CHAPTER - 4

AZO DERIVATIVES OF 1-HYDROXYANTHRACENE

INTRODUCTION

INTRODUCTION

The chemistry of diazo and azo compounds possess a surprising number of facts and a glance at the historical development of this field, reaching as it does into both aliphatic and aromatic chemistry, shows in how many directions progress has been made. The history and the development in the field has been reviewed (1-3). The various aspects of chemistry of azo compounds is discussed by Zollinger(4).

Preparation of Aromatic Diazo Compounds :

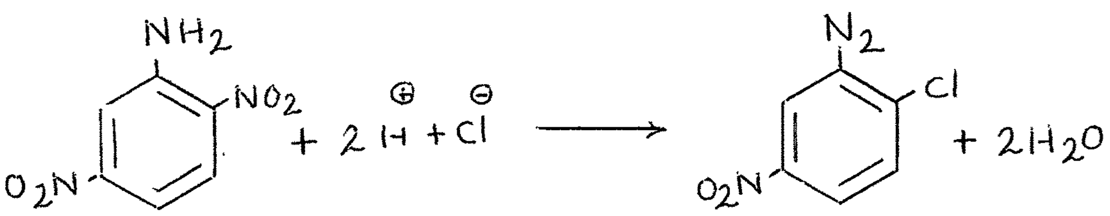
Several methods are reported for the preparation of aromatic azo compounds. Saunders has given different routes for preparing aromatic azo compounds in a tabular form in his book(5). The important method is the rearrangement of nitrosoacylarylamines(6,7). Later on Huisgen et. al. studied this rearrangement and elucidated the mechanism(8-12).

Tedder has described an interesting way of introducing a diazonium group into aromatic systems(13-17). In this method phenols are treated with two equivalents of nitrous acid and give, via the intermediate nitroso compound, the diazonium salt in good yield. The equation can be given as :

$$ArH + 2HNO_2 + HX \longrightarrow ArN_2^+X^- + 2H_2O + 2O.$$

The formation of diazonium compounds by reactions of nitroso compounds with nitric oxide was first observed by Bamberger(18). Gowenlock and Luttke discussed its mechanism(19).

Noteworthy is also the so-called self-diazotization discovered by Sinlbohm(20-22), several nitroaniline derivatives on treatment with hydrochloric acid in acetic acid solution form the corresponding chlorodiazobenzenes e.g.



The usual method for preparing diazo compound is diazotization with alkali nitrite in aqueous solution. In this method diazotization is carried out by allowing sodium nitrite to act on a solution of aromatic amine in mineral acid at low temperature i.e. about 0-5°C. The overall equation for this process is :

$$Ar\text{-}NH_2 + 2HX + NaNO_2 \longrightarrow Ar\text{-}N_2X + NaX + 2H_2O$$

$$(X = Cl,\ Br,\ NO_3,\ HSO_4,\ etc.)$$

A newer technique for monodiazotization of aromatic diamines is claimed by Hoechst A.G.(23). With some modification Shah and Upasani have monodiazotized several aromatic diamines and have coupled them with different naphthol sulphonic acids(24).

Absorption Spectra of Azo Compounds :

Colour, the most important property of the dyestuff, is the interpretation by the mind of the response of the retina to stimulation by light, which is that portion of electromagnetic radiation to which the eye is sensitive. Electromagnetic radiation is energy propagated through space in the form of an oscillating electric and magnetic field, which can be represented as a sinusoidal wave with the characteristic of wavelength(λ), frequency(ν) and energy (E). Human eyes are sensitive only to the visible portion of the spectrum, that is to light of wavelength between 400 and 750 mμ. A knowledge of the extent to which different frequencies of radiation are absorbed by a substance allows the colour of that substance to be determined for a given set of circumstances. If a substance is illuminated by radiation that is uniformly intense throughout the visible region of the spectrum (i.e. white light), then bands of wavelengths, when absorbed, will give rise to the colours listed in the following Table.

Wavelength(mμ)	750	605	595	580	560	500	490	480	435	400
Absorbed light	R	O	Y	YG	G	BG	GB	B	V	
Resulting colour	BG	GB	B	V	RV	R	O	Y	YG	

(V=violet, B=blue, G=green, Y=yellow, O=orange, R=red).

The absorption spectra of azo compounds have been the subject of some investigations, Brode has studied the absorption spectra of benzeneazo-benzene(25). He observed that the absorption band is not simple, but consists of a smaller bands on the lower frequency side of the principal band. Later on Uymura reported absorption spectra of azo derivatives(26). Some more data are given by Costa (27), and sixteen aminoazobenzene dyes have has been investigated in 50% alcoholic hydrochloric solution using ultraviolet and visible spectra(29). Absorption spectra of azobenzene derivatives are redetermined and are analysed in terms of simplified L.C.A.O. - M.O. theory(30). The spectra of azo dyes derived from 4-hydroxy and 4-acetoxybenzene is reported by Skulski et. al.(31). Effect of alkali on the spectra of azo dyes has been studied by McDowell(32). In the recent years different workers have discussed absorption spectra of azo dyes(33-36).

<u>The Infra Red Spectra of Azo Dyes</u> :

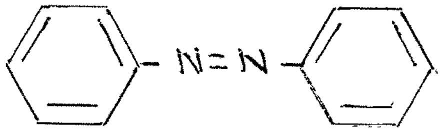
The group frequencies of the azo compounds are constantly attracting the researchers. Herzberg has reported -N=N- streching vibration of azomethane at 1575 cm^{-1}(37). Later on in 1950, Tetlow suggested the possibility that the characteristic frequency for the skeleton -C-N=N-C- may exist at 927 cm^{-1}(38). He observed that cis-and trans-azobenzenes show absorption at 927 cm^{-1}, which is absent in hydrazobenzene. Also this band shows a Christiansen Alter effect only in the trans form, which indicates its association with a skeleton group along the direction of maximum polarizability. Le Feyre et. al. have studied many aromatic diazo-compounds(39-41). They find common absorptions at 1406 ± 14 cm^{-1} and at 1577 ± 8 cm^{-1}, and although they assign the latter to the -N=N- link, they point out that it could well arise from ring vibrations The Controversy on whether bands at 1600 or 1450 cm^{-1} should assign for -N=N- has been resolved by some elegant work of Luttke et. al.(42). Using N^{15} substitution they have been able to show that in aromatic azo compounds in the trans configuration, the -N=N- band occurs between 1440 and 1410 cm^{-1}. Morgan has given some further data on the -N=N- frequencies of some aryl azo naphthols(43). These show -N=N- bands near 1450 cm^{-1}, but they are of little use for identification purposes.

Fluorescence Spectra of Azo Dyes :

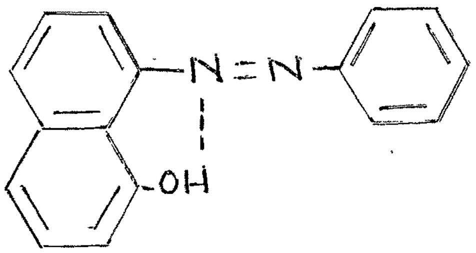
As early as in 1949, Pringsheim has noted that among more than 700 azo dyes, there is not a single example which is known to have fluorescence(44). This fact was understood on the basis of properties of the chemical bond in the azo group. It is known that π bond between the nitrogen atoms has a greater energy value (50 K.cal) than a σ-bond (30 K.cal). When the molecules are excited, a loosening of π bonds takes place, during which the bond in the -N=N- group is considerably weakened. The energy of an absorbed light quantum is either quickly transformed to thermal energy by way of vibration of single bonds, or leads to photodecomposition of the compound(45).

Nurmukhametov et. al. have attempted to clarify the conditions for the appearance of fluorescence in azo compounds and have tried to establish the connection between emission spectra and molecular structure(46). Their study has derived following conclusions :

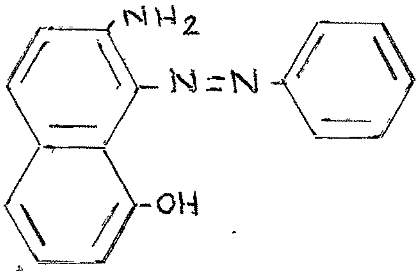
Unsubstituted azobenzene (I) has no luminescence either as powder or in solution. An intense fluorescence appears when an -OH group is introduced on the benzene or naphthalene ring in the position ortho to the azo group. The compounds with the highest symmetry have the most spectral structure. The substituted benzazo-naphthalenes having an OH group in the peri-position to the azo group (II & III) do not fluoresce.



I

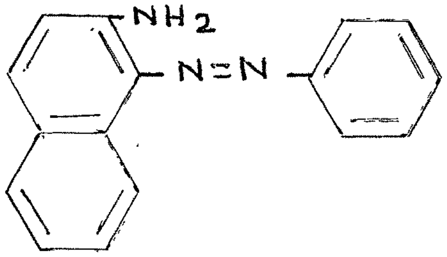


II

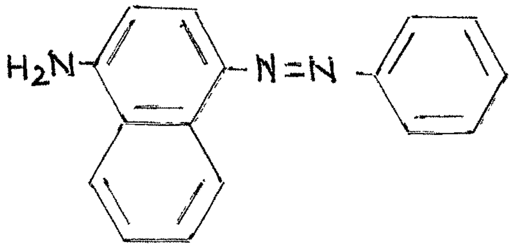


III

Ortho-amino derivatives (e.g.IV) show no luminescence under any condition while para-amino derivative(V) fluoresces only as a powder.



IV



V

Present Work

Logodinski was first to suggest that 1-hydroxyanthracene combines with diazonium salts to form bluish red azo compounds, but he did not isolate any of them(47). In 1916 Sircar prepared azo derivatives of 1-hydroxyanthracene by reacting 1-hydroxyanthracene with diazonium salts of aniline, p-nitroaniline, p-bromoaniline and sulphanilic acid. He examined these dyes for their dyeing properties on cotton and wool and compared it with the corresponding azo-a-naphthol dyes and azo anthranol dyes(48). A series of long-chain alkyl aromatic azo compounds based on 1-hydroxyanthracene has been prepared and their spreading properties on water have been examined(49). Osponson has studied the absorption spectra of 4-phenylazo-1-hydroxyanthracene(50).

It was proposed to synthesize some more azo derivatives of 1-hydroxyanthracene and to study their visible, i.r. and fluorescent spectra. Eight new azo derivatives have been synthesized by coupling different diazonium salts with alcoholic 1-hydroxyanthracene. Their spectral properties viz. visible, i.r. and fluorescent spectra have been studied.

EXPERIMENTAL

EXPERIMENTAL

Synthesis of 1-Hydroxyanthracene :

It was prepared by sulphonation of anthraquinone in presence of yellow mercuric oxide(51) followed by reduction to anthracene-1-sulphonic acid(52) and then fusion with potassium hydroxide to yield 1-hydroxyanthracene(53). The detailed procedure is described in chapter 3.

Synthesis of 4-Arylazo-1-Hydroxyanthracene :

The aromatic amines were obtained from B.D.H. or Koch-light Laboratories Ltd. These were used as such without any purification. Sodium nitrite used were of E.Merck, G.R. grade. All other chemicals used were A.R. or B.D.H. chemicals.

The diazotization was carried out in the usual way by dissolving aromatic amine in dil. HCl and adding sodium nitrite solution at 0-5°C. A typical procedure is described below(54).

o-Nitroaniline (0.1 mole) was dissolved in 1:1 hydrochloric acid (50 ml) in a conical flask. The mixture was cooled to 0°C in an ice-salt-bath with vigorous shaking with the addition of a little crushed ice. The salt, o-nitroaniline, hydrochloride separated as a finely divided crystalline precipitate. To this, aqueous sodium nitrite solution (0.1 mole) was added with shaking at a temperature of 0.5°C. Thus formed diazonium chloride solution was kept at this temperature for half an hour.

The coupling was carried out in alcoholic medium. To a alcoholic solution of 1-hydroxyanthracene, aromatic diazonium chloride solution was slowly added at 0-5°C with constant stirring. After complete addition, the mixture was stirred for one hour. The precipitate obtained was filtered and dissolved in potassium hydroxide (5% 25ml). The solution after filtration was acidified with concentrated hydrochloric acid. Again the precipitates obtained were filtered and washed with distilled water till the filtrate is free from acid. The precipitates were dried at 40°C under vaccum. These were crystallized till the constant melting point is obtained. The melting point and analytical data are given in Table 1. Melting points were recorded by using Toshniwal Melting Point Apparatus in open capillary and are uncorrected.

Visible Spectra :

The absorption spectra of these derivatives were taken on a SPEKOL Spectrophotometer using 10 mm cell in alcohol and in acetone. The absorption maximas are recorded in Table 2 and are shown in figures 1 to 8.

Infra Red Spectra :

The i.r. spectra were scanned on a Beckmann IR-20 spectrophotometer in nujol mull. The characteristic frequencies are tabulated in Table 3 and some representative spectra are shown in figures 9 to 11.

Fluorescence Spectra :

The fluorescence spectra (emission and excitation) were taken on a Aminco Fluorescence Spectrophotometer using alcohol as a solvent. The results are given in Table 4 and are shown in figures 13 to 16.

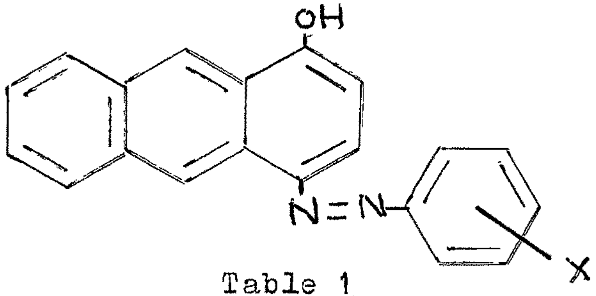


Table 1

4-Arylazo-1-hydroxyanthracene

No.	X	M.P. in °C	Elemental Analysis					
			Found			Required		
			%C	%H	%N	%C	%H	%N
1.	o-Nitro	240 (d)	69.74	3.56	12.50	69.97	3.79	12.24
2.	o-Chloro	250 (d)	72.08	3.810	8.231	72.22	3.912	8.427
3.	m-Chloro	222.3 (d)	71.83	3.765	8.551	72.22	3.912	8.427
4.	p-Chloro	275 (d)	72.15	3.814	8.128	72.22	3.912	8.427
5.	2,3-Dichloro	250 (d)	65.12	3.218	7.456	65.39	3.269	7.629
6.	2,4-Dichloro	179 (d)	65.00	3.111	7.621	65.39	3.269	7.629
7.	2,6-Dichloro	198.201 (d)	65.22	3.030	7.686	65.39	3.269	7.629
8.	p-Methoxy	145 (d)	76.60	4.536	8.531	76.82	4.878	8.536

Table 2

Absorption Spectra of 4-Arylazo-1-Hydroxyanthracene Derivatives:

No.	Aryl group	λ max in ethanol nm	E max x10^4	λ max in acetone nm	E max x10^4
1.	o-Nitrophenyl	495	1.25	490	2.25
2.	o-Chlorophenyl	495	6.00	480	6.00
3.	m-Chlorophenyl	505	4.80	490	5.20
4.	p-Chlorophenyl	515	4.00	505	4.08
5.	2,3-Dichlorophenyl	485	2.76	470	3.44
6.	2,4-Dichlorophenyl	510	1.8	505	2.00
7.	2,6-Dichlorophenyl	495	3.68	485	4.8
8.	p-Methoxyphenyl	530	2.96	525	3.26

Table 3

Infra Red Spectra of 4-Arylazo-1-Hydroxyanthracene Derivatives :

No.	Aryl group	Characteristics Frequencies in cm^{-1}				
		ν OH	ν N-H	ν C=N	ν N=N	ν C=O
1.	o-Nitrophenyl	-	1590	4590	-	1620
2.	o-Chlorophenyl	-	1600	1600	-	1640
3.	m-Chlorophenyl	-	1595	1595	-	1620
4.	p-Chlorophenyl	3405	-	-	1450	-
5.	2,3-Dichlorophenyl	-	1600	1600	-	1630
6.	2,4-Dichlorophenyl	-	1600	1600	-	1620
7.	2,6-Dichlorophenyl	-	1590	1590	-	1620
8.	p-Methoxyphenyl	-	1590	1590	-	1610

Table 4

Fluorescence Spectra of 4-Arylazo-1-Hydroxyanthracene Derivatives :

No.	Aryl group	Emission spectra in ethanol λ max.			Excitation spectra in ethanol λ max.		
1.	o-Nitrophenyl	383	400	430	338	350	370
2.	o-Chlorophenyl	380	410	420	335	350	370
3.	m-Chlorophenyl	387	405	425	335	350	375
4.	p-Chlorophenyl	385	405	425	335	350	370
5.	2,3-Dichlorophenyl	350	370	390	-	313	-
6.	2,4-Dichlorophenyl	-	-	-	-	-	-
7.	2,6-Dichlorophenyl	-	-	-	-	-	-
8.	p-Methoxyphenyl	360	380	410	-	340	360

VISIBLE SPECTRA

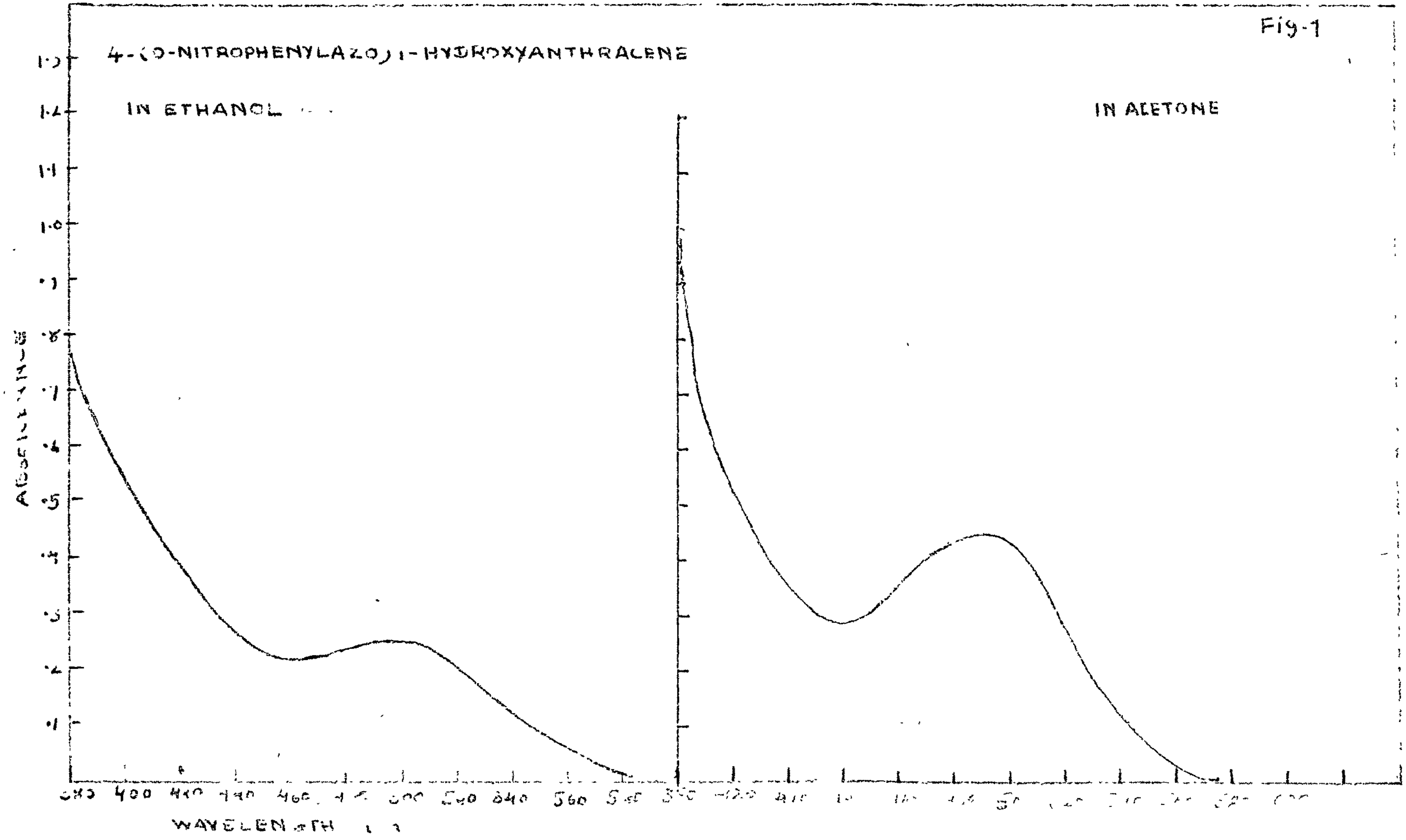
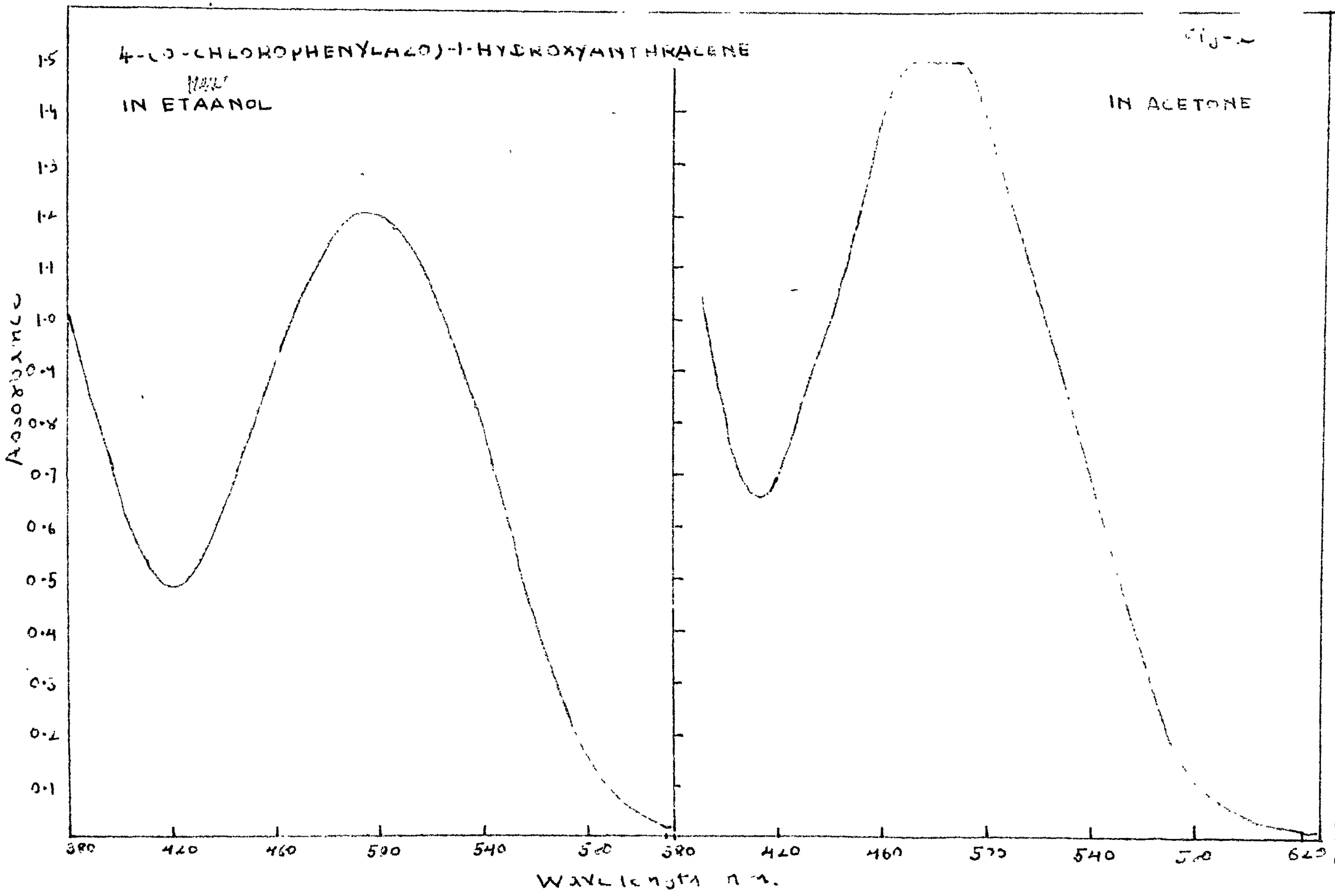
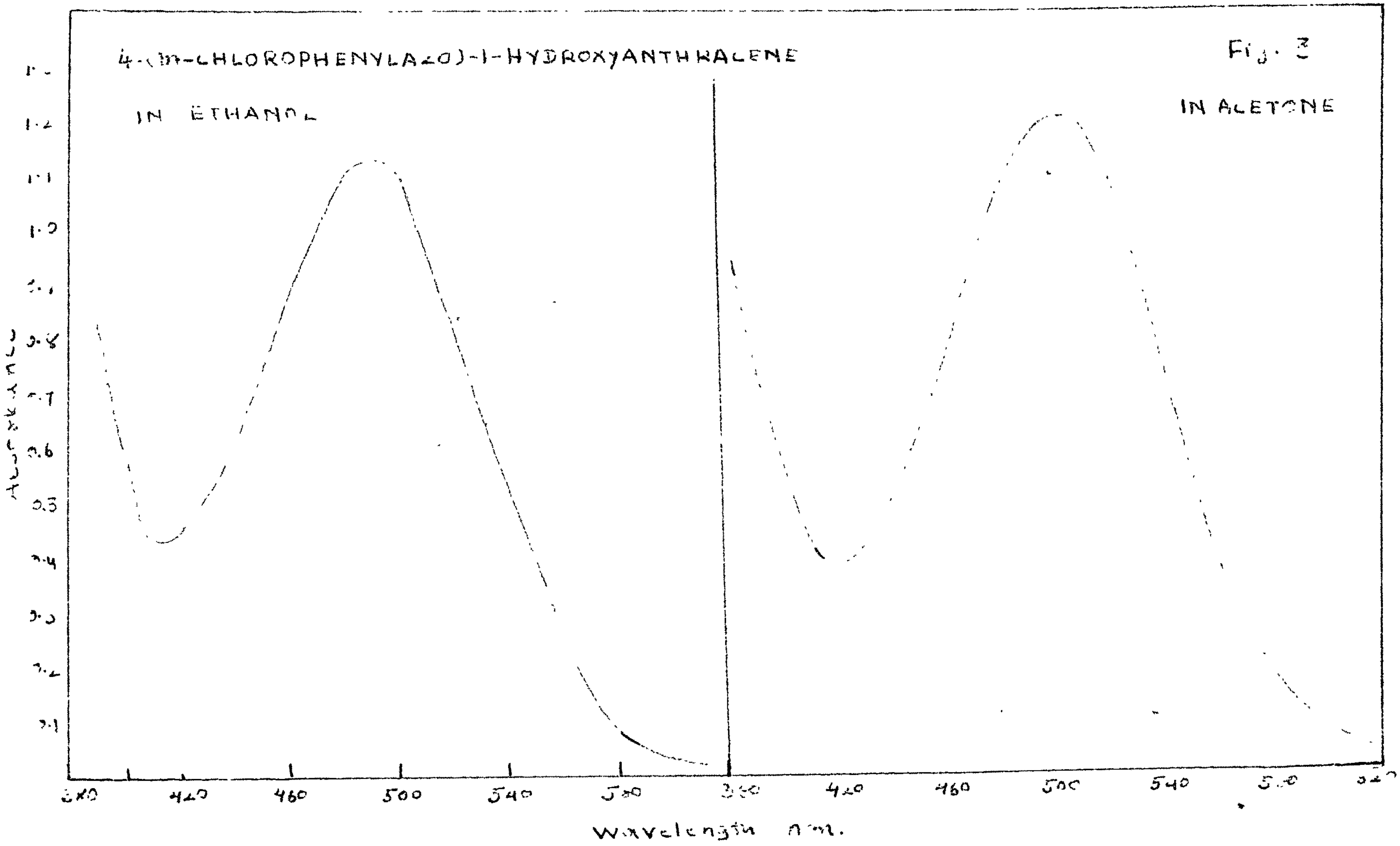


Fig-1

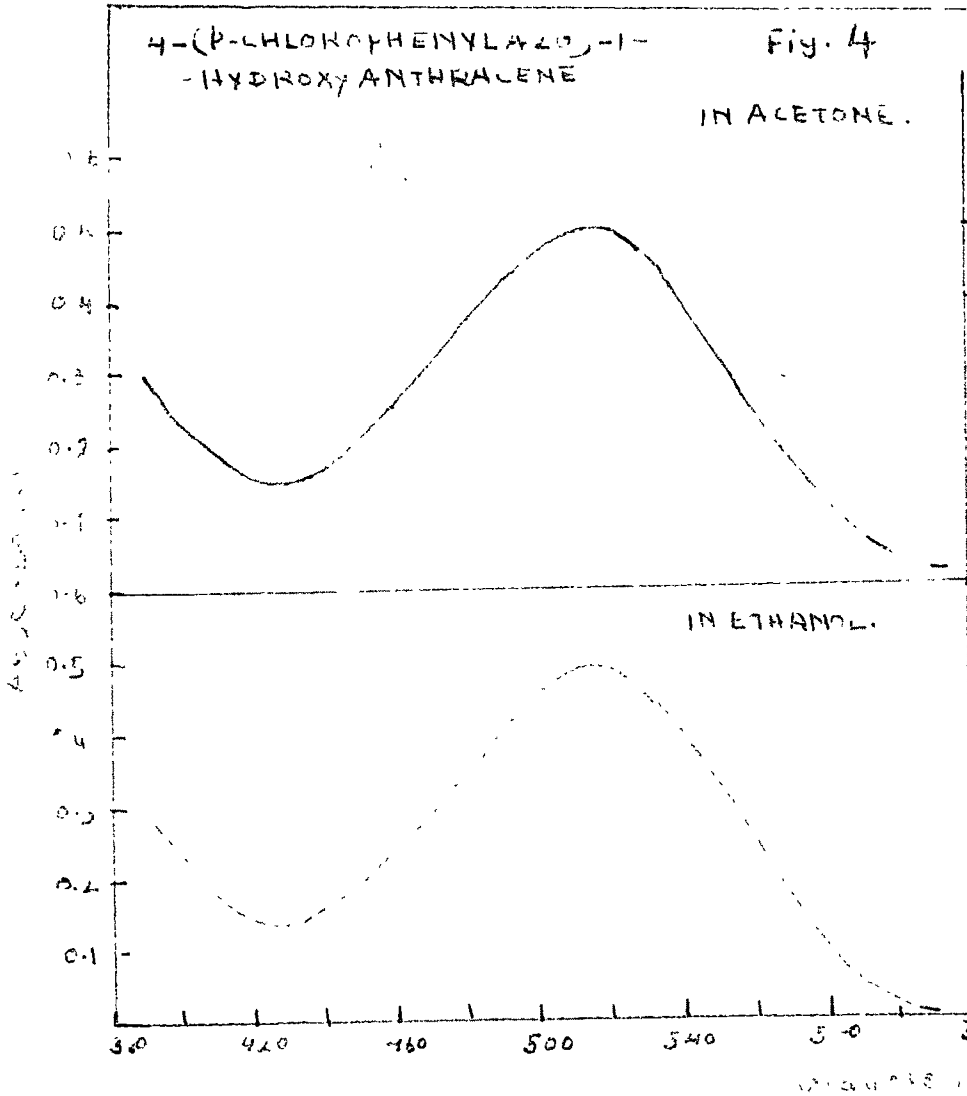
VISIBLE SPECTRA



VISIBLE SPECTRA

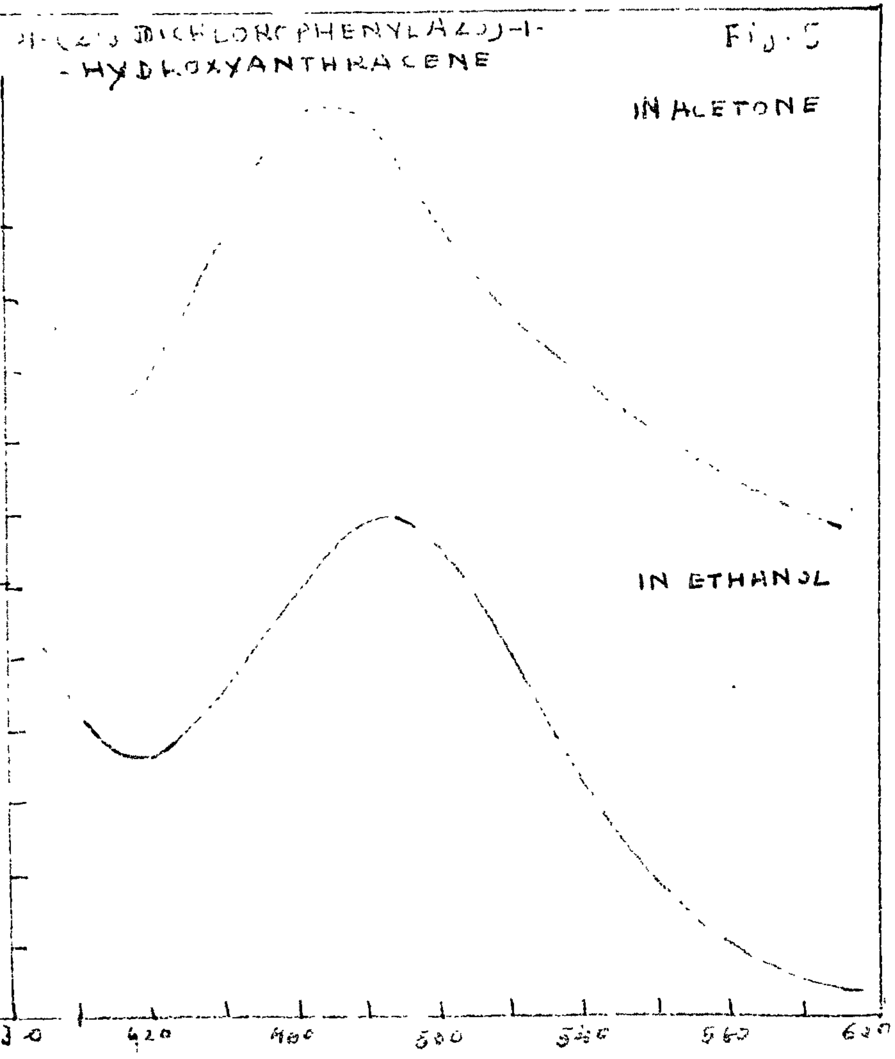


VISIBLE SPECTRA



4-(p-CHLOROPHENYLAZO)-1-HYDROXYANTHRACENE

Fig. 4



4-(2,5 DICHLOROPHENYLAZO)-1-HYDROXYANTHRACENE

Fig. 5

VISIBLE SPECTRA

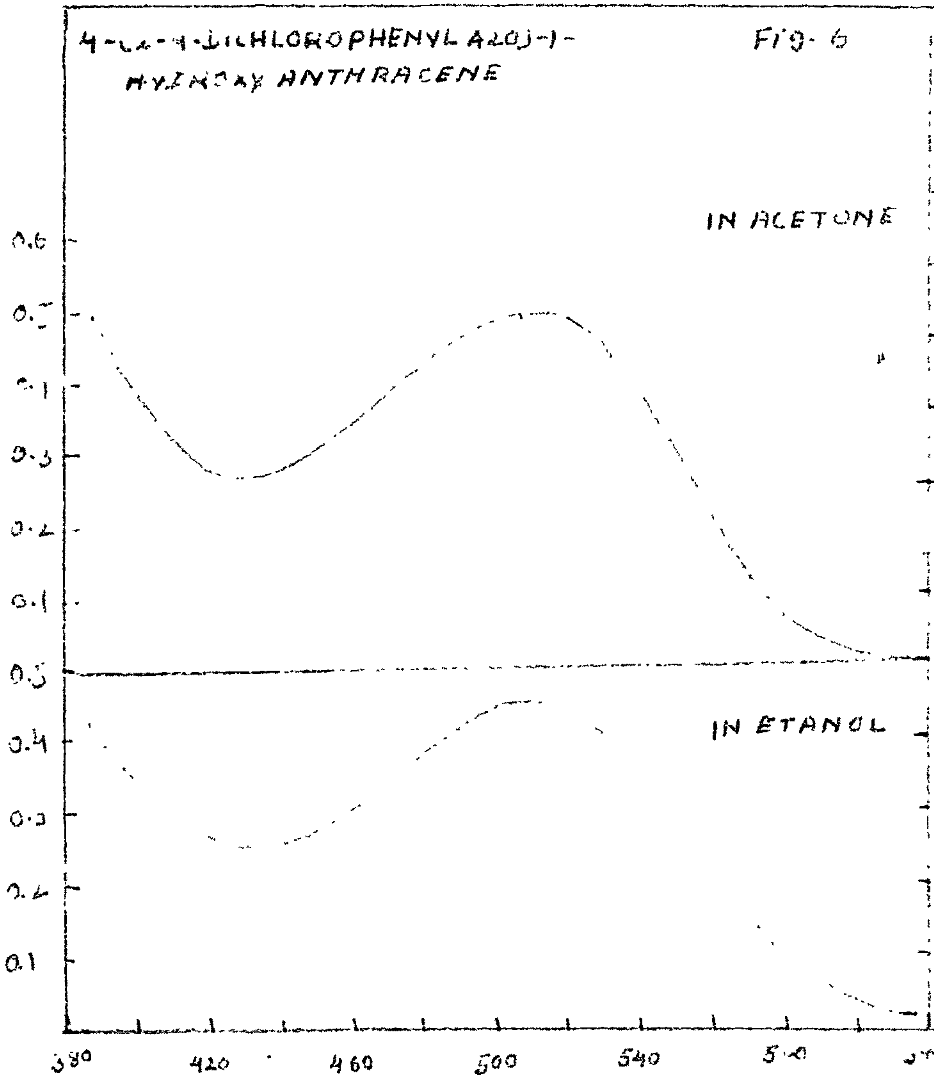


Fig. 6

4-(2-4-DICHLOROPHENYL AZO)-1-HYDROXY ANTHRACENE

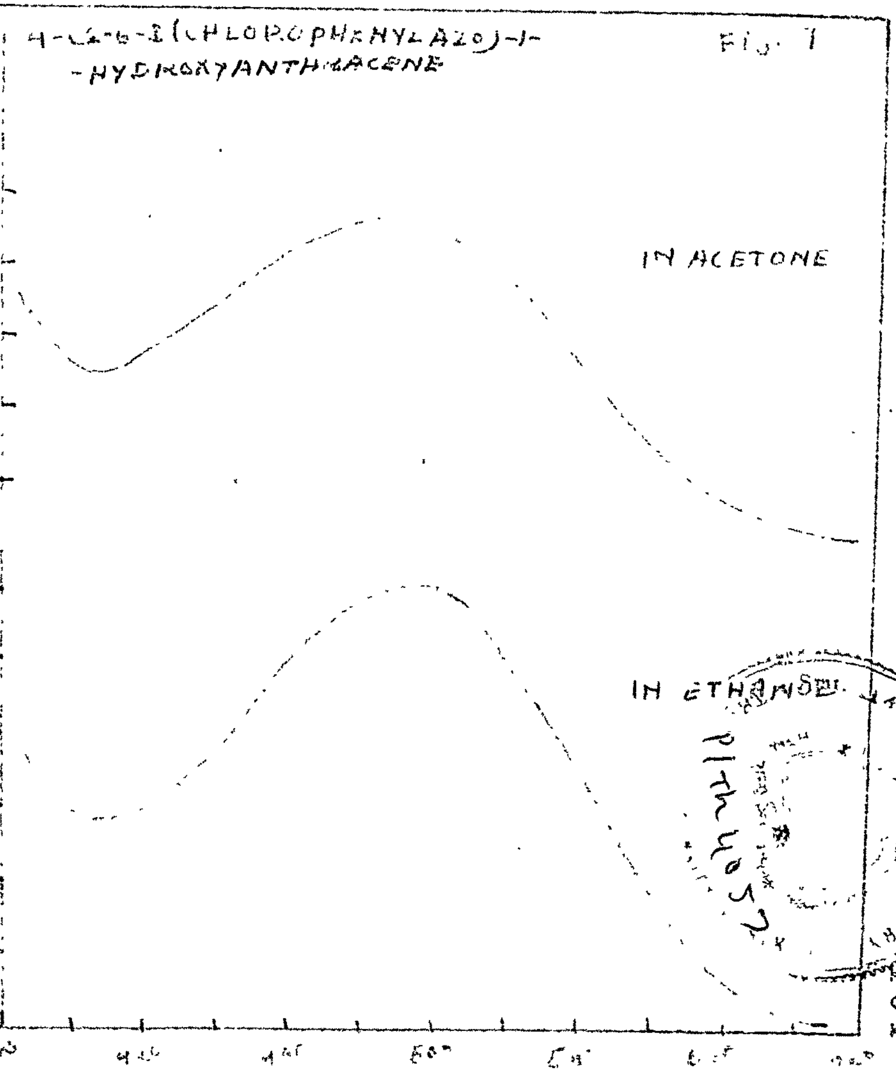


Fig. 7

4-(2-6-DICHLOROPHENYLAZO)-1-HYDROXYANTHRACENE

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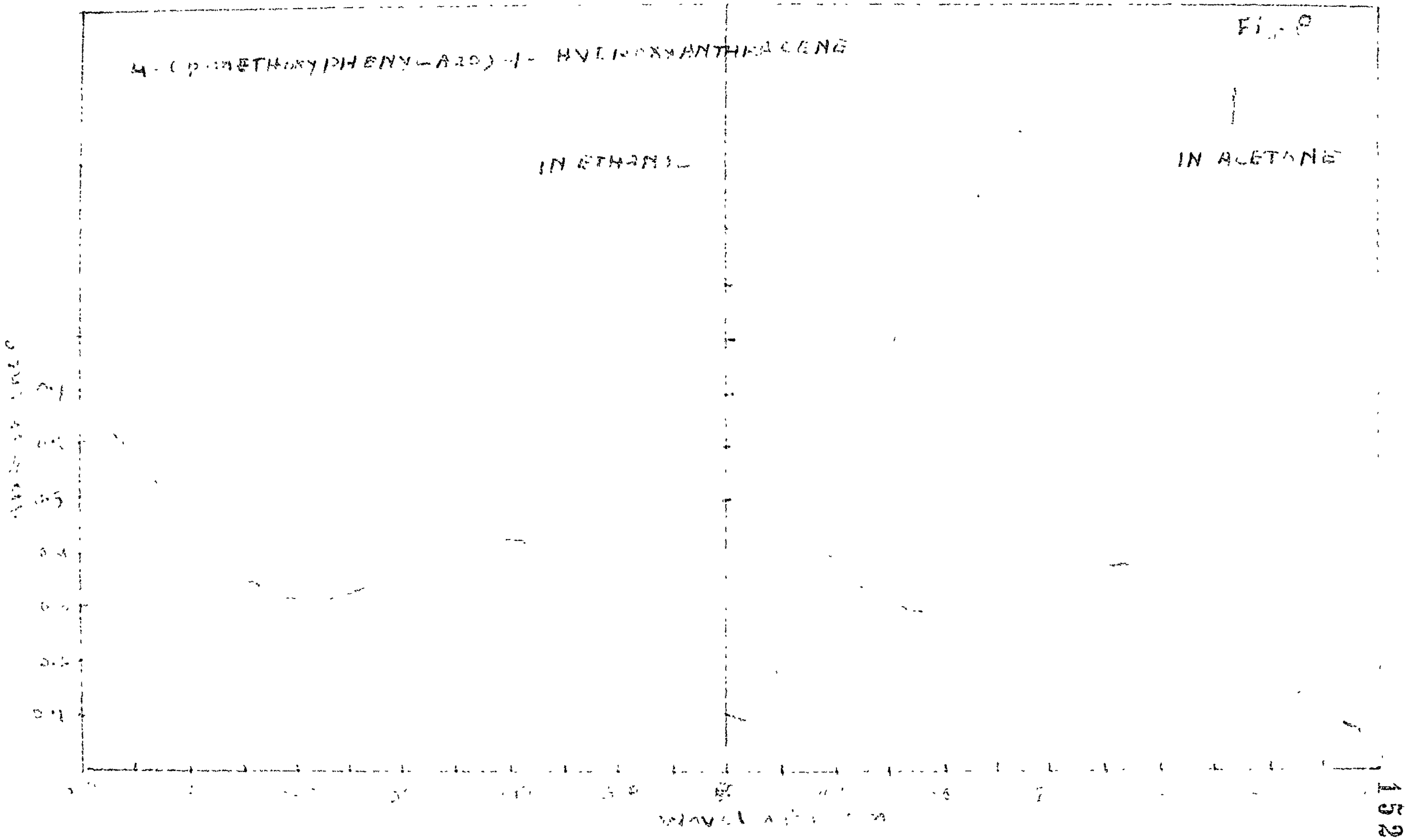
VISIBLE SPECTRA



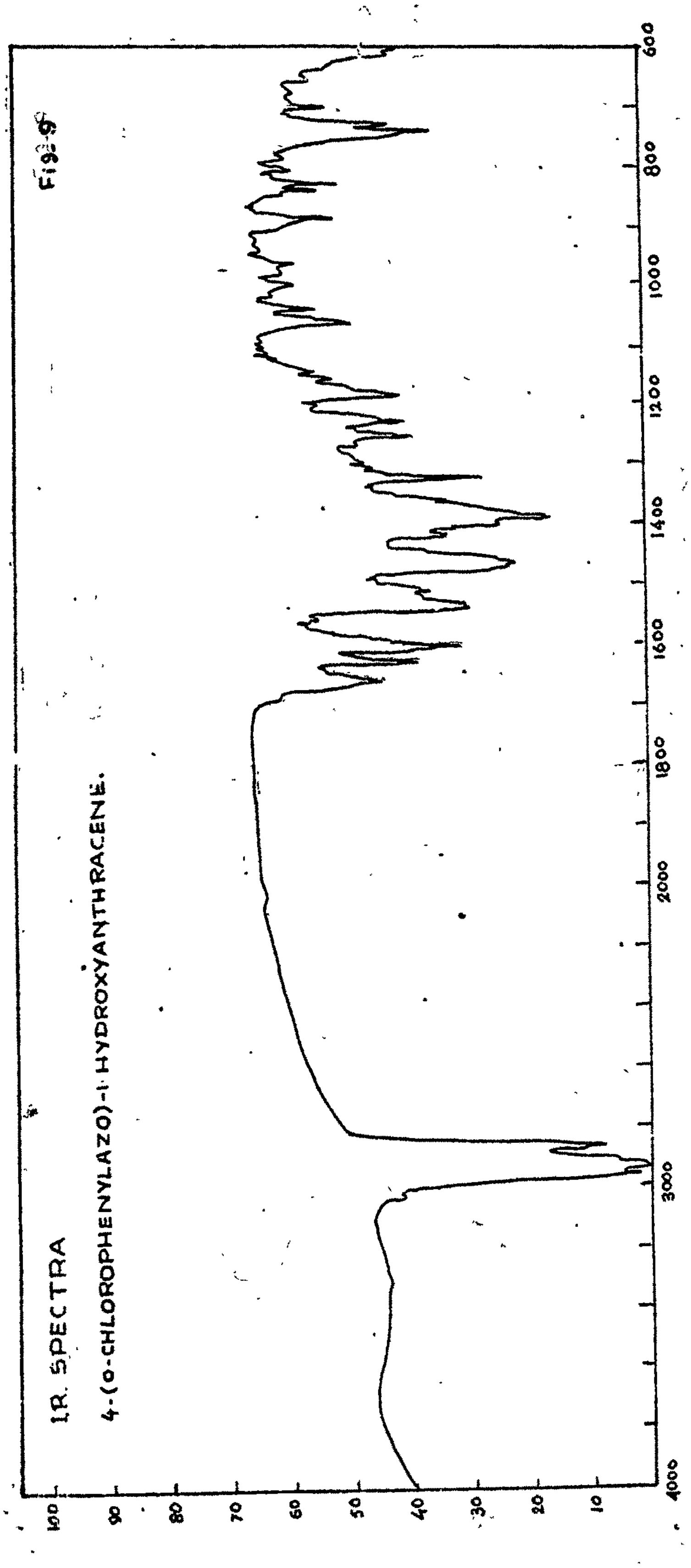
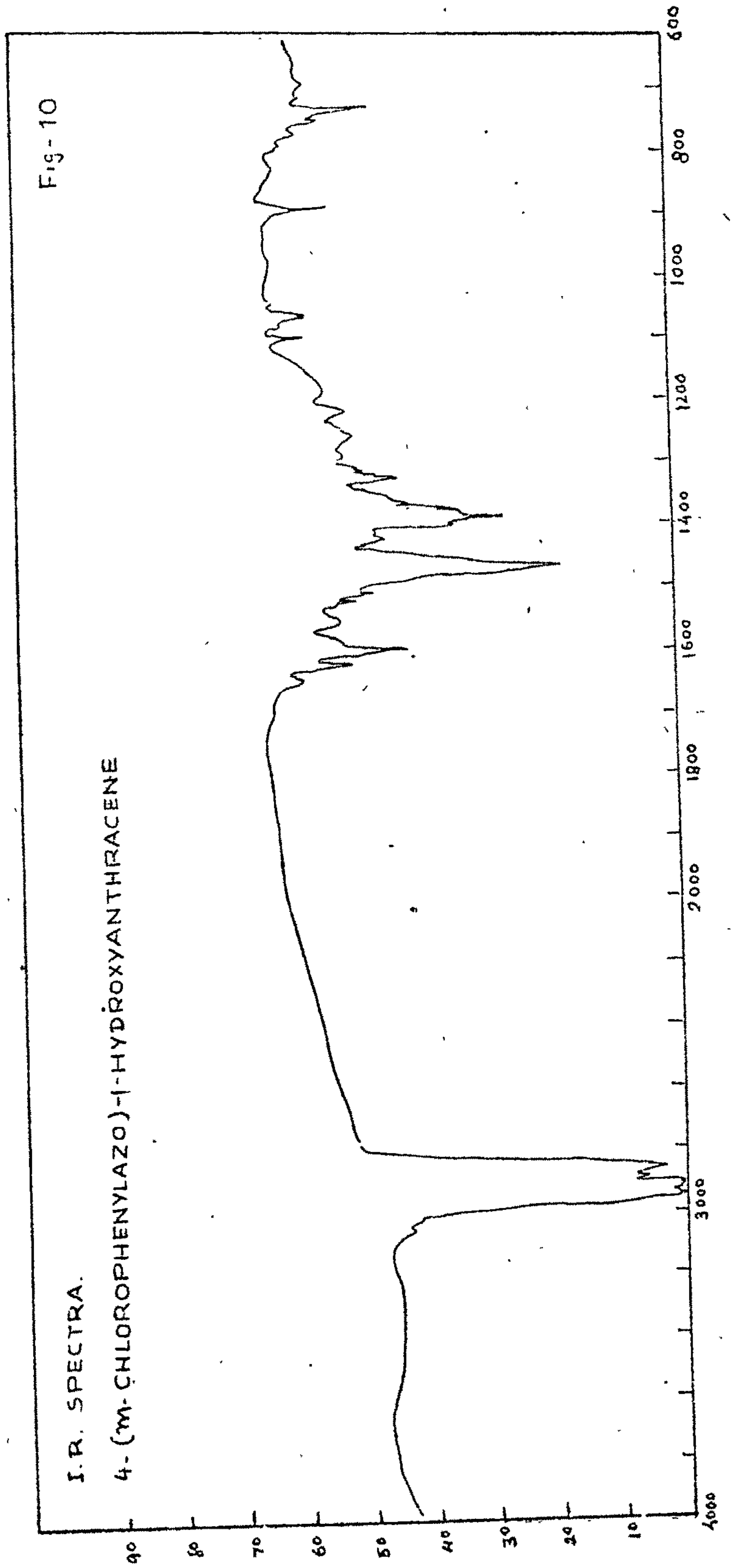


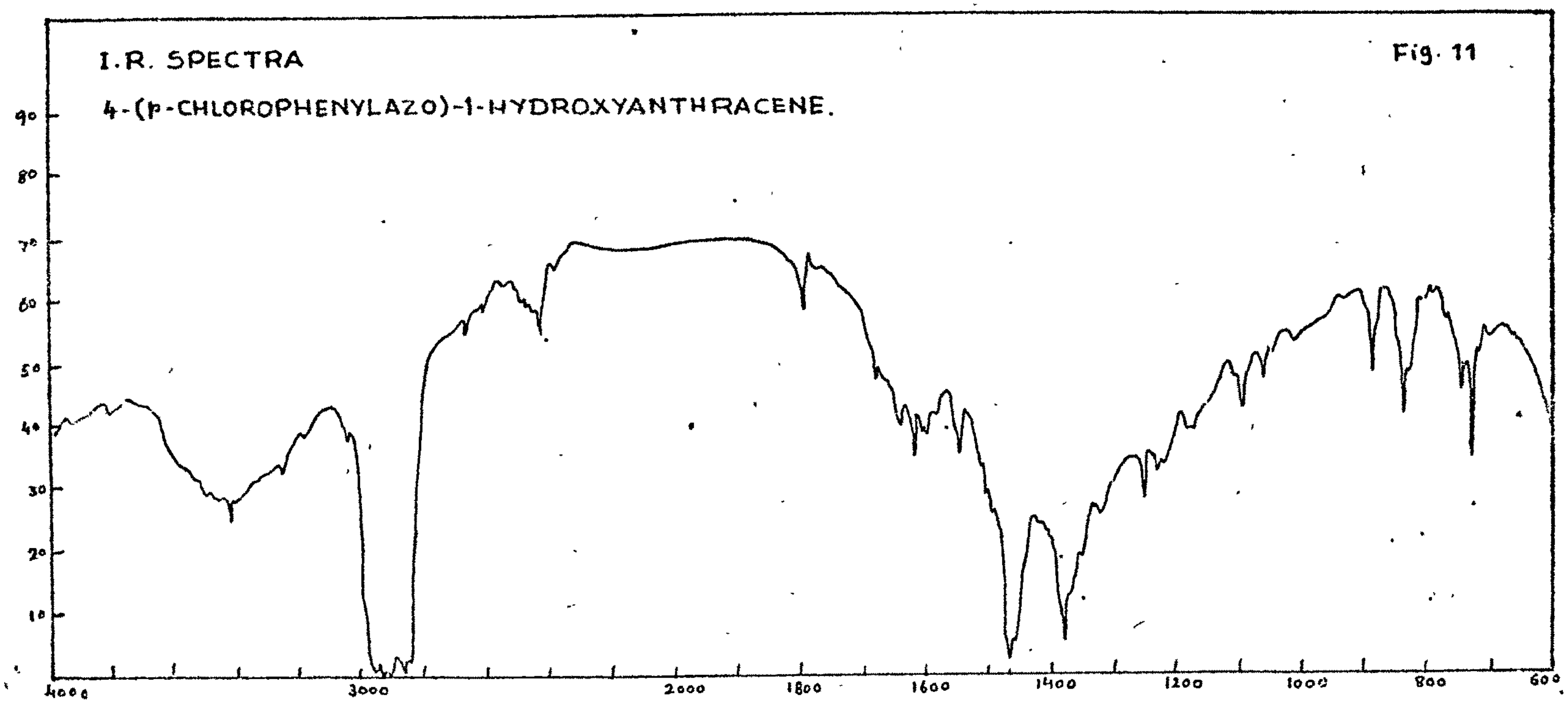
Fig- 9
I.R. SPECTRA
4-(o-CHLOROPHENYLAZO)-1-HYDROXYANTHRACENE.
600
800
1000
1200
1400
1600
1800
2000
3000
4000
100
90
80
70
60
50
40
30
20
10



I.R. SPECTRA.

4-(m-CHLOROPHENYLAZO)-1-HYDROXYANTHRACENE

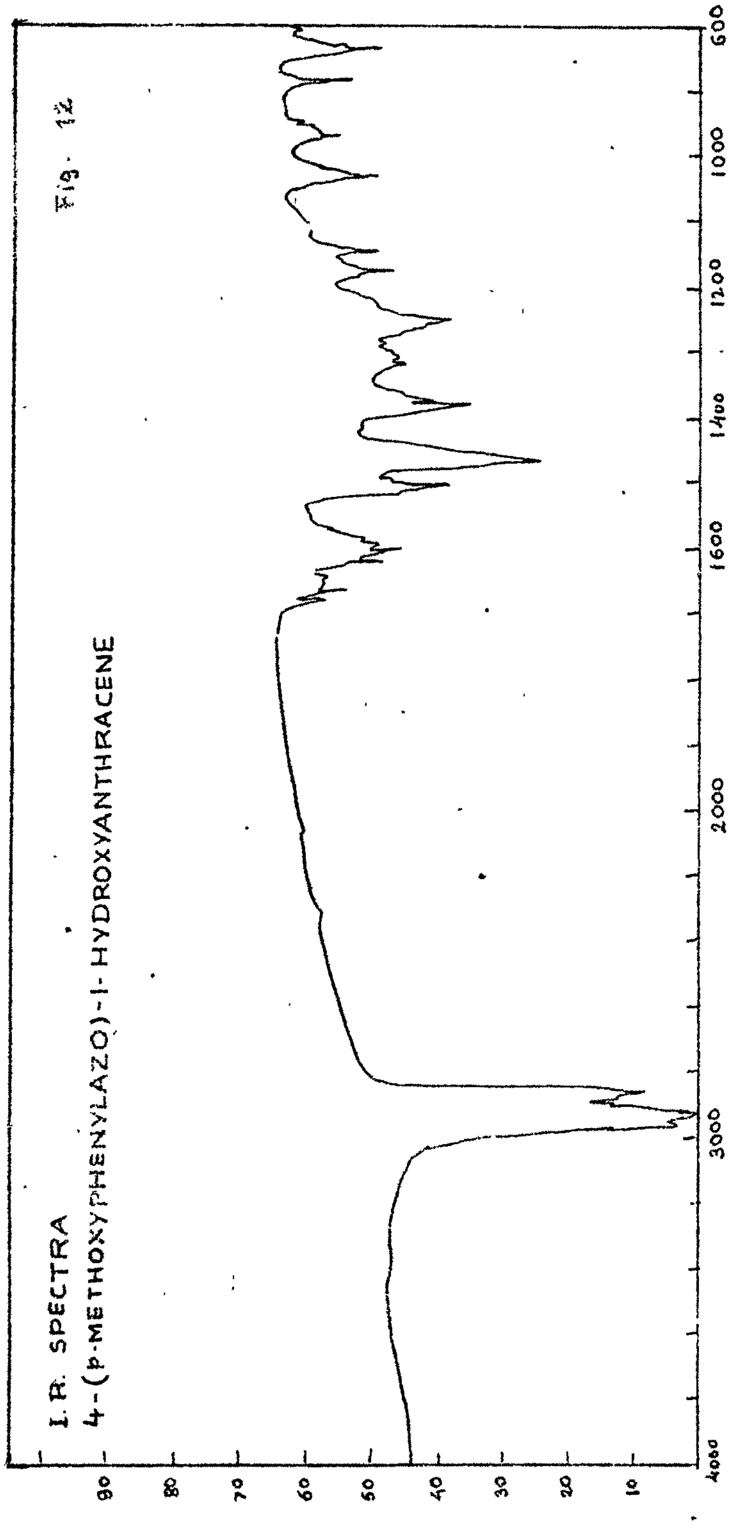
Fig-10



I.R. SPECTRA

4-(p-CHLOROPHENYLAZO)-1-HYDROXYANTHRACENE.

Fig. 11


I.R. SPECTRA
4-(P-METHOXYPHENYLAZO)-1-HYDROXYANTHRACENE
4000
3000
2000
1600
1400
1200
1000
600
90
80
70
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50
40
30
20
10

Fig. 12

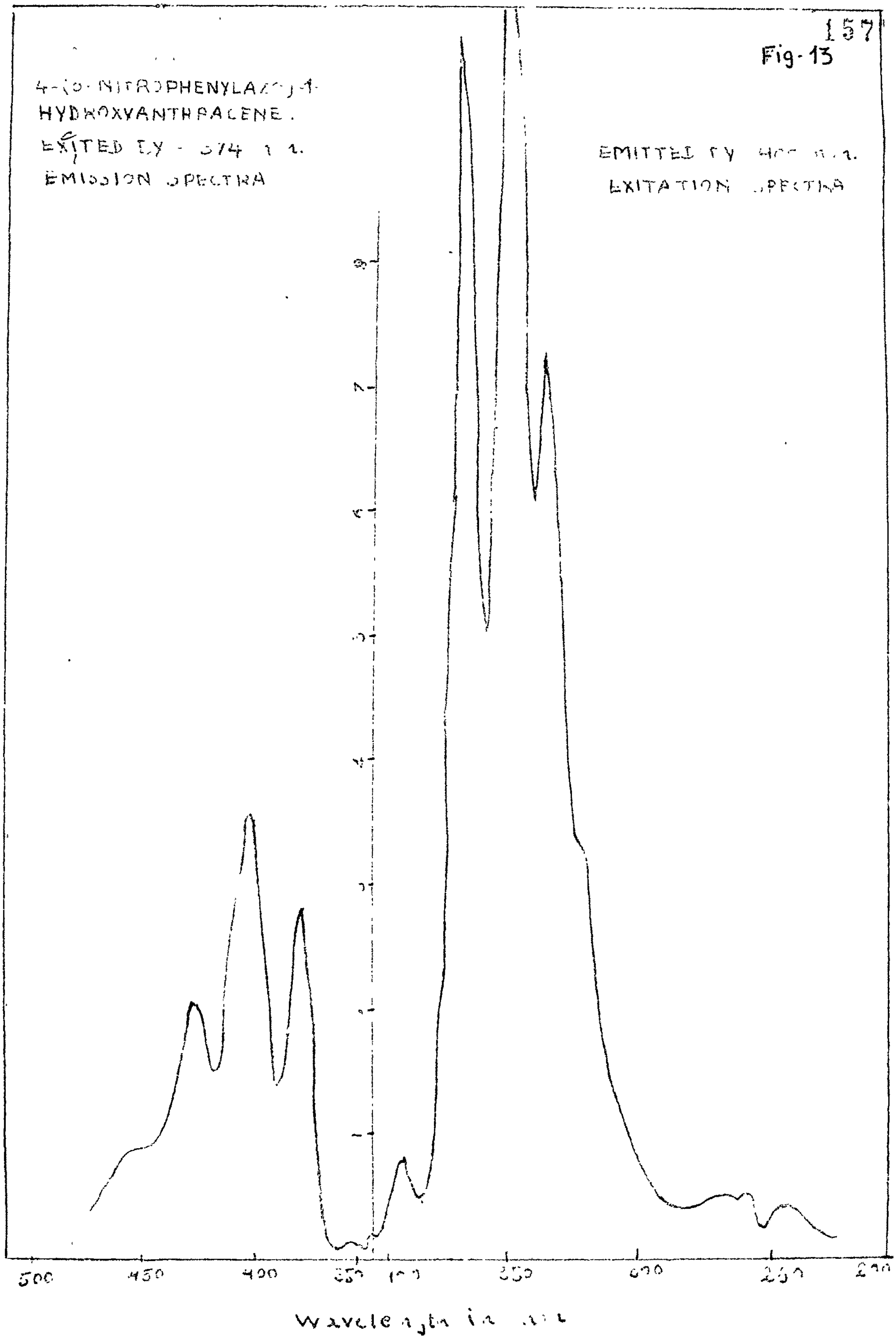


Fig-13

4-(O-NITROPHENYLAZO)-1-
HYDROXYANTHRACENE.
EXCITED BY - 374 n m.
EMISSION SPECTRA
EMITTED BY 400 n.m.
EXITATION SPECTRA
8
7
6
5
4
3
2
1
500
450
400
350
400
350
300
250
200
Wavelength in n.m

Fig-14

4-(O-CHLOROPHENYLAZO)-1-HYDROXYANTHRACENE

EXITED BY 274 nm

EMISSION SPECTRA

EMITTED BY 4[illegible]

EXITATION SPECTRA

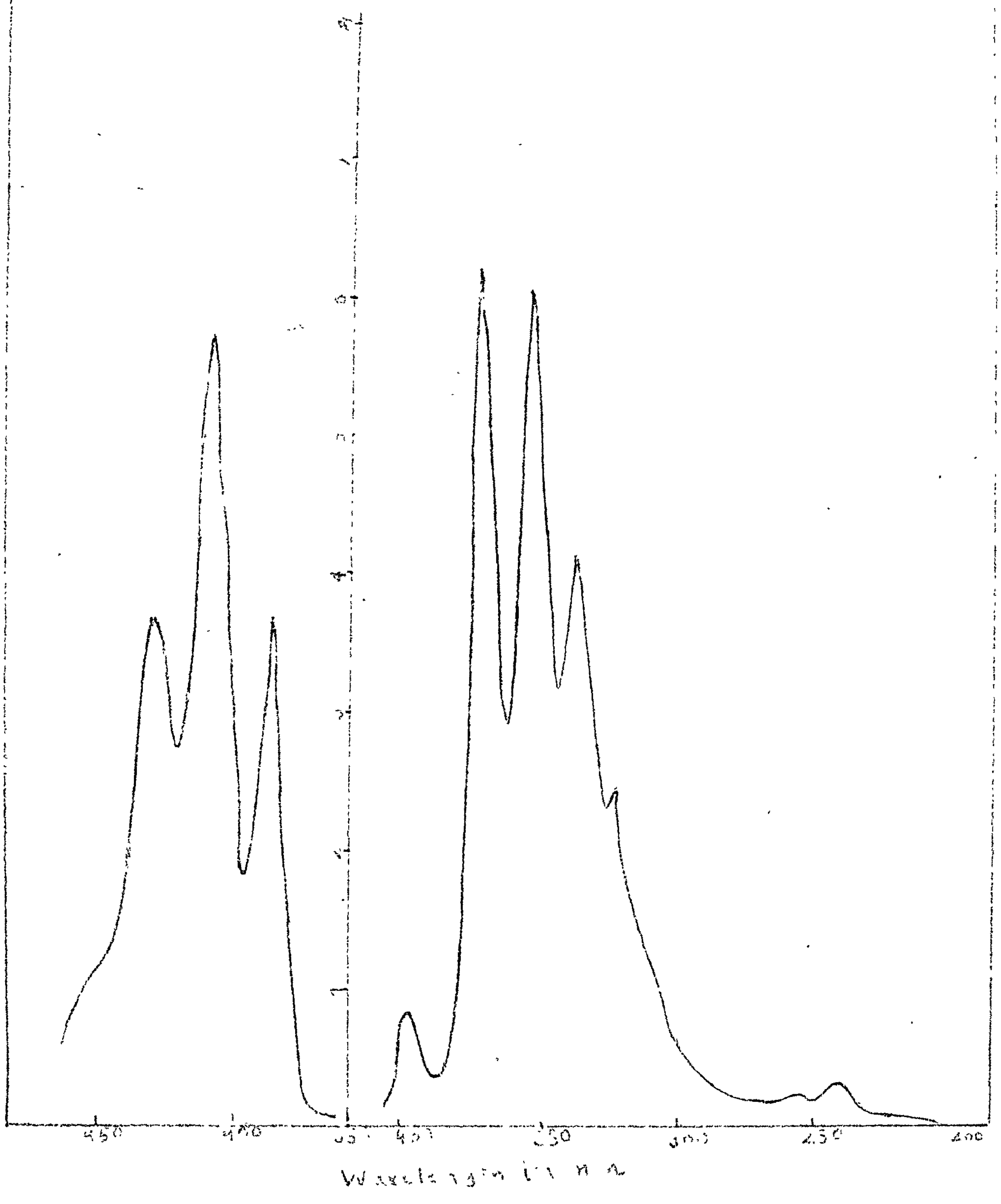


Fig- 15

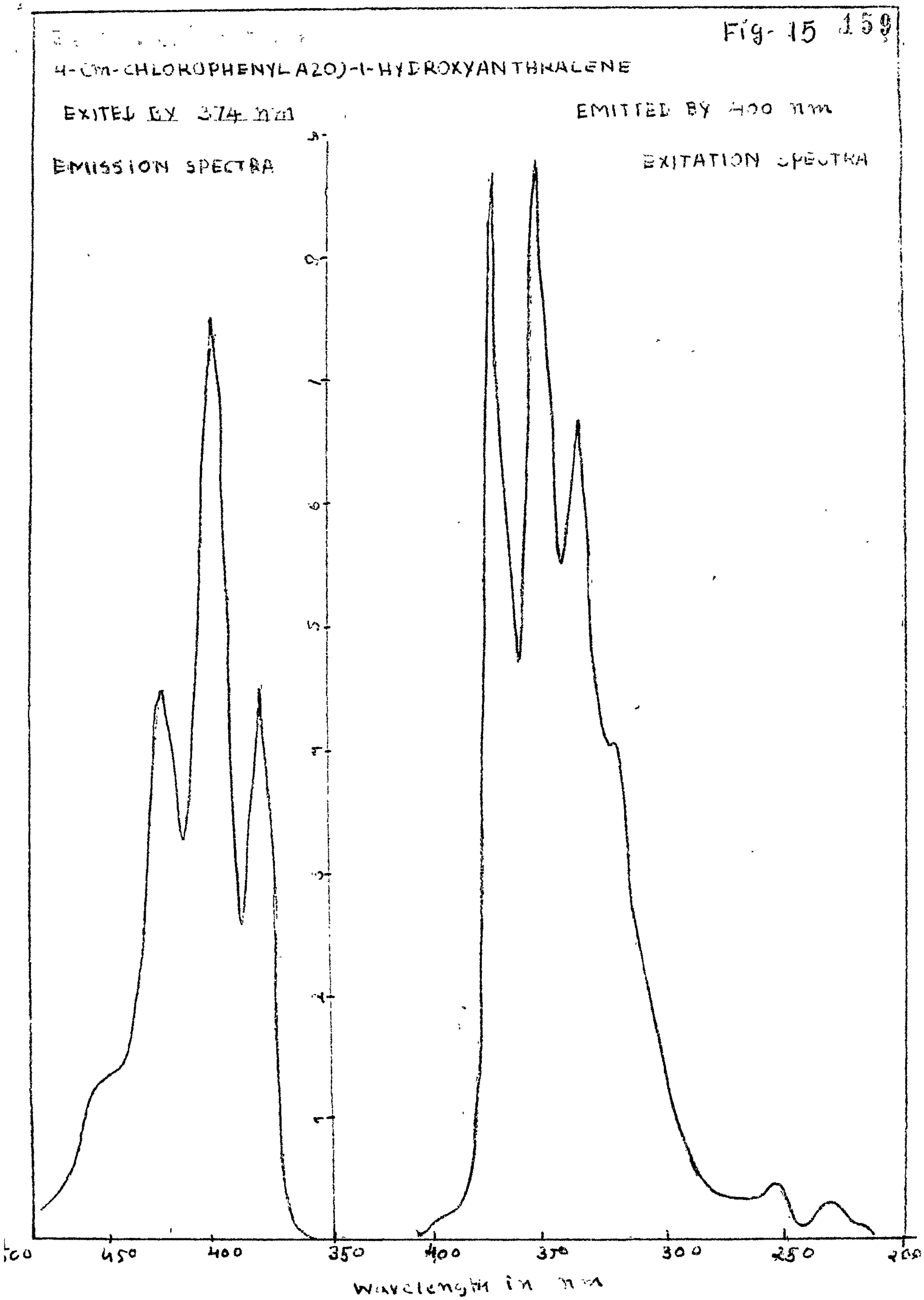
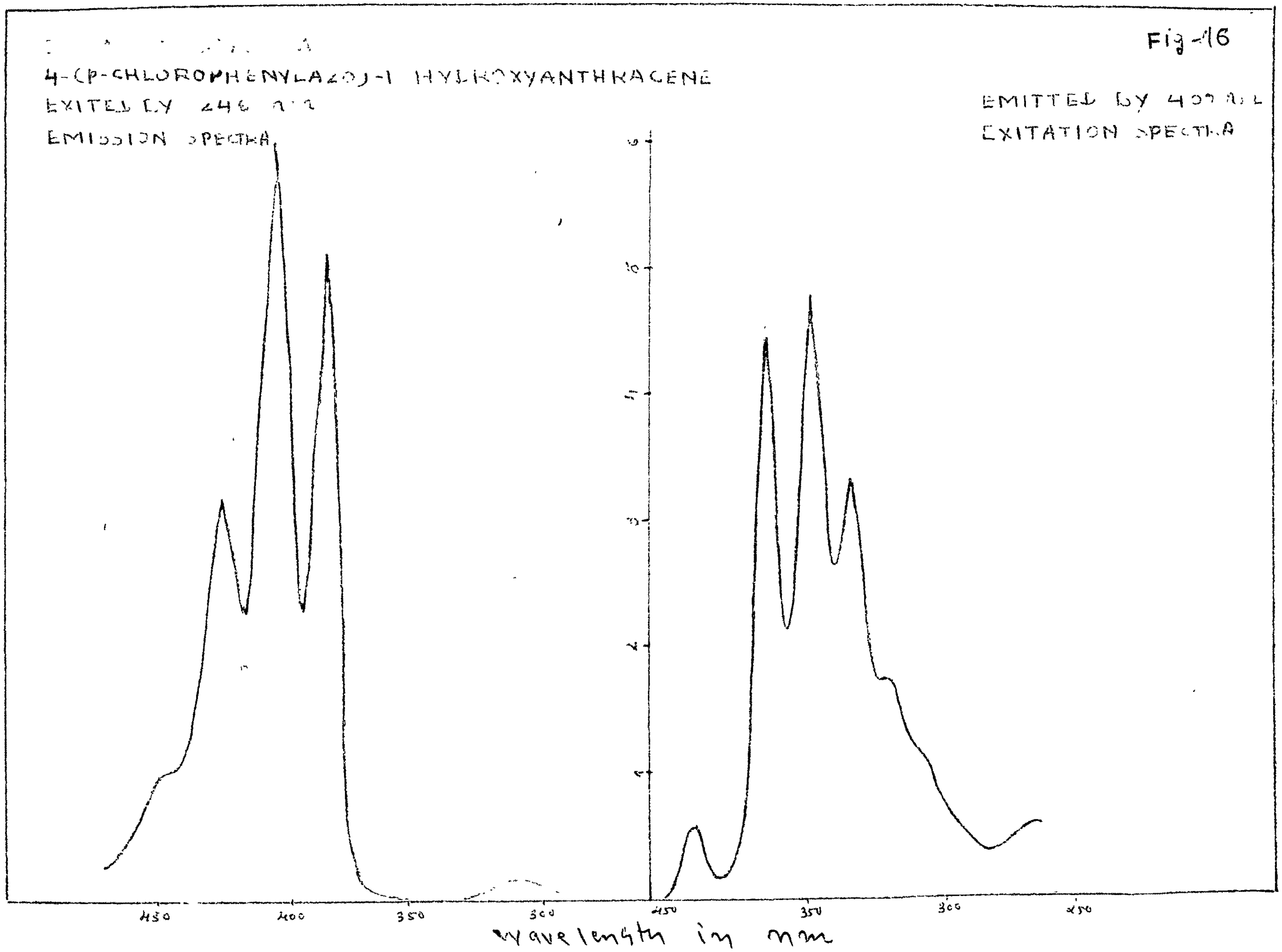

4-(m-CHLOROPHENYL AZO)-1-HYDROXYANTHRALENE
EXITED BY 374 nm
EMISSION SPECTRA
EMITTED BY 400 nm
EXITATION SPECTRA
9
8
7
6
5
4
3
2
1
500
450
400
350
400
350
300
250
200
Wavelength in nm

Fig-16


4-(P-CHLOROPHENYLAZO)-1 HYDROXYANTHRACENE
EXITED BY 246 nm
EMISSION SPECTRA
EMITTED BY 407 nm
EXITATION SPECTRA
6
5
4
3
2
1
450
400
350
300
450
350
300
250
wavelength in nm

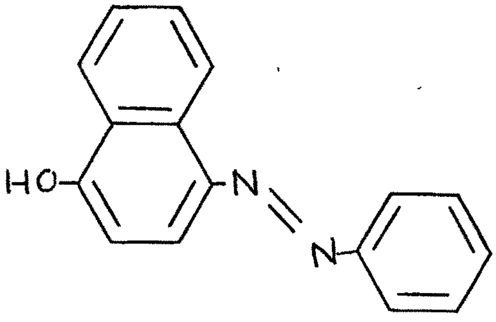
RESULTS AND DISCUSSION

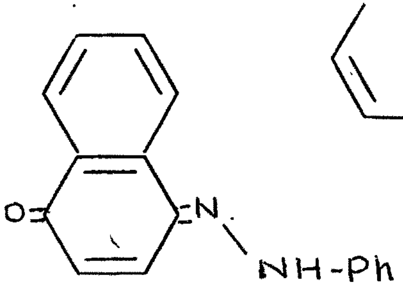
RESULTS AND DISCUSSION

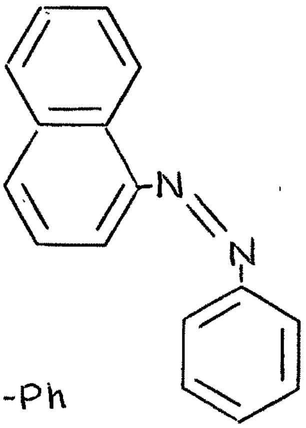
Visible Spectra :

Kuhn and Baer(55) were the first to point out that 4-phenylazo-1-naphthol(I) exist in solution as a tautomeric equilibrium mixture with the phenylhydrazone(II). Their results have been confirmed and extended by several authors(50,56-60).

Fischer and Frie studied tautomerism and geometrical iosmerism of arylazo-phenols and naphthols(61). They suggested cis- and trans- form of I, by in analogy with azobenzene(62), the azo naphthalene(63) and 4-hydroxy-azobenzene(64). They have obtained two bands, one around

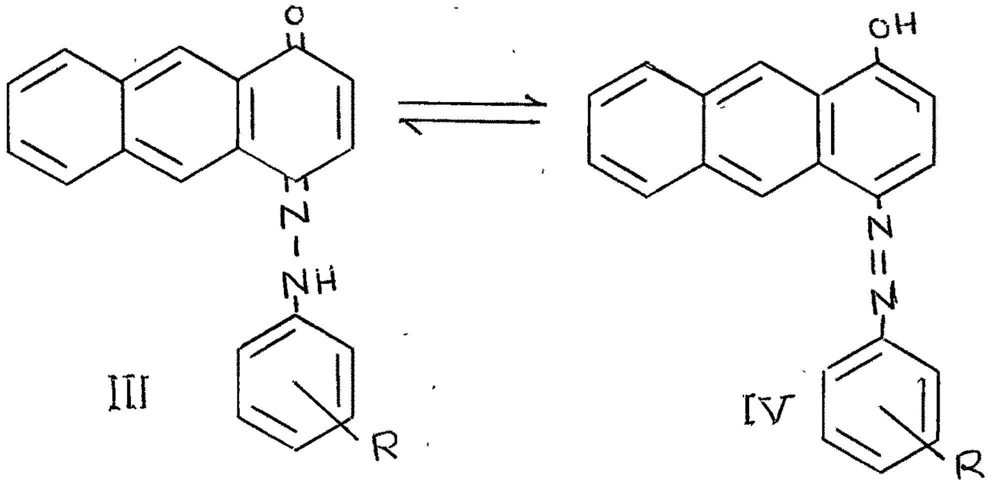

Ia


II


Ib

400 mμ and the other around 480mμ. The former band has been assigned due to the trans-azoisomer(Ia) and the earlier ~~later~~ to the hydrazone (II) in with conformity with ~~of~~ the results of Burawey and Thomson(58). In our study we have obtained

only one band around 500 nm region. This can be assigned due to the hydrazone form (III) of azo derivatives, instead of azo form (IV).



It is an established fact that the fine structure of the absorption curves and the intensities of bands are affected by the nature of the solvent used for spectroscopic examinations. In general with increasing solvent polarity the spectra suffer a loss of vibrational fine structure, because of a strong solvent-solute interaction in highly polar solvents especially when solute molecules possess induced or polar-dipolar characteristics. In ethanol the bands are very broad, but well defined. Similarly in acetone the bands are a little sharper than in ethanol. Among the striking observations of interest in the displacement of the bands to shorter wavelength with decreasing polarity and the dielectric constant of the solvent. However these observations are reversed with the found molar extinction coefficient e.g.

the molar extinction coefficient is greater when dielectric constant is lower. In all the dyes the following order is found :

Dielectric	Acetone	$<$	Ethanol
constant	20.5		25.0
λmax	Acetone	$<$	Ethanol
E max	Acetone	$>$	Ethanol

The introduction of the substituent group ~~are~~ also changing es the position of the bands and their molar absorbance absorbity. The introduction of the methoxy group is electropositive, the positive tautomeric effect is much more powerful than the inductive effect and causing es a bathochromic shift in~~to~~ the spectra, while the nitro and chloro groups ~~are having~~ have a mesomeric effect(65-67) arising from resonance benzenoid forms have the lower shift.

λmax methoxy $>$ λmax chloro and nitro.

It has also been observed that the position of the substituents into the benzene ring alters the spectrum. The introduction of the chlorine group in ortho, meta and para results in the ~~have~~ following order :

λmax ortho $<$ λmax meta $<$ λmax para

comp 2 $<$ comp 3 $<$ comp 4

Recently some azo derivatives of 9-hydroxyanthracene have been prepared and studied(68,69).The absorption maxima (in dioxane) of these dyes have been given in Table 5. Considering the solvent effect negligible, we have compared it with the maxima (in acetone) of our derivatives.

It is clearly seen from Table 5 that shifting ~~of~~ the hydroxy and azo groups from 9 and 10 positions to 1 and 4 position causes a bathochromic shift of average 60 nm.

Infrared Spectra :

In the IR spectra of substituted dyes only the most predominant peaks (C=O, N-H and C=N) are assigned for their characterisation (Table 3). In the i.r.spectrum of the compounds 1 to 8, no peak has been observed around 3500 cm^{-1} due to the -OH stretching vibrations, except the compound 4(p-Cl-aniline), in which the -OH stretching vibrations are observed around 3405 cm^{-1}(Table 3). It confirms that these compounds have the ketoenol tautomerism and only compound 4 exist in the enol form. Due to the absence of -OH stretching in other compounds, they are discussed on the basis of keto form. In all the compounds the carbonyl stretching vibrations are assigned around 1620 ± 20 cm^{-1}. Similarly the -NH banding vibrations are assigned around 1590 cm^{-1}. These peaks are very sharp and having a high intensity. The peak due to C=N is generally found around 1640-1690 cm^{-1} and 1630-1660 cm^{-1} in alkyl compounds and unsaturated compounds respectively(70). In the present

Table 5

Comparis~~s~~ion of the Absorption Maxima of 4-Arylazo-1-Hydroxyanthracene and 10-Arylazo-9-Hydroxyanthracene:

No.	Aryl group	1-Hydroxy anthracene derivative λmax in nm	9-Hydroxy anthracene derivative λmax in nm	$\Delta\lambda$
1.	o-Nitrophenyl	490	450	40
2.	o-Chlorophenyl	480	430	50
3.	m-Chlorophenyl	490	430	60
4.	p-Chlorophenyl	505	440	65
5.	p-Methoxyphenyl	525	440	85

$\Delta\lambda$ = λmax of 1-Hydroxyanthracene derivative – λmax of 9-Hydroxyanthracene derivative.

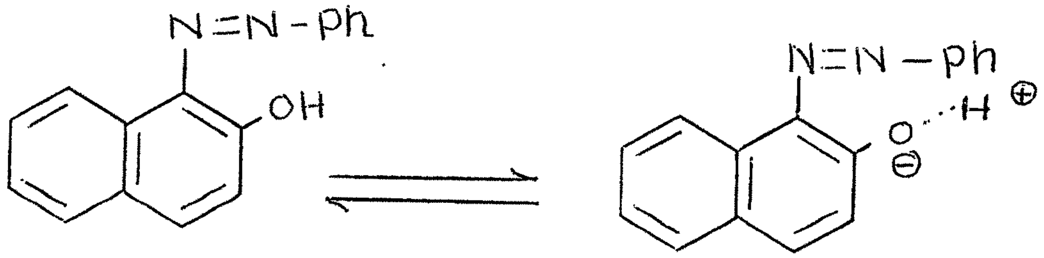
investigation peak around 1590 cm^{-1} due to C-N stretching vibration is overlaping with -NH banding vibration and no separate peak is observed. The vibration due to the chloro group in the benzene ring are assigned around 890 cm^{-1}.

Gawad et. al. have also observed the similar tautomerism in azo derivatives of 9-hydroxyanthracene(68).

<u>Fluorescence Spectra</u> :

The fluorescence spectra of 1- and 2-hydroxyanthracene has been studied by Suzuki et.al.(71,72). For characterising anthracene derivatives the use of fluorescence spectra is reported (73). In the present investigation the dyes derived from 1-hydroxyanthracene shows fluorescence in the region max 370-420 nm, except dyes 6 and 7, which have no fluorescence.

The fluorescence spectra of 1-phenylazo-2-hydroxynaphthalene is interpreted in terms of an equilibrium between enol form (I) and dipolar form (II)(74). In the excited state the equlibrium is shifted towards the bipolar ion, which is responsible for the fluorescence.



I

II

4-Phenylazo-1-hydroxynaphthalene in powder form gives fluorescence in the near i.r.spectra region but in hexane it does not fluorescence(46). 4-Arylazo-1-hydroxyanthracene in ethanol gives fluorescence. Thus increase in fused ring system results in fluorescence. Of course ethanol as a solvent strongly affects the fluorescence spectrum of a molecule containing a hydroxyl group (OH) or an amino group (NH_2). The effect of solvent on fluorescence spectra is discussed by Berlamn(75).

Generally the substituents alter the spectrum. An introduction of the chlorine into the benzene ring diminishes the fluorescence(76). The same observation is recorded in the present investigation in dyes 6 and 7. Further the 2,3-dichlorophenylazo derivative has lowered shift as compared to monochloro azo derivative. Also the introduction of $-NO_2$ in the benzene nucleus has a low band energy favouring predissociation(76) and a rapid dissipation of the energy of electronic excitation. The dye o-nitrophenylazo derivative ~~have~~ has some anomalies.

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