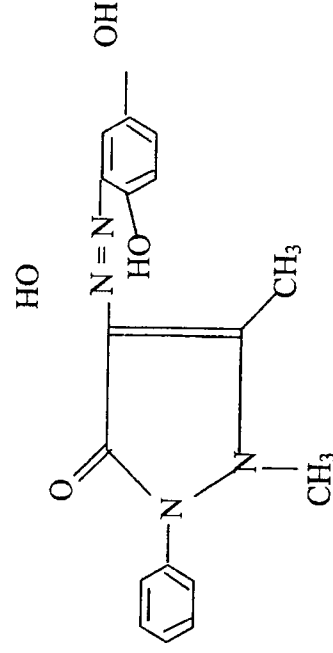
Table(1) lists some of physical and chemical properties of the prepared dyes; The R_f value of PAR and PAO dyes indicate the similarity of affinity of both dyes to eluent as a result of their containing of two hydroxyl groups (scheme 1)

Table(1): physical and chemical properties of dyes

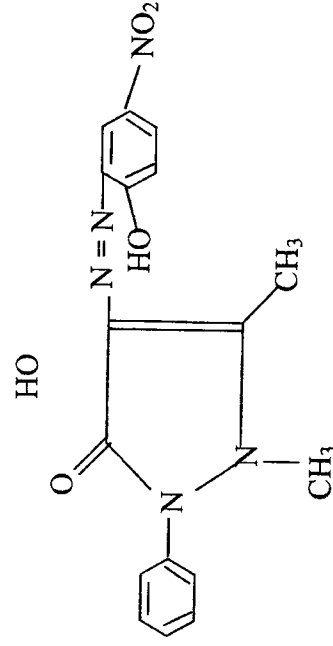
No.	Dye	Empirical formula	M. Wt. g. mol ⁻¹	colour	Yield %	M. P. C°	R _f
1	PAR	C ₁₇ H ₁₆ N ₄ O ₃	324	Brown	72	235	0.840
2	PAO	C ₁₇ H ₁₆ N ₄ O ₃	324	Red	68	214	0.795
3	PAPNP	C ₁₇ H ₁₅ N ₅ O ₄	353	Red-Brown	81	195	0.697



(PAR)

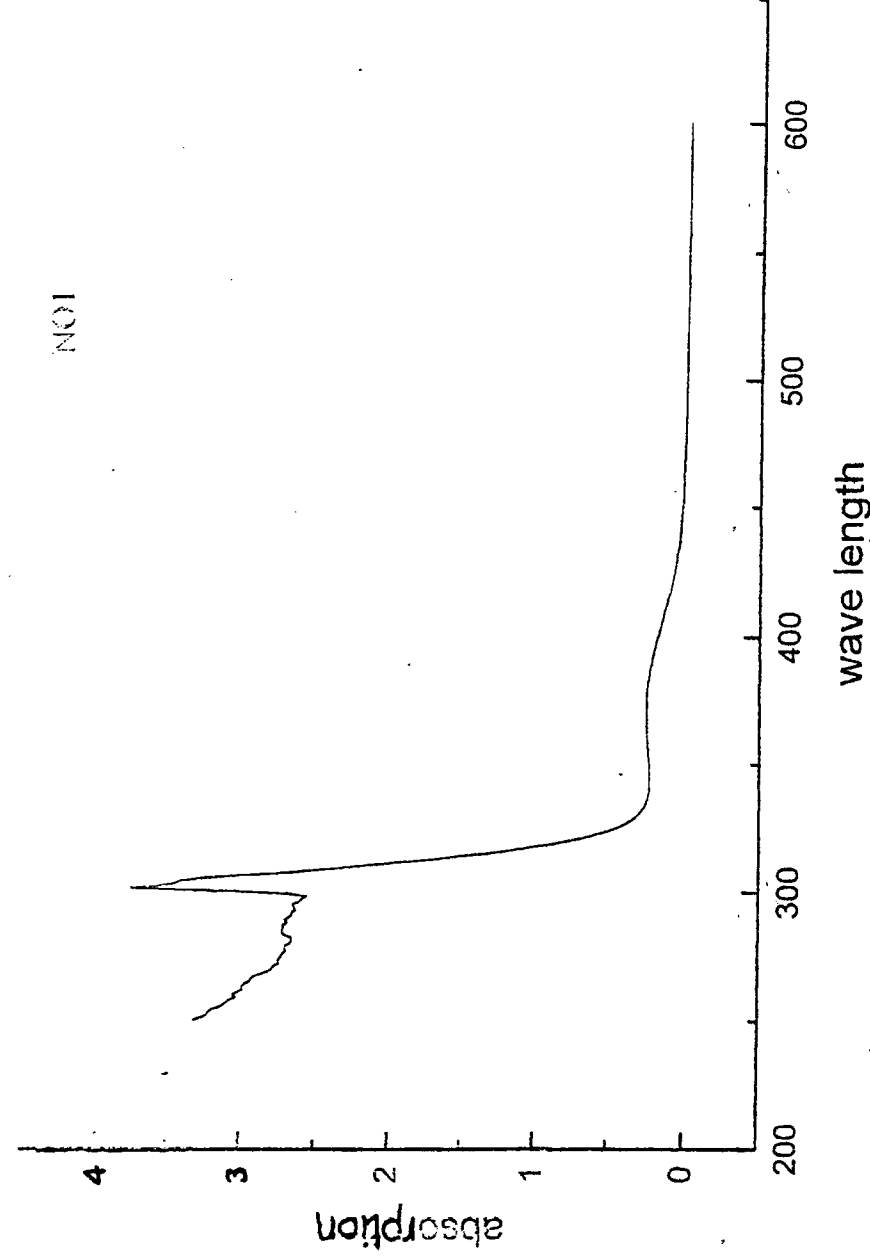


(PAO)



(PAPNP)

(Scheme 1)
Structural formula of dyes



Fig(1): UV-visible Spectrum of 4-amino phenazone

Figures (2), (3) and (4) show the FT-IR spectra of PAR, PAO and PAPNP dyes respectively; The absence of amine vibration band is considered as an essential indicator of the formation of dye beside the intensive color of crystals of product compound which was supported by UV-visible absorption spectra (Figures (5), (6) and (7) of PAR, PAO, PAPNP dyes respectively).

The main result of coloring crystals is the absorption of visible light as shown in table(2); The high value of E_{max} indicates the high absorptivity of those dyes of visible light. Also the λ_{max} of absorption and λ_{max} fluorescence (table(2)) are considered additional indicator of formation of dyes; The fluorescence spectra are showed in figures (8), (9) and (10).

Table (3) shows the effect of adsorbed dyes on the surface properties of TiO₂; It is clear that the stated dyes adsorb in monolayer which don't externally change the nature of TiO₂ surface, i.e. adsorption of dyes modifies the surface layer of TiO₂ particles which indicates that the chemisorption may be formed.

Table (4) shows the concentrations of dyes after photodegradation process of aqueous solutions of dyes; The data indicates that the presence of TiO₂ particles causes the increase in photodegraded molecules as a result of catalytic properties of TiO₂ are found in other studies (14-17).

Table(2): Spectral properties of dyes

No.	Dye	λ _{max} , nm Absorption	λ _{max} , nm Emission	E l.mol ⁻¹ . Cm ⁻¹	N=N Stretching Cm ⁻¹
1	PAR	405	575	1.8x10 ³	1520
2	PAO	515	580	5.1x10 ²	1504
3	PAPNP	540	550	6.6x10 ³	1511

Table(3): X-rays data of adsorbed dyes on TiO₂ surface (relation of hkl with d according to Bragg's equation)

Hkl	101	103	004	112	200	105	211	213	204	116	220	215
Intensity of Beak												
Dye/TiO ₂	Vst	Vw	St	Vw	St	M	M	W	M	Vm	Vm	M
PAR	3.519	2.431	2.377	2.338	1.894	1.699	1.667	1.493	1.481	1.361	1.339	1.264
PAO	3.516	2.430	2.378	2.337	1.890	1.698	1.664	1.493	1.484	1.369	1.335	1.262
TiO ₂	3.518	2.434	2.378	2.337	1.894	1.700	1.660	1.493	1.480	1.365	1.338	1.265
PAPNP	3.598	2.431	2.375	2.336	1.892	1.670	1.663	1.491	1.482	1.365	1.338	1.262

Table (4): The remain conc. Of photodegradation of dyes (1x10⁻³M) in absence and presence of TiO₂

No	Absence of TiO ₂	Presence of TiO ₂
PAR	0.65 x 10 ⁻³	0.50 x 10 ⁻⁴
PAO	0.41 x 10 ⁻³	0.63 x 10 ⁻⁴
PAPNP	0.70 x 10 ⁻³	0.21 x 10 ⁻³

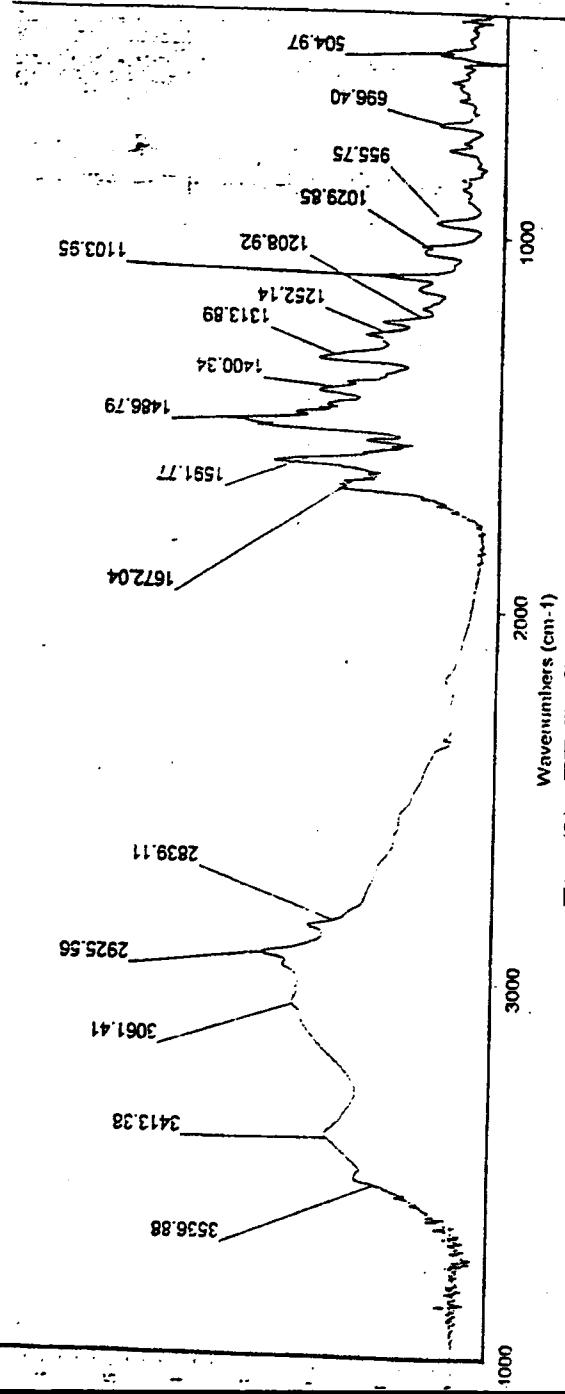


Fig.(2): FT-IR Spectrum of PAR dye

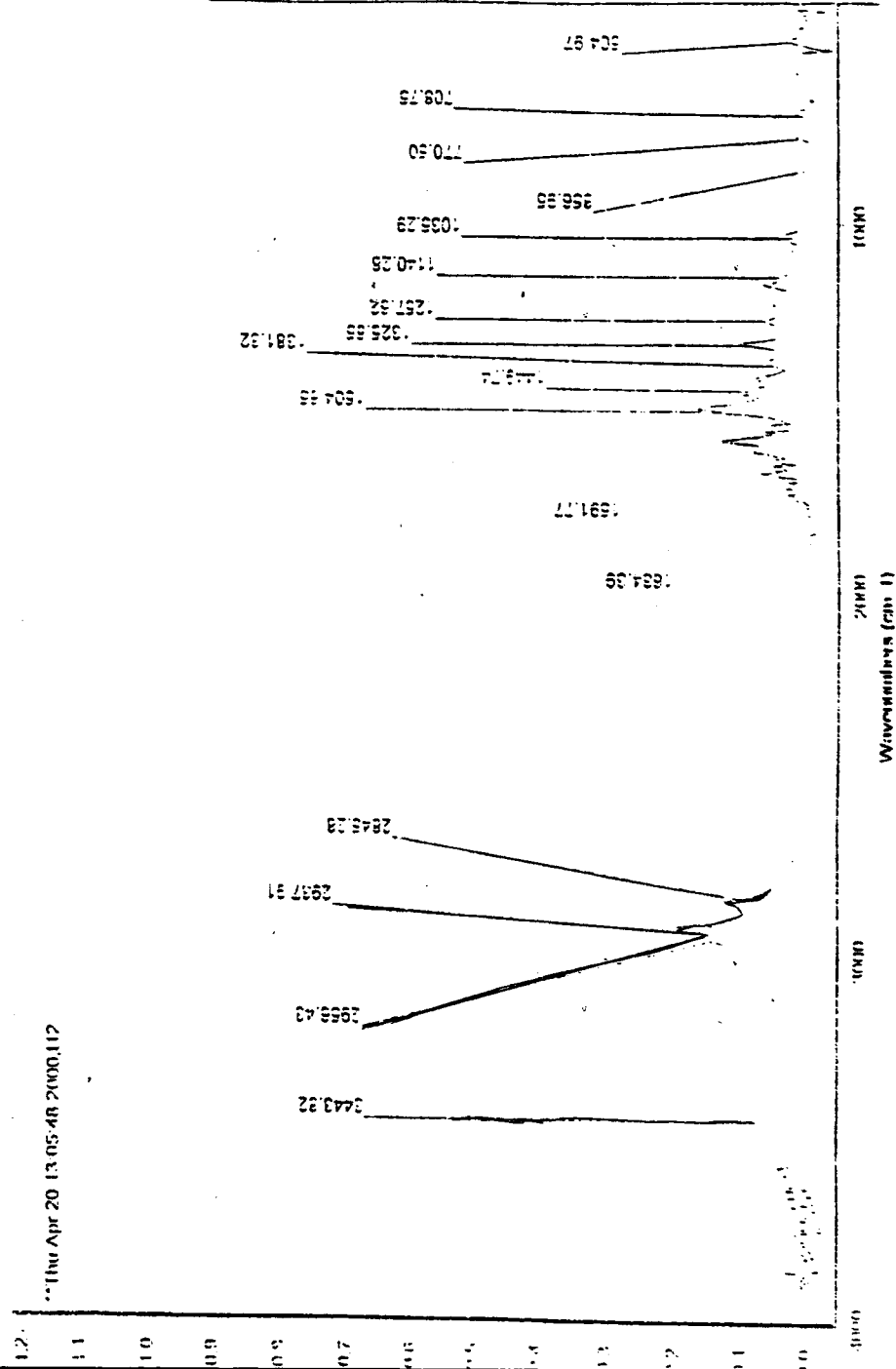


Fig.(3): FT-IR Spectrum of PAO dye

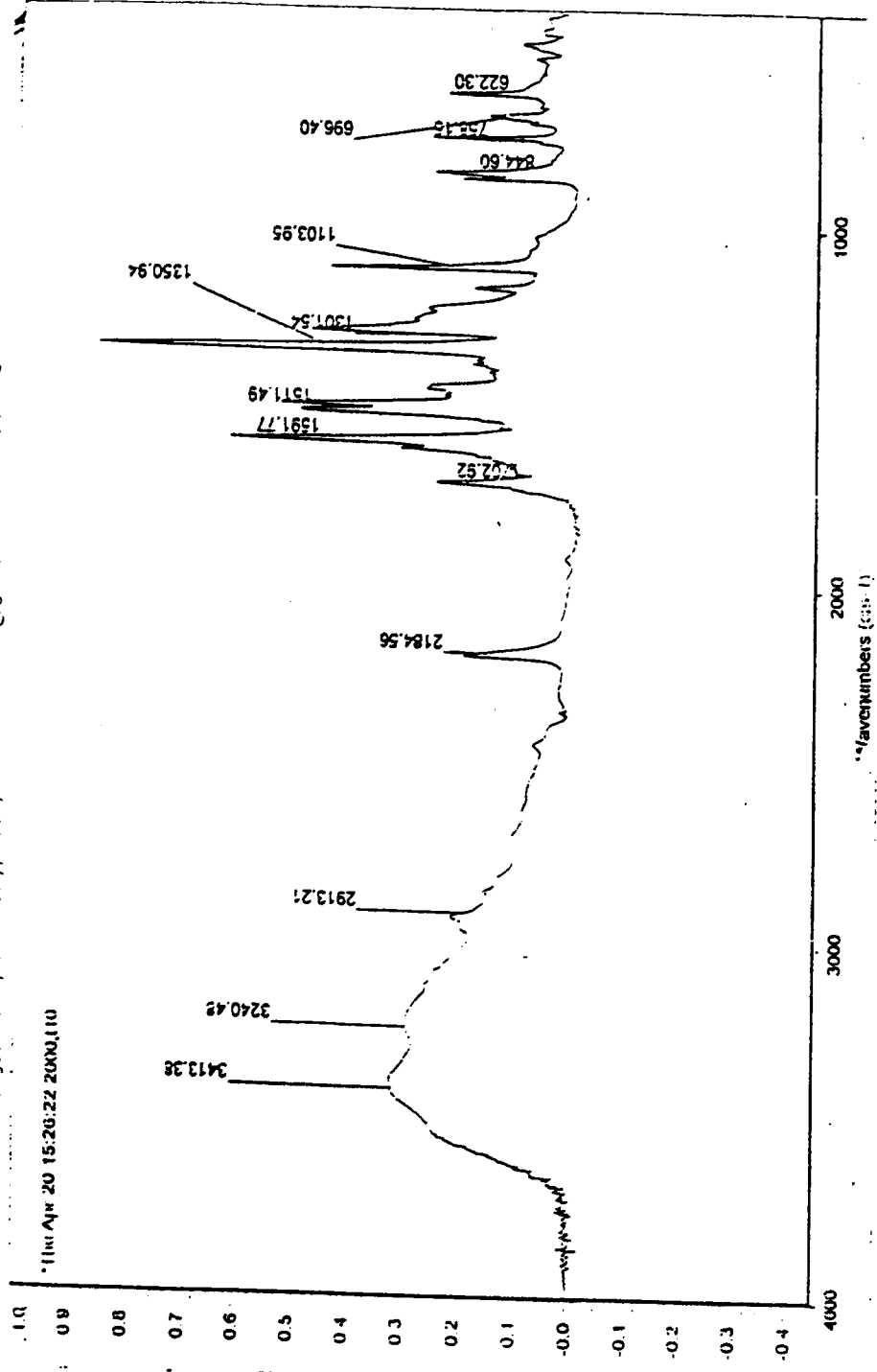


Fig.(4): FT-IR Spectrum of PAPNP dye

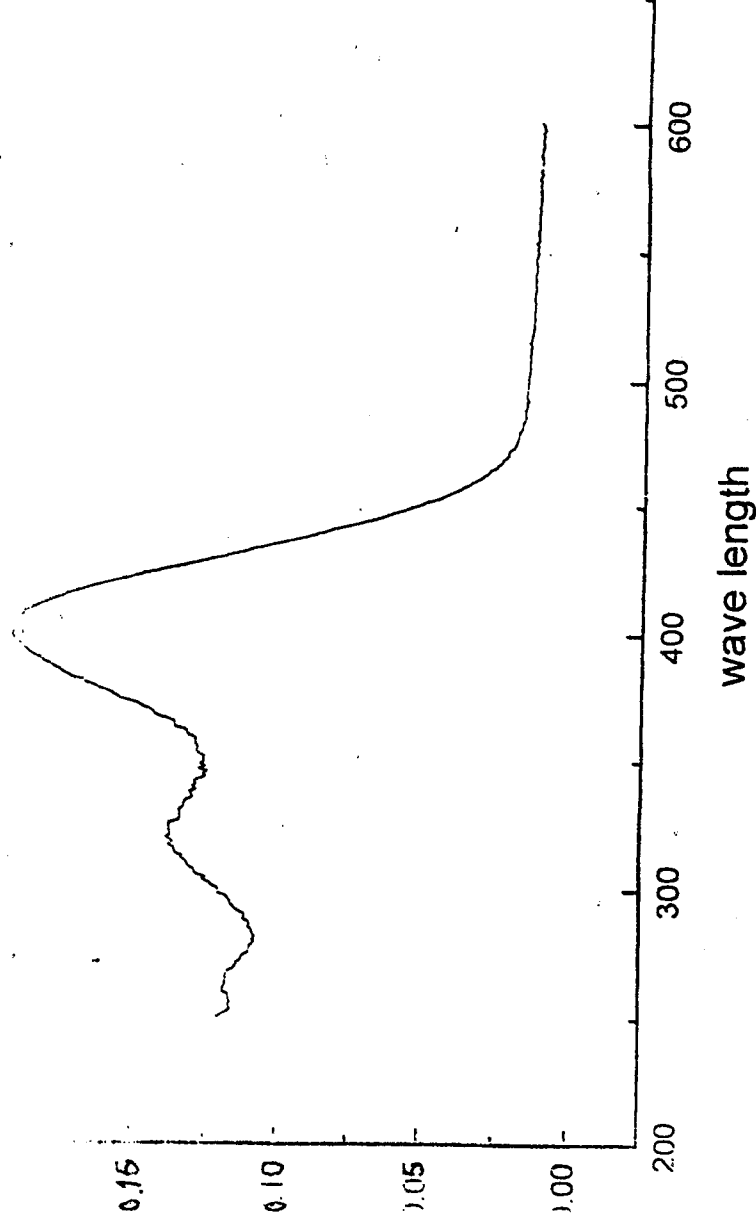


Fig.(5): UV-visible Spectrum of PAPNP dye

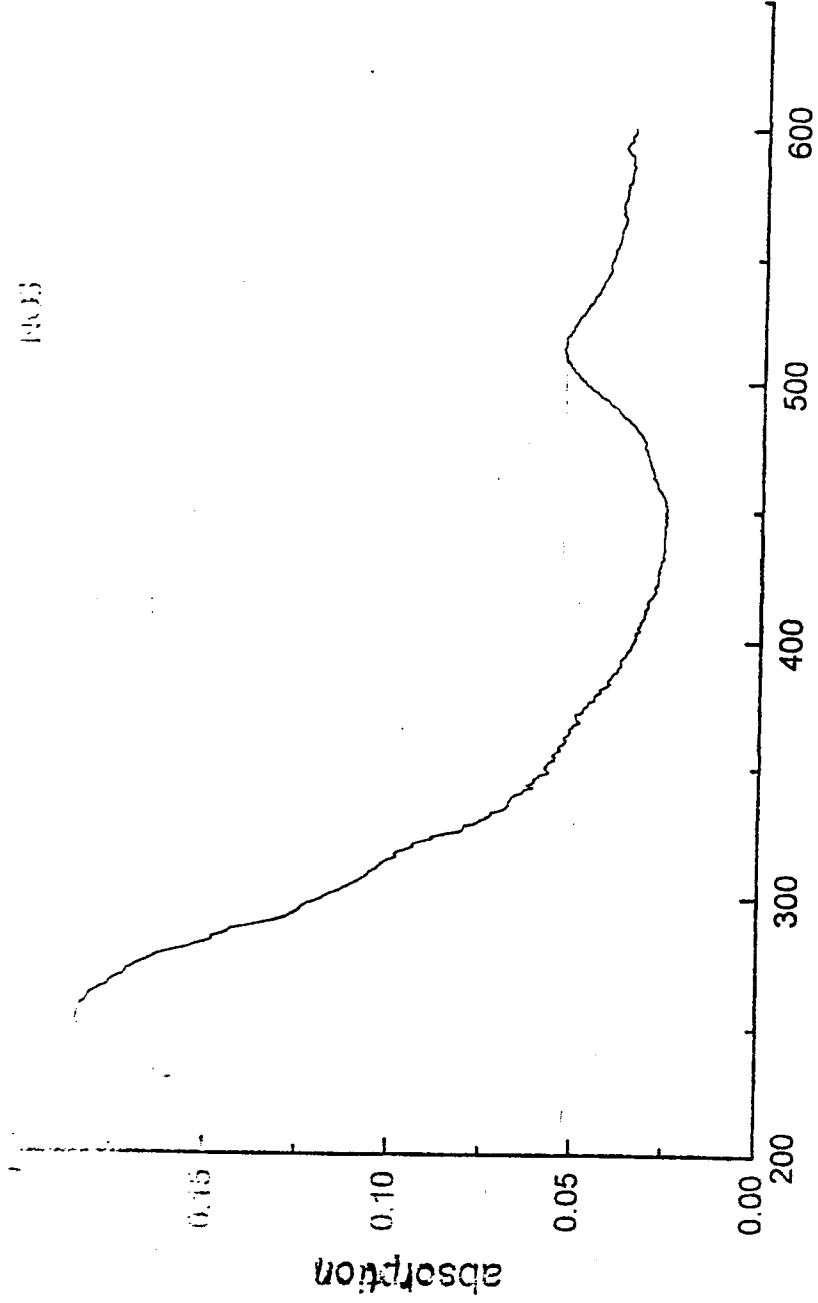


Fig.(6): UV-visible Spectrum of PAO dye

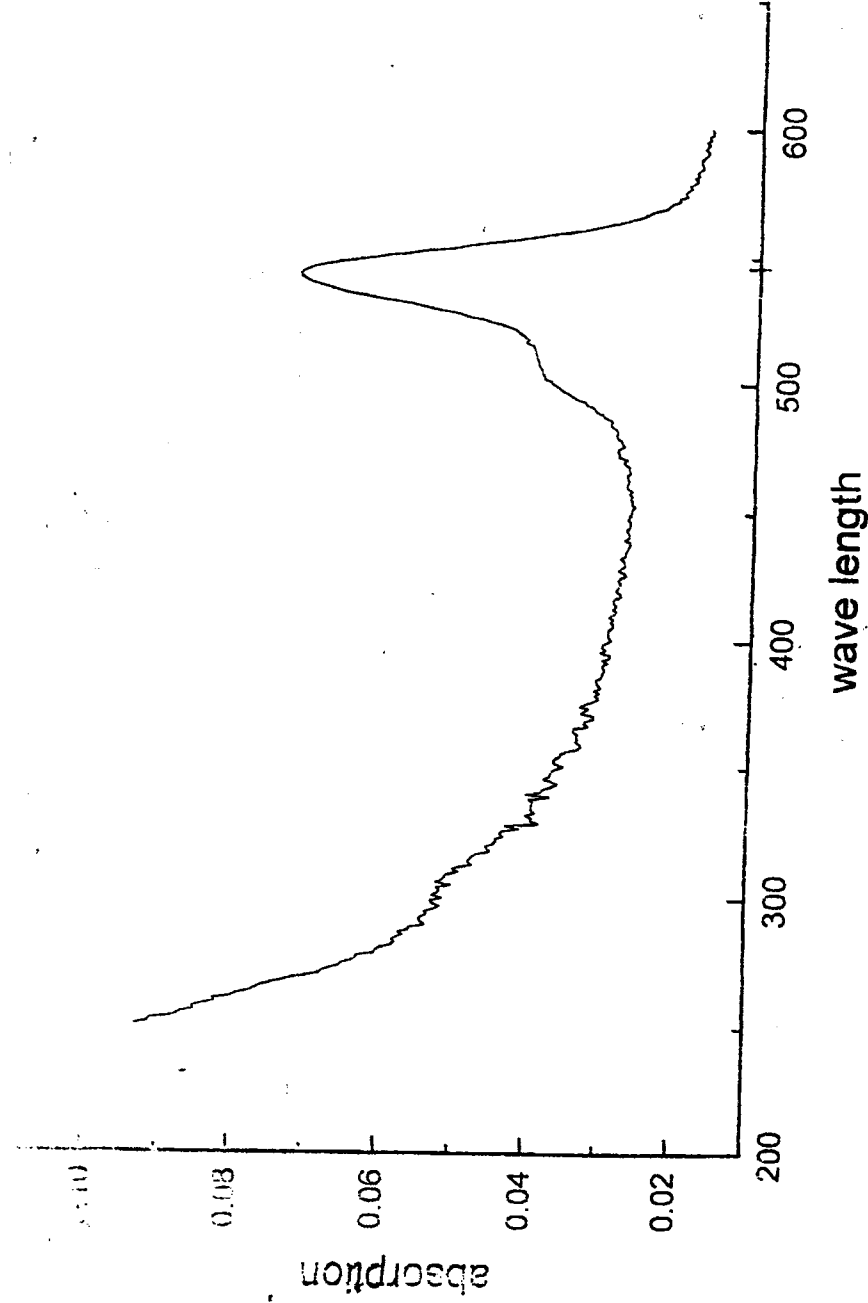


Fig.(7): UV-visible Spectrum of PAPNP dye

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