ELECTRONIC, INFRARED AND PROTON MAGNETIC RESONANCES SPECTRAL STUDIES ON SOME AZO AND AZO-AZOMETHINE DERIVATIVES

BY

M. E. MOUSTAFA

Chemistry Department, Faculty of Science, Benha University

Benha - Egypt.

ABSTRACT

The electronic absorption spectra of nine azo and azo-azomethine compounds are investigated in different organic solvents. The spectral bands have been assigned and the position of the charge transfer band (CT) is related to both the microscopic solvent polarity parameters viz Z and E_T or the macroscopic one viz $f(D), D-1/D+1, \phi(D)$ and $f(n)$. The solute-solvent specific association play an important role in shifting the spectral band where the emprical parameters α and β give a linear relations for HBD and HBD-A solvents. The molecular structure of the compounds is studied by the IR and ^1H NMR spectra. The electronic spectra of the compounds are investigated in universal buffer solutions of pH range 2-12, containing 40% (v/v) ethanol and the ionization constants for the various compounds are determined and discussed in relation to molecular structure.

INTRODUCTION

The absorption spectra of azobenzene and its derivatives have been the subject of many investigations [1-5].

However little attention has been given to the azo-azomethine dyes [6-7] and not much is reported about the solvent influence on azo and azo-azomethine spectra. The spectral behaviour of azodyes in acid and alkaline media as well as the determination of the pK_a values were also performed [8,9].

The present investigation aimed to assign the electronic, IR and ^{1}H NMR spectral bands of some azo and azo-azomethine dyes and discuss the spectral behaviour, in organic solvents and in buffer solutions containing 40% (v/v) ethanol, in the light of the molecular structure. The pK_a values of the compounds have been determined.

EXPERIMENTAL

Material and Solutions

The azodyes were prepared by coupling a cold solution of 1-amino 2-naphthol-4-sulphonic acid (0.01 M) in HCl and $NaNO_2$ with 0.01 M of 2,4-dihydroxybenzaldehyde, 2,4-dihydroxybenzoic acid or salicylaldehyde in NaOH solution. The solid products obtained in acid form were crystalized from methanol. The azo-azomethine derivatives were obtained by condensation of the appropriate azodye with the aniline derivatives and the products were crystallized from methanol. The compounds prepared have the following structural formula:

Y =

(I) , (II) , (III)

X= OH[8](IV),COOH[9](V),OCH$_3$[10](VI)   X=OH(VII),COOH(VIII),OCH$_3$(IX)
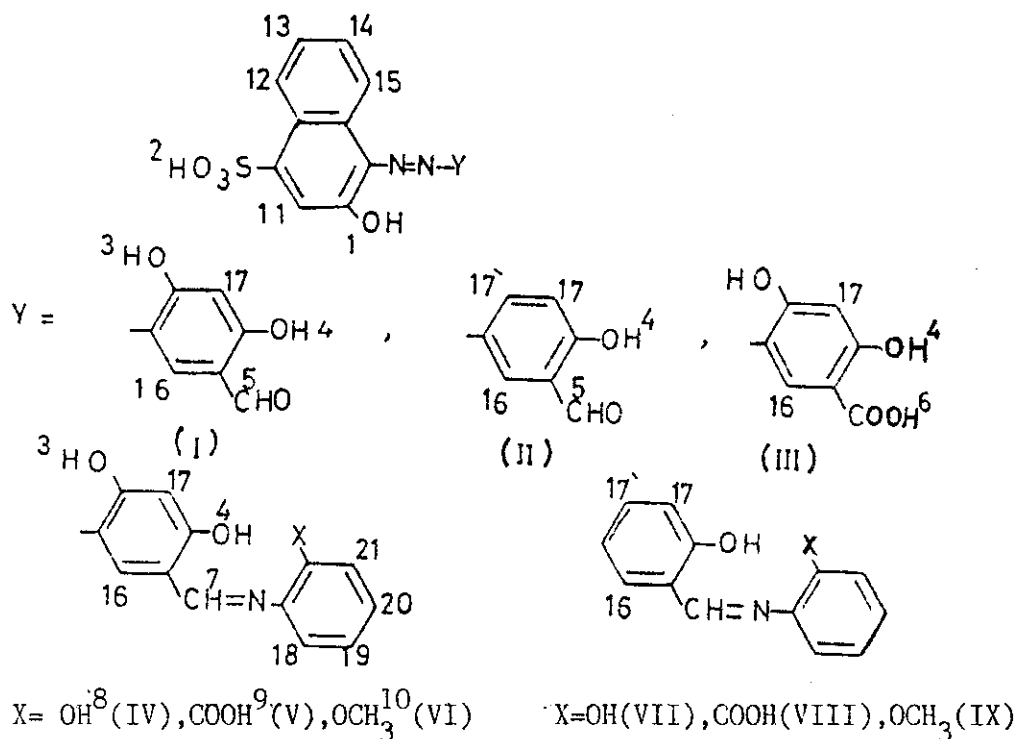
The solvents were obtained from commercial sources and purified according to recommeded procedures [10]. The buffers used for pH control were members of the universal series of Britton [11]. 10^{-3}M solutions of the dyes were prepared by dissolving an accurate weight of the recrystallized product in appropriate volume of pure solvent. Solutions for spectral measurements were obtained by accurate dilution of the stock ones. The media in buffers usually contain 40% (v/v) ethanol. The measured pH's were corrected as recommended by Pates and Rodinson [12].

APPARATUS

The electronic spectra, at 25°C, were recorded within
the range 190–700 nm Perkin–Elmer λ_{3B} spectrophotometer
using 1 cm matched silica cell. The IR spectra were recorded
on a Perkin–Elmer 683 IR spectrophotometer while the ^{1}H NMR
spectra were obtained with a Varian EM 390–90 MHz spectro-
meter using DMSO–d^6 as a solvent and TMS as internal
reference. The pH measurements were carried out on an Orion
research pH–meter model 601A/digital Ionolayzer

## RESULTS AND DISCUSSION

Spectra in Ethanol and Cyclohexane:

The electronic absorption spectra of the monoazo and
azo–azomethine compounds (I–IX) were recorded in polar
(ethanol) and nonplar (cyclohexane) solvents within the
wavelength range (190 – 500) nm. The spectra of these
compounds in ethanol display mainly Four absorption
bands (A, B, C, and D) in addition to one shoulder (C.F.
Table 1).

Inspection of the data cited in this Table, These
bands can be classified into two sets; firstly, the uv set
of the bands corresponding to the $\pi - \pi^*$ transitions within
the phenolic and naphthoic moeities which are slightly
influenced by the nature of substituents and solvent
polarity. The second set of bands appearing in the visible
region can be ascribed to the excitation of the π-electrons
of the azo group influenced by a charge transfer (CT) inter

action taking place through the whole molecule originating from the OH group as a source and terminating to the S = O group as sink which can be represented as follows:-

II
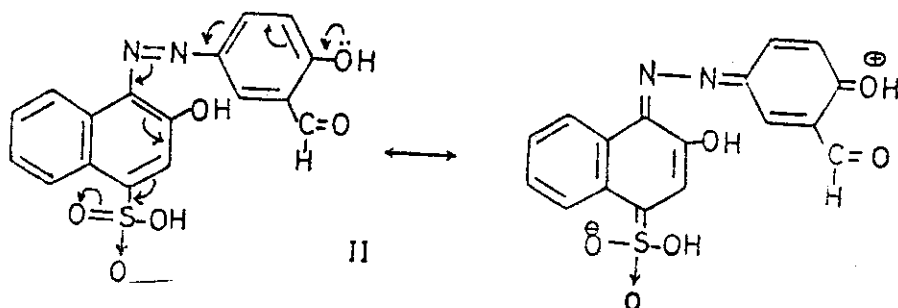
The CT nature of the band can be confirmed also by hypsochromic shift caused from the substituent (X) of electron withdrawing character of COOH group compared to the donor one of OCH_3 group. The study of the spectral behaviour in buffer media of varying pH's (Fig. 1) indicates that the CT band displays a bathochromic shift with increasing the pH of the medium due to ionization of the OH group.

Solvent Effect

The spectra of all compounds, recorded in different solvents of varying polarities, (e.g. Fig. 2) showed that the bands due to local exitations of the phenyl groups or naphthyl moieties displayed slight solvent effect. While

Electronic, Infrared

the behaviour due to the n -- * transition (of the N=N or
C=O groups) exhibits a blue shift inhydroxylic solvents
relative to hydrocarbon ones. However the shift in the
CT band position can be discussed in terms of the macro-
scopic solvent polarity via dielectric constant or refractive
index of the media. These are governed by the relations given
by Szalay [13] in which a plot of (cm^{-1}) vs D-1/D+1 gives
a non linear relation. Also, the more precise functions given
by Suppan [14] in which $_{max}$ of the CT band is plotted vs
f(D) = D-1/2D+1 or   (D) = D-1/D+2 giving non-linear relations.
The function of refractive index given by McRoa [15] $f_2(n)=n-1/n+2$
is plotted vs $_{max}$ where also non linear relation is obtained.
Accordingly, one can deduce that the macroscopic solvent
polarity parameters are not the predominant factors controlling
the change in intramolecular transition energy.

The correlation of the shift in λ_{max} of the CT band
with the microscopic solvent polarity parameters viz Z [16],
E_T[17] and β[18] (representativr example is given in
Fig. 3) indicates that:
i) The amphiprotic solvent class (HBA-D) gives positive
solvatochromic behaviour for all compounds, except IX,
as the solvent polarity is increased indicating the destabi-
lization of the ground state of the molecules consequently
a decrease in electronic transition energy is expected to
occure.
ii) The linear relations obtained for a group of solvents
of the same class confirm that there is a difficulty in

obtaining single solvent polarity parameters controlling the
shift of the band.

III) The plots of λ_{max} with α or β-scale of solvent polarity,
which measure the H-bonding strength for both the H-bond
acceptor (HBA) and hydrogen bond donors (HBD) solvents
respectively, are straight lines with slight deviation
for some solvents (Fig. 3). This denotes the specific
solute- solvent interaction which involves essentially the
change in solvation energy on going from the ground state
to the exited one, or propable formation of intermolecular
hydrogen bonding.

Accordingly, the shift in the CT band is actually
the net resultant effect of the bathochromic shift due to
increased polarity of the solvent and the hypsochromic
shift due to intermolecular H-bond interaction.

Spectra in Buffer Solution

The absorption spectra of the monoazo and azo-azo-
methine compounds in aqueous buffer solutions containing
40% (v/v) ethanol show regular changes with increasing
pH of the medium especially the CT band, Fig. 1. Generally,
increasing the pH of the medium results in increasing the
absorbance of the CT band of all compounds along with a
shift in its λ_{max} to longer wavelength. This indicates that
the ionized species of the compounds appeared and increased
in concentration leading to the bathochromic shift.

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The variation of absorbance with pH is utilized for
the determination of pK_a of the compounds, Table 2, using
half height [19], limiting absorbance [20] and Colleter
methods [21]. The pK_a value of the SO_3H groups was determined
by the Calvin and Bjerrum [22,23] pH titration technique
using the computation method of Irving and Rossotti [24].
It is evident that the pK_a value are related to the molecular
structure of the compounds. Thus, the pK_a value of compound
I is the highest for the monoazo compounds, whereas that
of VIII is the lowest one for azo-azomethine   dyes. This
is attributed to the strong intramolecular H-bonding of
the OH group ortho to the N=N of monoazodyes or the weaker
one for azo-azomethine dyes .

IR Spectra

The IR spectra of the compounds under investigation
were recorded as KBr discs; the $\bar{\nu}$ (cm^{-1}) of the important
bands are collected in Table 2. The band assignment is
achieved by a method indentical to that of Looker [25] and
by comparison with compounds having identical structures
to parts of these molecules. From the wavenumbers of the
different bands, the following points can be revealed (i)
In the 3500-3290 cm^{-1} range, the spectra of azo compounds
I-III display the ν_{OH} vibration band of the phenolic OH
group whereas that of the azo-azomethine compounds IV-IX
in 3400-3300 cm^{-1} range. The assymmetric N=N band lies

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in the range 1435–1445 cm^{-1} whereas that of the $\nu_{CH=N}$ vibration in the range 1570–1605 cm^{-1}. The low frequency values and the broadening of these bands denote that the OH as well as the N=N and CH=N groups are involved in an intramolecular H-bond:
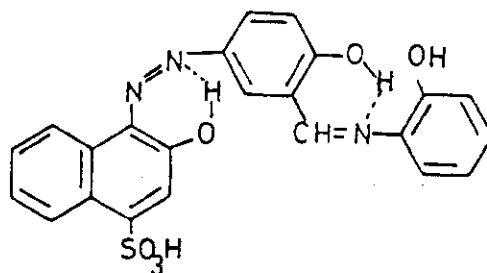
(ii) The band position of the CH=N group of compounds IV–VI, VIII and IX is shifted according to the nature of the substituent groups at the ortho position to the CH=N linkage.

^{1}H NMR Spectra

The signals of the ^{1}H NMR spectra of the compounds are given in Table 3. The spectra are given after deuteration by D_2O in which the signals due to OH, SO_3H and COOH groups are removed. The signals of the OH group at 1.2 and 4-positions has a chemical shift at 7.26–7.03, 7.33–6.73 and 6.40–6.13 ppm ranges respectively. The higher field of the OH signal indicates a weaker intramolecular hydrogen bond, which is attributed to the acceptance character of

the substituents $4-SO_3H$, CHO or COOH groups which lower
the contribution of the nitrogen ions pair to the intra-
molecular hydrogen bonding. Accordingly, the signal of
the o-OH group of the phenyl-azomethine (δ = 9.34 ppm)
or that of o-COOH group (δ= 10.96-9.35 ppm range) are
relatively at lower field i.e. forming stronger intra-
molecular H-bonding. Multible signals of the aromatic
protons of the phenyl or naphthyl rings appear at δ =8.80-
7.13 ppm. It is clear, generally, that the aromatic protons
H^{16}, H^{17} or H^{17} (compound II) as well as H^{18} –H^{21} (compounds
IV-IX) have signals of wide variation in chemical shift
depending on the nature of the substituent groups attached
to the ring.

Table 1: Assignment of the electronic absorption spectra of azo and azo-azomethine dyes.

Compd.	Solvent	Type of bands									
		λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}
I	EtOH	208	2.10	230	1.78	276	1.65	312	1.58	485	0.28
	Cyclohexane	215	s	230	s	274	s	310	s	450	s
II	EtOH	202	1.04	230	1.03	270	0.64	320	0.59	465	0.3
	Cyclohexane	203	s	244	s	270	s	330	s	450	s
III	EtOH	204	1.10	230	1.08	275	0.97	313	0.73	470	0.08
	Cyclohexane	204	s	240	s	275	s	330	s	480	s
IV	EtOH	204	1.80	230	1.40	275	0.63	313	0.78	420	0.50
	Cyclohexane	216	s	235	s	270	s	335	s	410	s
V	EtOH	214	1.20	230	0.64	275	0.40	313	0.22	490	0.16
	Cyclohexane	220	s	245	s	275	s	330	s	460	s
VI	EtOH	205	1.86	233	0.98	270	0.64	313	0.52	495	0.42
	Cyclohexane	212	s	235	s	275	s	340	s	490	s
VII	EtOH	202	1.65	235	1.40	275	0.25	313	0.22	445	0.44
	Cyclohexane	213	s	244	s	280	s	335	s	420	s
VIII	EtOH	202	2.10	230	0.92	276	0.84	313	0.85	480	0.24
	Cyclohexane	220	s	245	s	274	s	335	s	470	s
IX	EtOH	205	1.14	230	0.40	270	0.36	313	0.24	490	0.08
	Cyclohexane	211	s	234	s	285	s	330	s	475	s

$\lambda_{max}(nm)$ $\varepsilon_{max} = 10^{-3} \text{L.cm}^{-1} \text{M.}^{-1}$ s=saturated solution

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Table(2): The assignment of the frequencies(cm^{-1}) of IR bands and
pK_a values of the free ligands.

Compound	νOH	νCH	νC=O	νCH=N	νCN	νN=N	νOCH$_3$	δOH	νSO$_3$H	νC-O	δCH	p:
I	3290	2980	--	--	1550	1440	--	1395	1330	1255	745 1130	8
II	3500	3000	--	--	1550	1437	--	1385	1345	1265	755 1145	6.
III	3300	2880	1680	--	1550	1445	--	1380	1335	1260	750 1140	6.
IV	3400	2470	--	1620	1540	1440	--	1395	1334	1240	765 1124	7.
V	--	2935	1730	1627	1545	1442	--	1390	1310	1265	765 1145	9
VI	3390	3020	--	1615	1546	1440	1450	1390	1345	1265	770 1115	8.
VII	3300	2900	--	1605	1547	1435	--	1390	1340	1267	745 1140	9.
VIII	3400	2800	1730	1625	1545	1435	--	1385	1340	1267	755 1135	5.
IX	3390	3000	--	1670	1545	1440	1440	1390	1345	1265	755 1145	6

le (3): Assignment of the $^1H_{NMR}$ spectra of azo and azo-methine compounds (I-IX).

id	H_1	H_2	H_3	H_4	H_5	H_6	H_7	H_8	H_9	H_{10}	Aromatic Bands
						Chemical Shift (ppm)					
	7.1	5.50	7.2	6.3	9.63	--	--	--	--	--	7.34, 7.56, 7.7, 8.04, .18 8.3, 8.5
	7.26	5.5	--	6.13	8.97	--	--	--	--	--	7.4, 7.53, 7.6, 7.7, 7.8, 7.83, 7.95, 8.2
	7.1	4.6	7.33	6.36	--	10.1	--	--	--	--	7.4, 7.45, 7.63, 7.83, 8, 8.2, 8.3
	7.06	5.5	7.23	6.4	--	--	9.8	9.034	--	--	7.4, 7.34, 7.45, 7.53, 7.7 7.8, 7.83, 8.1, 8.2, 8.4, 8.5, 8.73
	7.034	4.76	6.73	6.3	--	--	9.79	--	10.96	--	7.13, 7.16, 7.2, 7.26, 7.4 7.53, 7.66, 7.7, 8.075, 8.1 8.2
	7.030	4.66	7.13	6.3	--	--	9.43	--	--	4.36	7.36, 7.5, 7.53, 7.63, 7.66 7.8, 7.56, 8.1, 8.2, 8.23 8.3
	7.200	4.35	--	6.35	--	--	--	--	--	--	7.35, 7.4, 7.5, 7.55, 7.7 7.79, 8.15, 8.2, 8.22, 8.33 8.6, 8.45
	7.100	5.20	--	6.35	--	--	9.66	--	9.35	--	7.36, 7.4, 7.56, 7.6, 7.8, 7.96, 8.16, 8.26, 8.46, 8.6 8.73, 8.8
	7.034	5.20	--	6.40	--	--	4.40	--	--	4.43	7.3, 7.43, 7.46, 7.6, 7.66, 7.7, 7.4, 7.961, 8.03, 8.035, 8.16, 8.3

Spectra Of Compound (III) In Buffer Solutions.

[L] = 1 × 10⁻⁴ M
EtOH = 40 %
pH = 2.14
pH = 3.60
pH = 4.00
pH = 5.16
pH = 6.16
pH = 7.05
pH = 7.73
pH = 9.16
pH = 9.83
pH = 11.24

LIGAND III

LIGAND III

a - AT 490 nm.
b - AT 480 nm

LIGAND III

a - AT 490 nm.
b - AT 480 nm.

Fig. (5)

THE ELECTRONIC SPECTRA OF COMPOUND VIII
IN DIFFERENT SOLVENTS

Ethanol
Methanol
n-propanol
iso-propanol
DMF
Cyclohexane
n-hexane
CCl_4
$CHCl_3$

λ(nm)

ABSORBANCE
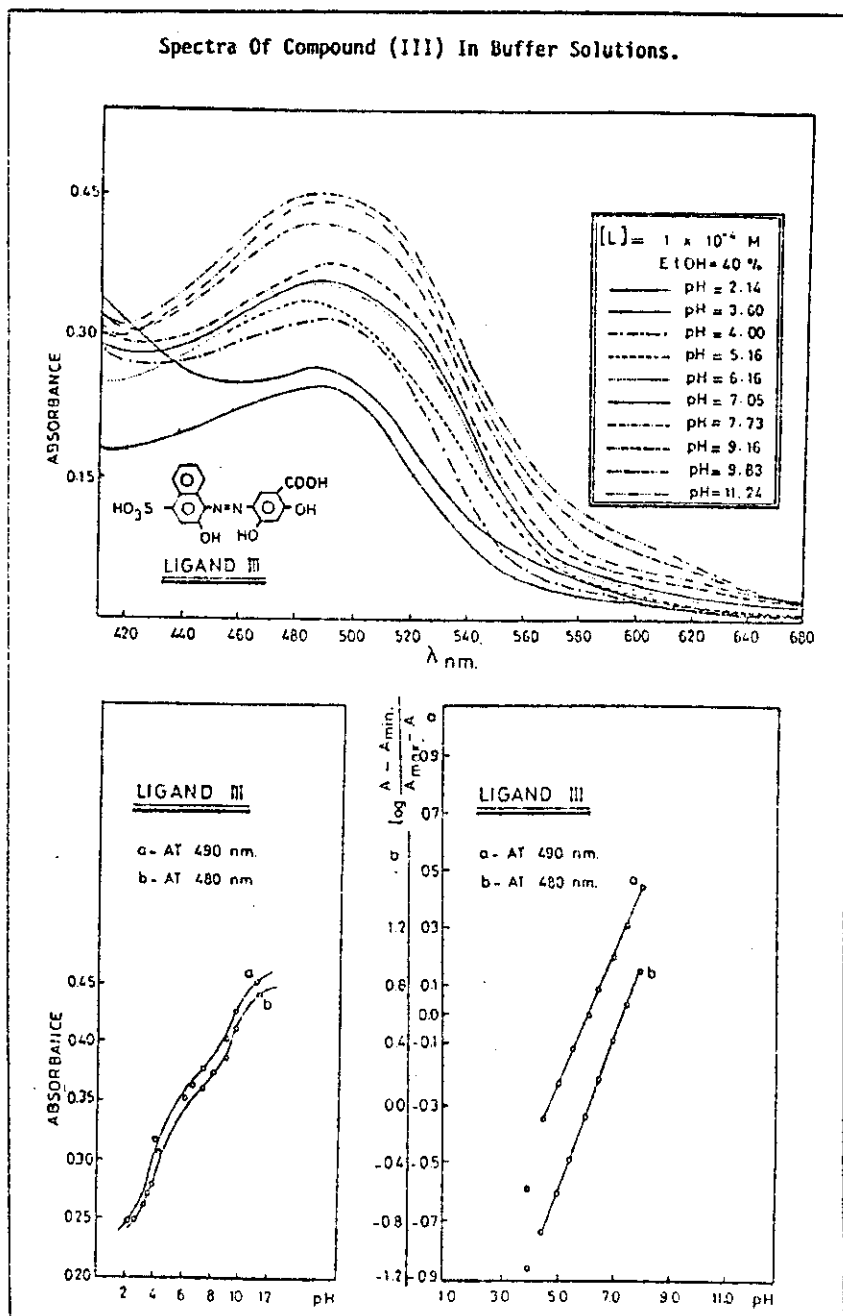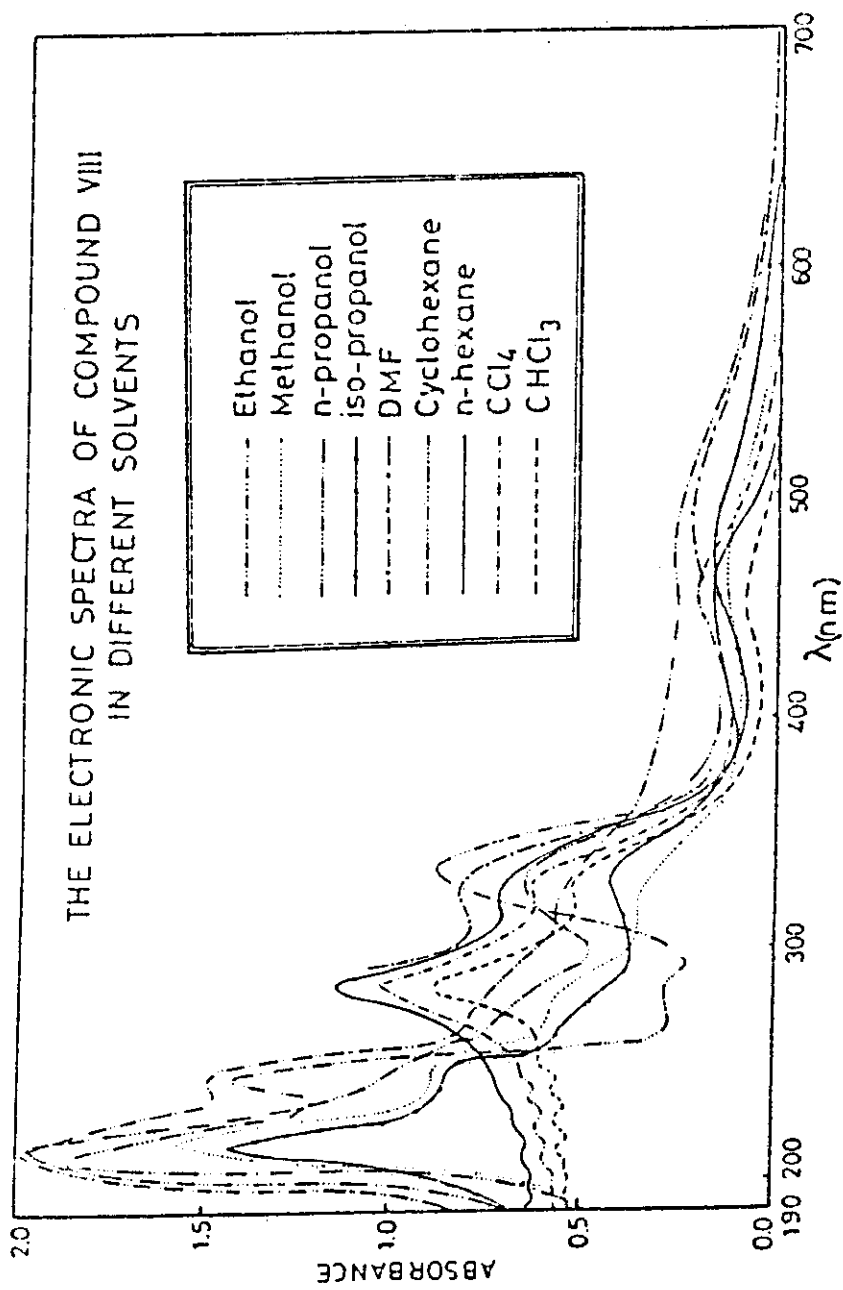
Fig (2)
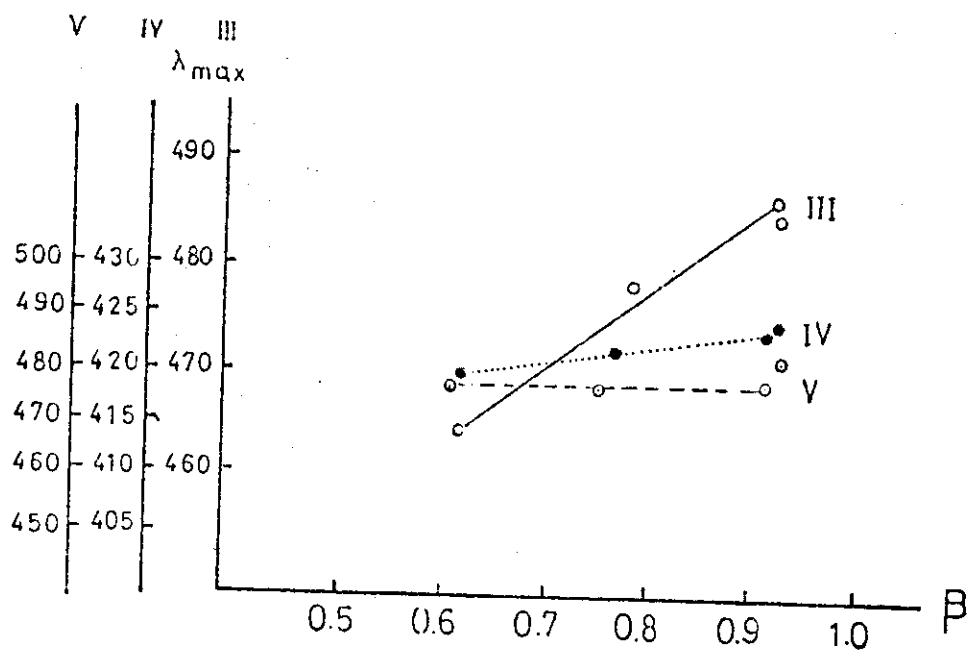
Fig. (3)

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دراسات عن الطيف الالكترونى والاشعة تحت الحمراء والرنين النووى المغناطيسى
لبعـض اصباغ الازو والازو – ازوميثين

مصطفـى ابراهيم مصطفـى

قسم الكيمياء ـ كلية العلوم ـ بنهـا

تمت دراسة طيف الامتصاص الالكترونى لبعض مركبات الازو والازو–
ازوميثين الجديدة فى بعض المذيبات العضوية ذات القطبية المختلفة وتـم
تعيين القيم العظمى لحزم الامتصاص وكذلك موضع الامتصاصية العظمـى
المناظرة لانتقال الشحنة داخل الجزىء الواحد وربطهما ببعض القيـم
الميكروسكوبية والماكروسكوبية للمذيبات المختلفة ، وقد لوحظ ان التداخـل
النوعى بين المذيب والمذاب يلعب دورا هاما فى موضع مناطق الامتصاصية
العظمى المناظرة لانتقال الشحنة· وقد تمت ايضا دراسة طيف الامتصاص
للمركبات قيد الدراسة فى المحاليل المنظمة ذات الاس الهيدروجينـى
المتغير والمحتوية على ٤٠٪ (بالحجم) كحول ايثيلى ومنها تم تعيين قيم
ثوابت التأين للمركبات المختلفة ومناقشتها فى ضوء تركيبها الجزيئى·
كما امتدت الدراسة الى اثبات التركيب الجزيئى لمركبات الازووالازو–
ازوميثيين المحضرة باستخدام طيف الاشعة تحت الحمراء والرنين النووى
البروتونى المغناطيسـى·