MULTINUCLEAR ORGANOTIN COMPLEXES OF POLYFUNCTIONAL LIGAND

Thesis

Submitted for the Degree of
Doctor of Philosophy (Science)
of the
UNIVERSITY OF NORTH BENGAL

By

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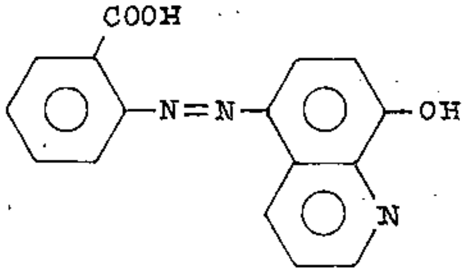
1983

PREFACE

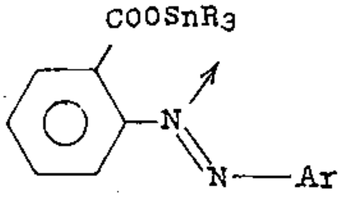
Although a great variety of organotin complexes have been reported during the last two decades, the extent literature contains no reference to mixed complexes of the type $(R_nSnL)_xM$ where the polyfunctional ligand L coordinates simultaneously to an organotin group as well as a metal, particularly a transition metal, M. Such complexes may be looked upon as the counterpart of the mixed complexes of the type $R_2SnL.L'$ (L and L' are different ligands) which are now quite well known. The present work was therefore undertaken as a part of a general programme aimed at the synthesis and study of such mixed complexes. The main difficulty in preparing transition metal-organotin mixed complexes arises from the usually much greater stability of the transition metal complex of a ligand compared to its organotin complex. This generally results in a facile replacement of the organotin group by the transition metal ion whenever an attempt is made to prepare the mixed complexes.

It was soon realised that such mixed complexes can only be obtained through the use of heterofunctional ligands having two coordinating sites which can be discriminated by the metal ions by means of widely different coordinating abilities of the two sites. A study of different factors, e.g., ease of synthesis, stabilities of the resulting complexes, easily accessible spectral features which may be utilised to study the structural characteristics etc., led to the choice of 5-(2'-carboxy phenyl) azo-8-quinolinol (I) as a model ligand for the present study.



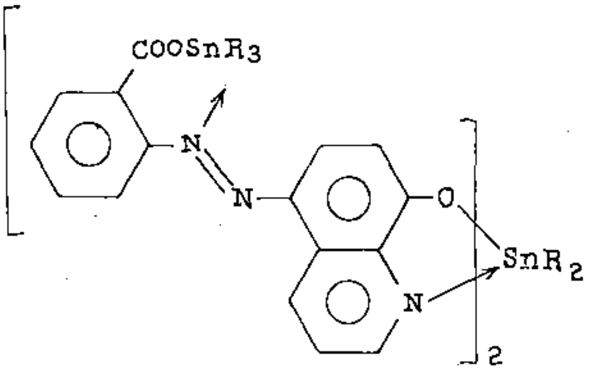
(I)

This ligand contains the 8-quinolinol moiety which is expected to form quite strong complexes with the transition metal ions, while the carboxylate group which has much lower coordinating power towards the transition metal compared to that of the quinolinol moiety, can be readily used to coordinate the organotin group since organotin arylazo benzoates (II) are quite well known.



(II)

In the present work more emphasis was laid on the preparation and study of the properties of the polynuclear organotin complexes of the type (III) because a study of such complexes would lead a better understanding of the transition metal-organotin mixed complexes (IV).



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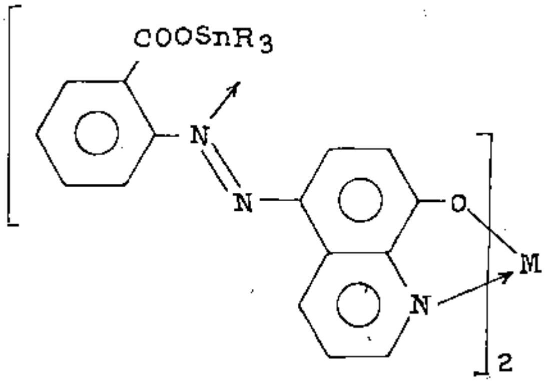

(IV)

The thesis is divided into four chapters. A survey of the azoderivatives of 8-quinolinols and their chemistry with emphasis on their metal complexes are reviewed in Chapter - I.

The synthesis of the ligands, 5-(phenyl) azo-8-quinolinol and 5-(2'-carboxy phenyl) azo-8-quinolinol and their organotin derivatives constitute the subject matter of Chapter - II. The structure of organotin derivatives has been discussed using IR absorption frequencies.

The asymmetric carboxylate stretch in the free ligand occurs at ~ 1650 cm^{-1} due to intramolecular H-bonding. Methylation of the -COOH group shifts the $\nu_{as}(COO)$ to normal position while stannylation leading to the derivatives of the type R_3SnL lowers it to the region ~ 1630-35 cm^{-1} which is same as that found in triorganotin arylazobenzoates. On the other hand, $\nu_{as}(COO)$ occurs at ~1700-1730 cm^{-1} in the diorganotin 5-(2'-carboxy phenyl) azo-8-quinolinolates.

The electronic absorption spectra and the effect of solvents have been discussed in Chapter - III. A CNDO/2 type calculation shows that the longest wave length transition is indeed a $\pi-\pi^*$ transition which involves mostly a transfer of electron density from the quinoline N and O_8 atoms to the azo group, the β-N atom getting greater share of the electron transfer during transition. The absorption spectral data supports the presence of $N \rightarrow Sn$ coordinate link in the organotin derivatives.

Preparation and properties of transition metal-organotin mixed complexes (IV) have been discussed in Chapter - IV using IR, electronic absorption spectra and magnetic moment data. These complexes are structurally quite similar to the binuclear organotin derivatives (III). The larger bathochromic shift of these complexes as compared to the corresponding organotin derivatives can be interpreted in terms of $d_{\pi} - p_{\pi}$ interaction involving the metal 'd' and ligand π-MO's. On the basis of the physicochemical studies, particularly, the magnetic moment data, the transition metal-organotin mixed complexes are expected to have tetrahedral stereochemistry about the transition metal atom.

C O N T E N T S

CHAPTER - I

A SHORT REVIEW OF ARYLAZO-QUINOLINOLS AND THEIR COMPLEXES:

CHAPTER - II

PREPARATION, PROPERTIES AND IR SPECTRA OF ORGANOTIN COMPLEXES OF 5-ARYLAZO-8-QUINOLINOLS:

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CHAPTER -III

ABSORPTION SPECTRA AND STRUCTURE OF THE ORGANOTIN COMPLEXES OF 5-ARYLAZO-8-QUINOLINOLS:

CHAPTER - IV

PREPARATION AND STRUCTURE OF TRANSITION METAL-ORGANOTIN MIXED COMPLEXES OF 5-ARYLAZO-8-QUINOLINOLS:

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CHAPTER - I

A SHORT REVIEW OF ARYLAZO-QUINOLINOLS AND THEIR COMPLEXES:

IA. INTRODUCTION

IB. ANALYTICAL APPLICATIONS OF ARYLAZO QUINOLINOLS

IC. ELECTRONIC SPECTRAL PROPERTIES

ID. BIOLOGICAL PROPERTIES OF ARYLAZO QUINOLINOLS

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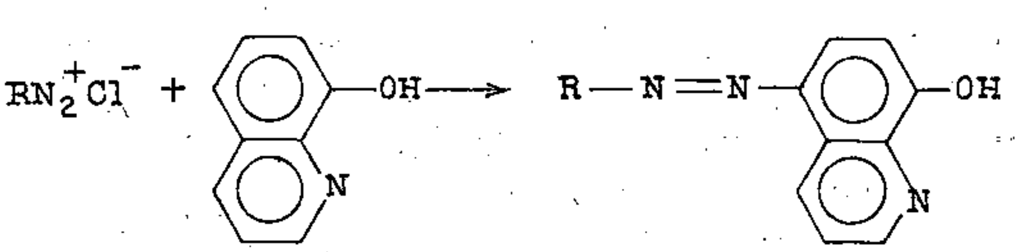
IA. Introduction:

8-quinolinol, first described by R.Berg[1], is now one of the most versatile analytical reagents[2,3]. This reagent behaves as a weak acid[1] (pK = 9.7) and reacts with metal ions to form inner complexes which can be extracted at pH 1.6 – 14. Control of the pH of the solution, therefore, permits the extraction and estimation of individual metal ions[1-7]. In principle, it is possible to prepare more useful organic reagents by preparing compounds having the properties of 8-quinolinol together with other desired features, e.g., having an intense light absorption in the visible region for colorimetric applications. Azo derivatives of 8-quinolinols, commonly known as azoxines mentioned by Chorkosov[8] and first described by Gutzeit and Monnier[9-12], constitute one such group of reagents.

Azoxines can be prepared by coupling 8-quinolinol with diazonium component obtained by diazotising the appropriate diazoforming moiety:

$$RNH_2 \xrightarrow{HCl\ /\ KNO_2} RN_2^+Cl^-$$



Although 5-azo-derivatives are generally formed[9-12], 7-azo-derivatives are also formed in many cases. However, the resulting reagents exhibit such differences in their chemical properties that they can be used for specific tasks in analytical chemistry. For example, while 7-azo derivatives are, as a rule, good complexometric indicator[13-23], the 5-azo derivatives are used for mercurimetric titrations and spectrophotometric applications[24-26]. The relative yield of the 5- and 7- azo derivatives depend on the structure of the diazo forming moiety as well as the pH of the solution, addition of catalysts etc[27,28]. Methods for separation of the two isomers where both are simultaneously formed have also been reported[29,30].

IB. <u>Analytical applications:</u>

The analytical applications of the azo derivatives of 8-quinolinol have been recently reviewed by Ivanov and Rudometkina[31]. The presence of 8-quinolinol group, the reagents have high reactivity towards all metal ions which makes the reagents non selective. However, the presence of the hetero atoms in the diazo system often increases the selectivity of these reagents[13]. Sherkesov observed that 7-azoxines in acid media, unlike 5-azoxines form complexes with metal ions with the participation of the azo group[8,32]. While 5-azoxines, reacting via the 8-quinolinol group, form in neutral media yellow or greenish yellow complexes, the 7-azoxines derivatives in acid media form red or red violet coloured complexes; these complexes are much less stable[8]. Azoxines are thus particularly useful for complexing easily hydrolyzable metal ions.

In addition, the shift of reactivity towards more acid conditions allows, in a number of cases, to increase the selectivity in determining elements, and has been utilized in complexometry where azoxines are used as metallochromic indicators[14-23,33-45]. However, an increase in the acidity of the reagent decreases the stability of the complex formed. It has been shown that the acidity of 8-quinolinol-5-sulphonic acid (I), 7-phenylazo-8-quinolinol-5-sulphonic acid (II), 7-(4-sulphophenyl azo-8-quinolinol-5-sulphonic acid (III), and 7-(4-sulphonapthyl azo-8-quinolinol-5-sulphonic acid (IV) increases in the sequence (I), (II), (III), (IV)[46]. The stability of the corresponding complex of Cr(IV), Mo(VI) and W(VI) with these reagents, as determined by potentiometry, decreases in all cases with the decreasing basicity of the reagent, i.e. in the sequence (I) > (II) > (III) > (IV)[46]. 8-quinolinol azo derivatives are used as complexometric indicators. The 7-azoxines are suitable for this purpose because only these derivatives give a sufficient contrast in the colour change near the titration end point[14]. It has been found that the presence of electrophilic groups (-COOH, -NO$_2$,

$-SO_3H$) in the structure of the reagent improve the sharpness of the colour change near the end point. The presence of the sulpho group improves the solubility of the reagent and the corresponding complexes in water[14-17]. In metal ions forming strongly dissociating complexes with the azoxines, a gradual change in colour of the indicator is usually observed; the titration end point can be determined in this case by adding 1-2 ml. of 0.005M copper or zinc salt solutions. The ions of Al, Cd, Co, Fe(II), Pb, Ni, Mo(IV), Rare earth elements, V(V), Sc, Hg, Th and La can thus be titrated[14,41,42]. When 7-(1-napthyl azo)-8-quinolinol-5-sulphonic acid (napthylazoxines) and, particularly, 7-(6-sulpho-2-napthyl azo)-8-quinolinol-5-sulphonic acid (napthyl azoxines S), which is an indicator for both acids and bases, are used some of the metals can be determined by a direct titration[15,16,42]. The specificity of titration in neutral and basic media can be increased by employing a suitable masking compound. Some of the titration modifications are given in Table (1)[22].

Table (1) . Uses of Azoxines as Indicator in complexometric titration.

Metal ion estimated	Indicator	Conditions	Remarks	Ref.
Ga	NA	$pH_{2.2}$ (CH_3COOH), 70-80°	Ca, Mg, Mn, Cd, Zn; Al masked with fluoride	21
In	DHOQ	$pH_{3.0-3.6}$ (CH_3COOH), 70-80°	Ca, Mg, Mn, Zn Cd; Al masked with fluoride	20
	NA	$pH \geqslant 2$	Cd, Al, Mg, Mn	18
	SHOQ	$pH_{2.8-3.0}$ (CH_3COOH), 60-70°	The same	18
Tl(III)	DHOQ	$pH \geqslant 2$ ($CH_2ClCOOH$)	Ca, Mg, Mn, Zn, Al, Fe, Bi	43
	PAOQ	$pH_{1.8-3.5}$	Cd, Mn, Mg, Zn, Al, Bi	23
Cu	PAOQ	$pH_{2.8-3.0}$	REE, Mg, Be and Al masked with fluoride	22

Contd..

Table 1 (Contd..)

Metal ion estimated	Indicator	Conditions	Remarks	Ref.
Co, Cd, Pb, Cu, Ni, Y, REE, Zn	NA	$pH_{6.5-6.8}$ (pyridine or CH_3COONH_4)	Th, Zr, and U(VI) masked with citrate; Be, Ta, Al, Nb masked with fluoride	41
Cu	NA	$pH_{4.0}$ (formate)	Th, Zr, U(VI) masked with citrate, Be, Nb, Ta, and Al masked with fluoride.	41
Mn(II)	NA	$pH_{6.5-7.0}$ (pyridine)	The same	41
Fe(III), Th	NA	$pH_{2.8-3.5}$ ($CH_2ClCOOH$)	The same	41
Zn	NA	$pH_{5.5-6.5}$ (CH_3COONH_4)	Masked with thiourea	41

Contd..

Table 1(Contd..)

Metal ion estimated	Indicator	Conditions	Remarks	Ref.
Al	NAS	$pH_{6.4}$; DT with copper salts		42
Bi	NAS	$pH_{6.0}$; DT, with copper salts		42
Ca	NAS	pH 10 (TEA) 50-70 Vol. % acetone		42
Co,Cu,Cd, Dy,Fe(III)	NAS	$pH_{6.0}$	All masked with citrate	42
Mn(II),Pb, Cu,Cd	NAS	$pH_{8.5}$;50 vol. % acetone	Fe masked with citrate, W(VI) masked with tartrate	42
V(IV)	BCAQ or SPA	$pH_{3.6-4.3}$	[illegible],Phosphates and fluorides; Cu,Cd,Hg,Zn,Co and Ni masked with cyanide; Al, Ti and Th masked with fluoride.	16

__Note:__ NA); 6-(1-napthyl azo)-8-quinolinol-5-sulphonic acid; DNQS); 7-(5,7-disulpho-2-napthyl azo)-8-quinoline sulphonic acid; SNQS); 7-(4-sulpho-1-napthyl azo)-8-quinolinol-5-sulphonic acid; PAQ4); 7-(2-pyridyl azo)-8-quinolinol; NAS); 7-(6-sulpho-2-napthyl azo)-8-quinolinol-5-sulphonic

(Contd..)

Interestingly the complex formation between metal ions and 7-azoxine not containing heteroatoms in the diazo forming moiety changes the colour of solution in reverse to the usually observed change on complexing with other heterocyclic hydroxy azo compounds. The colour changes from violet or crimson to yellow or lemon yellow usually; complexing with azo compounds containing heteroatoms in the diazo-forming moiety results in deepening of the colour of the solution; the reagent in its dissociated form has the deepest colour.

The dissociated form of 7-azoxines and of some 5-azoxines is orange or red in colour, as compare to its protonated form (in acid media) that is rose coloured or violet. The colour of complexes of these reagents is usually less deep than the colour of the uncomplexed reagent at the same pH value. During direct complexometric titration the colour of the titrated solution thus changes from yellow (the colour of the complex with an indicator) to bright crimson (the colour of the free reagent). The more acid is the medium during titration the brighter is the colour of the free reagent.

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acid; DAOQ); 7-(benzene azo)-8-quinolinol-5-sulphonic acid; SPA); 7-(4-sulphophenyl azo)-8-quinolinol-5-sulphonic acid; TEA); Triethanolamine; BT); back titration; REE); rare earth elements.

The azoderivatives of 8-quinolinols are used in mercurimeter. The formation of brightly coloured complexes between Hg (II) ions and azoxines is very convenient for detecting mercury ions in solution. The ability of mercury (II) to form stable complexes with halogens or thiocyanides and cyanides has been utilized for quantitative determination of these ions by titrating with mercury salts and indicating the end point with azoxines. Silver salts instead of mercury salts have also been used.

The ions of Hg or Ag bind chlorides less fully than bromides and iodides. All ions capable of binding to mercury more strongly than halogen will interfere with the determination. The reaction is, therefore, more sensitive to cyanide and thiocyanide. For the same reason, sulphides, thiosulphate, nitrilotriacetate and cations capable of binding the 8-quinolinol group more strongly than the mercury and silver ion also interfere with the determination. The specificity of these reaction can be increased by carrying out the titration in an acid medium. However, only mercury salts can be used since silver reacts with azoxines only in neutral media. Microquantities of mercury can be determined by titrating with iodides[47]. The reaction can be best followed by using the sodium salt of stilbene-4,4'-bis /¯(azo-5)-8-quinolinols_7-3-3'-disulphonic acid as the titration indicator. The ions of Pb, Cu, Ag, Co, Ni, Cd and Zn also give colour reactions with this reagents, forming compounds of various violet shades at weakly acid pH.

Its already mentioned azoxines are widely used as photometric reagents for the estimation of large number of metal ions[31]. Depending on the structure and position of the diazoforming moiety, the complexes results either via the 8-quinolinol group or via the participation of the heteroatoms or groups in a sterically suitable position in the diazo forming moiety. Almost all the complexes are formed in acid or weakly acid media. The difference between the absorption maxima of the reagent and the complex varies from 70 to 108 nm[48]. The high molar absorptivity of the complexes[31] ($\epsilon \sim 10^4$) allows the determination of trace amounts of elements. Ions of Cu, Cd, Co and Ni can be masked with cyanide[16,49], while those of Al, Ti(IV) and Th can be masked with fluoride. Introduction of a thiazo ring into azoxines increases considerably the selectivity of the reagent. 5-(2'-(4', 5', 6', 7' -tetrahydrobenzthiazolyl)-azo)-8-quinolinol reacts with Cu, Ag, Zn, Cd, Hg, Ga, In, Y, La, Ce, Nd, Gd, Dy, Yb, Sn, Pb, Zr, Th, V, Ta, Mo, Fe, Co and Ni ions[37]. The reagent is very sensitive to Ni[50].

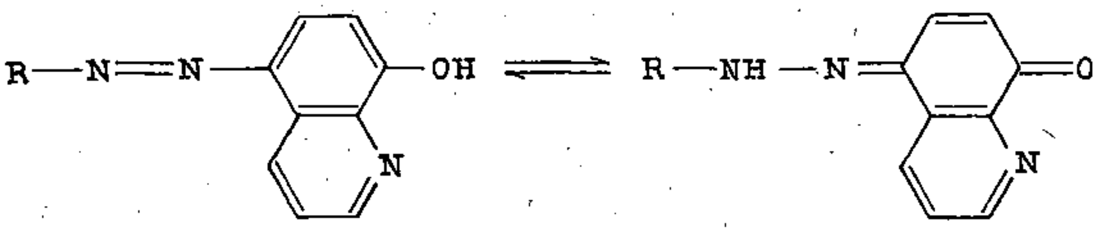
Efforts to obtain azoxine analogs of PAR led to the synthesis of 7-(2-pyridylazo)-5-methyl-8-quinolinol[51]. This reagent gives violet and blue violet chelates with Co, Ni, Cu, Cd, Zn, Pb, Bi, In, U(IV), Y, V(V) and Pb. Some of the complexes can be extracted with organic solvents. In a number of cases the sensitivity is higher than that obtained with PAR.

7-(2-quinolylazo)-8-quinolinol[52] was found very reactive toward the Fe(II,III), Ni, Co, Zn, Cd, Pb, Hg, Ce(III), In, Ga, Tl(III), V(V), Bi, As(III,V), Th, U(VI), Pd, Cr(III), Cu, and Hg(I) ions at pH 1-5, and toward Mn (II) and Al ions at pH 3-7. The colour of the resulting complexes varies from red (Mn, Pd) to red violet [As(V), Ce] and dark blue-violet [U(VI), Zn, Co, Fe, In, Tl, Bi, V, Hg and others].

The absorption maxima, reaction condition and the sensitivity of the various types of azoxines are given in reference[31].

10. Electronic Spectral Properties:

Despite the wide use of 5-phenylazo-8-quinolinol for spectrophotometric estimation of metal ions, the electronic absorption spectra of these compounds and their complexes have not been investigated in detail. The studies that have so far been made concern mainly azo-hydrazone tautomerism (I) exhibited by azo dyes containing -OH group in ortho - or para-position to the azo group[53].

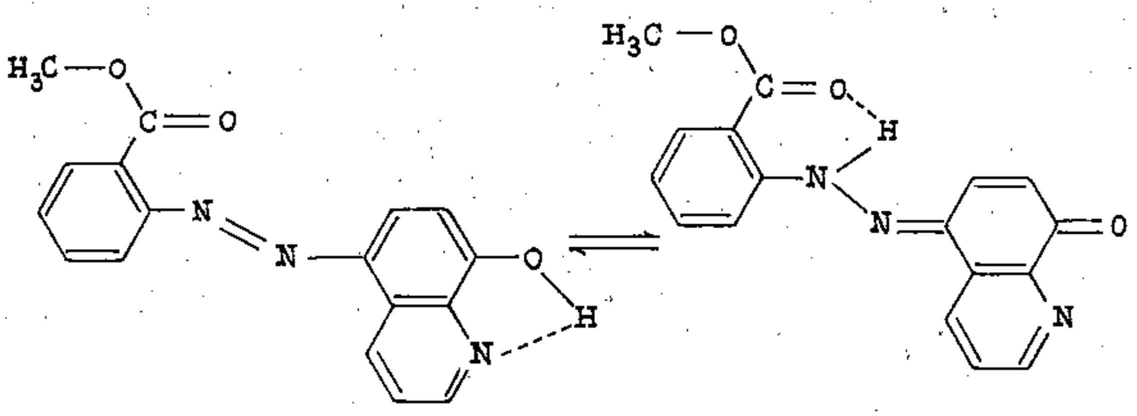


[Azo - Form] [Hydrozone - Form]

(I)

For example, 4-phenyl azo-1-napthol is know to exist in absolute alcohol as an equilibrium mixture of the azo and phenyl hydrazone tautomer, the absorption curve consisting of two broad bands at 408 nm (azo form) and 462 nm (hydrazone form)[54]. It has been well established that the hydrazone form always absorbs at longer wave-lengths compared to the azo form[53,55].

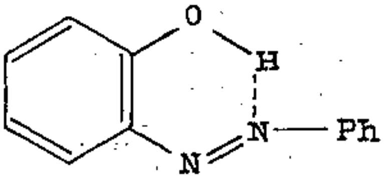
The existence of intramolecular hydrogen bonding in 8-quinolinol is shown by its high melting point, small wet m.p. depression (3°C), steam volatility and IR spectrum[54]. The intramolecular H-bonding involves the formation of a 5-membered ring between the heterocyclic nitrogen and the hydroxylic hydrogen. In the case of 8-quinolinol - N-oxide, such intramolecular H-bonding is much more extensive due to formation of a 6-membered ring[54]. It has been demonstrated that the existence of intramolecular H-bonding in the 8-quinolinol moiety influences the azo-hydrazone tautomeric equilibria in the azo dyes of 8-quinolinol. For example, 5-phenyl azo-8-quinolinol in absolute alcohol shows two regions of absorption at 387 nm ($\epsilon = 21.1 \times 10^3$) and 462 nm ($\epsilon = 5.5 \times 10^3$) but the longest wave length absorption appears only as an inflexion[56]. The intramolecular H-bond tends to stabilise the azo tautomer, ratio of the concentrations of hydrazone to azo tautomer being 0.26. In other solvents, only small difference in the relative intensities of the two absorption bands are observed, the absorption due to the phenyl hydrazone tautomer increasing in the order: CCl_4 $CHCl_3$ C_2H_5OH CH_3COOH. This shows that the greater the possibility of intramolecular H-bonding with the solvent, the smaller would be the influence of weak intramolecular H-bonding on the position of the equilibrium[54]. The spectra of 5-phenyl azo-8-quinolinol-N-oxide shows that the molecule exists almost completely in the azo form in ethanol. The spectra are identical in a series of solvents except for small shifts in $_{max}$ which means that the intramolecular H-bonding is so strong the intramolecular H-bonding with the solvent is without effect on the equilibrium[54]. Similarly, in 5-(2'-carbomethoxy phenyl azo)-8-quinolinol, the intramolecular H-bond involving a 5-membered ring in the azo form (IIA) is pitted against the intramolecular H-bond involving a 6-membered ring of the hydrazone form (IIB).



(IIA) (IIB)

The spectrum of 5-(2'-carbomethoxy phenyl azo)-8-quinolinol consists of two broad bands ($_{max}$ at 395 nm and 460 nm), the ratio of the concentrations of hydrazone to azo tautomers as deduced from the relative intensities of the bands is 1:1. The hydrazone form is, thus, stabilized to a greater extent than the azo form[56].

The situation is analogous to that prevailing in 1-phenyl azo napthol (III) which exists exclusively in the azo form. The azo form is stabilised by intramolecular H-bond due to formation of a 6-membered ring[57].



(III)

Matsunaga, in an attempt to study thermochromism in 5-arylazo-8-quinolinols, have shown that the molecules exhibit azo-hydrazone tautomeric equilibria in the solid state also[58].

Acid base transformations in solutions often lead to a change in the electronic absorption of the azoxines. Spectrophotometric studies of solutions of azoxines at various acidity show the existence of a number of equilibria. Introduction of an arylazo group into 8-quinolinol generally increases the acidity of the hydroxy group. At pH 1-3, protonation of the quinolinol N-atom occurs and in conc. H_2SO_4, azo group N-atom is protonated[31]. It has been observed that for 5-arylazo-8-quinolinols, the absorption spectra exhibit intense maxima in the long wave length region that decreases with decreasing acidity with an apperance of a maximum in the 400 nm region. The presence of a sharp isobestic is consistent with the existence of equilibrium (1). deprotonation of the azo-group nitrogen:

$$H_3R^{+2} \rightleftharpoons H_2R^{+} + H^{+} \qquad \dots (1)$$

deprotonation of the hetero atom nitrogen:

$$H_2R \rightleftharpoons HR + H^{+} \qquad \dots (2)$$

the hydroxy - group dissociation:

$$HR \rightleftharpoons R^{-} + H^{+} \qquad \dots (3)$$

At pH > 1, the absorption maximum moves bathochromically. The equilibrium is shifted toward the more deeply coloured form of the reagent (neutral form) as shown in equilibrium (2). With further increase in pH, the molecule dissociate and a sharp bathochromic shift of the absorption maximum is observed [equilibrium (3)][59].

The colour deepening, particularly in a basic medium, is characteristic only for 5-azoxines and is due to the formation of a longer conjugated chain. Usually, all the 7-arylazo-8-quinolinols show just the reverse behaviour i.e. the deepest colour (λ_{max} = 530-550 nm) is observed for solutions of azoxines in acid media ($pH < 2$) and with increasing pH the colour becomes lighter, the dissociated form of the molecules being yellow or orange in colour[31].

The primary interest in the azoxines being due to their potential use as analytical reagent, no theoretical studies on the electronic transitions in these molecules in terms of the molecular orbitals are still available. Although in the absence of such studies it is hazardous to make any conjecture about the nature of transitions responsible for the light absorption properties of the azoxines, their spectra may be understood, at least in part, by comparison with other azo compounds which have investigated in detail by several workers

In simple azo-dye, like substituted azobenzene, strong $\pi - \pi^*$ transition is responsible for the visible absorption[63]. The comparatively weak $n-\pi^*$ bands are fully masked in the trans-configurations in which the azo-dyes normally exist. The $n-\pi^*$ transition may, however, be observed in cis-form where the first $\pi-\pi^*$ transition occurs at shorter wave lengths[60,61]. According to MO descriptions, the upper MO for the longest wave length

π-π^* transition is the perturbed orbital originating from the anti bonding π-orbital of the azo group, while the lower one is the orbital arising from the perturbation of the highest bonding π-orbital of the aryl residue[60,62]. The electronic spectra of metal and organometallic derivatives of simple azo dyes have also been interpreted in terms of π-π^* transitions, the coordination of metal ion or organometal group exerting a bathochromic shift of the absorption maxima[53,60-65].

D. Biological Properties:

In the last decade there has been increasing interest in the biological properties of the azoxines which were so far used only as analytical reagents. Azoxines have received attention presumably for their stability and reactivity[46].

The survey of literature reveals that the biological effect is very dependent upon the nature of the reagents. Shrave and Bennett[66] prepared 5-R-8-quinolinols (R = substituted aryl azo groups) and studied their bacteriostatic power (B.P) towards *E. Coli* and *S. aureus*. The testing solution in gm/100 ml. is given for the base in 95% ethanol at 25°C and for the HCl-salt in glycol at 24°C and in 0.1 N HCl at 24°C, in some cases the standard solution was diluted. Observation shows that the lowest dilution supported some growth and the water dilution of HCl-salt just prevent the growth.

The azoxine derivatives were tested for the properties of diabetes[67] which shows no better results but induced diabetes and stained the Langerhans island cells. The reagents caused diabetes during chelation with metallic ions[68] in the β-cells of the pancreatic islets of Langerhans and, otherwise, did not cause diabetes.

A series of azoxines metal derivatives, tested by Rao and Sircar[69], shows low antibacterial activity. Some new fungistatic compounds of azoxines[70] were investigated on liquid mash containing 10% cattle-serum and on solid media containing 3% agar. A relation was sought between the chelate complex forming ability and fungistatic activity of these compounds. These compounds exercise their fungistatic activity by means of intercellular chelation of the heavy metal components in certain enzyme of fungus cells. These enzyme were inactivated and this prevented multiplication.

Mycobacterium phlei and *Staphy lococcus aurens* NCTC 8342 shows possible anti-microbial activity[71] against many aryl-azoquinolinol derivatives. The water soluble copper salt of azoxines shows some fungicidal properties[72]. Azoxines derivatives of Cu^{++}, Cd^{++}, Fe^{++}, Ni^{++} and Co^{++} complexes[73] exhibits antibacterial activity and found to be useful in the treatment of dysentery.

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CHAPTER - II

PREPARATION, PROPERTIES AND IR SPECTRA OF ORGANOTIN COMPLEXES OF 5-ARYLAZO-8-QUINOLINOLS:

IIA. INTRODUCTION

IIB. LIGANDS USED IN THE PRESENT STUDY

IIC. METHODS OF PREPARATION OF ORGANOTIN COMPLEXES

IID. ANALYTICAL DATA

IIE. IR SPECTRA

IIF. EXPERIMENTAL

(i) PREPARATION OF THE LIGANDS

(ii) SOURCE OF ORGANOTIN COMPOUNDS USED FOR SYNTHESISING THE ORGANOTIN COMPLEXES

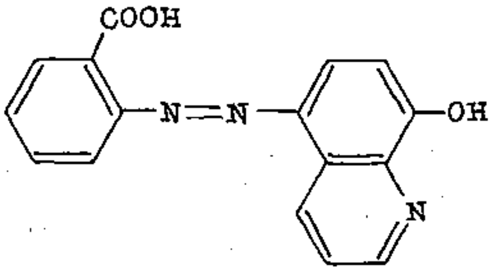
(iii) SYNTHESIS OF ORGANOTIN DERIVATIVES

BIBLIOGRAPHY

IIA. Introduction

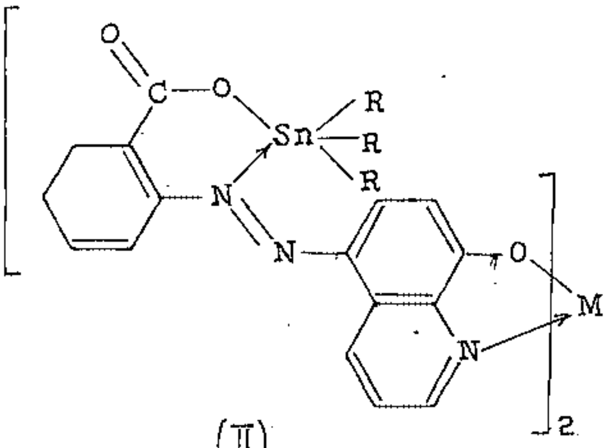
It was discussed in chapter - I that the Arylazoquinolinols are extremely efficient analytical reagents[1-5]. This class of azodyes forms complexes in solution with a wide variety of metals. However, there is no report in the extant literature of any metal complex having been isolated and characterised apart from a very recent example of organotin complexes of 5-phenyl-azo-8-quinolinol[6].

5-Arylazo-8-quinolinols, particularly the o-carboxy derivative 5-(2'-carboxyphenyl) azo-8-quinolinols (I) appears to be a very suitable ligand for preparing organotin as well as organotin-transitional metal mixed complexes. This ligand contains two functional groups capable of coordination with metal ion/ organometal group and are situated at different sites within the molecule. Such a heterofunctional ligand provides a rare opportunity of synthesising not only mixed metal complexes (II) but



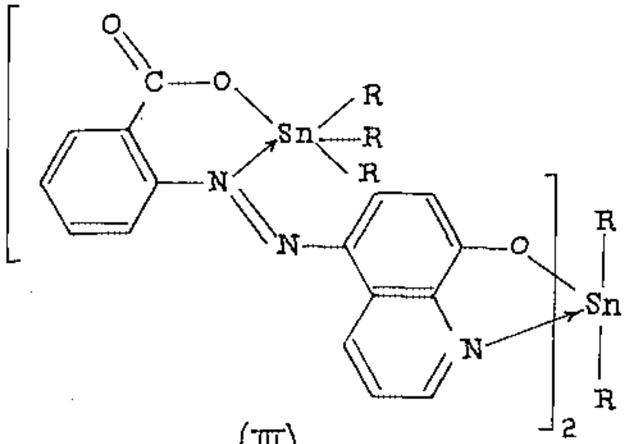
(I)

organotin complexes (III) having tin atoms of different coordination numbers in the same molecule.



(II)

(M = Cu, Ni etc. and R = alkyl or aryl groups)



(III)

(R = alkyl or aryl groups)

In addition, simple organotin complexes like the organotin carboxylates and the organotin quinolinolates can also formed. This prompted us to undertake the synthesis and spectro-chemical studies on the organotin complexes and mixed complexes of o-carbaoxine.

The reason for choosing 5-(2'-carboxy phenyl) azo-8-quinolinol or o-carbaoxine may be summarised as follows:

(i) The presence of the 8-quinolinol group is certain to impart high reactivity towards many metal ions as well as organotin group.

(ii) The compound has intense light absorption in the visible region which may be utilised in the study of the complexes.

(iii) The much higher reactivity of the metal ions, e.g., Cu(II), Ni(II) etc. towards the quinolinol part compared to the carboxylate group offers a favourable chance for synthesising the novel transition metal-organotin mixed complexes (II). In general transition metal ions reacts with organotin complexes through a facile replacement of the organotin group by the fomrer primarily due to the higher stability of the complexes due to lower effective size. Presumably, of this, no report of organotin-transition metal mixed complex is still available in the literature.

(iv) The influence of the triorganotin group in the electronic spectral characteristics can be easily ascertained by a comparative study of the complexes of 5-phenyl azo-8-quinolinols.

(v) The organotin quinolinolate type derivatives may be made water soluble by treating with aqueous sodium bicarbonate solution. Such water soluble organotin complexes are likely to find wide use because of their biocidal properties of organotin compounds.

(vi) The ligand can be easily prepared in high yield by coupling 8-hydroxy-quinoline with diazotised anthranilic acid.

In the present chapter, methods of preparation of the ligands and their organotin complexes are described.

IID. Ligands used in the present study

The ligands used in the present study are given in Table 1.

Table 1

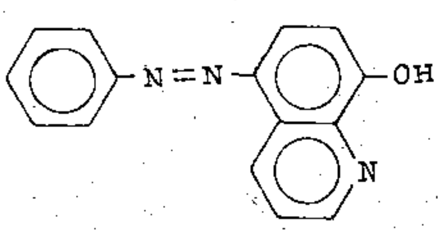
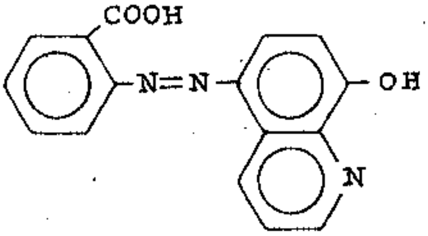
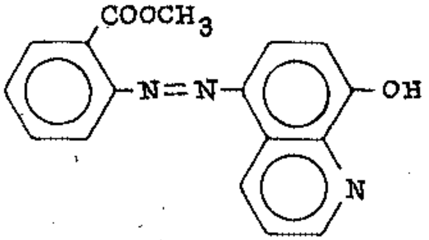
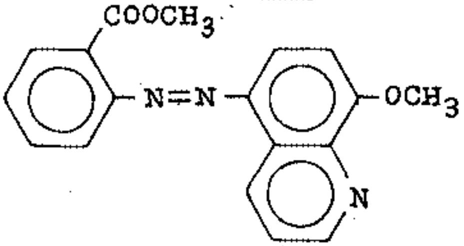
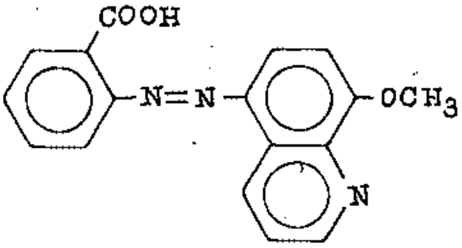
Structure	Name	Abbreviation[a]
A.		
1. 	Phenyl-5-azo-8-quinolinol	LH[b]

Table 1 (Contd..)

Structure	Name	Abbreviation[a]
8. 	5-(2'-carboxyphenyl) azo-8-quinolinol	L'HH'
B.		
1. 	5-(2'-carbomethoxyphenyl)azo-8-quinolinol	L'MeH
2. 	5-(2'-carbomethoxyphenyl)azo-8-methoxy quinoline	$L'Me_2$
3. 	5-(2'-carboxyphenyl) azo-8-methoxyquinoline	L'MeH'

---

a) H and H' denote, respectively, the phenolic (-OH) and carboxyl (-COOH) protons of the ligand to specify the site of complexation in their organotin complexes.

b) Several organotin complexes of this ligand have been recently reported (see ref. 6).

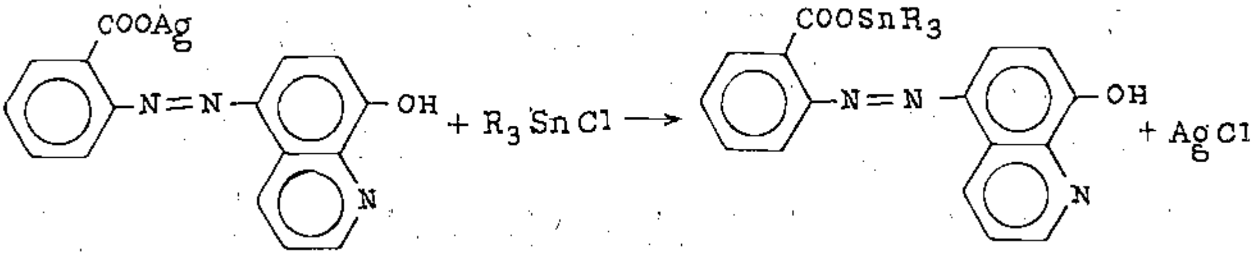
IIC. Methods of preparation of organotin complexes:

While the mono basic ligand LH, forms only one type of organotin complexes, viz., the organotin quinolinolates[6], the dibasic ligand L'HH' can form three types, viz, the organotin carboxylate, organotin quinolinolate and the binuclear di/tri-organotin (triorganotin carboxyphenyl) azo-quinolinolates.

(A) In order to prepare the triorganotin carboxylates, the following methods were employed:

(i) Reaction of the organotin halide with the silver salt of the 5-(2'-carboxyphenyl) azo-8-quinolinol.

Ag - salt of the ligand and R_3SnCl (1:1) were taken in dry benzene and the mixture was refluxed. The reaction mixture was filtered off and the benzene solution was concentrated and then pet -ether was gradually added. The crystallised compound was purified from unreacted dye by extraction with cold benzene followed by recrystallisation from benzene-petroleum ether mixture. The reaction may be represented as follows:

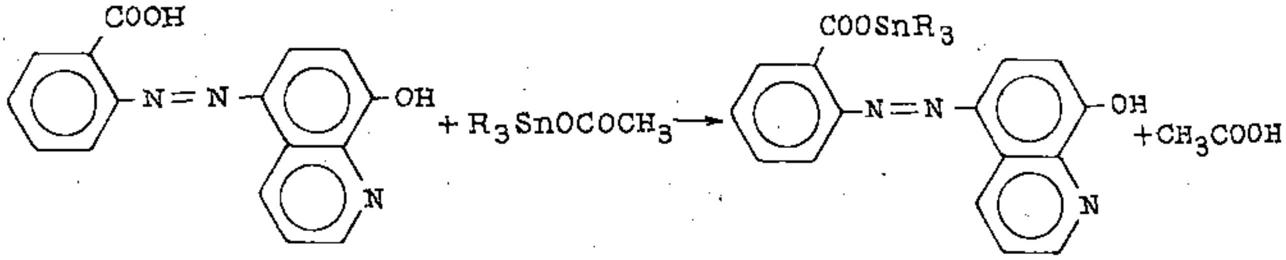


... (1)

This reaction was found particularly suitable for preparing the triphenyl tin derivative. With other triorganotin compounds, the reaction was too slow to be of any practical value.

(ii) Reaction of the organotin acetate with the 5-(2'-carboxyphenyl) azo-8-quinolinol.

The ligand and $R_3SnOCOCH_3$ (1:1) were taken in dry THF and the mixture was stirred. The reaction mixture was filtered and evaporated. Solid was extracted with cold benzene and concentrated, petroleum ether was gradually added. The crystallised compound was purified from unreacted dye by extraction with cold benzene and 2% $NaHCO_3$ solution, followed by recrystallisation from benzene-pet. ether mixture. The reaction may be represented as follows:



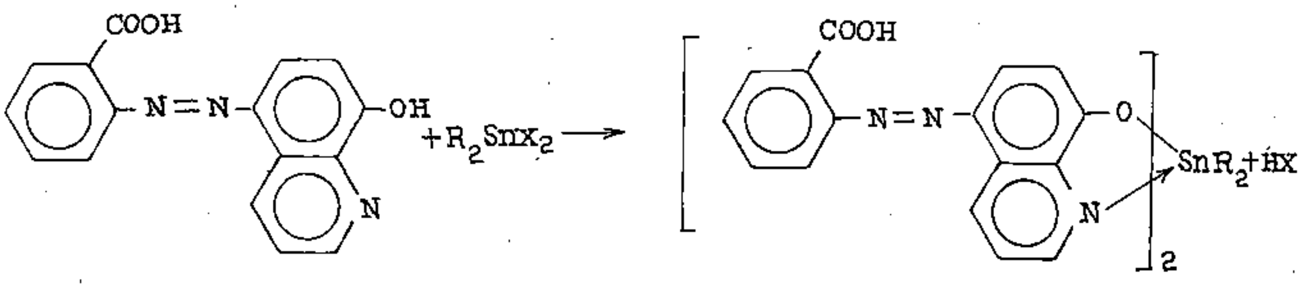
... (2)

This offers a convenient route for the preparation of the tributyl tin derivative.

(B) Preparation of the quinolinate derivatives of the type $R_2Sn(L'H')_2$ and $R_2Sn(L'Me)_2$:

(1) Reaction of diorganotin dihalide with the 5-(2'-carboxyphenyl) azo-8-quinolinol.

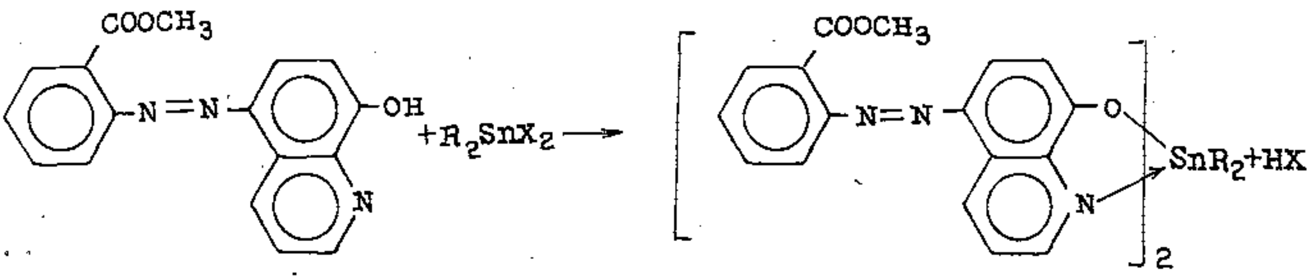
The ligand and R_2SnX_2 (2:1) were taken in dry THF and mixture was stirred. The reaction mixture was filtered and distilled off. Solid was extracted with cold benzene and concentrated, petroleum ether was gradually added. The crystallised compound was purified from unreacted dye by extraction with cold benzene and recrystallised from benzene - pet. ether mixture. The reaction may be represented as follows:



... (3)

(ii) Reaction of diorganotin dihalide with the 5-(2'-carbomethoxyphenyl) azo-8-quinolinol.

The ester (L'MeH) and R_2SnX_2 (2:1) were taken in dry benzene and refluxed. On addition of petroleum ether to the concentrated benzene solution, the diorganotin derivative could be obtained.



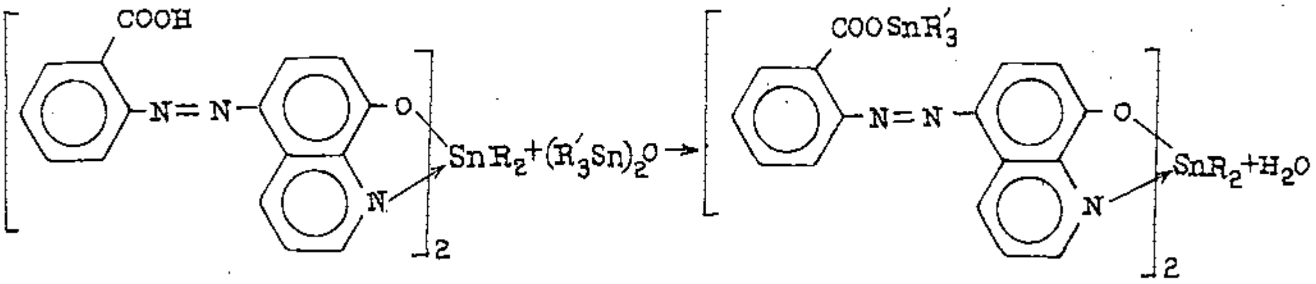
... (4)

(R = Phenyl, Octyl, Butyl and Methyl)

(C) <u>The binuclear di/tri-organotin (triorganotin carboxyphenyl) azo-quinolinolates are conveniently prepared by the following methods:</u>

(i) Reaction of diorganotin complexes of the ligand $[(L'H')_2SnR_2]$ with the Bis-(triorganotin)oxide:

The $(L'H')_2SnR_2$ and $(R'_3Sn)_2O$ (1:1) were taken in dry benzene and refluxed. On addition of petroleum ether to the concentrated benzene solution, the binuclear di/tri-organotin (triorganotin) azo-quinolinolates could be obtained.



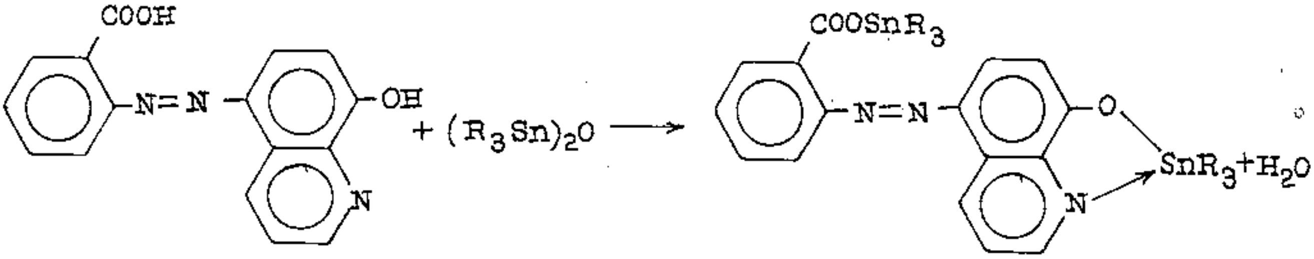
... (5)

R = Phenyl, Octyl, Butyl and methyl

R' = Phenyl and butyl

(ii) Reaction of the 5-(2'-carboxyphenyl) azo-8-quinolinole with Bis-(tri-organotin) oxide.

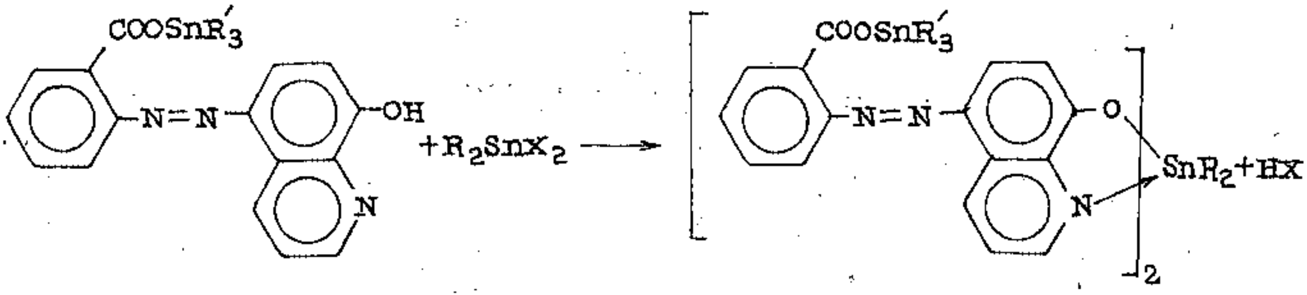
The ligand and $(R_3Sn)_2O$ (1:1) were taken in dry benzene and refluxed. On addition of pet. ether to the concentrated benzene solution. The organotin derivatives could be isolated. The reaction may be written as:



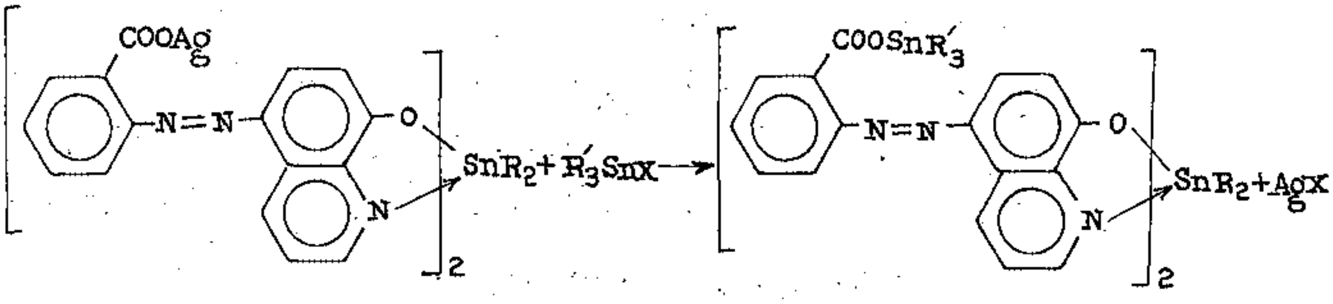
... (6)

(R = Phenyl and Butyl)

(iii) Reaction (7) and (8) were also tried for the preparation of the binuclear organotin complexes. However, reaction (5) is found to be the best one for the preparation of $R_2Sn(L'SnR'_3)_2$ type complexes.



... (7)



... (8)

[R' = Phenyl and Butyl
R = Phenyl, Butyl, Octyl and Methyl]

A reference to the methods of preparation of organotin complexes (III) would show that the yield of the desired organotin carboxylate and quinolinolate are dependent on the nature of the group R and R' and also on the method employed. The addition of a small amount of pyridine to the reaction mixture to neutralise the acid formed in reaction (2), (3), (4) and (7) improves the yield. However, in the case of stannylation of the quinolinolates this method gives considerably lower yields and increase of reaction time even with refluxing does not increase the yield significantly.

The binuclear di/tri-organotin (triorganotin carboxyphenyl) azo quinolinolates were obtained in 20-70% yield by the reaction (5) and (6). The yield in reaction (7) is not good though the reaction time is short. The reverse holds good for reaction (8).

A summary of the reaction products together with the yields and the experimental condition used in the present investigation are given in Table 2.

Table 2

Reactants[a] (Mole ratio)	Experimental condition used	Product (m.p. °C, yield %)
1. L'H -Ag + Ph_3SnCl (1:1)	Refluxing for 25 hours in dry benzene, product crystallised from benzene-pet. ether mixture.	$Ph_3SnL'H$ (> 300°, 75)

Table 2 (Contd..)

Reactants^{c} (Mole ratio)	Experimental condition used	Product (m.p. °C, yield %)
2. $L'HH' + Bu_3SnOOCCH_3$ (1:1)	Stirring at RT for 8 hours in dry THF^{a}, product crystallised from benzene-pet. ether mixture.	$Bu_3SnL'H$ (220°, 40)
3. $L'HH' + Ph_2SnCl_2$ (2:1)	Stirring at RT for 10 hours in dry THF^{a}, product crystallised from benzene-pet. ether mixture.	$Ph_2Sn(L'H')_2$ (259°^{b}, 45)
4. $L'HH' + Bu_2SnBr_2$ (2:1)	Stirring at RT for 15 hours in dry THF^{a}, product crystallised from benzene-pet. ether mixture.	$Bu_2Sn(L'H')_2$ (163°, 25)
5. $L'HH' + Oct_2SnCl_2$ (2:1)	Stirring at RT for 10 hours in dry THF^{a}, product crystallised from benzene-pet. ether mixture.	$Oct_2Sn(L'H')_2$ (144°, 35)

Table 2 (Contd..)

Reactants^c (Mole ratio)	Experimental condition used	Product (m.p. °C, yield %)
6. $L'HH' + Me_2SnCl_2$ (2:1)	Stirring at RT for 10 hours in dry THF^a, product crystallised from benzene-pet. ether mixture.	$Me_2Sn(L'H')_2$ (169^o, 40)
7. $L'MeH + Ph_2SnCl_2$ (2:1)	Refluxing for 10 hours in dry benzene^a, product crystallised from benzene-pet. ether mixture.	$Ph_2Sn(L'Me)_2$ (178^o, 55)
8. $L'MeH + Bu_2SnBr_2$ (2:1)	Refluxing for 10 hours in dry benzene^a, product crystallised from benzene-pet. ether mixture.	$Bu_2Sn(L'Me)_2$ (174^o, 45)

Table 2 (Contd..)

Reactants (Mole ratio)	Experimental condition used	Product (m.p. °C, yield %)
9. $L'MeH + Oct_2SnCl_2$ (2:1)	Refluxing for 10 hours in dry benzene[a], product crystallised from benzene-pet. ether mixture.	$Oct_2Sn(L'Me)_2$ (175°, 80)
10. $L'MeH + Me_2SnCl_2$ (2:1)	Refluxing for 10 hours in dry benzene[a], product crystallised from benzene-pet. ether mixture.	$Me_2Sn(L'Me)_2$ (175°, 60)
11A. $Ph_2Sn(L'H')_2$ + $(Ph_3Sn)_2O$ (2:1)	Refluxing in dry benzene for 15 hours, product crystallised from benzene-pet. ether mixture.	$Ph_2Sn(L'SnPh_3)_2$ (>300°, 65)

Table 2 (Contd..)

Reactants (Mole ratio)	Experimental condition used	Product (m.p. °C, yield %)
11B. $Ph_3SnL'H$ + Ph_2SnCl_2 (2:1)	Stirring in dry benzene[a] for 5 hours, product crystallised from benzene-pet. ether mixture	$Ph_2Sn(L'SnPh_3)_2$ (>300°, 25)
11C. $(L'Ag)_2SnPh_2$ + Ph_3SnCl (1:2)	Refluxing in dry benzene for 15 hours, product crystallised from benzene-pet. ether mixture.	$Ph_2Sn(L'SnPh_3)_2$ (>300°, 35)
12. $Bu_2Sn(L'H')_2$ + $(Ph_3Sn)_2O$ (1:1)	Refluxing in dry benzene for 25 hours, product crystallised from benzene-pet. ether mixture.	$Bu_2Sn(L'SnPh_3)_2$ (211°[b], 35)

Table 2 (Contd..)

Reactants (Mole ratio)	Experimental condition used	Product (m.p. °C, yield %)
13. $Oct_2Sn(L'H')_2$ + $(Ph_3Sn)_2O$ (1:1)	Refluxing in dry benzene for 20 hours, product crystallised from benzene-pet. ether mixture.	$Oct_2Sn(L'SnPh_3)_2$ ($165^{\circ b}$, 40)
14. $Me_2Sn(L'H')_2$ + $(Ph_3Sn)_2O$ (1:1)	Refluxing in dry benzene for 15 hours, product crystallised from benzene-pet. ether mixture.	$Me_2Sn(L'SnPh_3)_2$ (175°, 50)
15. $Ph_2Sn(L'H')_2$ + $(Bu_3Sn)_2O$ (1:1)	Refluxing in dry benzene for 25 hours, product crystallised from benzene-pet. ether mixture.	$Ph_2Sn(L'SnBu_3)_2$ (242°, 30)

Table 2 (Contd..)

Reactants (Mole ratio)	Experimental condition used	Product (m.p. °C, yield %)
16. $Bu_2Sn(L'H')_2$ + $(Bu_3Sn)_2O$ (1:1)	Refluxing in dry benzene for 30 hours, product crystallised from benzene-pet. ether mixture.	$Bu_2Sn(L'SnBu_3)_2$ (102°, 30)
17. $Oct_2Sn(L'H')_2$ + $(Bu_3Sn)_2O$ (1:1)	Refluxing in dry benzene for 25 hours, product crystallised from benzene-pet. ether mixture.	$Oct_2Sn(L'SnBu_3)_2$ (182°, 40)
18. L'HH' + $(Ph_3Sn)_2O$ (1:1)	Refluxing in dry benzene for 25 hours, product crystallised from benzene-pet. ether mixture.	$Ph_3SnL'SnPh_3$ (180°, 70)

a) The acid formed in the reaction was neutralised with pyridine.

b) Decomposition point.

c) Ph- phenyl; Bu - n-butyl; Oct - n - Octyl; and Me- methyl.

IID. Analytical data

Analytical data on the organotin derivatives are given in Table -3. Analytical data clearly indicate the formation of well defined organotin compounds.

Table - 3

Formula*	Found (calculated) (%) C	H	N	Sn
1. $C_{34}H_{25}O_3N_3Sn$ $(Ph_3SnL'H)$	63.36 (63.58)	3.30 (3.89)	6.50 (6.54)	18.62 (18.49)
2. $C_{28}H_{37}O_3N_3Sn$ $(Bu_3SnL'H)$	57.72 (57.76)	6.30 (6.36)	7.28 (7.22)	20.12 (20.40)
3. $C_{44}H_{30}O_6N_6Sn$ $[Ph_2Sn(L'H')_2]$	60.98 (61.63)	3.52 (3.50)	9.79 (9.80)	13.90 (13.85)
4. $C_{40}H_{38}O_6N_6Sn$ $[Bu_2Sn(L'H')_2]$	58.78 (58.77)	4.60 (4.65)	10.12 (10.28)	14.70 (14.53)
5. $C_{48}H_{54}O_6N_6Sn$ $[Oct_2Sn(L'H')_2]$	61.95 (62.02)	6.02 (5.81)	9.15 (9.04)	12.50 (12.78)
6. $C_{34}H_{26}O_6N_6Sn$ $[Me_2Sn(L'H')_2]$	56.01 (55.63)	3.60 (3.54)	11.50 (11.46)	16.23 (16.20)
7. $C_{46}H_{34}O_6N_6Sn$ $[Ph_2Sn(L'Me)_2]$	62.42 (62.39)	3.90 (3.84)	9.36 (9.49)	13.39 (13.41)

Contd..

Table - 3 (Contd..)

Formula*	Found (Calculated) (%) C	H	N	Sn
8. $C_{42}H_{42}O_6N_6Sn$ $[Bu_2Sn(L'Me)_2]$	59.50 (59.66)	4.92 (4.97)	10.10 (9.94)	14.12 (14.05)
9. $C_{50}H_{58}O_6N_6Sn$ $[Oct_2Sn(L'Me)_2]$	63.07 (62.71)	6.10 (6.06)	7.97 (8.78)	12.34) (12.40)
10. $C_{36}H_{30}O_6N_6Sn$ $[Me_2Sn(L'Me)_2]$	57.10 (56.78)	3.90 (3.94)	10.73 (11.04)	15.96 (15.60)
11. $C_{80}H_{58}O_6N_6Sn_3$ $[Ph_2Sn(L'SnPh_3)_2]$	61.70 (61.77)	3.70 (3.75)	5.39 (5.40)	22.80 (22.91)
12. $C_{76}H_{57}O_6N_6Sn_3$ $[Bu_2Sn(L'SnPh_3)_2]$	60.70 (60.59)	3.19 (3.78)	5.72 (5.58)	23.69 (23.65)
13. $C_{84}H_{82}O_6N_6Sn_3$ $[Oct_2Sn(L'SnPh_3)_2]$	62.50 (61.98)	5.25 (5.04)	5.30 (5.16)	21.89 (21.90)
14. $C_{70}H_{54}O_6N_6Sn_3$ $[Me_2Sn(L'SnPh_3)_2]$	57.95 (58.75)	3.60 (3.77)	5.62 (5.87)	25.10 (24.90)
15. $C_{68}H_{82}O_6N_6Sn_3$ $[Ph_2Sn(L'SnBu_3)_2]$	57.25 (56.89)	5.80 (5.71)	6.12 (5.85)	24.95 (24.83)

Contd..

Table - 3 (Contd..)

Formula*	Found (Calculated) (%)			
	C	H	N	Sn
16. $C_{64}H_{90}O_6N_6Sn_3$ [$Bu_2Sn(L'SnBu_3)_2$]	54.50 (55.03)	6.62 (6.45)	6.22 (6.02)	25.79 (25.54)
17. $C_{72}H_{106}O_6N_6Sn_3$ [$Oct_2Sn(L'SnBu_3)_2$]	56.92 (57.36)	6.96 (7.03)	5.50 (5.57)	24.10 (23.64)
18. $C_{52}H_{39}O_3N_3Sn_2$ ($Ph_3SnL'SnPh_3$)	62.50 (63.00)	3.92 (3.90)	4.10 (4.24)	24.15 (23.97)

* The abbreviated structural formulae are given in parenthesis.
Ph- phenyl; Bu - n-butyl; Me-methyl; Oct - n-octyl.

IIE. Infrared Spectra:

The IR spectra of 5-phenyl azo-8-quinolinol (LH) and 5-(2'-carboxy phenyl)-azo-8-quinolinol (L'HH') and their organotin derivatives are very complex due to the presence of a large number of vibrational modes due to ring stretch, deformation, in plane and out of plane ring and CH deformations[11,12 etc.]. However, these modes are of little value in the understanding of the structure and bonding in the complexes. Valuable information can, however, be obtained from the frequencies of carboxylate stretch, Sn-O stretch, Ar - OH (C - O vibration involving the 8-hydroxy group) and the N = N stretch. Unfortunately, even those modes can not be identified with certainity in all the cases because of the presence of strong ligand vibrations in the regions where these modes are expected. For example, the N = N stretch mode is of little use though variation of $\nu(N = N)$ in the complexes is expected to provide valuable clue to the participation or otherwise of the azo group in the organotin complexes. This is because the substitution on the azo group in dyes are fairly symmetrical (as far as the local symmetry is concerned, the grouping in azo-dyes always being $>C-N = N - C<$) and is, therefore, likely to be weak in IR spectrum. Although this vibration has been reported by some authors to occur at 1400-1450 cm^{-1} region[13], Miller[14] has emphasised that no diagnostically useful band can be found in this region in azo dyes. The later studies involving complexes of aryl azo benzoic acids[15-18] also confirm this. In view of this we shall confine our discussion primarily to ν(COO), ν(Sn-O) and ν(Ar-O) modes.

The O-H stretch in LH occurs at 3330 cm^{-1} as broad band and at 3480 cm^{-1} and ~ 3360 cm^{-1} (very broad, shoulder) in L'HH' indicating the presence of H-bonding interactions involving the -OH group. The two frequencies in the L'HH' are presumably due to the carboxylic -OH and phenolic -OH groups respectively. Since the 3480 cm^{-1} absorption disappears on methylation of the carboxyl group, this may be assigned to carboxyl O-H stretch while the very broad band at ~ 3360 cm^{-1} to the phenolic -OH group which is known to form intra molecular H- bond with the quinoline N-atom in such systems[19].

As expected, the OH stretching modes disappears in the esters or the organotin derivatives (Figs. 2,3,5-11) confirming bonding through the O-atom of the ligand.

The carboxylate stretch, ν_{as}(COO) occurs at ~ 1650 cm^{-1} in the free ligand (L'HH'). The lower value of ν_{as}(COO) is due to H-bonding involving the H-atom of the COOH group since methylation of the carboxyl group results in the shift of ν_{as}(COO) to the normal position 1700 cm^{-1} (Fig. 2, 8).

In the carboxylate derivatives of the type $R_3SnL'H$ or $(R_3'SnL')_2SnR_2$, the asymmetric carboxylate stretch is lowered to 1630-35 cm^{-1} (Fig. 6,9-11) organotin carboxylates, which are not polymeric, are known to absorb in this region[20-23]. Organotin aryl azobenzoates which are closely similar to these compounds also absorb in this region. This suggests a similar 5-coordinated structure at the tin atom involving the azo-N-atom[15-18].

A strong absorption at 1235 cm^{-1} in LH which moves to ~ 1245 cm^{-1} in the organotin derivatives of the type R_2SnL_2 can be assigned to the C(aryl)-O [ν_s - O]. An upward shift of this stretching frequency is expected in the organotin compounds because the large polarity of -O-Sn$\leftarrow$ bond[24] increases the conjugative interaction of the oxygen atom with the π-ring resulting in an increase of the C-O bond order.

All organotin derivatives are characterised by a strong band at 1290 - 1310 cm^{-1}.

However, this band can not be assigned to ν_{as}(OCO) as the band is present even in the R_2SnL_2 type compounds which contain no carboxylate group.

Both ν(Sn-O) and ν(Sn-O) are expected to occur in ~400-600 cm^{-1} region[20-23,26]. ν(Sn-O) is probably very weak in these compounds. However, medium to strong intensity bands in 480-500 cm^{-1} are found in R_2SnL_2, $R_2Sn(L'H')_2$, $R_2Sn(LMe)_2$ and $R_2Sn(LSnR'_3)_2$ type compounds. One can, therefore, assign this band to ν(Sn-O) [oxygen of the S-OR group] with reasonable certainty. Another weaker band is also observed at ~440 cm^{-1} in the triorganotin carboxylate derivatives of the type $R_3SnL'H$ and $(R'_3SnL')_2SnR_2$ only.

Presumably, this represents the ν(Sn–OCO) stretch. The appearance of new absorptions in the organotin complexes assignable to ν(Sn–O) confirms the formation of O–Sn bonds.

As most of the spectra were run in nujol mull using KBr optics, the region below 400 cm^{-1}, where ν(N ⟶ Sn) is expected[21,26,27], could not be explored. The electronic spectra of the Organotin derivatives (Chapter – III), however, suggests the formation of complexes through N ⟶ Sn bond.

The characteristics vibrational frequencies in the organotin complexes studied in this work are given in Table – 4 and some typical spectra are shown in Figures.

The important vibrational modes that could be identified with reasonable certainty are given in Table –4.

Table – 4.

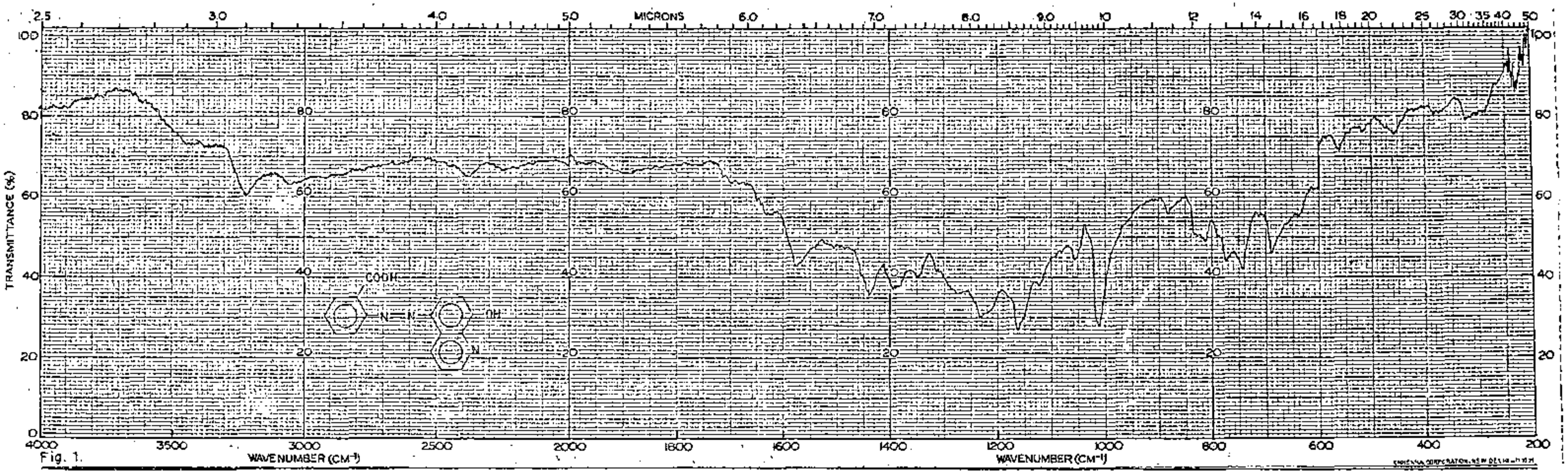
Compound	Frequencies (in cm^{-1}) of [a]			
	$\nu_{as}(COO)$	$\nu^{b}_{Sn-O_{I}}$	$\nu^{c}_{Sn-O_{II}}$	$\nu^{d}_{C(Ar)-O}$
1. Me_2SnL_2		495		1250
2. Bu_2SnL_2		495		1250
3. Oct_2SnL_2		495		1250
4. Ph_2SnL_2		485		1250
5. Ph_3SnL		480		1250
6. $Ph_3SnL'H$	1630		440	1250

Table - 4 (Contd..)

Compound	Frequencies (in cm^{-1}) of [a]			
	ν_{as}(COO)	$\nu^{b}_{Sn-O_{I}}$	$\nu^{c}_{Sn-O_{II}}$	$\nu_{C(Ar)-O}^{d}$
7. $Bu_3SnL'H$	1635			1245
8. $Me_2Sn(L'H')_2$	1720	495		1250
9. $Bu_2Sn(L'H')_2$	1725	495		1250
10. $Oct_2Sn(L'H')_2$	1725	495		1250
11. $Ph_2Sn(L'H')_2$	1725	495		1250
12. $Me_2Sn(L'Me)_2$	1720	495		1255
13. $Bu_2Sn(L'Me)_2$	1720	485		1255
14. $Oct_2Sn(L'Me)_2$	1720	490		1250
15. $Ph_2Sn(L'Me)_2$	1720	490		1250
16. $Ph_2Sn(L'SnPh_3)_2$	1650	490	445	1240
17. $Bu_2Sn(L'SnPh_3)_2$	1630	485	440	1240
18. $Oct_2Sn(L'SnPh_3)_2$	1630	490	445	1245
19. $Me_2Sn(L'SnPh_3)_2$	1630	500	445	1250
20. $Ph_2Sn(L'SnBu_3)_2$	1635	485	440	1245
21. $Bu_2Sn(L'SnBu_3)_2$	1630	500		1245
22. $Oct_2Sn(L'SnBu_3)_2$	1635	490		1245
23. $Ph_3SnL'SnPh_3$	1630	495	445	1245

a) Values may be in error by ± 5 cm^{-1}.
b) Refers to the oxygen atom at 8-position of the quinoline ring.
c) Refers to carboxylate O-atom.
d) Refers to C_8 – O stretch of the quinoline ring.

IR SPECTRA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35
40
50
TRANSMITTANCE (%)
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40
20
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WAVENUMBER (CM⁻¹)
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1400
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OH
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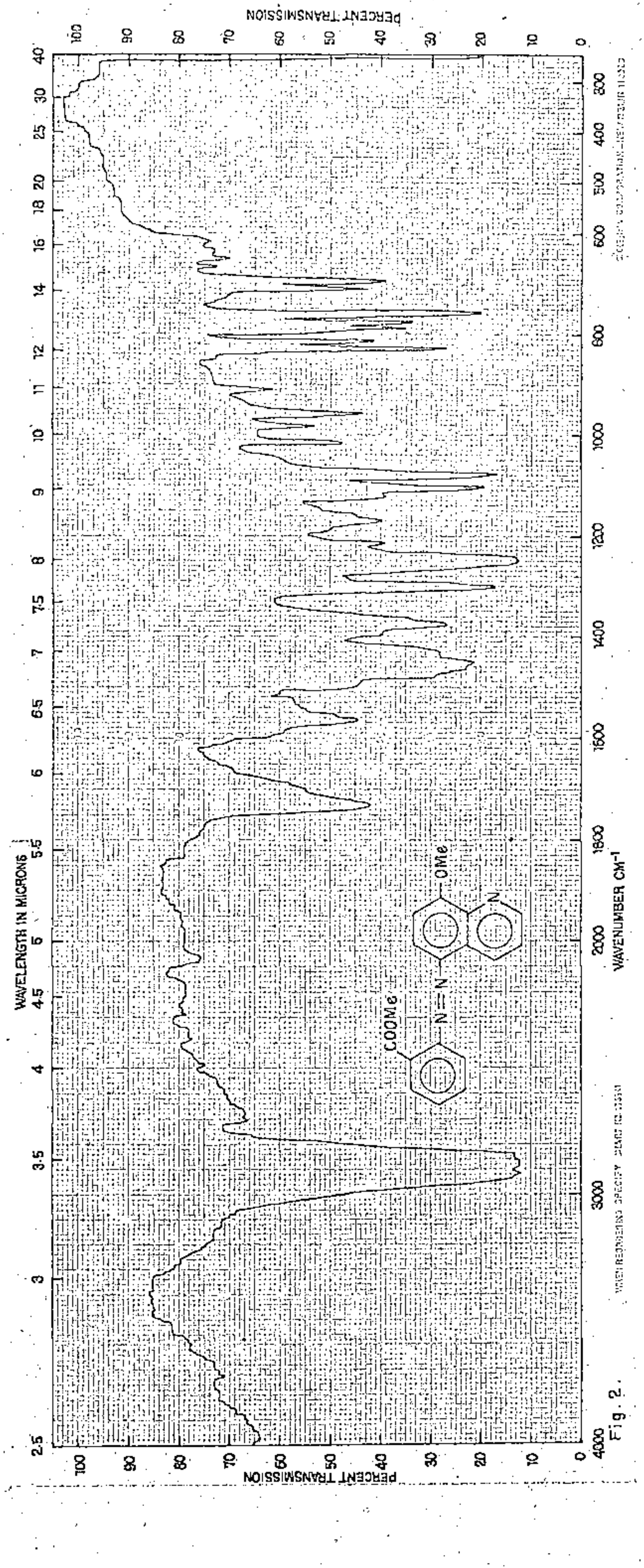
Fig. 1.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18
20
25
30
40
PERCENT TRANSMISSION
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50
40
30
20
10
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300
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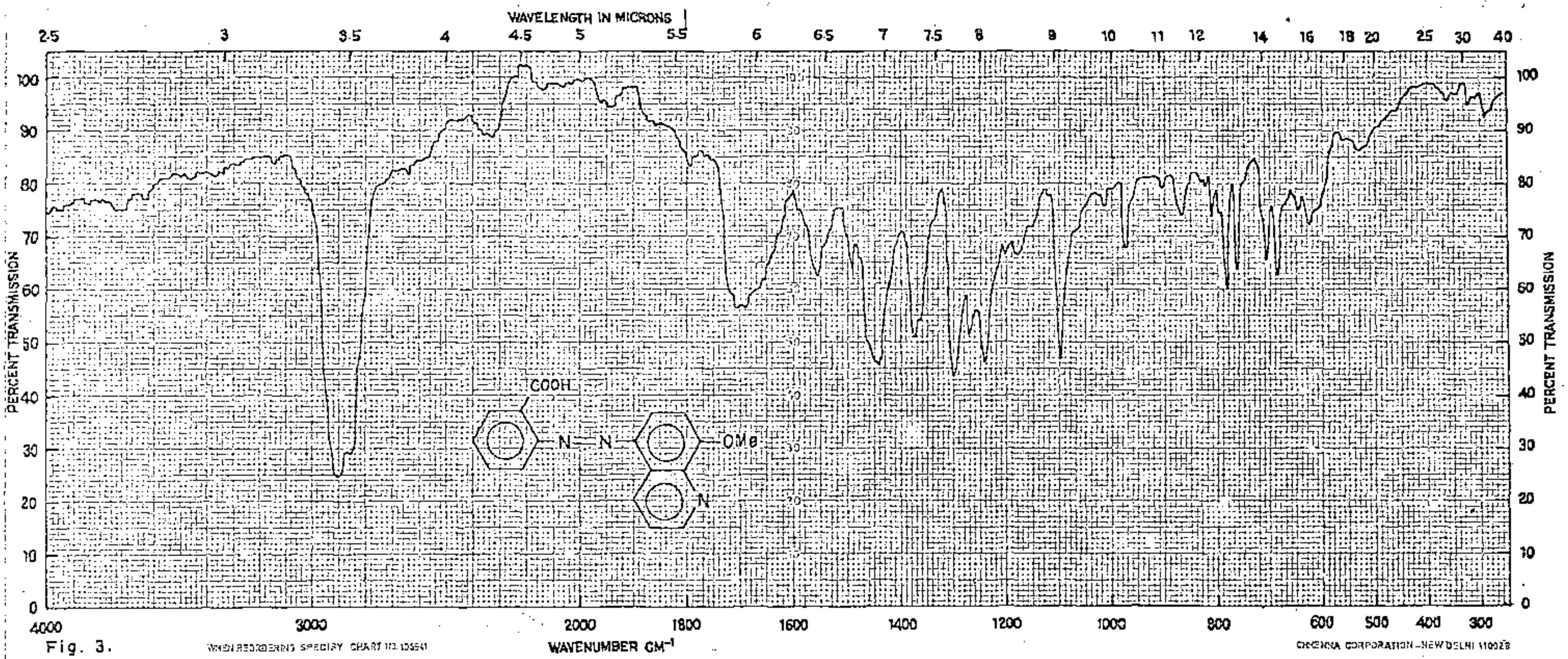
OMe
N

Fig. 2.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14
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18
20
25
30
40
PERCENT TRANSMISSION
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90
80
70
60
50
40
30
20
10
0
4000
3000
2000
1800
1600
1400
1200
1000
800
600
500
400
300
WAVENUMBER CM⁻¹
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N
OMe
N
WHEN REORDERING SPECIFY CHART NO. 105541
CHEMNA CORPORATION—NEW DELHI 110028

Fig. 3.

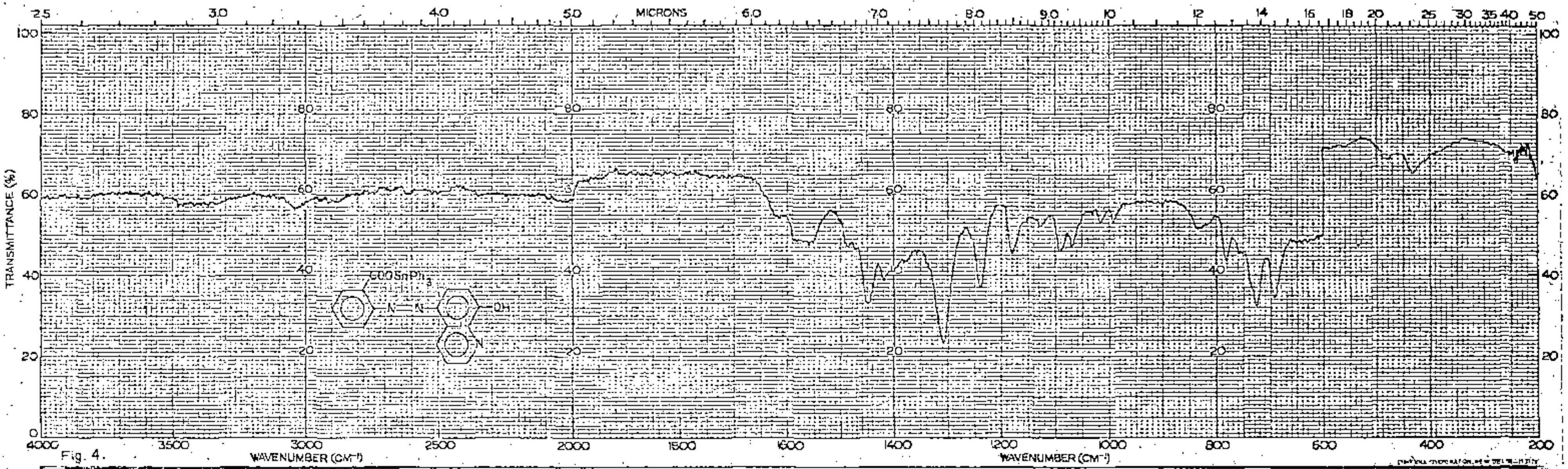
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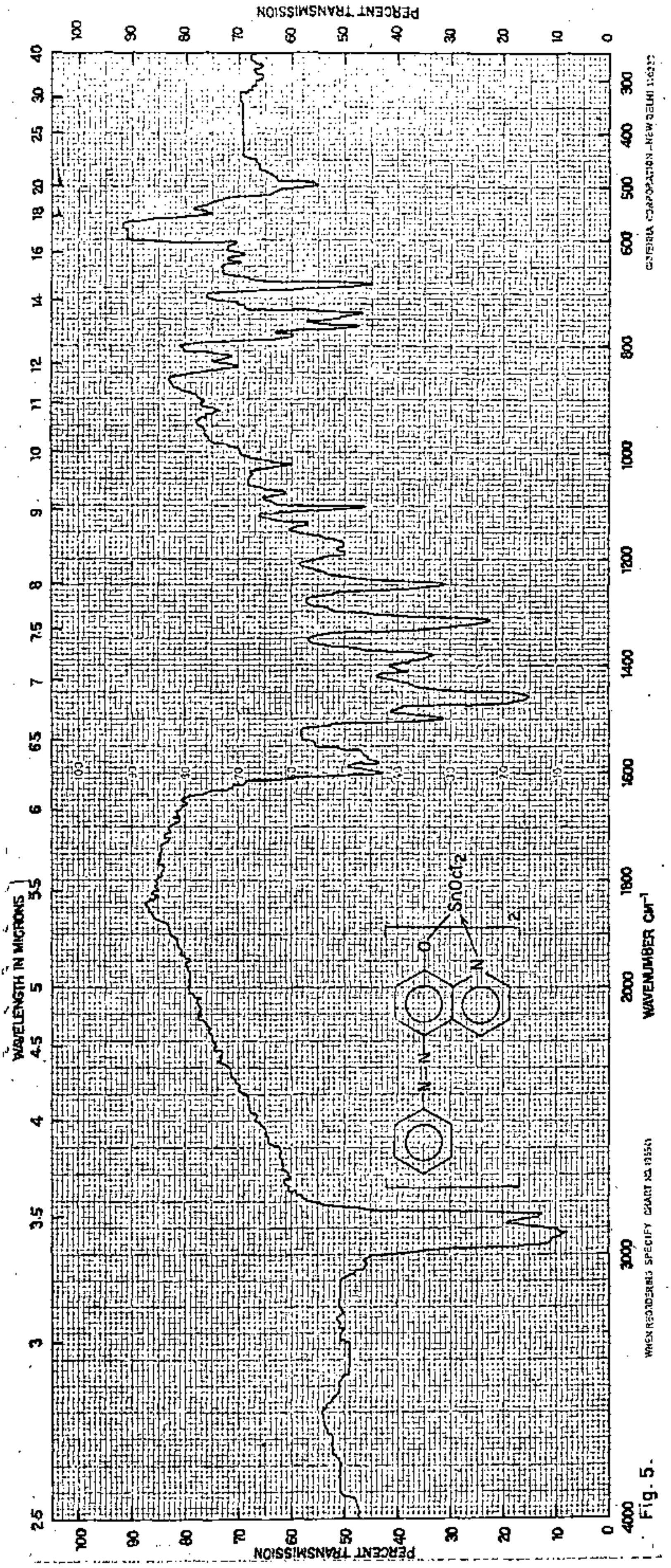
Fig. 4.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30
40
WAVENUMBER CM⁻¹
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300
PERCENT TRANSMISSION
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O
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SnOCl2
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Fig. 5.

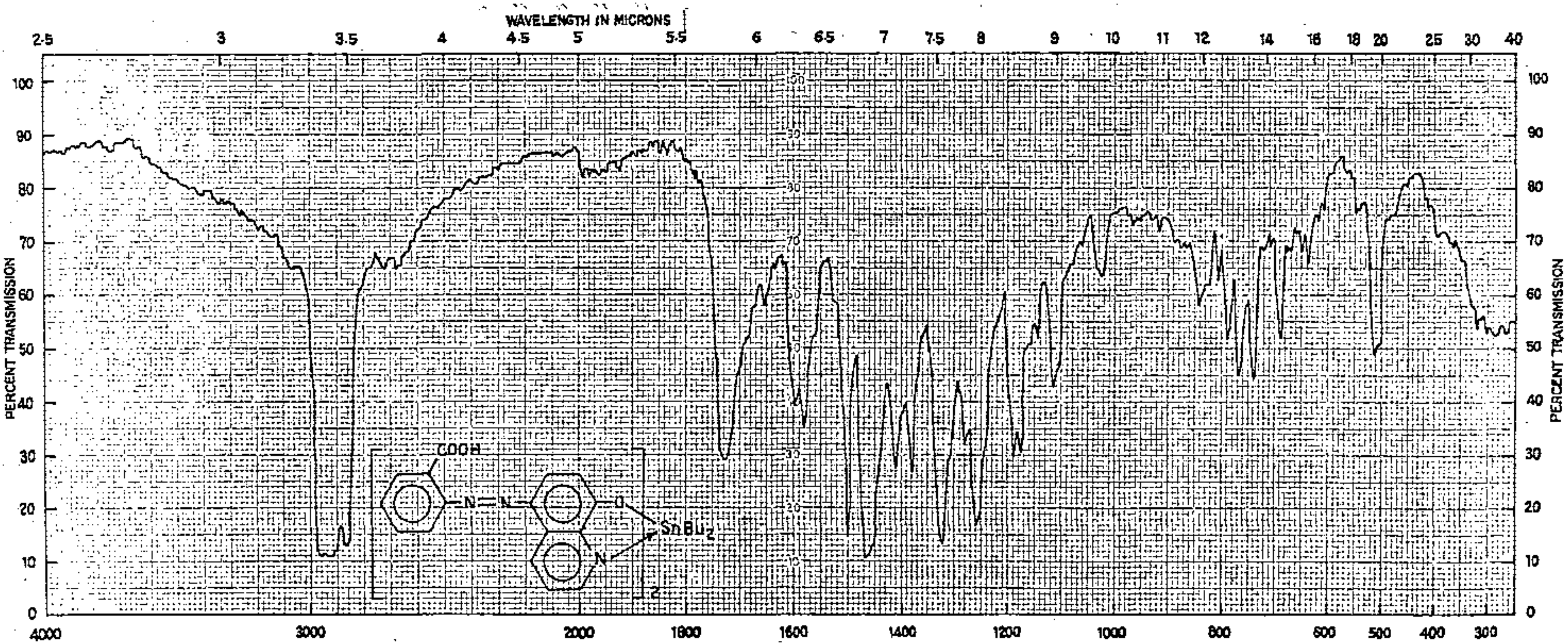
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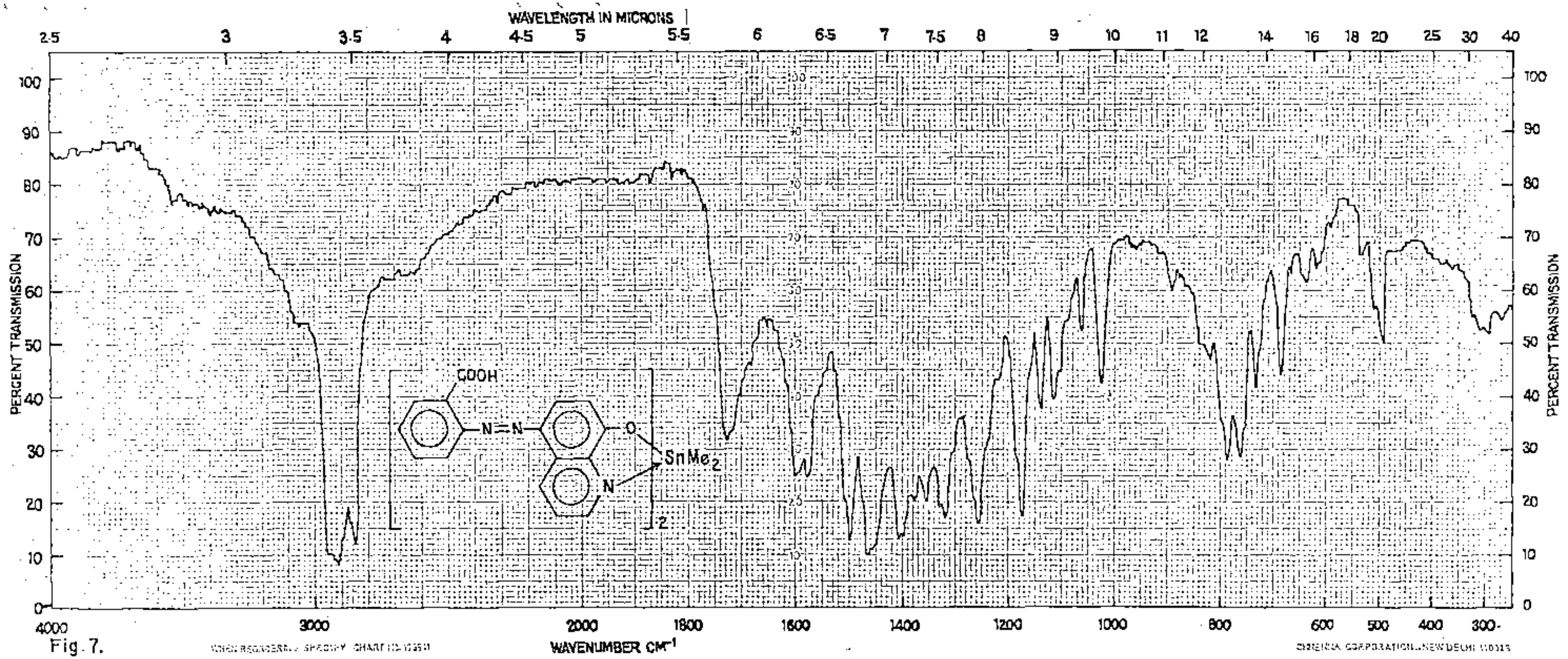
Fig. 6.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18
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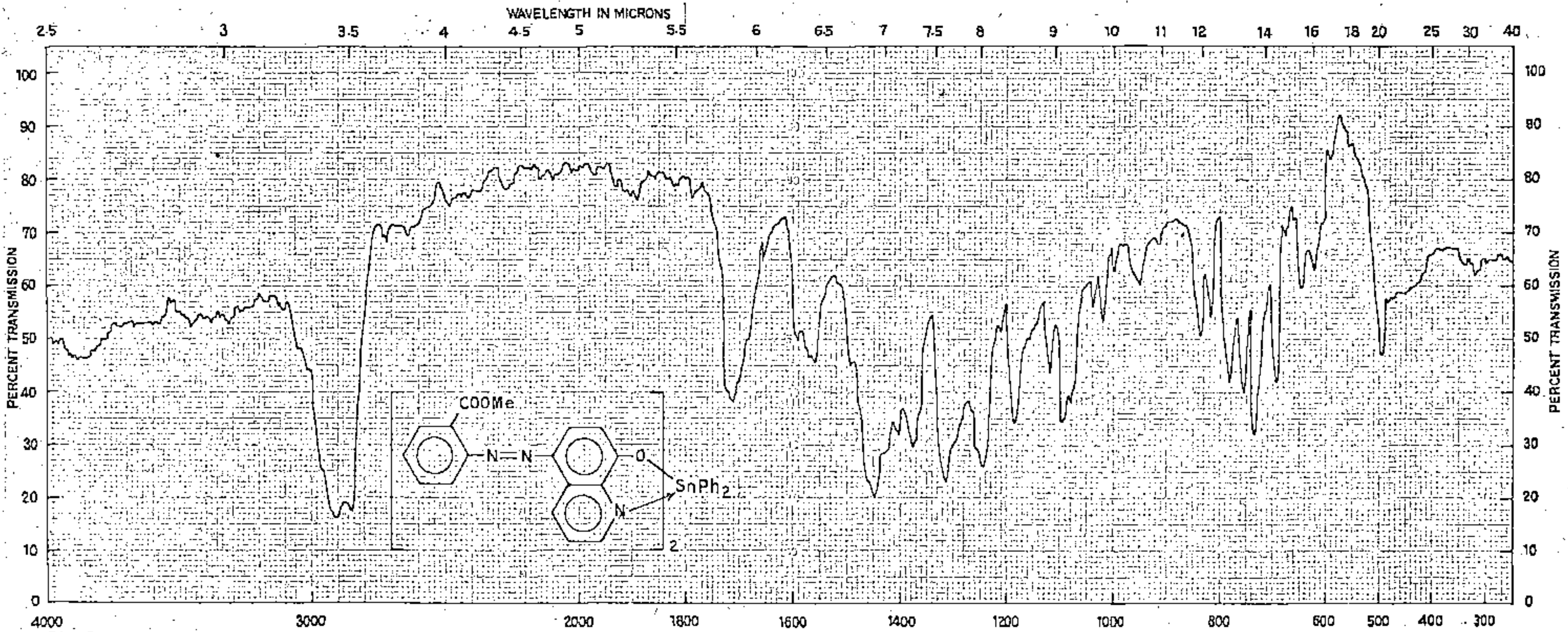
Fig. 7.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18
20
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30
40
PERCENT TRANSMISSION
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N=N
O
SnPh2
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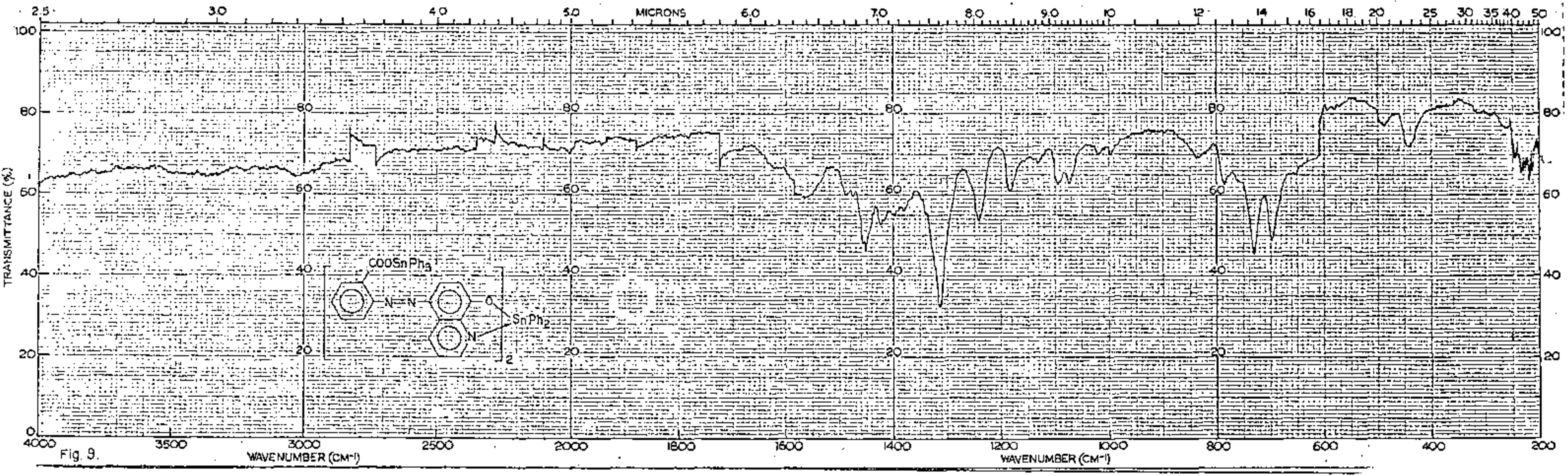
WAVENUMBER CM⁻¹

Fig. 8.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TRANSMITTANCE (%)
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40
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WAVENUMBER (CM⁻¹)
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3000
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2000
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SnPh2
N
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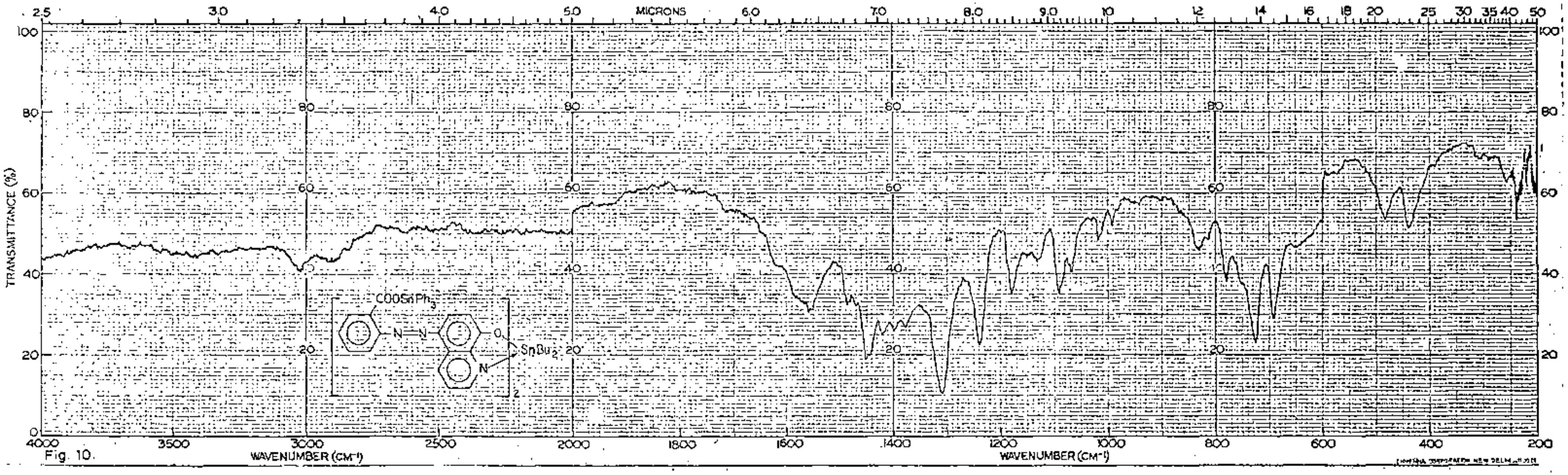
Fig. 9.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TRANSMITTANCE (%)
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60
80
100
WAVENUMBER (CM⁻¹)
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SnBu$_2$
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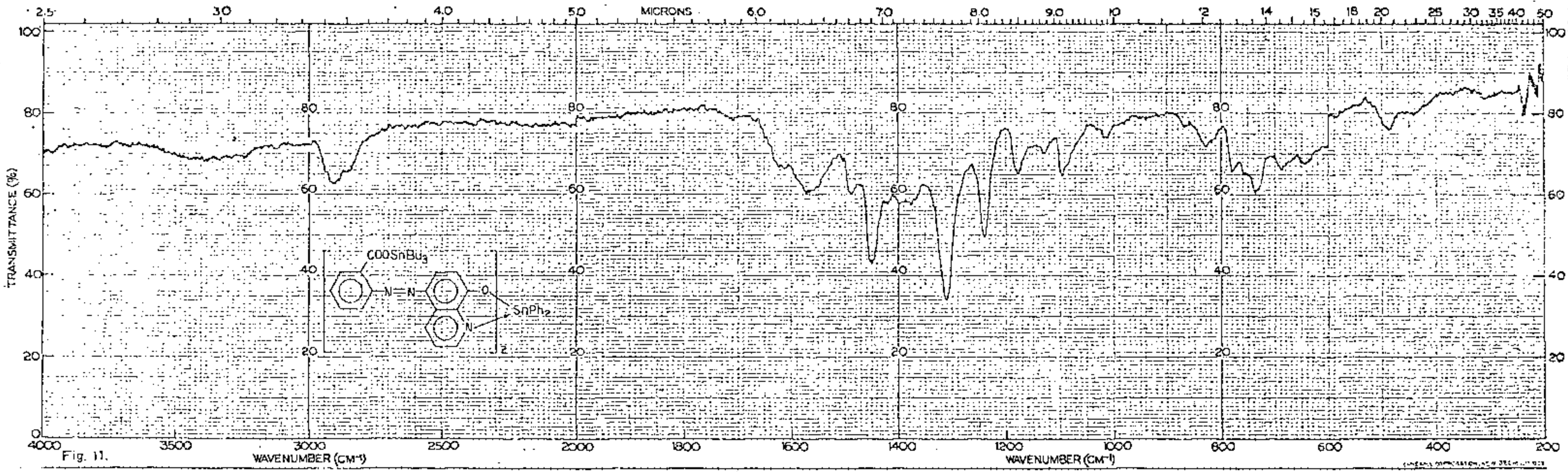
Fig. 10.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20
25
30
35
40
50
TRANSMITTANCE (%)
100
80
60
40
20
0
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
WAVENUMBER (CM⁻¹)
COOSnBu3
N=N
O
SnPh2
N
2

Fig. 11.

III. Experimental

The preparation of the ligands, organotin compounds used for the synthesis of the organotin complexes, are described in this section.

All solvents were purified and dried as described in Vogel[7] unless otherwise stated. Petroleum ether used in the present investigation refers to the fraction with the boiling range 60-80°C. All melting points are uncorrected.

All IR spectra were recorded in Nujol mull/CsI using Beckman IR-20/Perkin Elmer Spectrophotometer.

(i) Preparation of the ligand:

1. Preparation of [L'HH'][5]

5 gm of anthranilic acid was dissolved in a little water with 6-8 ml of concentrated hydrochloric acid, was diazotised with 12 ml of cold 20% sodium nitrite. 5 gm of 8-hydroxy quinoline was dissolved in aqueous 2N sodium hydroxide solution and was cooled to 5°C in an ice bath which was then added to the cold diazonium salt solution with vigorous stirring when a red colour developed. It was kept overnight in a refrigerator followed by 2 hrs. at R.T. and then acidified with conc. hydrochloric acid when a deep red precipitate separated out. It was filtered, washed several times with water, dried in air. Crystallisation from methanol yielded L'HH'.

m.p. : 235°C

Yield : 80%

IR : ν_{as}(COO) 1645 cm^{-1}(broad)

$\frac{m}{e}$ (M^+) : 293

	C	H	N (%)
Analytical data Found:	65.27	3.70	14.32
Calculated for $C_{16}H_{11}O_3N_3$:	65.30	3.74	14.28

2. Preparation of $[LH]^{2-3}$:

5 ml. of concentrated hydrochloric acid was mixed with 3.2 gm of aniline and was dissolved with the addition of 50 gm of ice. Then it was cooled and added 25 ml. of a 20% solution of sodium nitrite. 5 gm of 8-hydroxy quinoline was dissolved in 2N sodium hydroxide and cooled to 5°C in an ice bath which was then added to the cold diazonium salt solution with vigorous stirring. It was kept over night in a refrigerator followed by 2 hrs. at R.T. It was filtered, washed several times with water, dried in air. Crystallisation from methanol yields the desired product.

m.p. : 179°C

Yield : 80%

3. Preparation of [L'MeH]^{8}:

A diazotised solution of methyl anthranilate in aqueous hydrochloric and was added to a stirred cold solution of 8-hydroxyquinoline in methanol. Enough potassium acetate was added to neutralize the hydrochloric acid. The mixture was kept below 5°C for 12 hours after which the mixture was filtered and washed thoroughly with water. Several crystallisations from methanol gave an orange coloured product of the dye.

m.p : 164°C

Yield : 80%

IR $\nu_{as}(COO)$ 1720 cm^{-1}

$\frac{m}{e}$ (M^{+}) : 307

		C	H	N (%)
Analytical data				
Found	:	66.45	4.31	13.50
Calculated for				
$C_{17}H_{13}O_3N_3$	:	66.44	4.23	13.68

4. Preparation of [L'Me$_2$]:

Methylation of L'HH' was done using standard procedure^{7}.

2 gms of L'HH' was dissolved in 5 ml. of methanol and little amount of concentrated sulphuric acid was added. Then the mixture was refluxed for 5 hours. Enough sodium bicarbonate was added to

neutralise the acid. The mixture was extracted with cold benzene, washed several times with water and benzene layer was separated. On evaporation on water bath, a gummy paste was obtained which was extracted with solvent ether. Repeated crystallisations gave the desired orange coloured product.

m.p. : 112°C

Yield : 85%

PMR (δ) : 3.78 ($COOCH_3$), 4.03 (aryl - OCH_3)

IR : ν_{as}(COO) : 1730 cm^{-1}

$\frac{m}{e}$ (M^+) : 321

6. Preparation of [L'MeH']

L'MeH' was prepared by saponification of $L'Me_2$ using standard procedure[7].

1 gm of $L'Me_2$ was dissolved in 30 ml. 10% sodium hydroxide. Then the mixture was refluxed for 1 hour. Acetic acid was added to neutralise the alkali. The mixture was extracted with cold benzene, washed successively with 5% sodium hydroxide and finally with water. To the concentrated benzene solution was added petroleum ether, an orange coloured product separated as a crystal. Product was further purified by repeated crystallisation.

m.p. : 205°C

Yield : 73%

$\frac{m}{e}$ (M^+) : 307

(ii) <u>Source of organotin compounds used for synthesising the organotin complexes:</u>

Triphenyl tin chloride (MERCK - Schuchardt) was used after recrystallisation from petroleum ether, m.p. 105° - 106°C (Lit. m.p. 106°C) and when necessary, triphenyl tin chloride was also prepared from tetraphenyl tin by the reaction of stannic chloride[9].

Bis-(triphenyl tin) oxide (m.p. 122° - 124°C) was prepared by the reaction of triphenyl tin chloride and sodium hydroxide[10]. The product was purified by crystallisation.

Tributyl tin chloride, b.p. 152°C/10 mm (Fluka A.G.) was used without further purification.

Bis-(tributyl tin) oxide, b.p. 210-4°C/10 mm (RIEDEL - DE HAEN AG SEELZE - HANNOVER), Tributyl tin acetate (Fluka A.G.), Dibutyl tin dibromide (Alfa - Division, Ventron Corporation), and Dimethyl tin dichloride (Fluka A.G.) were used without further purification. Diphenyl tin dichloride was prepared by the method of Gilman et al[11] from tetraphenyl tin.

Dioctyl tin dichloride was obtained as a gift from Dr. S. Banerjee of ALA Industry, Bombay, was used without further purification.

(iii) Synthesis of organotin derivatives:

(1) Preparation of $Ph_3SnL'H$:

A mixture of triphenyl tin chloride (2.03 g, 5.2 m. mole) and silver salt of L'HH' (2.1 g, 5.2 m. mole) in 250 ml dry benzene was refluxed for about 25 hours. The reaction mixture was cooled and filtered. To the concentrated filtrate was added petroleum ether when an orange coloured solid separated out which was filtered off and washed with hot petroleum ether. The solid was then washed with 2% sodium bicarbonate solution followed by water to remove any unreacted ligand. The solid was extracted with cold benzene and concentrated by evaporation. On addition of petroleum ether to concentrated solution, orange coloured solid separated. The product was purified by several recrystallisation from benzene-petroleum ether mixture. $Ph_3SnL'H$ was obtained as a bright orange solid. The purified solid was dried in vacuum over calcium chloride.

m.p. : > 300 °C

Yield : 70%

Analytical data		C	H	N	Sn (%)
Found	:	63.85	3.80	6.50	18.62
Calculated for					
$C_{34}H_{25}N_3O_3Sn$	:	63.58	3.89	6.54	18.49

I.R. : $\nu_{as}(COO)$ 1630 cm^{-1}

2. Preparation of $Bu_3SnL'H$:

A mixture of tributyl tin acetate (1.18g, 3.4 m.mole) and L'HH' (1.0g, 3.4 m.mole) were taken in 150 ml dry THF and a few drops of pyridine were added for the neutralisation of acid formed in the reaction. The reaction mixture was stirred for 8 hours at room temperature. The volume was reduced to about 70 ml by distillation, cooled and filtered. On addition of petroleum ether to the concentrated filtrate, a brown coloured product separated which was filtered. The solid was washed with hot petroleum ether, followed by 2% sodium bicarbonate solution to remove unreacted ligand and finally with water. The solid was extracted with cold benzene and concentrated. To the concentrated solution was added petroleum ether, cooled and filtered. The brown coloured product was further purified by recrystallisation from benzene-petroleum ether mixture.

m.p. : 220°C

Yield : 55%

Analytical data		C	H	N	Sn (%)
Found	:	57.73	6.30	8.28	30.12
Calculated for					
$C_{28}H_{37}N_3O_3Sn$	:	57.76	6.56	7.22	20.40

I.R. : $\nu_{as}(OCO)$ 1635 cm^{-1}

3. Preparation of Ph_3SnL :

A mixture of bis-(triphenyl tin) oxide (0.71g, 1.0 m.mole) and LH (0.5g, 2.0 m. mole) in 75 ml dry benzene was refluxed for 20 hours. The solution on hot filtration gave a residue of unreacted ligand. The filtrate was concentrated by evaporation on water bath followed by addition of hot petroleum ether. On cooling, an orange coloured solid was obtained which was extracted with 25 ml of cold and dry benzene. The extract was concentrated, hot petroleum ether was added to reprecipitate the product which was separated and dried in vacuum. The product was purified by recrystallisation from benzene-petroleum ether mixture.

m.p. : 166°C

Yield : 80%

Analytical data:	C	H	N	Sn (%)
Found :	66.20	4.10	7.0	19.80
Calculated for $C_{33}H_{25}N_3O_3Sn$	65.95	4.20	7.1	19.62

4. Preparation of Ph_2SnL_2 :

A mixture of bis-(diphenyl tin) oxide (0.35g, 1.5 m.mole) and LH (0.75g, 3.0 m.mole) in 100 ml dry benzene was refluxed for 20 hours. The reaction mixture was cooled and filtered. The filtrate was concentrated by evaporation and hot petroleum ether was added when a precipitate appeared. On cooling, the orange coloured product was separated by decantation and dried in a vacuum desiccator. This was treated with a little cold and dry benzene and filtered. The filtrate was treated as before when an orange coloured solid was obtained.

m.p. : 143°C (d)

Yield : 80%

Analytical data :	C	H	N	Sn (%)
Found :	65.50	3.90	10.90	15.40
Calculated for $C_{42}H_{30}N_6O_2Sn$:	65.25	3.50	10.95	15.36

5. Preparation of Bu_2SnL_2 :

A mixture of dibutyl tin dibromide (1.03g, 2.6 m.mole) and LH (1.3g, 5.2 m.mole) were taken in 200 ml of dry benzene. To this reaction mixture was added few drops of pyridine for the neutralisation of acid formed in the reaction. This reaction mixture was then refluxed for 25 hours. The volume of the solution was reduced to about 90 ml by evaporation on water bath and filtered. The filtrate was concentrated to about 50 ml followed by addition of hot petroleum ether. On cooling a gummy material was obtained which was separated by decantation. The gummy material was treated with about 25 ml of cold and dry benzene and filtered. The filtrate was concentrated, hot petroleum ether added. The precipitate was separated and dried in vacuum. The brown coloured product was further purified by recrystallisation from benzene-petroleum ether mixture.

Decomposition point: 70°C

Yield : 60%

Analytical data:	<u>C</u>	<u>H</u>	<u>N</u>	<u>Sn</u> (%)
Found :	62.70	4.90	11.60	16.30
Calculated for $C_{32}H_{36}N_6O_2Sn$:	62.69	4.79	12.60	16.22

6. Preparation of Oct_2SnL_2 :

A mixture of dioctyl tin dichloride (1.24g, 3.0 m. mole) and LH (1.6g, 6.0 m. mole) were taken in 250 ml of dry benzene containing a few drops of pyridine and refluxed for 23 hours. The solution was then evaporated almost to dryness. The solid was extracted with cold, dry benzene, boiled for 15 minutes and then allowed to cool and filtered. The filtrate was concentrated, added a little hot petroleum ether, cooled and filtered. The concentrated filtrate afforded a brown coloured solid. The solid product was treated with a little volume of cold and dry benzene and filtered. The product was reprecipitated by adding hot petroleum ether to the cold concentrated solution. The brown coloured product was dried in vacuum. Oct_2SnL_2 was further purified by recrystallisation from benzene-pet ether mixture.

m.p. : 93°C

Yield : 63%

Analytical data:	C	H	N	Sn (%)
Found :	66.60	6.20	9.70	13.70
Calculated for $C_{48}H_{54}N_6O_2Sn$:	66.25	6.35	9.72	13.50

7. Preparation of Me_2SnL_2 :

A mixture of dimethyl tin dichloride (0.36g, 1.6 m.mole) and LH (0.8g, 3.2 m.mole) were taken in 150 ml of dry benzene containing a few drops of pyridine and the mixture was then refluxed for 25 hours. The volume of the solution was reduced to 50 ml by distillation, cooled and filtered. On addition of petroleum ether to the concentrated filtrate, a reddish brown product separated which was filtered off and the filtrate was concentrated. To the hot filtrate was added hot petroleum ether, cooled and filtered. The product was dried, washed several times with hot petroleum ether. It was then boiled with 60 ml of benzene-petroleum ether mixture (20:80) and filtered. The reddish brown coloured product was further purified by repeated crystallisation from benzene-petroleum ether mixture.

M.p. : 187°C

Yield : 65%

Analytical data :	C	H	N	Sn (%)
Found :	59.50	4.0	13.0	18.40
Calculated for $C_{32}H_{26}N_6O_2Sn$:	60.20	3.95	13.20	18.35

8. Preparation of $Ph_2Sn(L'H')_2$:

L'HH' (2.8g, 8.5 m. mole) was extracted by soxhlet in 300 ml Tetrahydrofuran. To the solution of L'HH' was added diphenyl tin dichloride (1.46g, 4.2 m. mole) containing a few drops of pyridine and the mixture was stirred at room temperature for 10 hours. The solvent was distilled off and the residue dried in vacuum, boiled with dry benzene for about 15 minutes and extracted. The benzene extract was concentrated, added petroleum ether, cooled and filtered. The orange coloured solid was boiled with petroleum ether for 10 minutes and filtered. The solid was extracted with cold benzene and concentrated by evaporation. Upon addition of petroleum ether a bright orange coloured solid separated which was purified by recrystallisation from benzene-petroleum ether. The solid was dried in vacuum over calcium chloride.

Decomposition point : 259°C

Yield : 45%

Analytical data:	C	H	N	Sn (%)
Found :	60.92	3.52	9.72	13.90
Calculated for				
$C_{44}H_{30}N_6O_6Sn$:	61.63	3.60	9.80	13.85

I.R. : ν_{as}(COO) 1725 cm^{-1}

9. Preparation of $Bu_2Sn(L'H')_2$:

L'HH' (2.5g, 8.5 m. mole) was extracted by soxhlet in 300 ml tetrahydrofuran. To the solution of L'HH' was added dibutyl tin dibromide (1.67g, 4.3 m. mole) and a few drops of pyridine. The mixture was stirred at room temperature for 15 hours, tetrahydrofuran was distilled off and the residue was dried in vacuum. The solid obtained was dissolved in dry benzene and filtered. The filtrate was concentrated, hot petroleum ether added, allowed to cool and the precipitate A, reddish brown powder (m.p. 159-160°C) was separated by filtration. The filtrate was concentrated, hot petroleum ether was added and cooled when a gummy material was obtained. This, on trituration with petroleum ether, gave a product B; (m.p. 157-158°C). Both the product (A and B) were dissolved in boiling benzene, concentrated, hot petroleum ether added, cooled and filtered. The solid obtained was washed with hot petroleum ether by boiling. The solid was then extracted with cold benzene and concentrated and petroleum ether was added when a reddish brown product separated. The product was purified by recrystallisation from benzene-pet. ether mixture and dried in vacuum.

m.p. : 165°C

Yield : 25%

Analytical data :	C	H	N	Sn (%)
Found :	58.75	4.60	10.18	14.70
Calculated for $C_{40}H_{36}N_6O_6Sn$:	58.77	4.65	10.28	14.53

IR : $\nu_{as}(COO)$ 1725 cm^{-1}

10. Preparation of $Oct_2Sn(L'H')_2$:

L'HH' (2.5 g, 8.5 m. mole) was extracted by soxhlet in 300 ml THF. To this solution was added (1.75g, 4.3 m. mole) dioctyl tin dichloride and few drops of pyridine. The reaction mixture was stirred at room temperature for about 10 hours. THF was then distilled off. The residue was washed with hot petroleum ether and extracted with cold benzene. Addition of petroleum ether to the concentrated solution furnished a brick red coloured solid which was recrystallised several times from benzene-petroleum ether mixture and dried in vacuum.

m.p. : 144°C

Yield : 35%

Analytical data:	C	H	N	Sn (%)
Found :	61.95	6.02	9.15	12.50
Calculated for				
$C_{48}H_{54}N_6O_6Sn$:	62.02	5.81	9.04	12.78

IR : $\nu_{as}(COO)$ 1725 cm^{-1}

11. Preparation of $Me_2Sn(L'H')_2$:

L'HH' (2.5g, 8.5 m. mole) was extracted by soxhlet in about 350 ml THF. To the solution was added dimethyl tin dichloride (0.94g, 4.2 m. mole) and few drops of pyridine. The reaction mixture was stirred at room temperature for 10 hours. THF was then distilled off, the solid washed with hot petroleum ether and extracted with cold benzene. On addition of petroleum ether to the concentrated solution a red coloured solid, m.p. 166°C separated which after several recrystallisation from benzene-petroleum ether mixture afforded the desired product.

m.p. : 169°C

Yield : 40%

Analytical data:	C	H	N	Sn (%)
Found :	56.01	3.50	11.50	16.25
Calculated for				
$C_{34}H_{26}N_6O_6Sn$:	55.68	3.54	11.46	16.20

IR : $\nu_{as}(COO)$ 1730 cm^{-1}

12. Preparation of $Ph_2Sn(L'Me)_2$:

A mixture of L'MeH (1.3g, 4.2 m. mole), diphenyl tin dichloride (0.73g, 2.1 m. mole) and few drops of pyridine in 150 ml dry-benzene was refluxed for 10 hours, cooled and filtered off. To the concentrated filtrate was added petroleum ether, when a solid separated out. The solid was filtered, washed successively with hot petroleum ether, 2% sodium bicarbonate solution and finally with water. The residue was extracted with cold benzene and concentrated. On addition of petroleum ether, an orange product separated. The product was purified by recrystallisation from benzene-petroleum ether mixture and dried in vacuum.

m.p. : 179°C

Yield : 55%

Analytical data :	C	H	N	Sn (%)
Found :	62.42	3.90	9.36	13.89
Calculated for $C_{46}H_{34}N_6O_6Sn$:	62.39	3.84	9.49	13.41

IR : ν_{as}(COO) 1720 cm^{-1}

13. Preparation of $Bu_2Sn(L'Me)_2$:

A mixture of L'MeH (1.3g, 4.2 m. mole), dibutyl tin dibromide (0.83g, 2.1 m. mole) were taken in 150 ml dry benzene containing a few drops of pyridine. The reaction mixture was refluxed for 10 hours, cooled and filtered. Addition of petroleum ether to the concentrated filtrate yielded the crude product which was filtered, washed with hot petroleum ether, 2% sodium-bicarbonate solution and finally with water. The product was extracted with cold benzene and concentrated. To this solution was added petroleum ether, the brown coloured product was separated and crystallised from benzene and petroleum-ether.

m.p. : 174°C

Yield : 45%

Analytical data :	<u>C</u>	<u>H</u>	<u>N</u>	<u>Sn</u> (%)
Found :	59.80	4.82	10.1	14.12
Calculated for :				
$C_{42}H_{42}N_6O_6Sn$:	59.66	4.97	9.94	14.05

IR : ν_{as}(COO) : 1720 cm^{-1}

14. Preparation of $Oct_2Sn(L'Me)_2$:

A mixture of L'MeH (1.3g, 4.2 m. mole) and dioctyl tin dichloride (0.87g, 2.1 m. mole) were taken in 200 ml dry benzene containing a few drops of pyridine. The mixture was refluxed for 10 hours, cooled and filtered. Addition of petroleum ether to the concentrated filtrate yielded the crude product which was filtered, washed with hot petroleum ether. The product was then washed with aqueous 2% sodium bicarbonate and finally with water to remove unreacted ligand. The brown coloured compound was then extracted with cold benzene, concentrated and reprecipitate by adding petroleum-ether. The process was repeated several times.

m.p. : 178°C

Yield : 50%

Analytical data:	C	H	N	Sn (%)
Found :	63.57	6.10	7.97	12.34
Calculated for				
$C_{50}H_{58}N_6O_6Sn$:	62.71	6.06	8.78	12.40

IR : $\nu_{as}(C=O)$: 1720 cm^{-1}

15. Preparation of $Me_2Sn(L'Me)_2$:

A mixture of L'MeH (1.3g, 4.2 m. mole), dimethyl tin dichloride (0.47g, 2.1 m. mole) and few drops of pyridine in 175 ml dry benzene was refluxed for 10 hours and the residue was filtered off. To the concentrated filtrate was added petroleum ether when a solid separated which was filtered, washed successively with hot petroleum ether, 2% sodium bicarbonate solution and finally with water. The solid was extracted with cold benzene and concentrated. On addition of petroleum ether a brown coloured product separated. The product was purified by repeated crystallisation from benzene-petroleum ether mixture.

m.p. : 175°C

Yield : 60%

Analytical data:	C	H	N	Sn (%)
Found :	57.10	3.80	10.73	15.96
Calculated for $C_{36}H_{30}N_{6}O_{6}Sn$:	56.78	3.94	11.04	15.60

IR : ν_{as} (COO) : 1720 cm^{-1}

16. Preparation of $Ph_2Sn(L'SnPh_3)_2$:

A. To a suspension of the silver salt of $Ph_2Sn(L'H')_2$ (0.5g, 0.47 m. mole) in 100 ml of dry benzene was added (0.350g, 0.91 m. mole) of triphenyl tin chloride and the mixture was refluxed for 20 hours. Benzene was distilled off to about 50 ml and filtered. To the concentrated solution was added petroleum ether, cooled and filtered. The solid was extracted with cold and dry benzene and filtered. The filtrate was further concentrated, added a little petroleum ether, cooled and filtered. The product was purified by recrystallisation from benzene-petroleum ether mixture. The orange product was dried in vacuum.

m.p. : > 300°C

Yield : 30%

B. To a solution of (0.3g, 0.78 m. mole) of $Ph_3SnL'H$ in 100 ml of dry benzene was added (0.134g, 0.39 m. mole) of diphenyl tin dichloride and a few drops of pyridine for the neutralisation of acid formed in the reaction. The reaction mixture was then stirred for about 10 hours at room temperature. Benzene was distilled off to about 50 ml, cooled and filtered. To the concentrated filtrate was added hot petroleum ether, cooled and filtered. The product was separated by filtration and washed with hot petroleum ether, 2% aq. solution of sodium bicarbonate and finally with water to remove unreacted $Ph_2Sn(L'H')_2$. Then the solid was extracted with cold dry benzene and filtered. The filtrate was concentrated, added petroleum ether when an orange coloured solid separated. The orange product was purified by repeated crystallisation from benzene-petroleum ether mixture and dried in vacuum.

m.p.	: $>300^{\circ}$C
Yield	: 32%

C. A mixture of $Ph_2Sn(L'H')_2$ (1.0g, 1.1 m. mole) and bis-(triphenyl tin) oxide (0.83g, 1.1 m. mole) in 200 ml of dry benzene was refluxed for 15 hours. Then the reaction mixture was concentrated on water bath and filtered. To the concentrated filtrate was added petroleum ether. The orange coloured precipitate was filtered, washed successively with hot petroleum ether, 2% aq. solution of sodium bicarbonate and finally with water to remove unreacted $Ph_2Sn(L'H')_2$. The residue was extracted with cold, dry benzene and concentrated. The concentrated filtrate was treated as before. The orange solid was further purified by recrystallisation from benzene-petroleum ether mixture and dried.

m.p. : >300°C

Yield : 65%

Analytical data :	C	H	N	Sn (%)
Found :	61.70	3.70	5.39	22.30
Calculated for $C_{80}H_{58}N_6O_6Sn_3$:	61.77	3.73	5.40	22.91

IR : $\nu_{as}(OCO)$: 1630 cm^{-1}.

17. Preparation of $Bu_2Sn(L'SnPh_3)_2$:

A mixture of $Bu_2Sn(L'H')_2$ (1.0g, 1.2 m.mole) and bis-(triphenyl tin) oxide (0.83g, 1.2 m. mole) in about 250 ml dry benzene was refluxed for 26 hours, cooled and filtered. Addition of petroleum ether to the concentrated filtrate yielded the crude product which was filtered, washed with hot petroleum ether. The product was further purified by washing with 2% sodium-bicarbonate solution and finally with water. The product was purified by repeated crystallisation from benzene-petroleum ether mixture.

Decomposition point : 211°C

Yield : 40%

Analytical data:	<u>C</u>	<u>H</u>	<u>N</u>	<u>Sn</u> (%)
Found :	60.70	3.19	5.72	23.63
Calculated for				
$C_{76}H_{57}N_6O_6Sn_3$:	60.59	3.78	5.58	23.65

IR : ν_{as} (COO) : 1630 cm^{-1}

18. <u>Preparation of $Cot_2Sn(L'SnPh_3)_2$:</u>

A mixture of $Cot_2Sn(L'H')_2$ (1.0g, 1.0 m. mole) and bis-(triphenyl tin) oxide (0.77g, 1.0 m. mole) in 200 ml dry benzene was refluxed for 20 hours, cooled and filtered. Addition of petroleum ether to the concentrated filtrate yielded the crude product which was filtered and washed successively with hot petroleum ether, 2% sodium bicarbonate solution and water. The solid was extracted with cold benzene and the solution was concentrated. On addition of petroleum ether to the concentrated benzene solution, an orange coloured solid separated which after several recrystallisation from benzene-petroleum ether mixture afforded the pure product. The solid was dried in vacuum.

Decomposition point : 185°C

Yield : 40%

Analytical data:	<u>C</u>	<u>H</u>	<u>N</u>	<u>Sn</u> (%)
Found :	62.50	5.25	6.30	21.89
Calculated for				
$C_{84}H_{82}N_6O_6Sn_3$:	61.98	5.04	5.16	21.90

IR : ν_{as}(COO) : 1630 cm^{-1}

19. Preparation of $Me_2Sn(L'SnPh_3)_2$:

A mixture of $Me_2Sn(L'H')_2$ (1.0g, 1.4 m. mole) and bis-(triphenyl tin) oxide (0.98g, 1.4 m. mole) in 300 ml dry benzene was refluxed for 15 hours, cooled and filtered. The filtrate was concentrated to about 75 ml, and pet. ether was added when the crude product m.p. 173°C separated. The product was filtered and washed successively with 2% sodium bicarbonate solution, and water. The reddish orange solid was purified by repeated crystallization from benzene-petroleum ether mixture.

m.p. : 175°C

Yield : 50%

Analytical data:	<u>C</u>	<u>H</u>	<u>N</u>	<u>Sn</u> (%)
Found :	57.95	3.50	5.62	25.10
Calculated for				
$C_{70}H_{54}N_6O_6Sn_3$:	58.73	3.77	5.87	24.9

IR : $\nu_{as}(COO)$ 1630 cm^{-1}

20. Preparation of $Ph_2Sn(L'SnBu_3)_2$:

A mixture of $Ph_2Sn(L'H')_2$ (1.0g, 1.1 m. mole) and bis-(tributyl tin) oxide (0.7g, 1.2 m. mole) in 300 ml dry benzene was refluxed for 25 hours, cooled and filtered and concentrated. Addition of petroleum ether to the concentrated filtrate yielded the crude product, which was filtered, washed successively with hot petroleum ether, 2% sodium bicarbonate solution and water. The orange solid was extracted with cold benzene and the filtrate was treated as before. The product was further purified by crystallisation from benzene-petroleum ether mixture.

m.p.	: 242°C				
Yield	: 30%				
Analytical data:		<u>C</u>	<u>H</u>	<u>N</u>	<u>Sn</u> (%)
Found	:	57.25	5.60	6.12	24.92
Calculated for					
$C_{63}H_{82}N_6O_6Sn_3$:		56.89	5.71	5.95	24.83
IR	:	$\nu_{as}(COO)$ 1635 cm^{-1}			

21. <u>Preparation of $Bu_2Sn(L'SnBu_3)_2$:</u>

A mixture of $Bu_2Sn(L'H')_2$ (1.0g, 1.2 m. mole) and bis-(tributyl tin) oxide (0.73g, 1.2 m. mole) in 300 ml dry benzene was refluxed for 30 hours, cooled and filtered. Addition of petroleum ether to the concentrated filtrate yielded a product m.p. – 160°C, which was filtered and washed successively with hot petroleum ether, 2% sodium bicarbonate solution and water. The product was then purified by recrystallisation from benzene-petroleum ether mixture. The product was obtained as orange coloured crystals.

m.p. : 162°C

Yield : 30%

Analytical data:	C	H	N	Sn (%)
Found :	54.80	6.62	6.22	25.79
Calculated for $C_{64}H_{90}N_6O_6Sn_3$:	55.08	6.45	6.02	25.54

IR : $\nu_{as}(COO)$ 1630 cm^{-1}

22. Preparation of $Oct_2Sn(L'SnBu_3)_2$:

A mixture of $Oct_2Sn(L'H')_2$ (1.0g, 1.0 m. mole) and bis-(tributyl tin) oxide (0.64g, 1.0 m. mole) in 250 ml dry benzene was refluxed for 23 hours, cooled and filtered. Addition of petroleum ether to the concentrated filtrate yielded the crude product which was filtered and washed with hot petroleum ether, 2% sodium bicarbonate solution and finally with water. The orange coloured product was then purified by repeated crystallisation from benzene-petroleum ether mixture.

m.p. : 182°C

Yield : 40%

Analytical data:	C	H	N	Sn (%)
Found :	56.92	6.96	5.50	24.10
Calculated for $C_{72}H_{106}N_6O_6Sn_3$:	57.36	7.03	5.57	23.64

IR : $\nu_{as}(COO)$ 1635 cm^{-1}

23. Preparation of $Ph_3SnL'SnPh_3$:

A mixture of L'HH' (1.5g, 5.1 m. mole) and bis-(triphenyl tin) oxide (3.7g, 5.2 m. mole) in 500 ml dry benzene was refluxed for 25 hours. The reaction mixture was cooled and filtered. The filtrate was concentrated, petroleum ether added when the crude product, m.p. 178°C separated. This was filtered, washed with hot petroleum ether, 2% sodium bicarbonate solution, and finally with water to remove unreacted L'HH'. The orange product was extracted with cold dry benzene and concentrated. Filtrate was treated as before. The product was purified by crystallisation from benzene-petroleum ether mixture. The orange crystals of triphenyl tin derivatives was dried in vacuum.

m.p. : 180°C

Yield : 70%

Analytical data:	C	H	N	Sn (%)
Found :	62.50	3.92	4.10	24.15
Calculated for $C_{52}H_{39}N_3O_5Sn_2$:	63.0	3.90	4.24	23.97

IR : ν_{as} (OCO) 1630 cm^{-1}.

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CHAPTER - III

ABSORPTION SPECTRA AND STRUCTURES OF THE ORGANOTIN COMPLEXES OF 5-ARYLAZO-8-QUINOLINOLS:

IIIA. INTRODUCTION

IIIB. NATURE OF ELECTRONIC TRANSITIONS IN AZOXINES AND ITS DERIVATIVES

IIIC. RESULT AND DISCUSSION

IIID. EXPERIMENTAL

BIBLIOGRAPHY

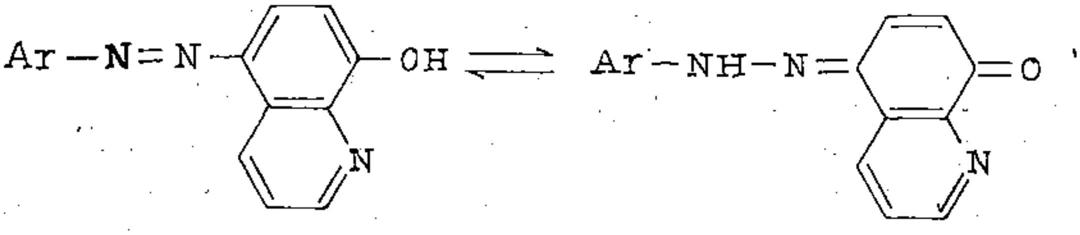
IIIA. Introduction

The electronic spectra of azobenzene and related compounds have been studied extensively by several workers[1-14] and have been interpreted in terms of molecular orbital discussion[15-16]. On the basis of these studies, the absorption bands in the UV-Visible region, which are generally, three to four in number may be divided into two types. The longest wave length, weak to moderate intensity band in azobenzene and related compounds ($\epsilon_{max} \approx 10^2-10^3$), is ascribed to the $n-\pi^*$ transition and the other more intense absorption bands ($\epsilon_{max} \approx 10^4$) are ascribed to $\pi-\pi^*$ transitions. While the position of the first $\pi-\pi^*$ band varies considerably from compound to compound, the position of the $n-\pi^*$ band is almost unaffected by the aryl groups and occurs at about 440-460 nm. MO treatment of the azobenzene[1,2] shows that the upper MO for the first $n-\pi^*$ as well as that for longest wave length $\pi-\pi^*$ transitions is the perturbed orbital originating from the antibonding π-orbital of the azo group and its energy is not very much affected by the nature of the aryl groups. The lower orbital of the first $\pi-\pi^*$ transition is the orbital arising from the perturbation of the highest bonding π-orbitals of the aryl groups and hence its energy largely depends on the aryl groups. On the other hand, the lower orbital of the $n-\pi^*$ transition being a non bonding orbital of the azo group, its energy is unaffected by the aryl groups.

Substituents like $-NH_2$, $-NMe_2$, $-OH$, $-COOH$ etc. which are capable of producing large bathochromic shift of the $\pi-\pi^*$

transitions by extending the conjugation, may often shift the first π-π^* band in the azo compounds to such an extent that the characteristic n-π^* absorption is masked by the strong absorption. Thus, in methyl red which contains -COOH and -NMe$_2$ groups in 2 and 4 positions respectively, no weak absorption band could be observed in the 440-60 nm region due to the presence of strong π-π^* absorption in this region[6]. Almost all the 5-Arylazo-8-quinolinols and their derivatives investigated in the present work belong to this category and no separate band due to n-π^* transition could be observed in these compound.

In the absence of specific solvent solute interactions the electronic absorption spectra of the azo compounds do not show any strong solvent dependence apart from a small red shift of both the π-π^* and n-π^* bands[1-17]. However, the presence of -OH group in the ortho or para-position relative to the azo group often leads to a strong solvent dependent absorption spectrum due to the possibility of: (a) hydrogen bond formation by the phenolic -OH and/or (b) Azo-hydrazone tautomerism, as shown below(I).



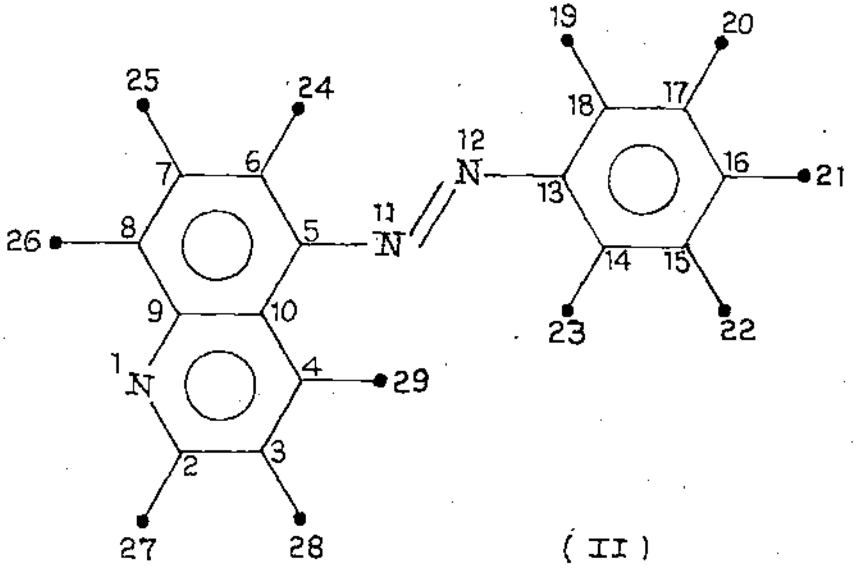
(I)

The azo-hydrazone tautomerism in hydroxy azo derivatives has been studied in great detail by several workers[3,7,9,10,18] because of its importance in determining the observed colour of azo dyes.

Although the azoxines, particularly 5-aryl azo-8-quinolinols are known for a long time[19-21] (Chapter IB), the electronic absorption spectra of this class of azo-dyes have not been studied in detail. Neither their metal complexes were subjected to such investigation. Organotin 5-phenyl azo-8-quinolinolates have only recently been prepared[22], but the authors studied their Mossbauer spectra only.

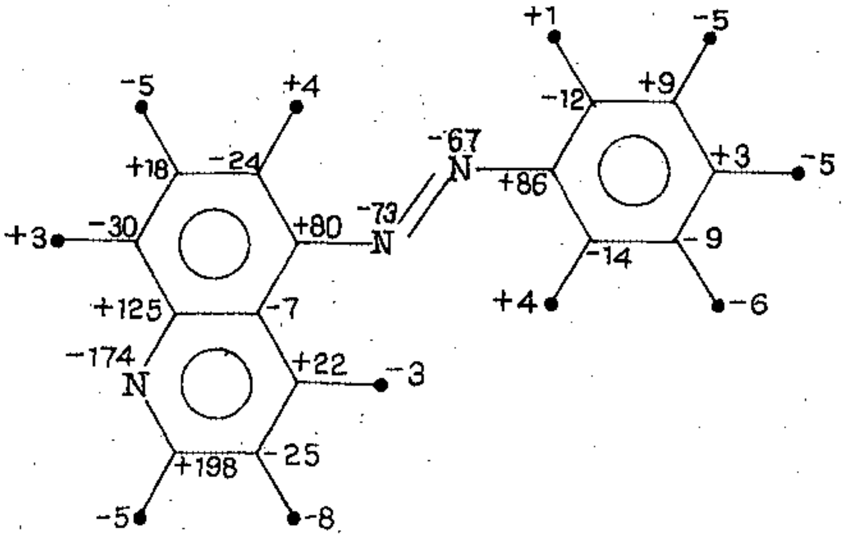
IIIB. Nature of electronic transitions in Azoxines and its derivatives:

In order to have a better understanding of the observed electronic spectra of the azoxine derivatives, we have a CNDO/2 type calculation[32-36] on molecule (II) which may be regarded as the parent molecule from which our ligands LH, L'HH' and their derivatives can be obtained by substitution at appropriate positions.



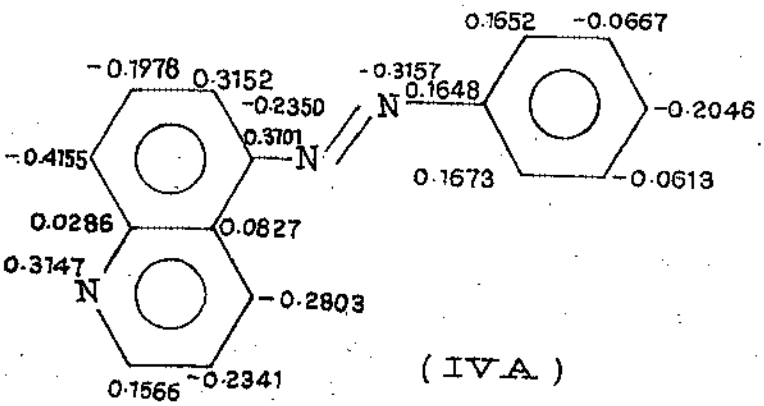
(II)

Of the 83 Molecular orbitals obtained by linear combination of the valence atomic orbitals of the atoms, 18 are of π-type. The highest occupied orbital is a π-type orbital; the lowest unoccupied one is also of the same type showing that the longest wave length intense transition in the azoxines are indeed a π-π* transition. The energy diagram of the π-type MO's are shown in Fig. 1 . The net atomic charges (σ+π) on the atoms are shown in (III) while the AO co-efficients of the highest occupied orbital (HOMO) and the lowest unoccupied orbital (LUMO) are shown in (IVA) and (IVB).



Net atomic charges (in units of 10^{-3} electron)

(III)



(IV.A.)

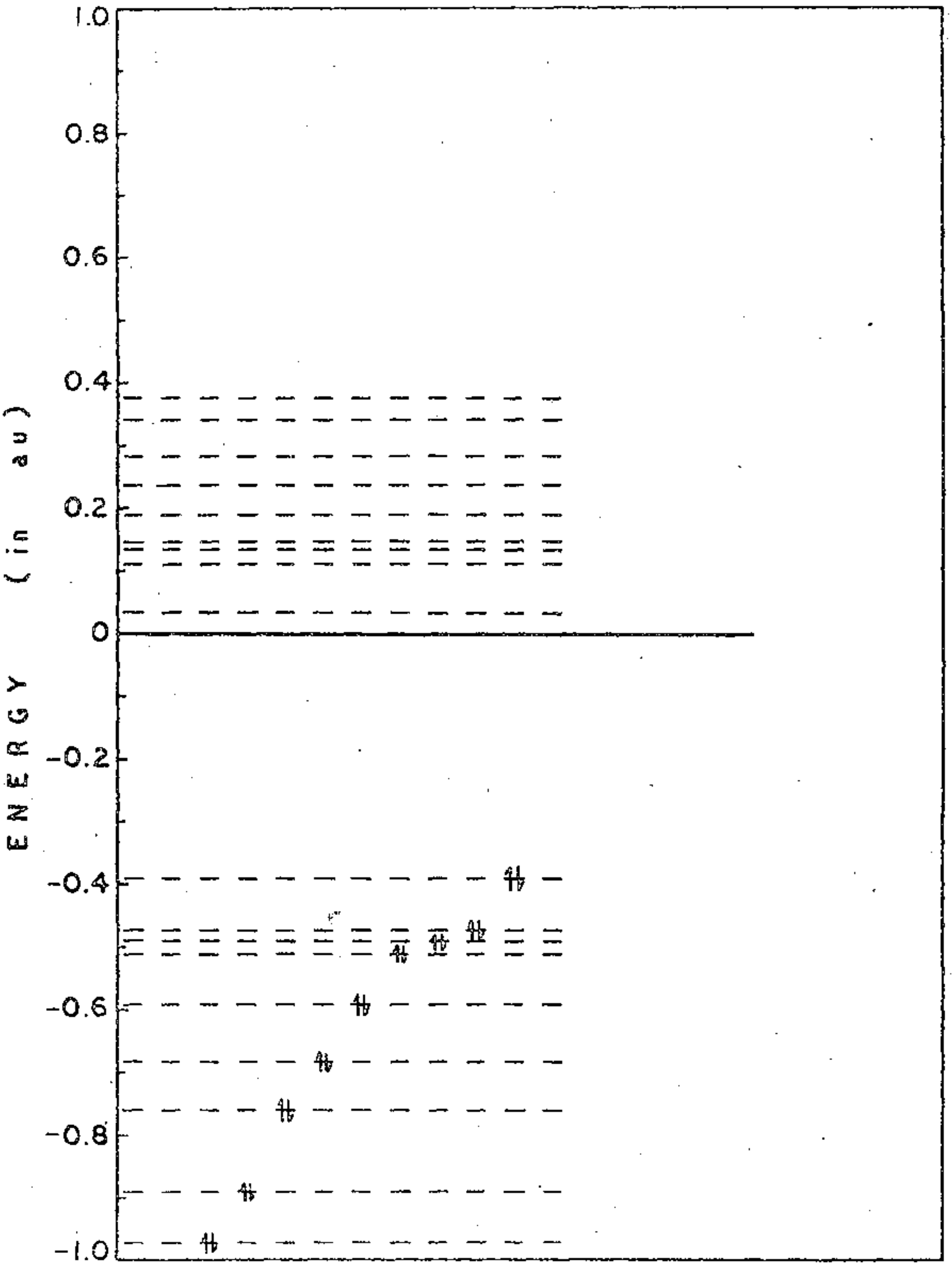
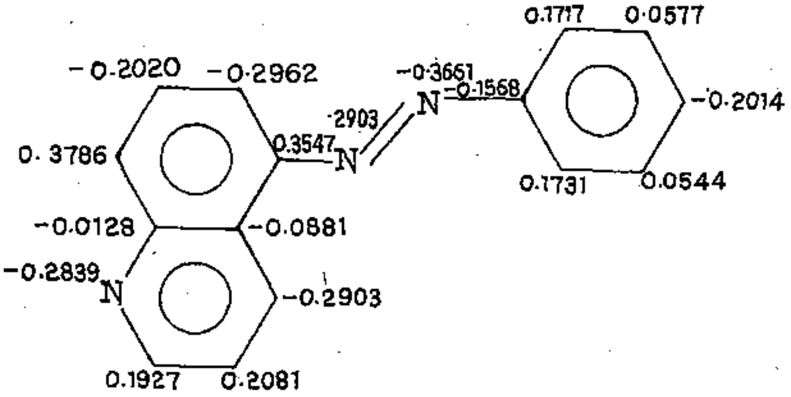
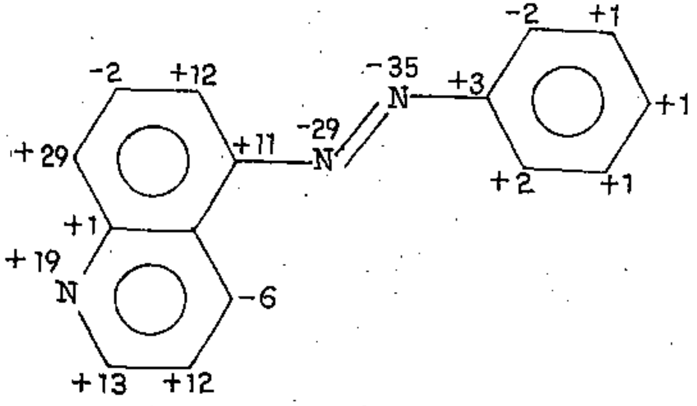


FIG. I. ENERGIES OF π - MO'S OF 5 - (PHENYL) AZO - 8 - QUINOLINE AND ELECTRON OCCUPANCIES IN THE GROUND STATE.

The transition density (charge migration) of the first π-π* transition is shown in (V) which shows that the longest wave length transition involves mostly a transfer of electron charge from the quinoline ring, more particularly the N-atom and C_8 to the azo-group, the β-N-atom getting somewhat greater share of the electron transfer during the transition.



(IVB)

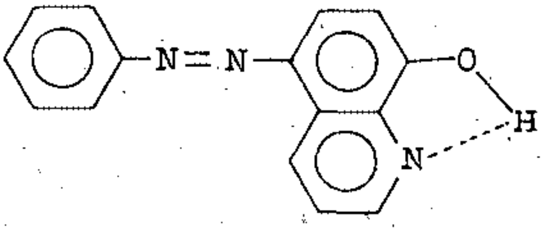


Charge migration in the lowest energy π − π* transition (in units of 10^{-3} electron, + ve sign indicates decrease of electron density on excitation and vice-versa).

(V)

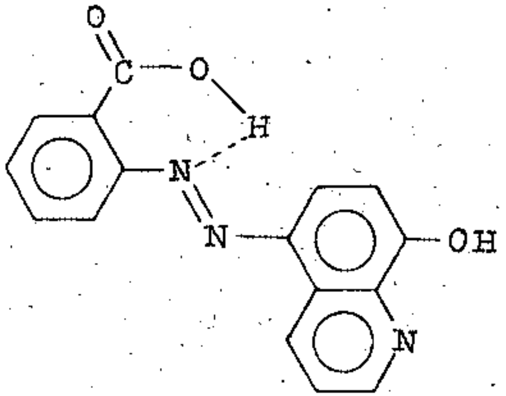
The ligands and their complexes studied in this work differs from the molecule (II) is having substituent at C_8 only (LH and its complexes) and at C_8 and $C_{8'}$ (L'HH' and its complexes). As far as the electronic spectra is concerned, those substituents can be discussed in terms of appropriate perturbations.

A substitution of H-atom at C_8 by an electron releasing substituent like -OH or -OR group would obviously lower the transition energy of the first $\pi-\pi^*$ transition because it involves a transfer of electron from the C_8 atom to the azo group. In the organotin derivatives where the O-atom is expected to have large negative charge because of the high polarity of tin -oxygen bond[37,38] ($\overset{\delta+}{Sn} - \overset{\delta-}{O}$), the $\pi-\pi^*$ transition energy is expected to further lowered. Therefore, the organotin quinolinolate derivatives are expected to show a bathochromic shift relative to the -OMe derivatives. It must be remembered that the free ligand, i.e., phenyl azo-8-quinolinol (LH) shows not only azo-hydrazone tautomeric equilibrium in solution[23,24], but the azo form is intramolecularly H-bonded (VI). This makes any meaningful comparison difficult.

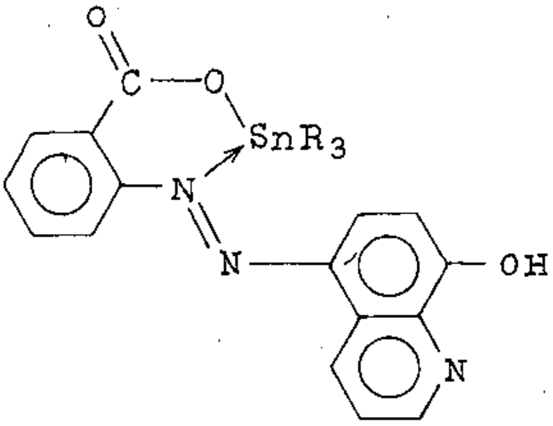


(VI)

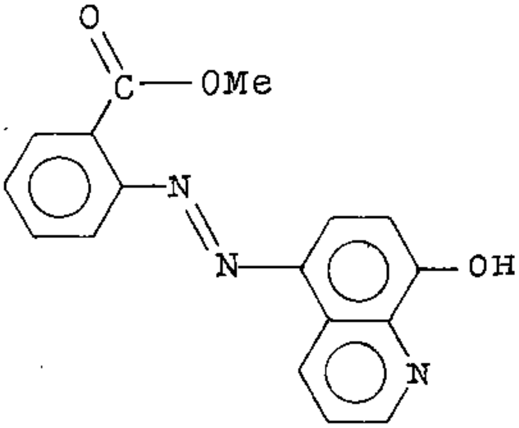
Since the 2'-position is not greatly affected in the first $\pi-\pi^*$ transition (V), a substitution at 2'-position is not going to affect this transition unless the substitution has some intra- or inter-molecular interaction with the other part of the molecule, particularly the azo group and the O_8 and quinoline N-atoms. However, any interaction with the azo-N-atoms, either through intramolecular H-bond as in L'HH' (VII) or in the organotin derivatives with N → Sn bonds (VIII) is expected to lead to a bathochromic shift relative to that in the non-interacting system, such as the ester (IX), because such an interaction would facilitate the electron flow from the quinoline ring to the azo group, thereby, lowering the transition energy.



(VII)



(VIII)



(IX)

Before we present the spectral data on the molecules studied, it must be pointed out that the discussion in this section applies to the azo form only, since the charge migration in the hydrazone form is very different (usually opposite[27]) from that in the azo form.

IIIC. Results and Discussion:

Electronic absorption spectra of the ligands and the abbreviation used for ligands are given in the preceding chapter. The spectral data for the 5-Aryl azo-8-quinolinols and their organotin derivatives are given in Table - 1. Absorption curves are also shown in Figs. 1-18. The electronic absorption spectra have been obtained in protic as well as non protic solvents. Although saturated hydrocarbon solvents, e.g., hexane etc., would have been better choice as non protic as well as non polar solvent, solubility considerations led to the choice of benzene.

Table -I

Absorption Maxima in 5-Aryl azo-8-quinolinols and their organotin derivatives.

Compound	Electronic spectra [λ_{max} nm]	
	Methanol	Benzene
A. Ligands:		
1. LH	380, ~ 460[a]	380
2. L'H'	485	410

Table - 1 (Contd..)

Compound	Electronic spectra $[\lambda_{max}\ nm]$	
	Methanol	Benzene
3. $L'MeH$	370, ~ 450^{a}	370
4. $L'Me_2$	380	380
B. Organotin derivatives of the ligand:		
(i) The Organotin carboxylates:		
5. $Ph_3SnL'H$	410, 480^{a}	420
6. $Bu_3SnL'H$	410, 450^{a}	420
(ii) The Organotin quinolinolates:		
7. Ph_3SnL	410	410
8. $Ph_2Sn(L)_2$	430	430
9. $Bu_2Sn(L)_2$	430	430
10. $Oct_2Sn(L)_2$	430	430
11. $Me_2Sn(L)_2$	430	430
12. $Ph_2Sn(L'H')$	415	450, ~420^{a}
13. $Bu_2Sn(L'H')_2$	420	430, ~420^{a}
14. $Oct_2Sn(L'H')_2$	410	430, ~420^{a}
15. $Me_2Sn(L'H')_2$	410	430, ~420^{a}
16. $Ph_2Sn(L'Me)_2$	420	420
17. $Bu_2Sn(L'Me)_2$	420	420
18. $Oct_2Sn(L'Me)_2$	420	420
19. $Me_2Sn(L'Me)_2$	420	420

Table - 1 (Contd..)

Compound	Electronic spectra [λ_{max} nm] Methanol	Benzene
(iii) The binuclear organotin carboxylates quinolinolates:		
20. $Ph_2Sn(L'SnPh_3)_2$	420	420
21. $Bu_2Sn(L'SnPh_3)_2$	410	415
22. $Oct_2Sn(L'SnPh_3)_2$	410	415
23. $Me_2Sn(L'SnPh_3)_2$	410	410
24. $Ph_2Sn(L'SnBu_3)_2$	410	410
25. $Bu_2Sn(L'SnBu_3)_2$	410	410
26. $Oct_2Sn(L'SnBu_3)_2$	415	410
27. $Ph_3SnL'SnPh_3$	410	420

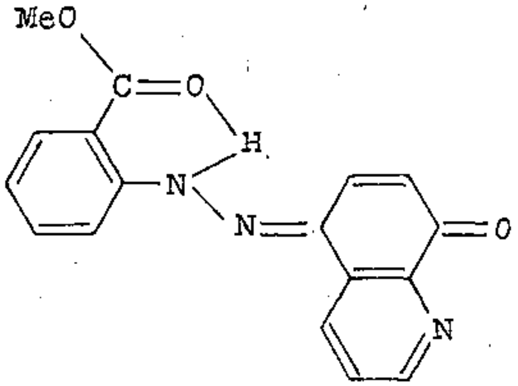
a) Inflection or shoulder

The azo-hydrazone tautomerism exhibited by the azoxines has been discussed in Chapter - I (Section IC). Like the ligands, organotin complexes in which the 8-OH group is present, show two absorption bands (Figs. 5 and 6) in the visible region at ∼ 400 nm and ~ 460-480 nm [Table -1B(i)] due to azo-hydrazone tautomerism. The lower wave length band must be assigned to the π-π* transition of the azo form since all compounds in which the -OH group is complexed with organotin group [Table -1B(ii)] and, thus, exist only in the azo form, show a single intense absorption at 400 nm. The same behaviour is observed when the 8-OH, group is methylated. For example, 5-(2'-carboxy phenyl) azo-8-methoxy quinoline, L'MeH' and 5-(2'-carbomethoxy phenyl) azo-8-methoxy quinoline, L'Me_2 [Table - 1A] have a single intense absorption maxima at ~ 380 nm in methanol and benzene. The longest wave length band at ~ 460-480 nm must, therefore, be attributed to the hydrazone form in agreement with earlier observations that the hydrazone form generally absorbs at a longer wave lengths[24,27]. The relative intensities of the two bands are dependent on the polarity of the solvent, intensity of the longest wave length band increasing with the solvent polarity. This is consistent with the known trends in similar molecules[23,24].

For convenience of discussion the organotin derivatives are classified into three types:

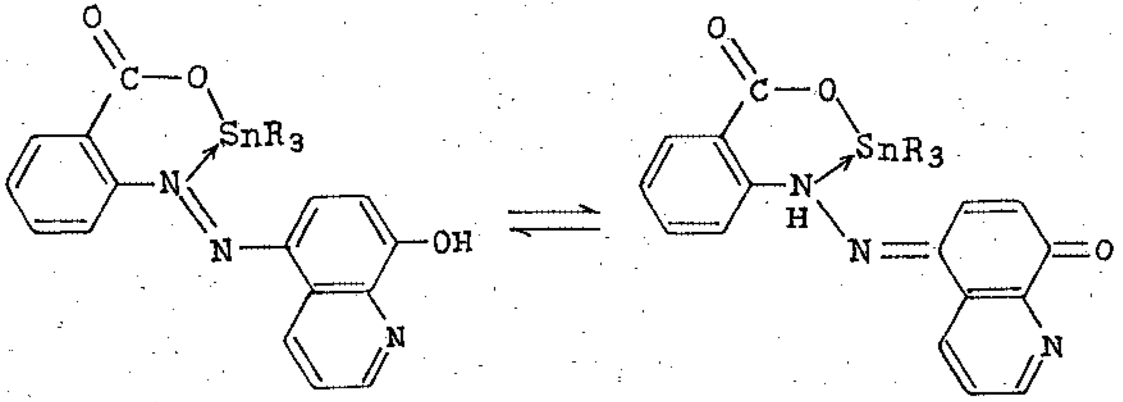
(a) <u>The organotin carboxylates</u>:

The relative intensities of the ~ 400 nm and ~ 460 nm band (Figs. 5 and 6) show that the azo-hydrazone equilibrium in the carboxylate derivatives is considerably shifted towards the azo form compared to that in the methyl ester L'MeH. In the latter, the hydrazone form is stabilized by the formation of a 6-membered ring[24] due to intra molecular H-bonding (X).



(X)

In the organotin complexes (XI), the presence of N → Sn coordinate bond prevents the formation of any such intra molecular H-bond in the hydrazone form. The latter form is, therefore, less favoured. As discussed in section-II, the large bathochromic shift of the $\pi-\pi^*$ transition in the azo form in $R_3SnL'H$ type complexes ($\lambda_{max} \sim 420$ nm) compared to that in the corresponding methyl ester L'MeH ($\lambda_{max} = 385$ nm) is an evidence of N → Sn coordination.



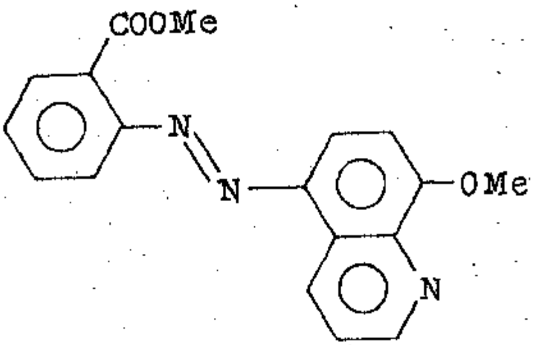
(XIA)
Azo form

(XIB)
Hydrazone form

(b) <u>The organotin quinolinolates:</u>

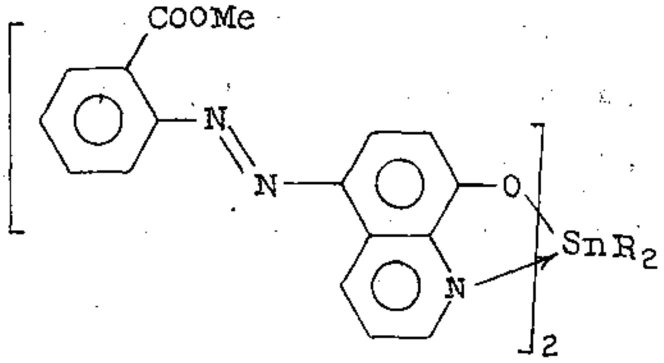
The electronic absorption spectra of the organotin-quinolinolates of the type $R_2Sn(L'H')_2$ are strongly influenced by the nature of solvent although the possibility of azo-hydrazone tautomerism is eliminated. It is, however, well known that the absorption spectra of azo benzene and substituted azobenzenes in different solvents are generally similar in nature except for some shift in the absorption maxima, the magnitude of the shift being dependent on the nature of the solvent[1,26]. A bathochromic shift of 10-15 nm is generally observed in going from non-polar to polar solvents. Any unusual solvent dependence is, therefore, indicative of some chemical equilibria in the system[26,38].

A similar behaviour is observed in case of the azoxines also. For example, the ester 5-(2'-carbomethoxy phenyl) azo-8-methoxyquinoline, L'Me$_2$ (XII), a model for the azo form, shows a single absorption maxima at 380 nm in polar as well as non-polar solvents.



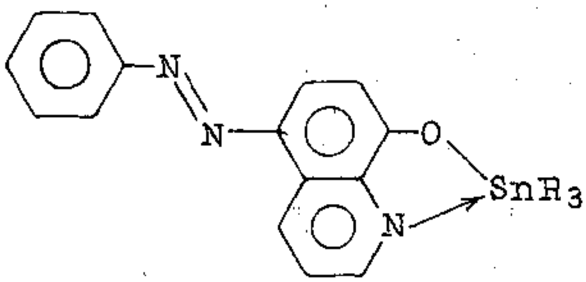
(XII)

The corresponding organotin derivatives, R$_2$Sn(L'Me)$_2$, absorb at considerably longer wave length (λ_{max} = 420 nm) and the spectra are not influenced by the nature of solvent [Table 1B(ii)]. The bathochromic shift, therefore, results from the complexation by the ligand. Such bathochromic shifts are quite well known in oxinate complexes and the organotin azoxinates are thus structurally quite similar to the organotin oxinates[26,28-31] and should be formulated as shown in (XIII).

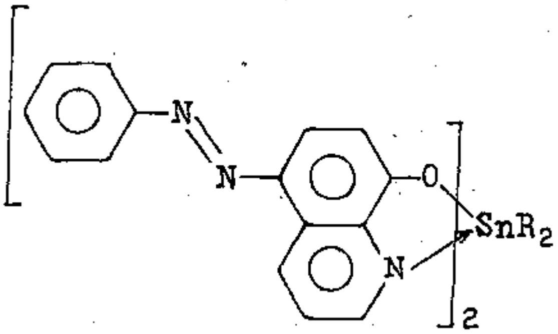


(XIII)

Similar solvent independent spectra are also shown by the organotin complexes of 5-phenyl azo-8-quinolinol (XIV) [Table - 1B(ii)].

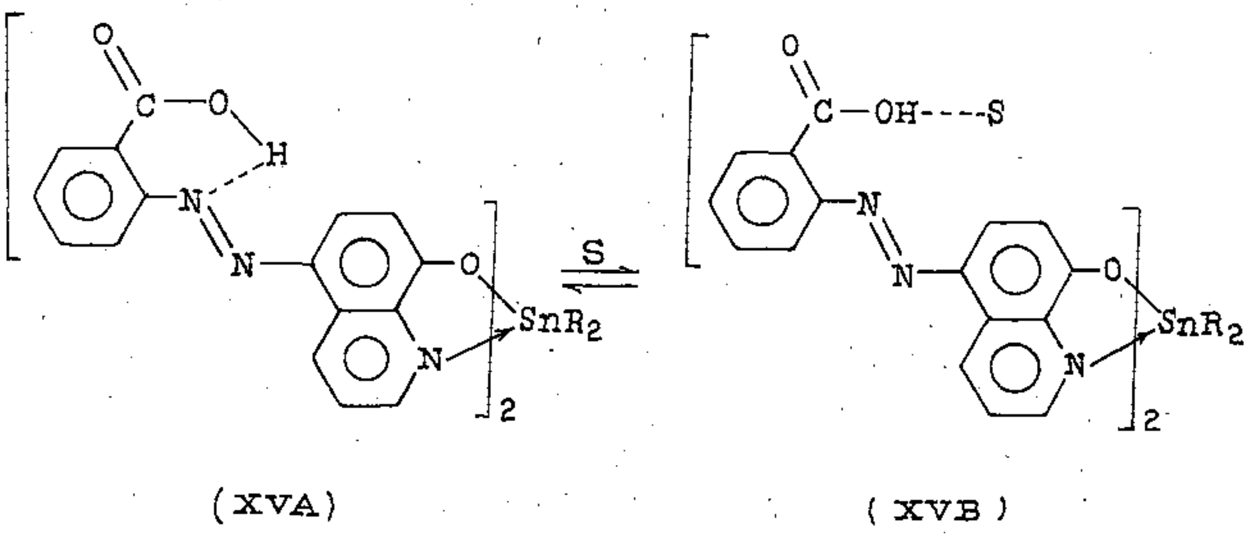


(XIV A)



(XIV B)

On the other hand, the complexes $R_2Sn(L'H')_2$ in which the carboxyl group is free, exhibit solvent-dependent spectra [Table-1B(ii)]. The compounds absorb predominantly at 415-420 nm in donor solvents like methanol, acetone, DMSO etc. and at 480 nm in non polar solvents like benzene and CCl_4. All compounds of this series in which the carboxylic proton has been replaced, e.g. $R_2Sn(L'Me)_2$ [Table -1B(ii)], $R_3SnL'H$ [Table - 1B(i)] and $R_2Sn(L'SnR'_3)_2$ [Table - 1B (iii)], have a single intense absorption at ~410 nm in all solvents mentioned above. Since, only donor solvents capable of forming strong H-bond give rise to a blue shift, we believe the following equilibrium involving a competition between the intra molecular H-bonded form (XVA) and intermolecular H-bonded species (XVB) is involved. The presence of



(XVA) (XVB)

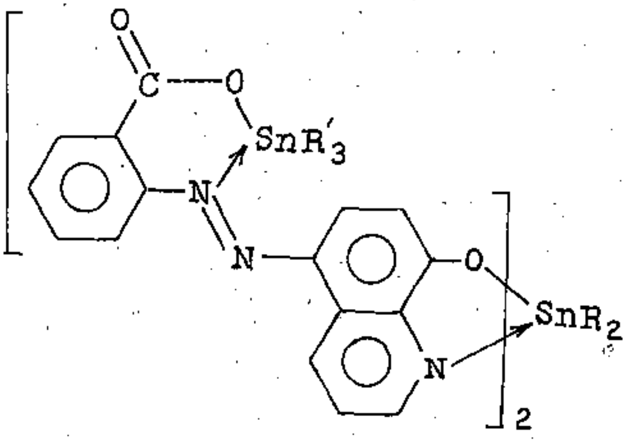
intramolecular H-bond involving the -COOH group is easily demonstrated by methylation of the -COOH group. The corresponding carbomethoxy derivatives show only a single absorption maximum.

Since the H-atom is not directly involved in the π-system, such interaction (VIB) will have little influence on the $\pi-\pi^*$ transition and consequently, the absorption spectra closely resemble to those of the corresponding carbomethoxy compounds, $R_2Sn(L'Me)_2$. However, formation of intramolecular H-bond involving the azo-N-atom (XVA) would certainly result in a large red shift of the $\pi-\pi^*$ transition (see Section IIIB). Such behaviour is well known in o-carboxy azo compounds. The 480 nm and ~ 410 nm absorptions should, therefore, be attributed to the species (XVA) and (XVB) respectively. Clearly, the intramolecular H-bonded form (XVA) will be the main species in aprotic solvents, while donor solvents will tend to form solvent-solute or intermolecular H-bond, thereby shifting the equilibrium towards the form (XVB).

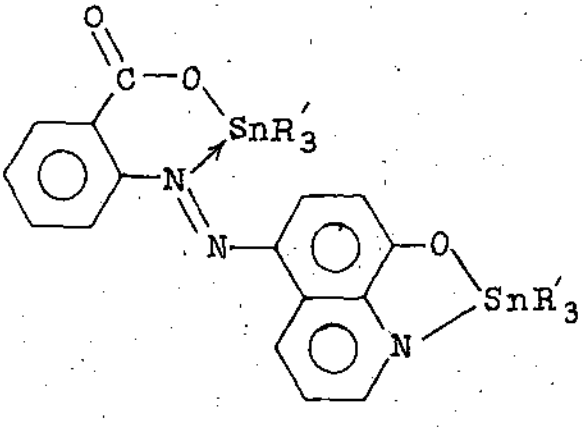
(c) The binuclear organotin carboxylate - quinolinolates:

In these organotin complexes, the possibilities of azo-hydrazone tautomerism or solvent-solute interactions through intermolecular H-bond are eliminated. Consequently, the absorption spectra are similar to the dimethoxy derivative (XII) and have a single intense absorption maxima at 410 nm in both types of solvent

[Table - 1B(iii)]. The bathochromic shift as compared to L'Me$_2$ (XII) is indicative of N → Sn coordination. The compounds should thus be formulated as (XVI) and (XVII).



(XVI)



(XVII)

ELECTRONIC SPECTRA

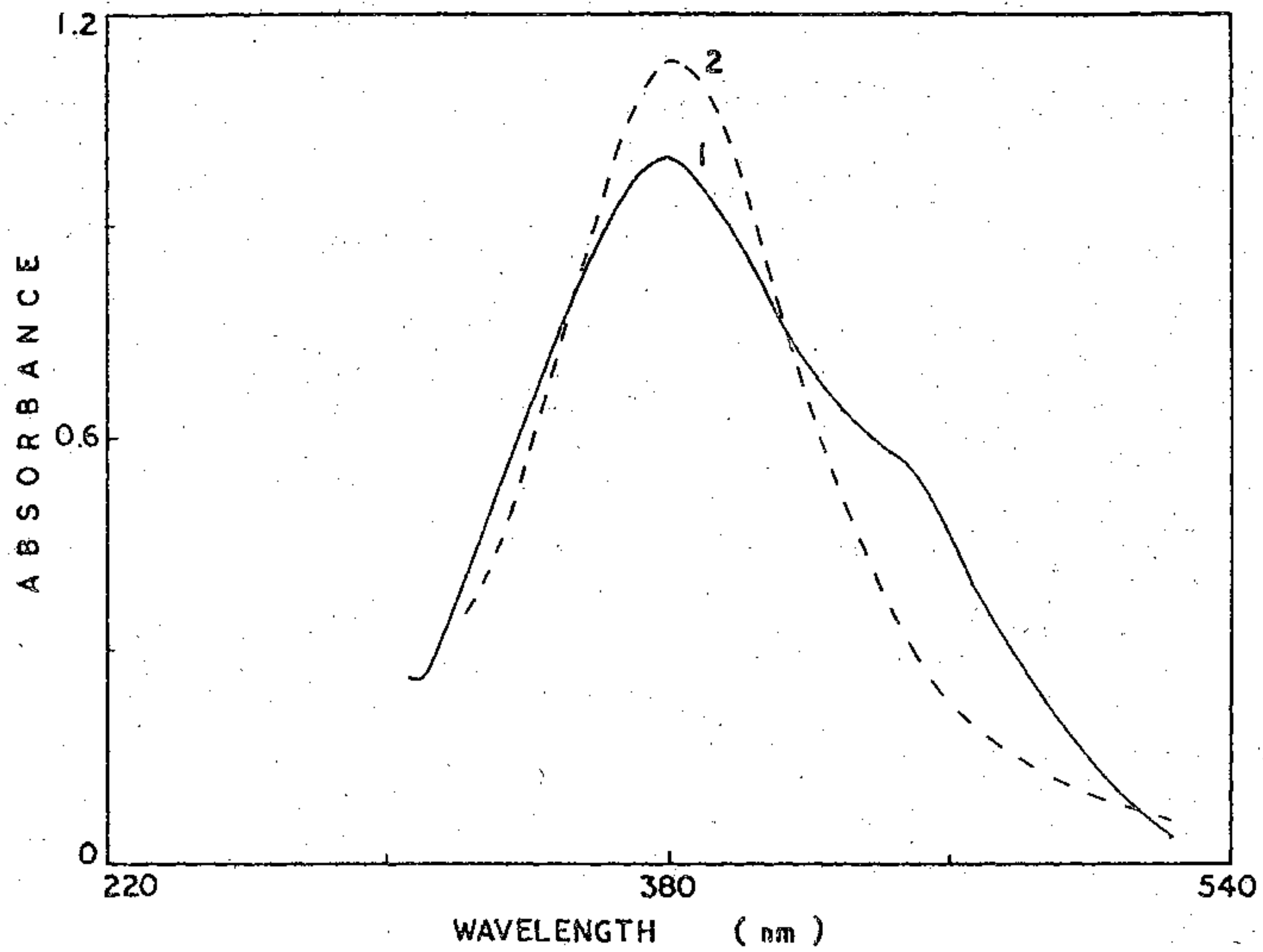


FIG. I. ABSORPTION SPECTRA OF LH. I. IN METHANOL AND 2. IN BENZENE.

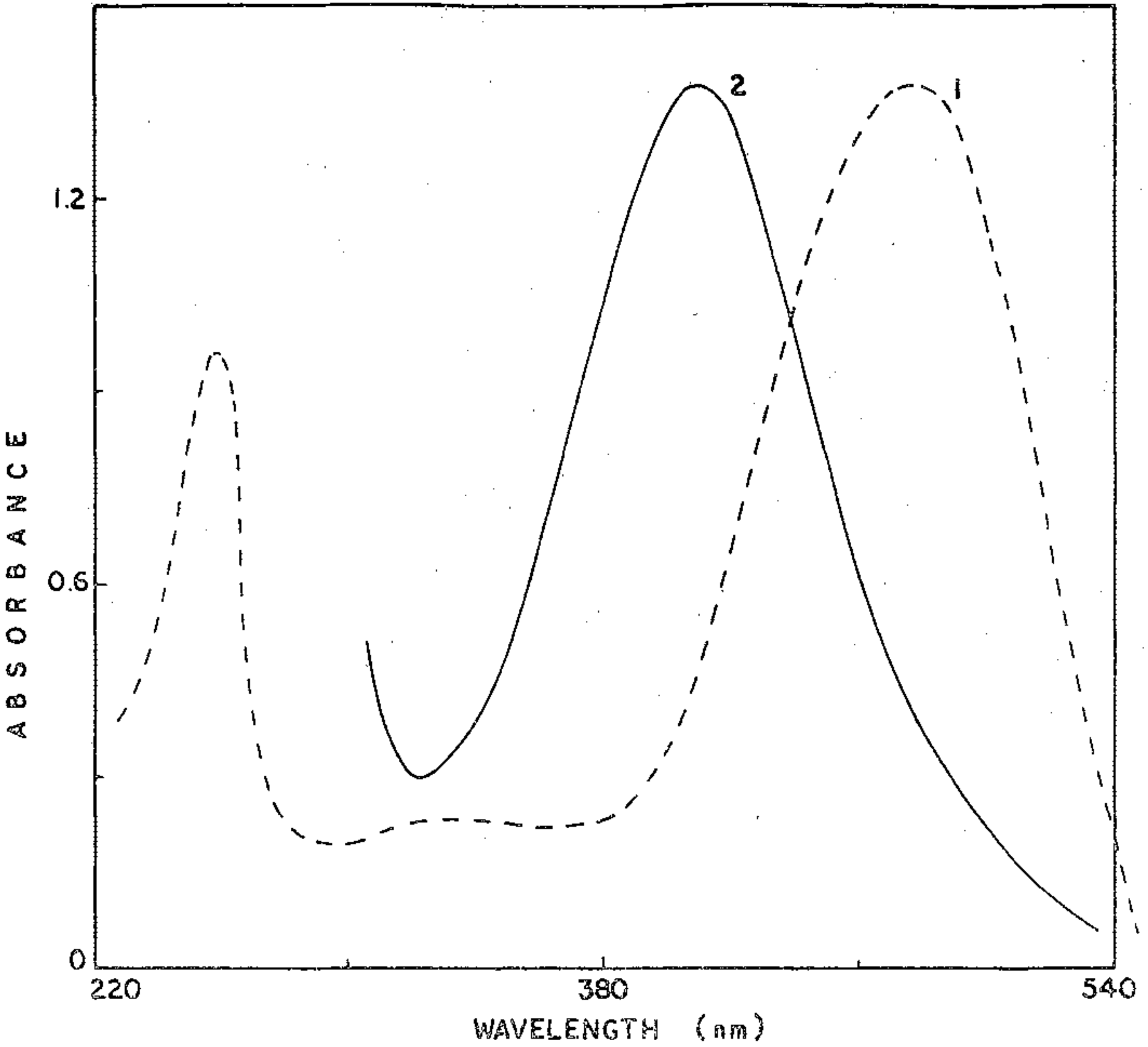


FIG.2. ABSORPTION SPECTRA OF L'HH' 1. IN METHANOL AND 2. IN BENZENE.

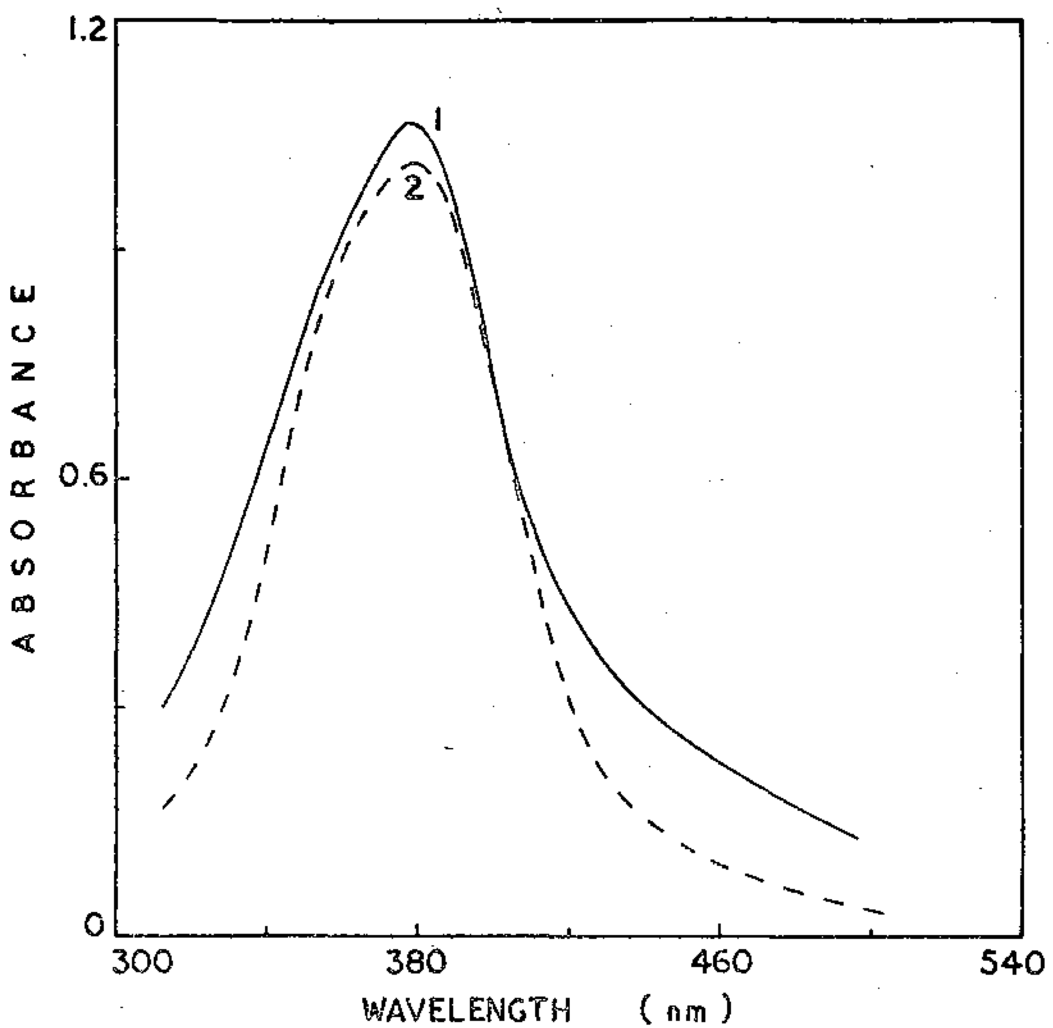


FIG. 3. ABSORPTION SPECTRA OF $L'Me_2$.
1. IN METHANOL AND 2. IN BENZENE.

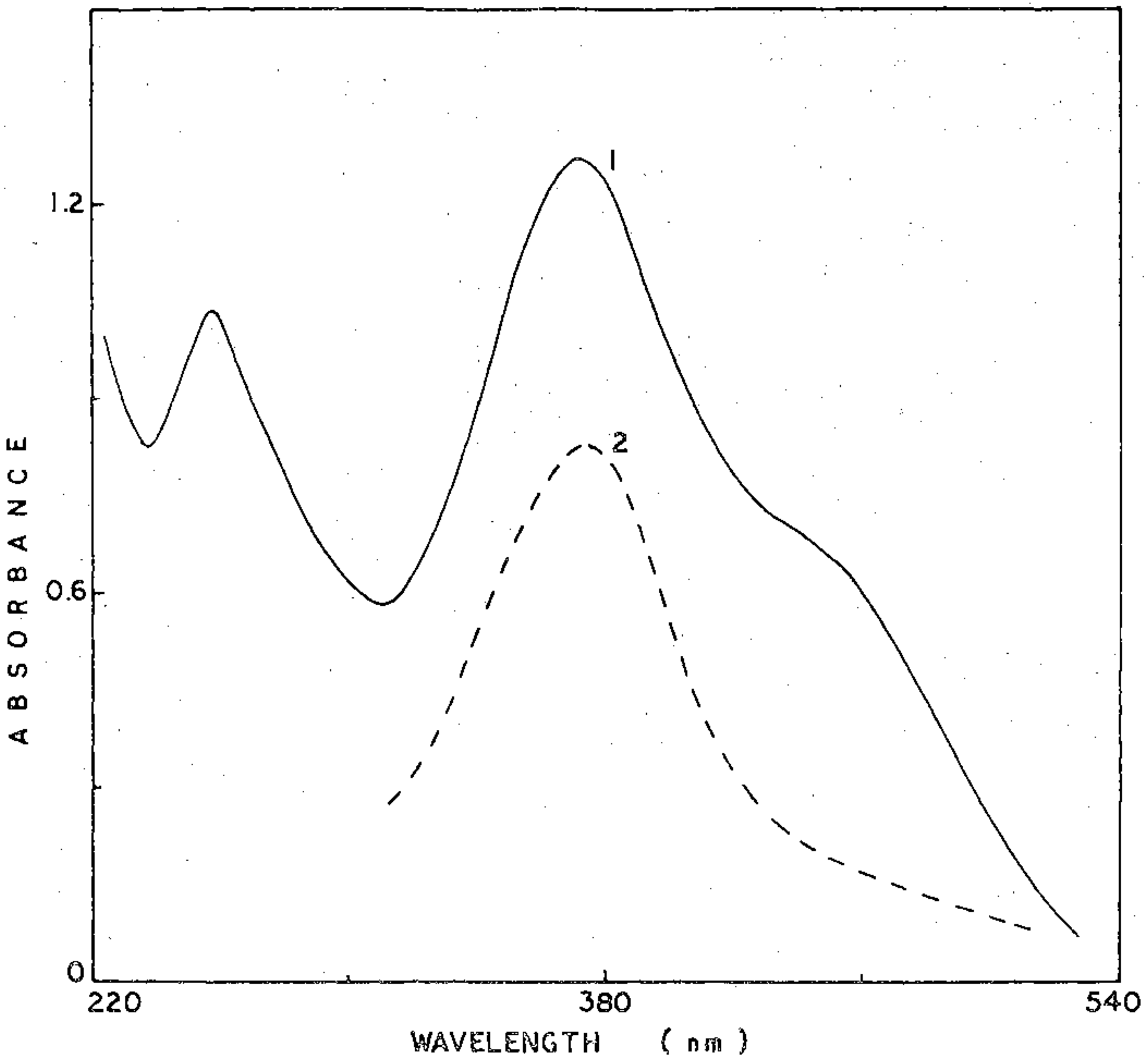


FIG. 4. ABSORPTION SPECTRA IN METHANOL OF L′MeH. 1. IN METHANOL AND 2. IN BENZENE.

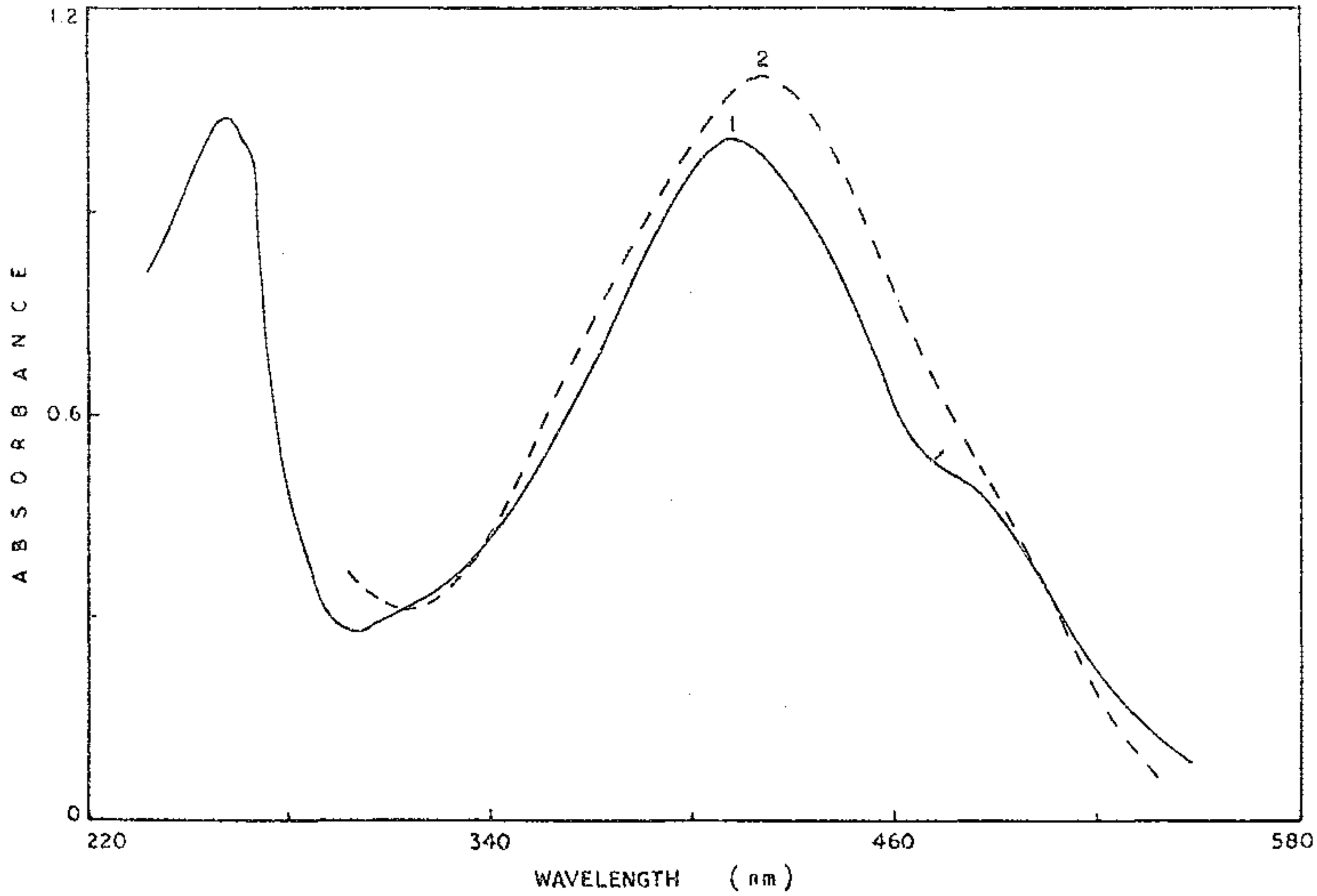


FIG. 5. ABSORPTION SPECTRA OF $Ph_3SnL'H$, 1. IN METHANOL. 2. IN BENZENE.

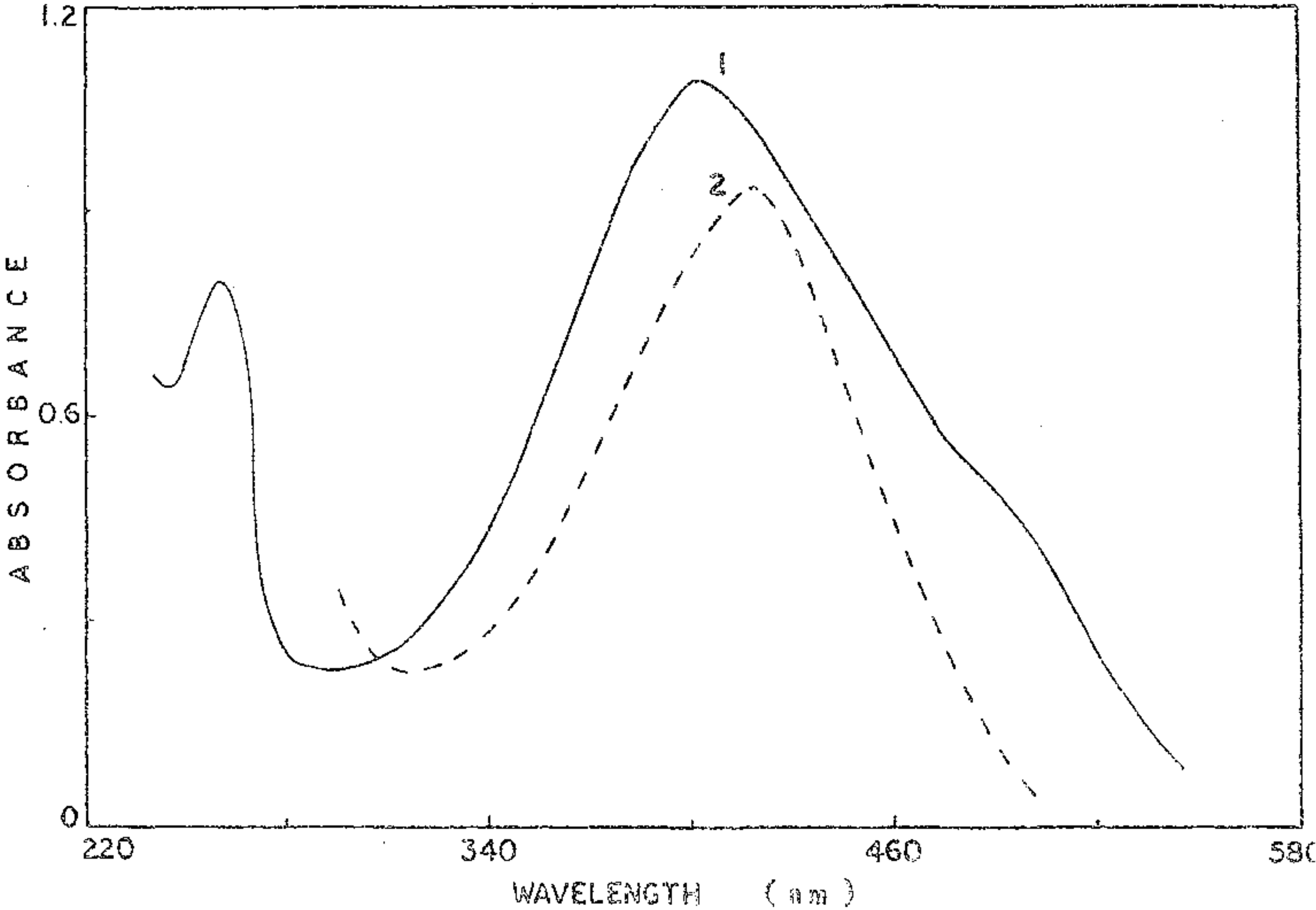


FIG. 6. ABSORPTION SPECTRA OF $Bu_3SnL'H$. 1. METHANOL, 2. BENZENE.

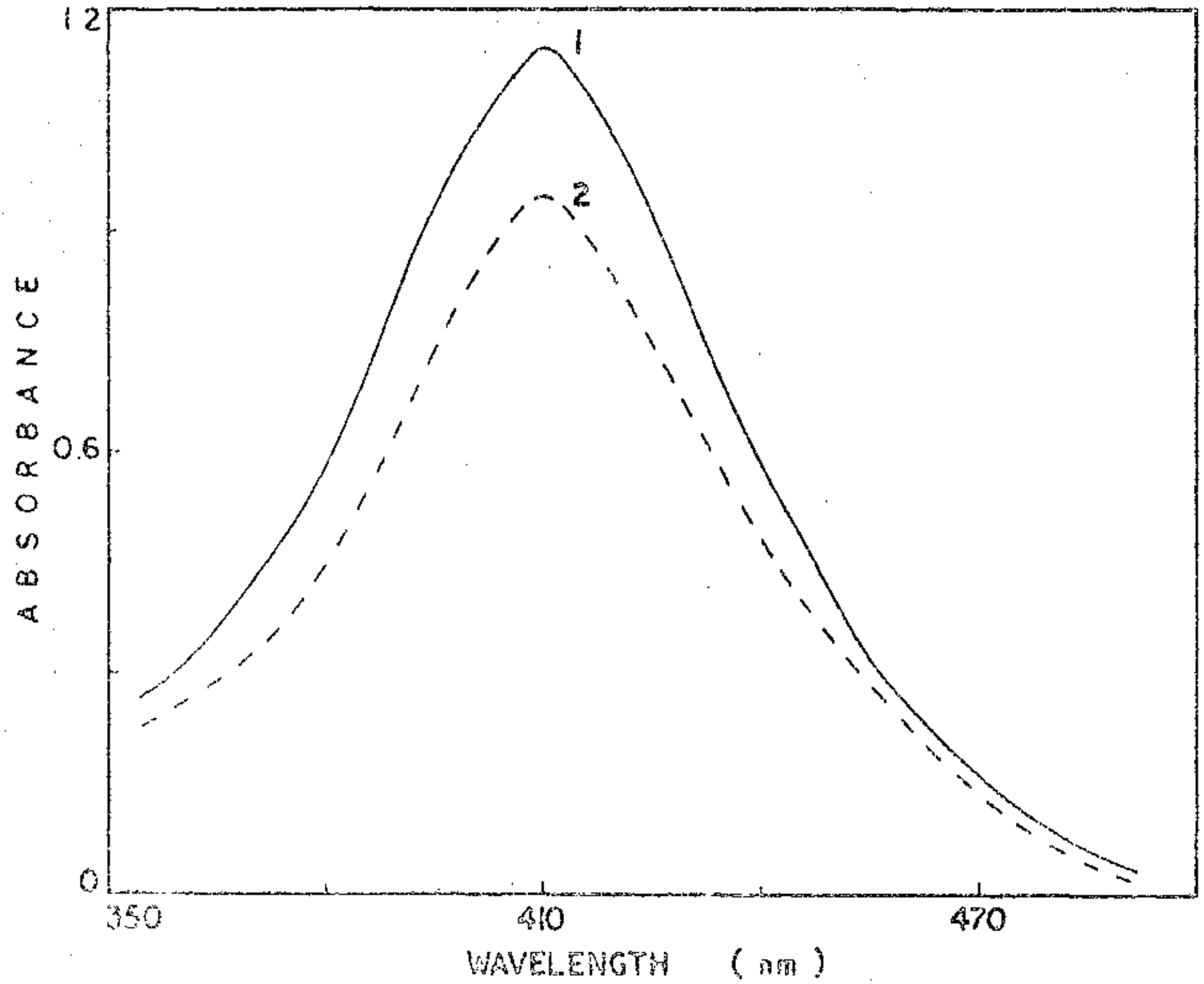


FIG. 7. ABSORPTION SPECTRA OF Ph_3SnL.
1. IN METHANOL AND 2. IN BENZENE.

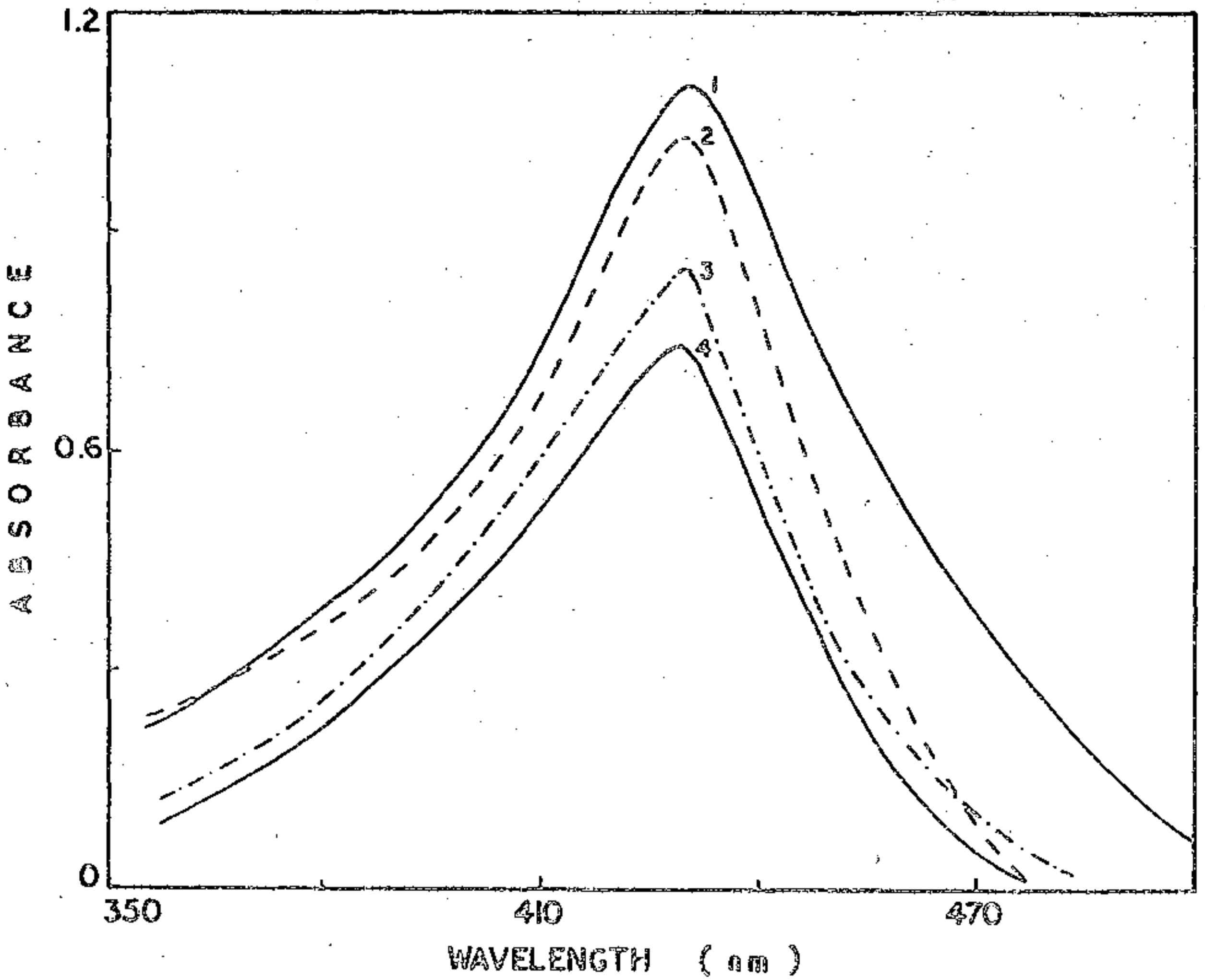


FIG. 8. ABSORPTION SPECTRA IN METHANOL OF 1. Ph_2SnL_2, 2. Bu_2SnL_2, 3. Oct_2SnL_2 AND 4. Me_2SnL_2.

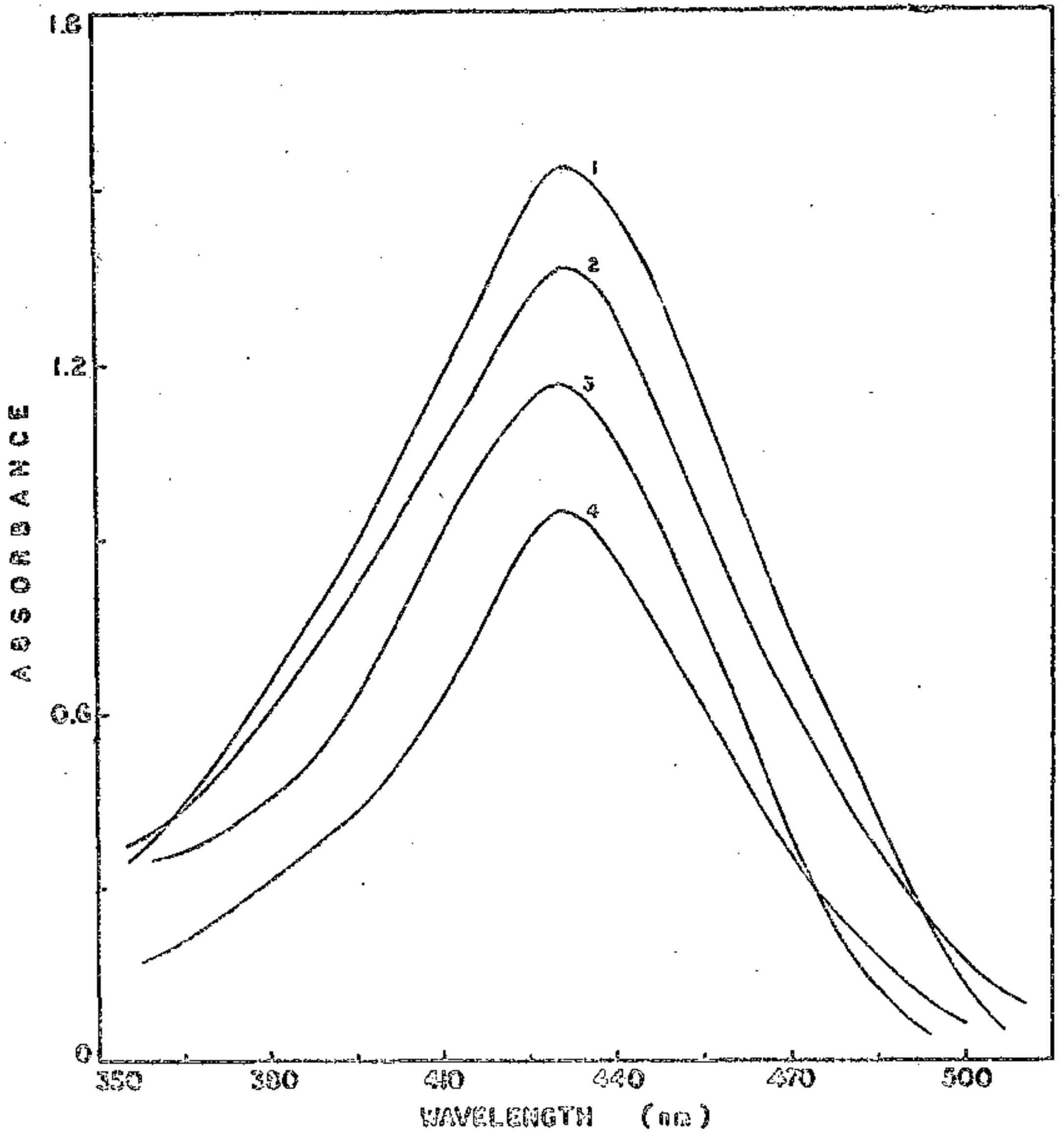


FIG. 9. ABSORPTION SPECTRA IN BENZENE OF
1. Ph_2SnL_2, 2. Bu_2SnL_2, 3. Oct_2SnL_2 AND 4. Me_2SnL_2.

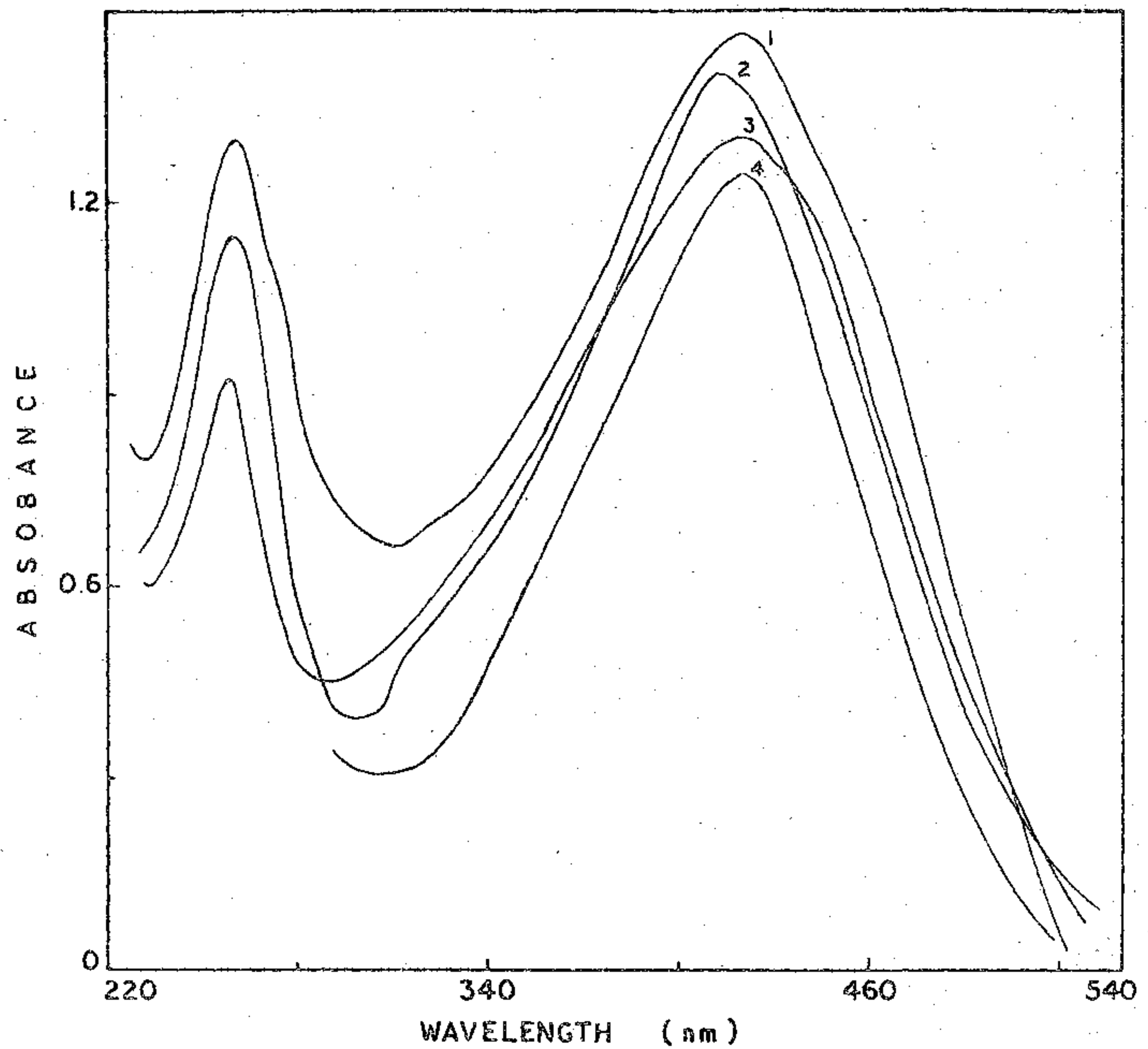


FIG. 10. ABSORPTION SPECTRA IN METHANOL OF 1. $Ph_2Sn(L'H')_2$, 2. $Bu_2Sn(L'H')_2$, 3. $Oct_2Sn(L'H')_2$ AND 4. $Me_2Sn(L'H')_2$.

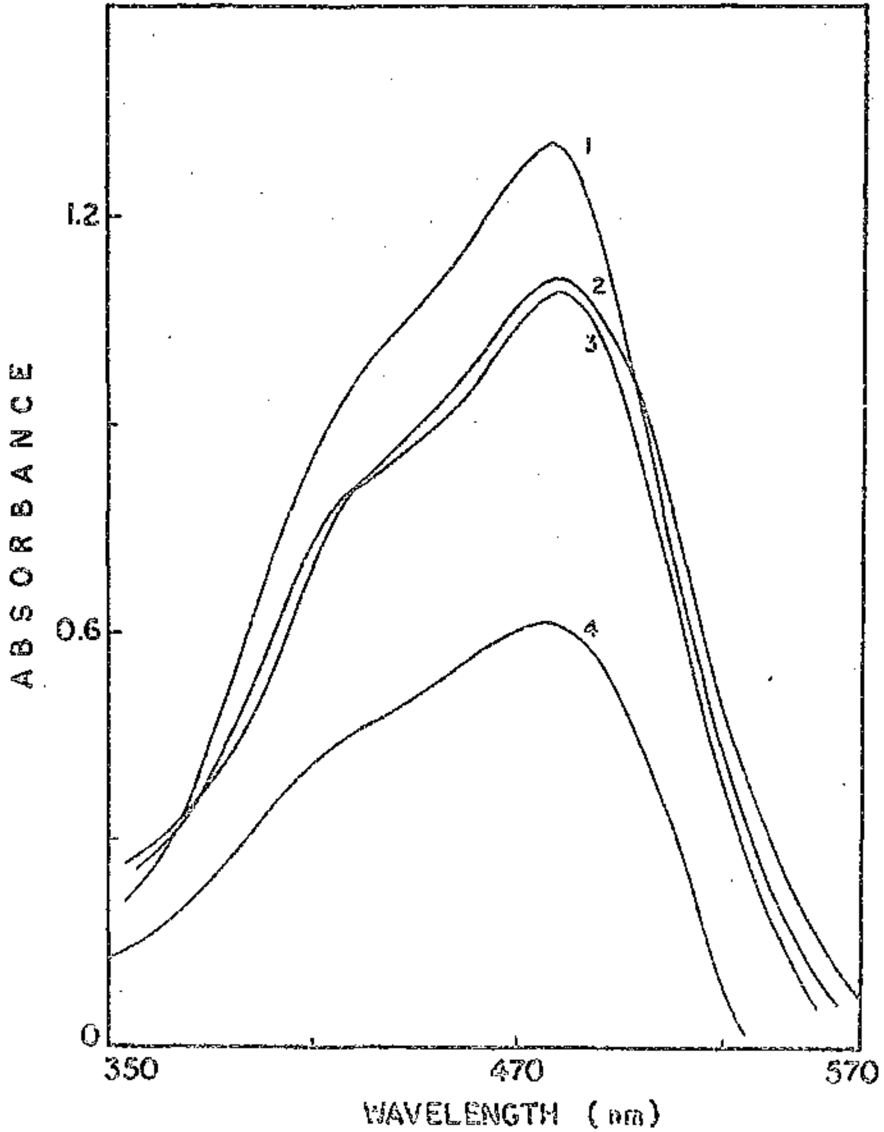


FIG. 11. ABSORPTION SPECTRA IN BENZENE OF 1. $Ph_2Sn(L'H')_2$, 2. $Bu_2Sn(L'H')_2$, 3. $Oct_2Sn(L'H)_2$, 4. $Me_2Sn(L'H')_2$.

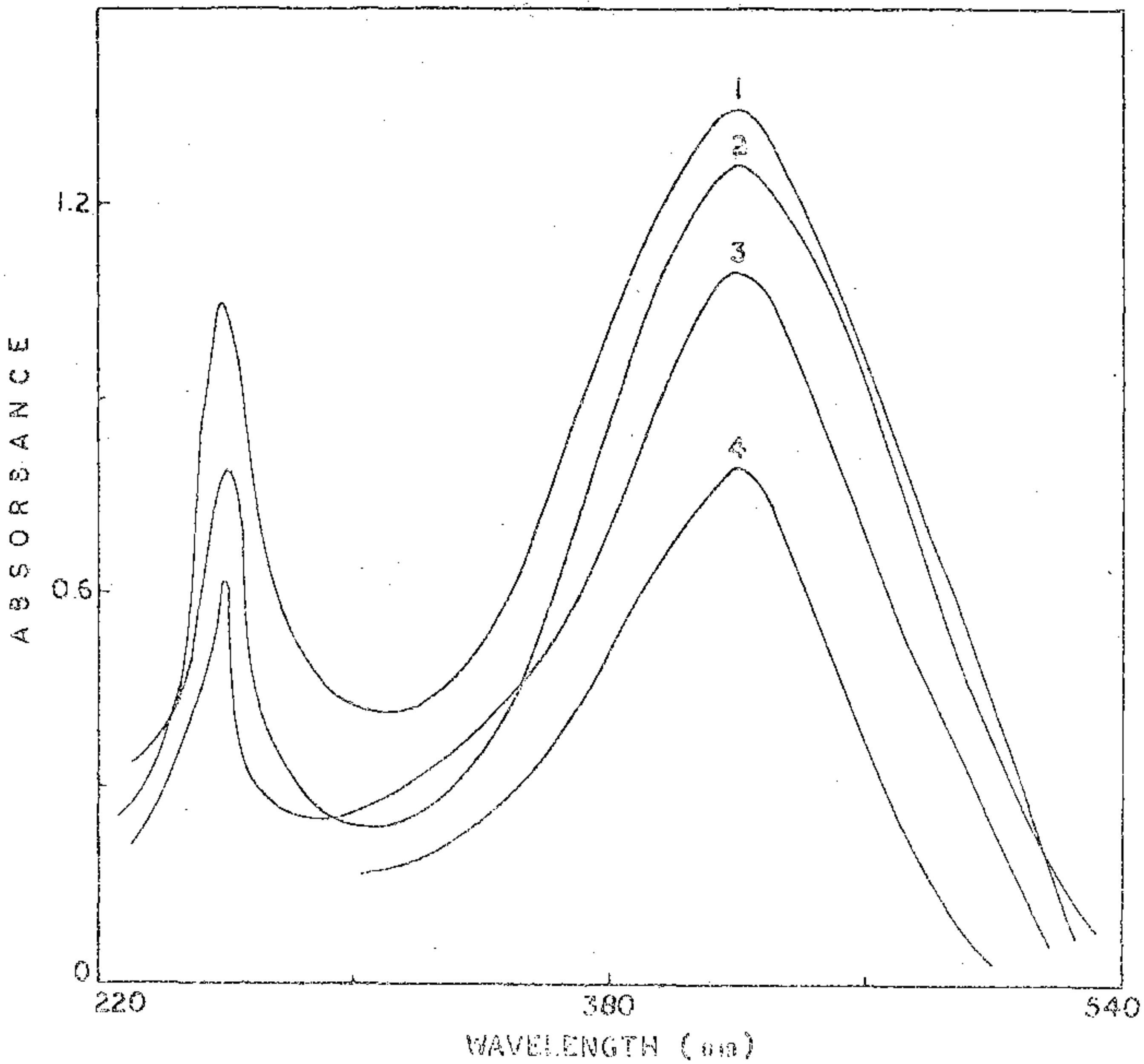


FIG.12. ABSORPTION SPECTRA IN METHANOL OF 1. $Ph_2Sn(L'Me)_2$, 2. $Bu_2Sn(L'Me)_2$, 3. $Oct_2Sn(L'Me)_2$ AND 4. $Me_2Sn(L'Me)_2$.

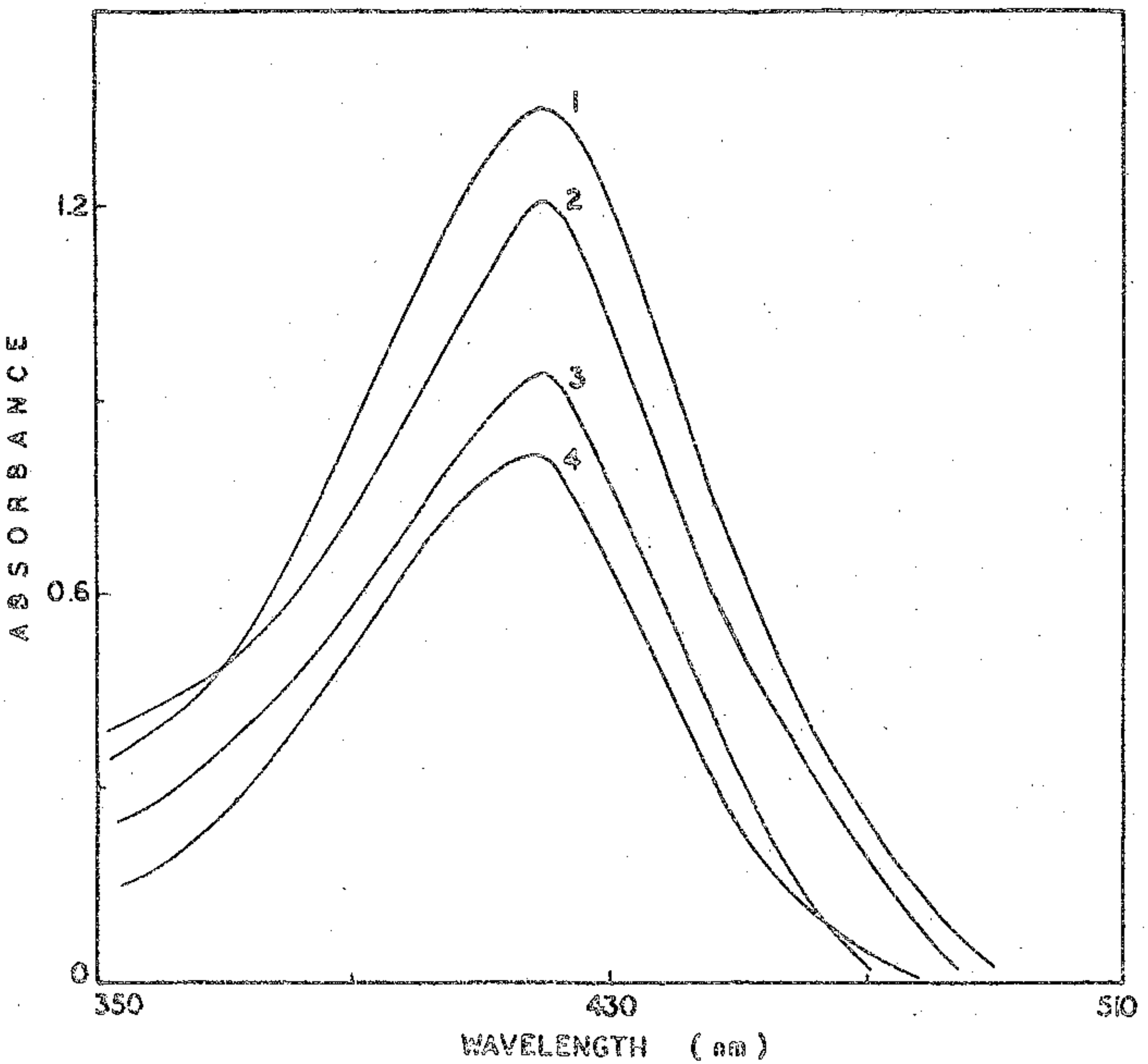


FIG. 13. ABSORPTION SPECTRA IN BENZENE OF 1. $Ph_2Sn(L'Me)_2$, 2. $Bu_2Sn(L'Me)_2$, 3. $Oct_2Sn(L'Me)_2$, 4. $Me_2Sn(L'Me)_2$.

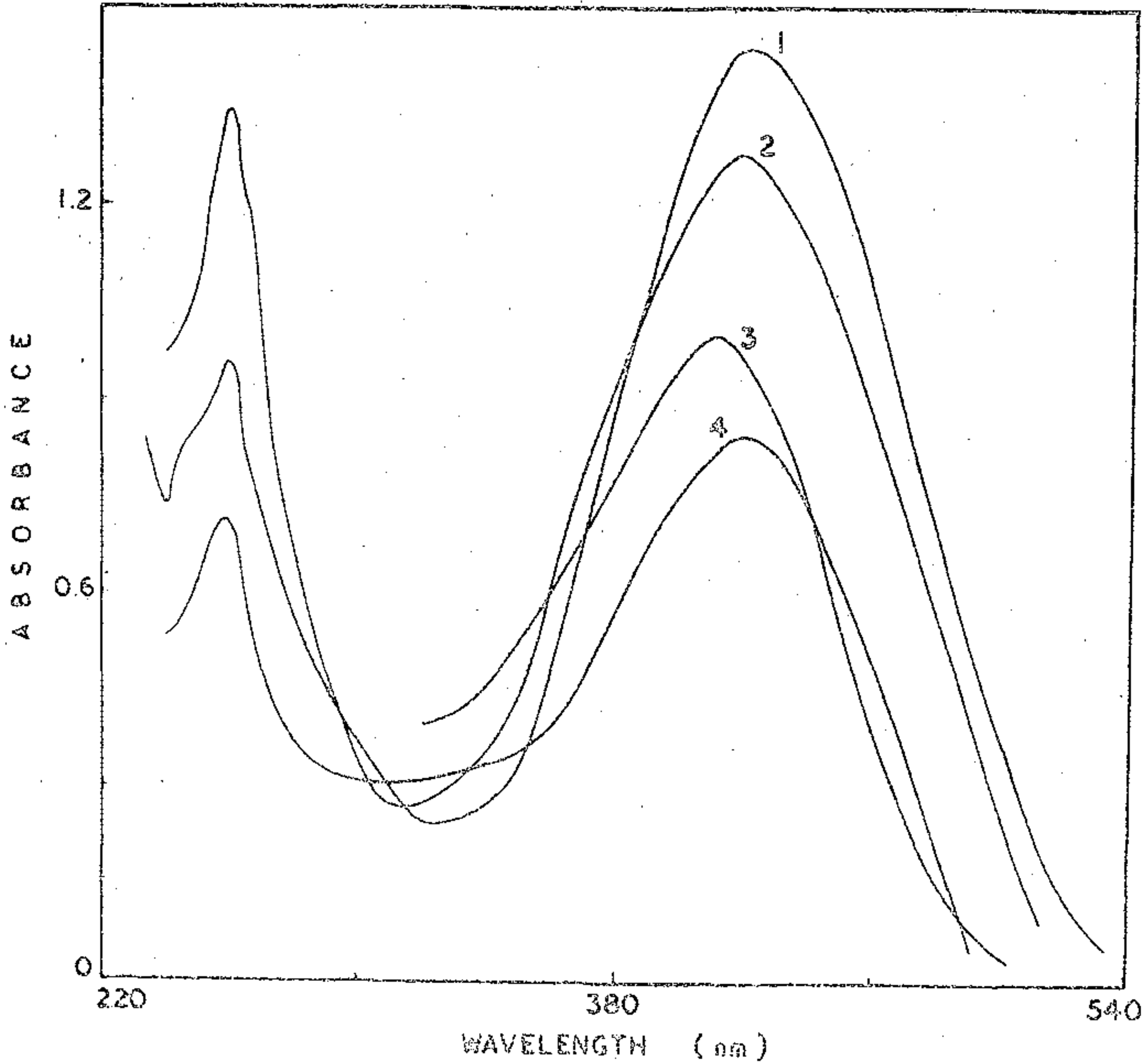


FIG. 14. ABSORPTION SPECTRA IN METHANOL OF 1. $Ph_2Sn(L'SnPh_3)_2$ 2. $Bu_2Sn(L'SnPh_3)_2$, 3. $Oct_2Sn(L'SnPh_3)_2$ AND 4. $Me_2Sn(L'SnPh_3)_2$.

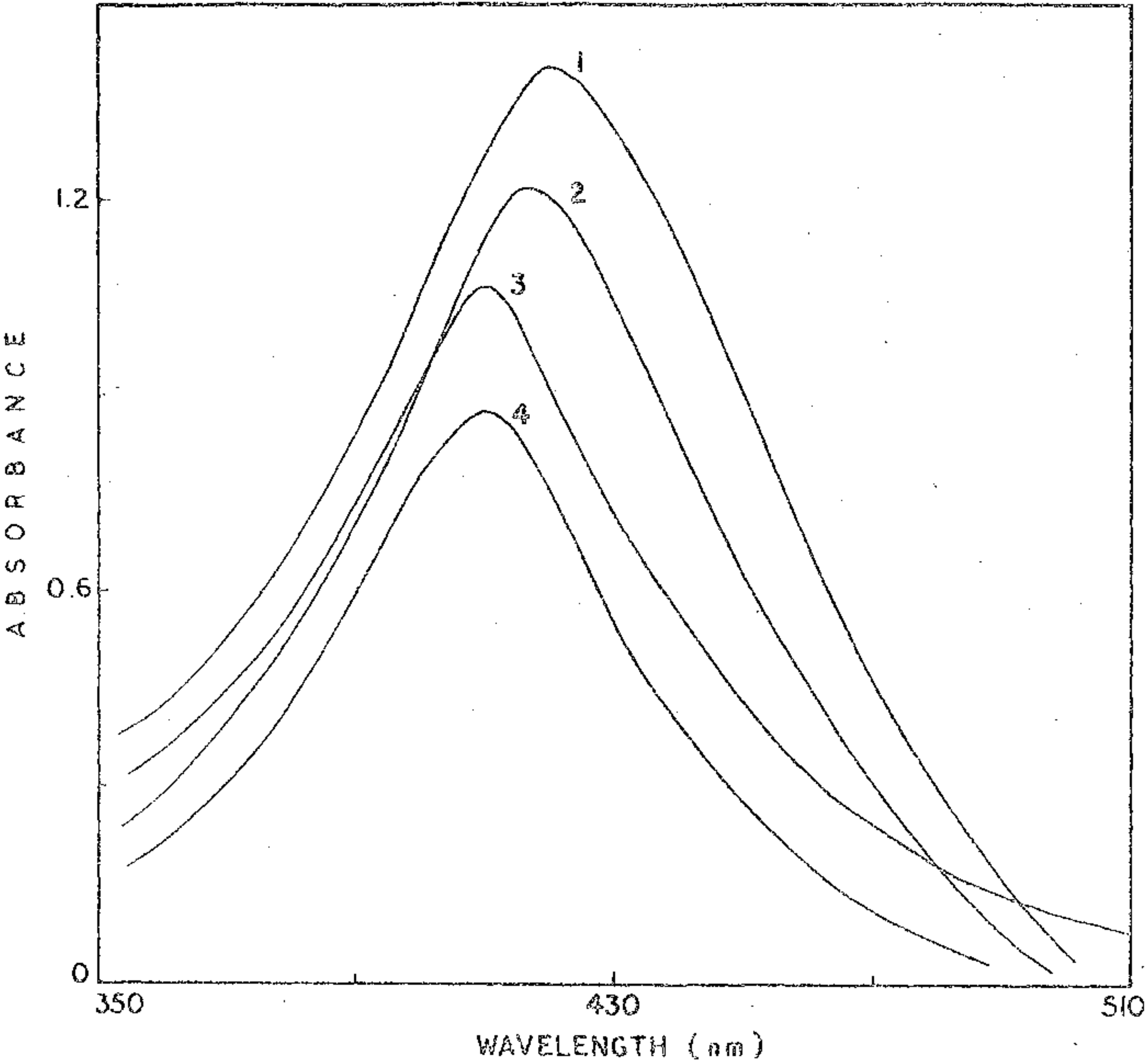


FIG. 15. ABSORPTION SPECTRA IN BENZENE OF 1. $Ph_2Sn(L'SnPh_3)_2$, 2. $Bu_2Sn(L'SnPh_3)_2$, 3. $Oct_2Sn(L'SnPh_3)_2$ AND 4. $Me_2Sn(L'SnPh_3)_2$.

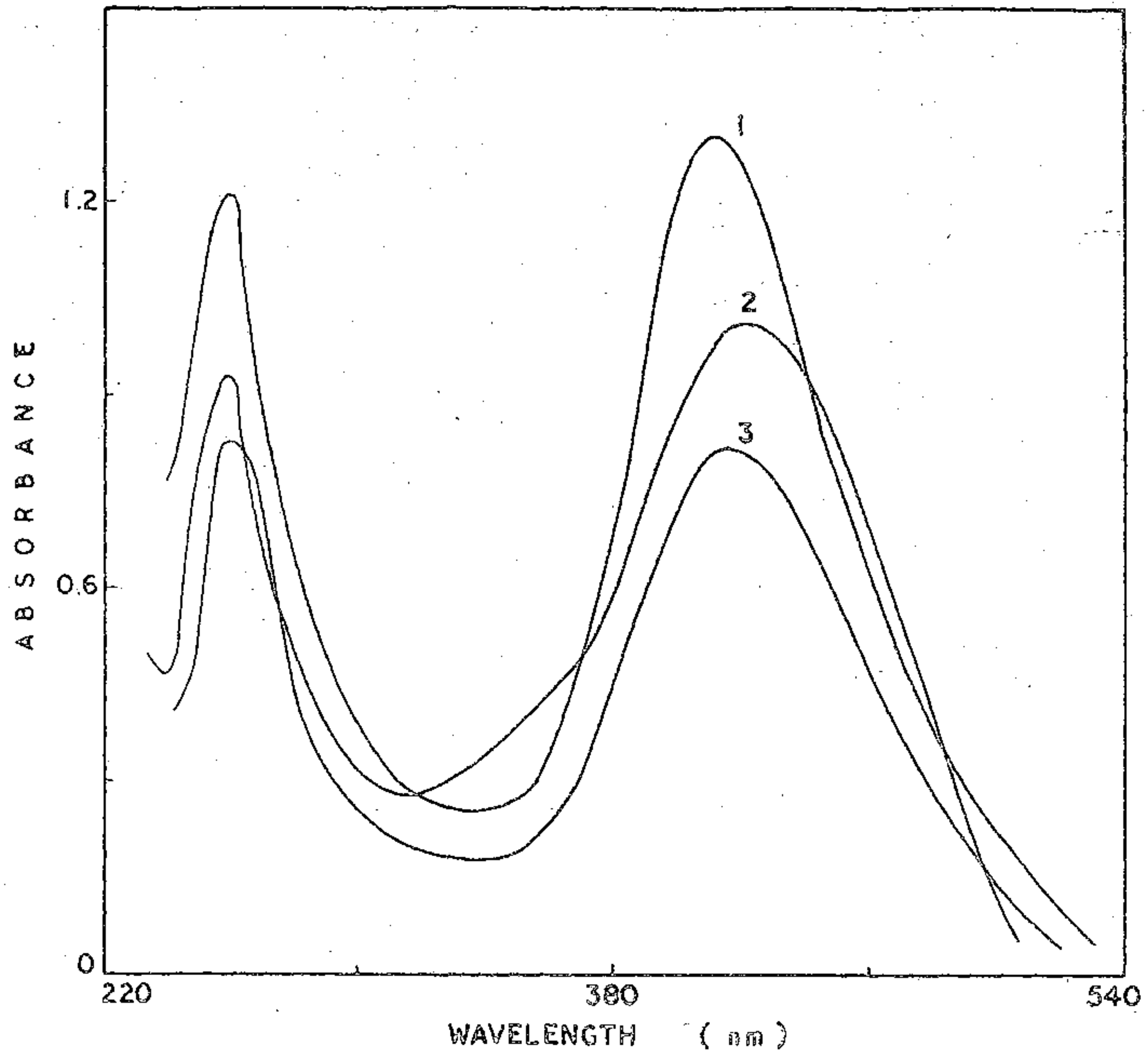


FIG. 16. ABSORPTION SPECTRA IN METHANOL OF 1. $Ph_2Sn(L'SnBu_3)_2$, 2. $Bu_2Sn(L'SnBu_3)_2$ AND 3. $Oct_2Sn(L'SnBu_3)_2$.

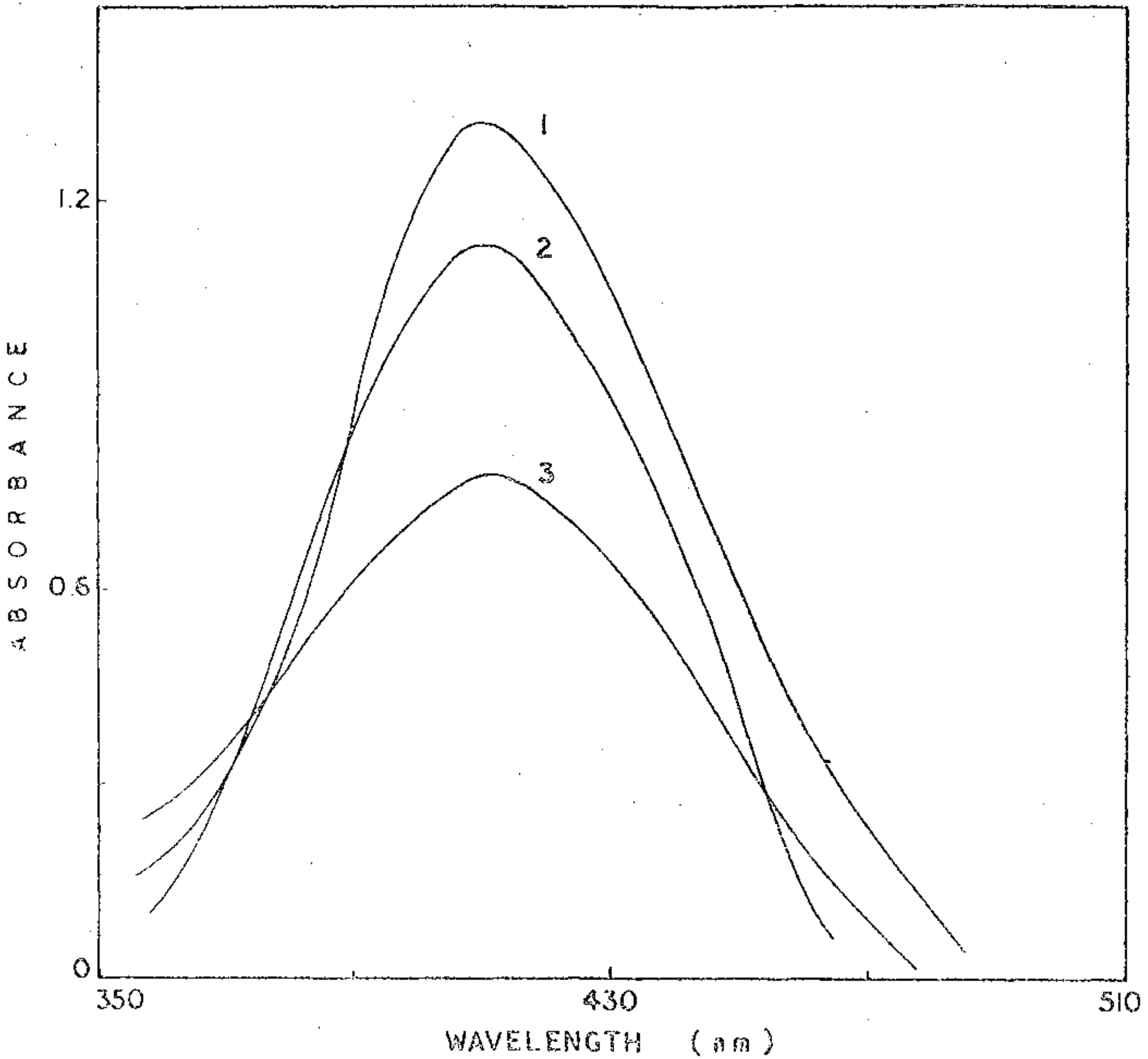


FIG. 17. ABSORPTION SPECTRA IN BENZENE OF 1. $Ph_2Sn(L'SnBu_3)_2$, 2. $Bu_2Sn(L'SnBu_3)_2$ AND 3. $Oct_2Sn(L'SnBu_3)_2$

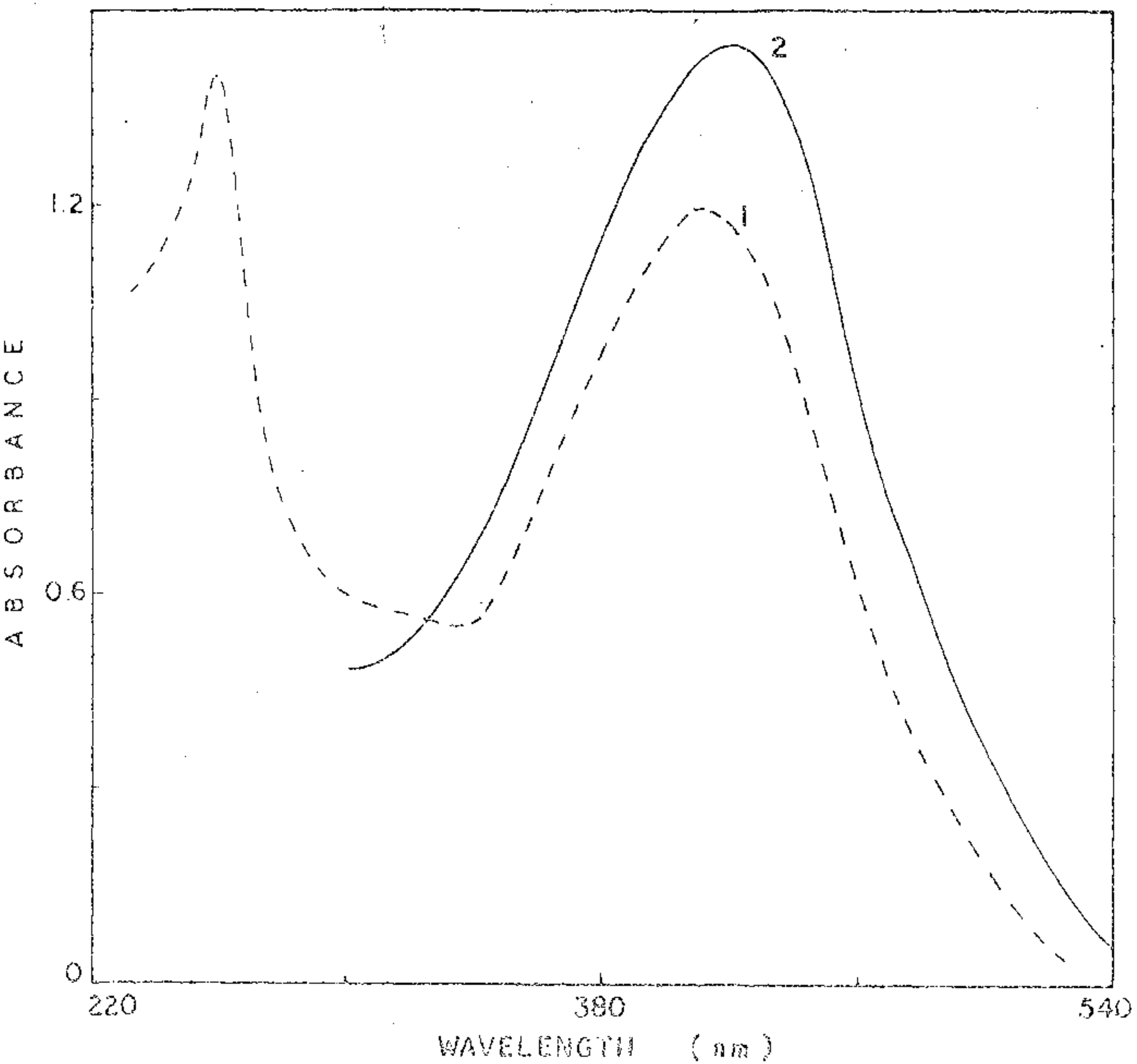


FIG. 18. ABSORPTION SPECTRA OF $Ph_3SnL'SnPh_3$
1. IN METHANOL AND 2. IN BENZENE.

IVD. Experimental

The UV-Visible spectra reported in this work were Obtained with Beckman DU-2 Spectrophotometer using 1 cm quartz cells.

All solvents used were of spectroscopic (UVASOL, E.Merck) grade.

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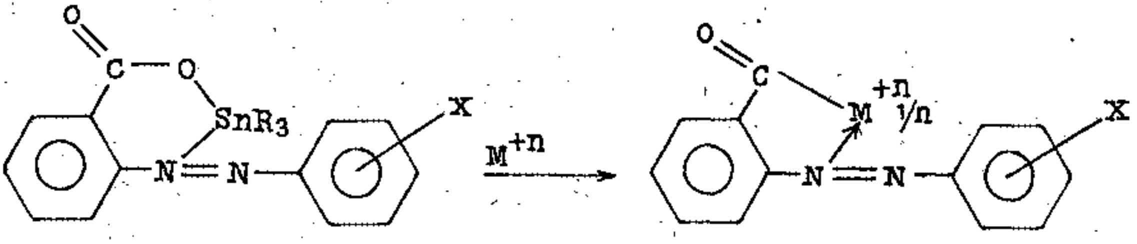
CHAPTER - IV

PREPARATION AND STRUCTURE OF TRANSITION METAL - ORGANOTIN MIXED COMPLEXES OF 5-ARYLAZO-8-QUINOLINOLS:

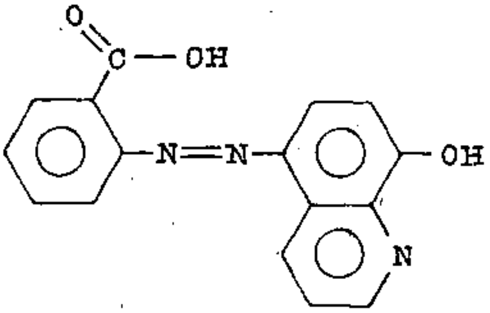
IVA. Introduction

In chapters II and III we have amply demonstrated the use of o-carbazoxine for preparing a variety of interesting organotin complexes including the binuclear organotin complexes having tin atoms with different coordination numbers. One of the primary aims of our present study was to explore the possibility of preparing organotin-transition metal mixed complexes which, to the best of our knowledge, are still unknown. The difficulty in the realisation of such mixed complexes lies in the facile replacement of organotin groups by the transition metal ions (eqn. 1) due to the much greater stability of the corresponding transition metal complexes[1].

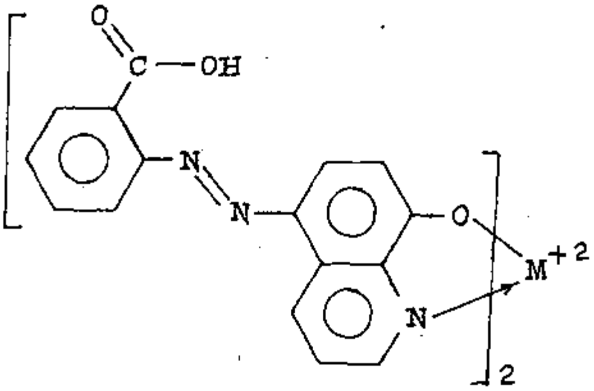


------- (1)

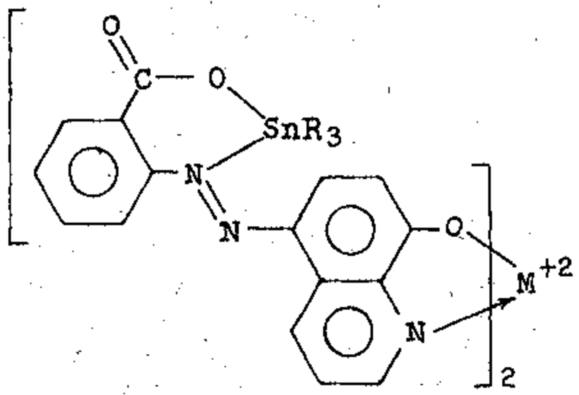
Obviously, the ideal ligand should be one in which the functional groups have different coordinating properties such that the ligand is able to distinguish between an organometal group and a transition metal ion. In o-carbaxoxine (I), the coordinating site on the quinoline moiety is expected to bind transition metal ions in preference to organotin groups because of the much greater stability of the transition metal oxinates. For example, the formation constant of copper oxinate is 2.5×10^{23} while that of copper acetate is only $2.0 \times 10^{3^{2}}$. Therefore, it is possible to prepare the quinolinolate derivative, i.e., the oxinate type complexes of (I) with Cu^{2+}, Ni^{2+} etc. (II) in the first step which can then be reacted with R_3SnX or $(R_3Sn)_2O$ to give the mixed complexes of type III.



(I)



(II)



(III)

$[M^{+2} = Cu, Ni]$

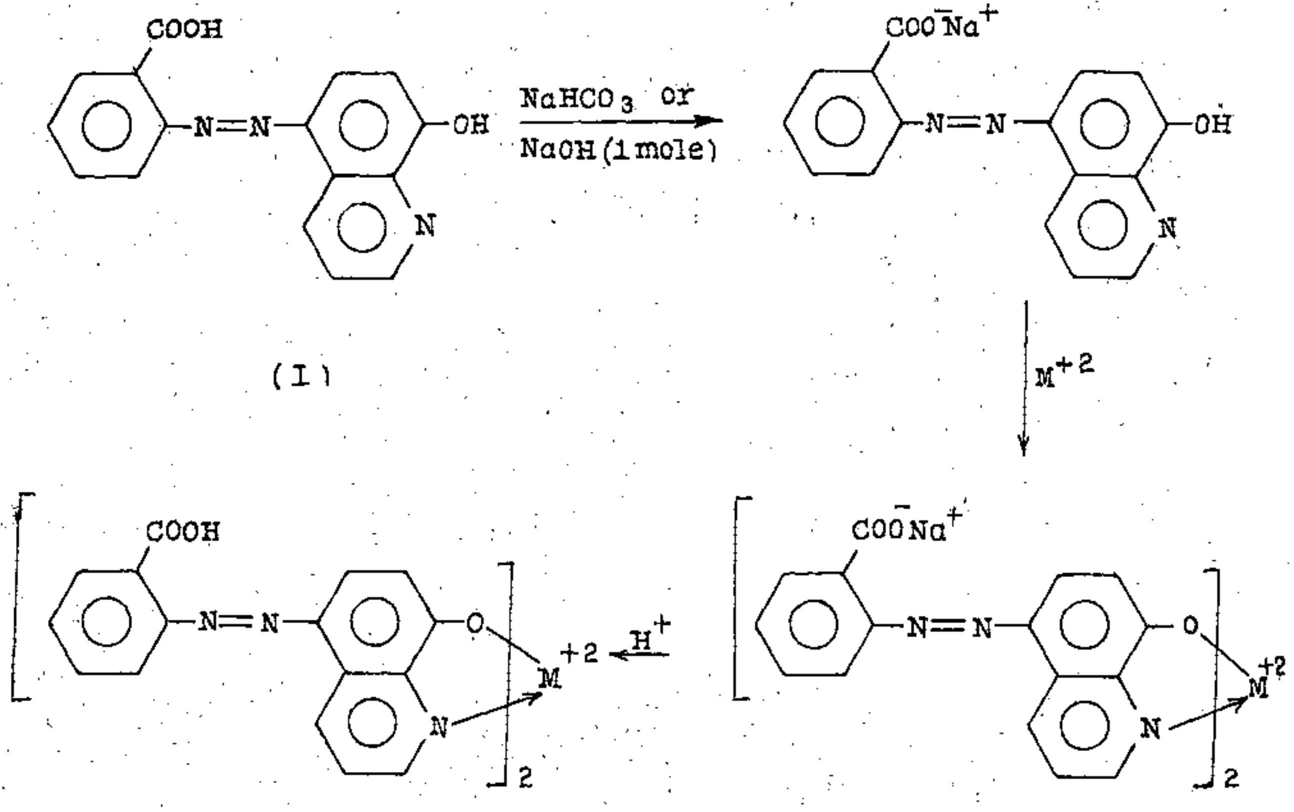
In this concluding chapter, we report the results of our exploratory investigation on the preparation and characterisation of such mixed complexes.

IVB. Methods of preparation of transition metal-organotin mixed complexes:

It was discussed in Chapter - II that the dibasic ligand, 5-(2'-carboxyphenyl) azo-8-quinolinol (o-carbazoxine) can form three types of organotin derivatives, viz., the organotin carboxylates, organotin quinolinolates and the binuclear di/tri organotin (triorganotin carboxyphenyl) azo-quinolinolates. As already indicated, the preparation of transition metal-organotin mixed complexes, involve the following two steps:

1. Preparation of the transition metal complexes of the ligand.
2. Preparation of the transition metal-organotin complexes of the ligand.

The first step, viz, the preparation of transition metal 5-(2'-carboxyphenyl) azo-8-quinolinolates (II), is a straight forward process. The desired complexes can be obtained by the reaction of the ligand with the metal in 2:1 molar proportion. However, the ligand being insoluble in water, it is dissolved either in an aqueous solution of $NaHCO_3$ or in a solution of containing equivalent amount of NaOH. To this solution, equivalent amount of the metal acetate or the metal sulphate is then added when the corresponding complex is precipitated. The solution is slightly acidified with acetic acid to complete the precipitation.



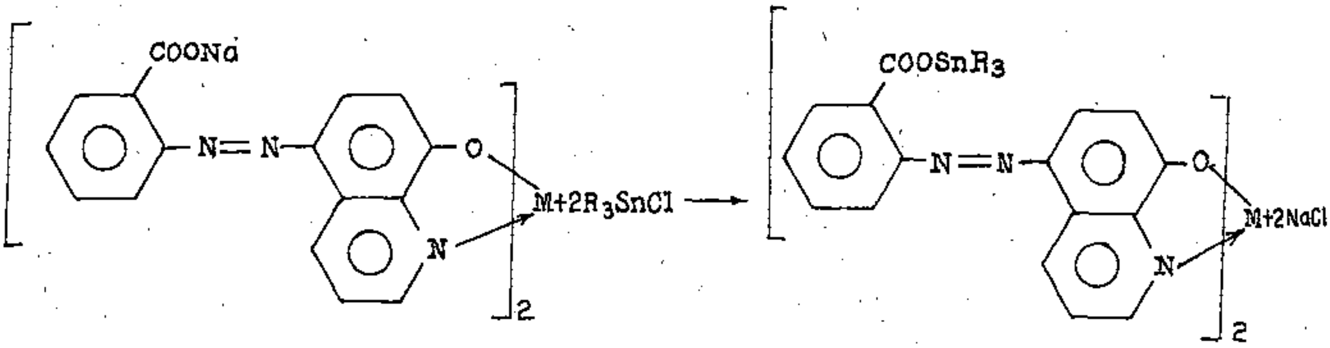
(I)

(II)

The polymeric, polynuclear complexes which may be formed in small amounts are removed by extracting the crude product with $NaHCO_3$ solution and reprecipitating the metal complex by acidification.

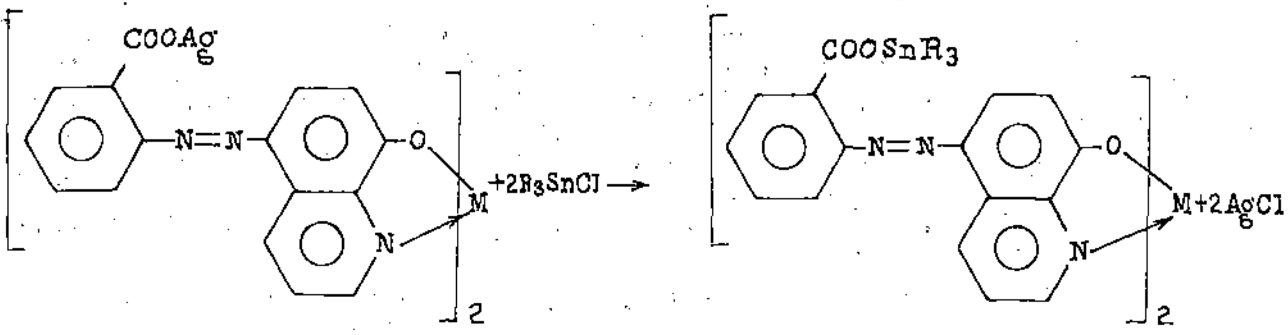
In order to prepare the transition metal-organotin mixed complexes, the following methods were tried:

(i) Reaction of the Na-Salt of the transition metal complex with R_3SnCl:



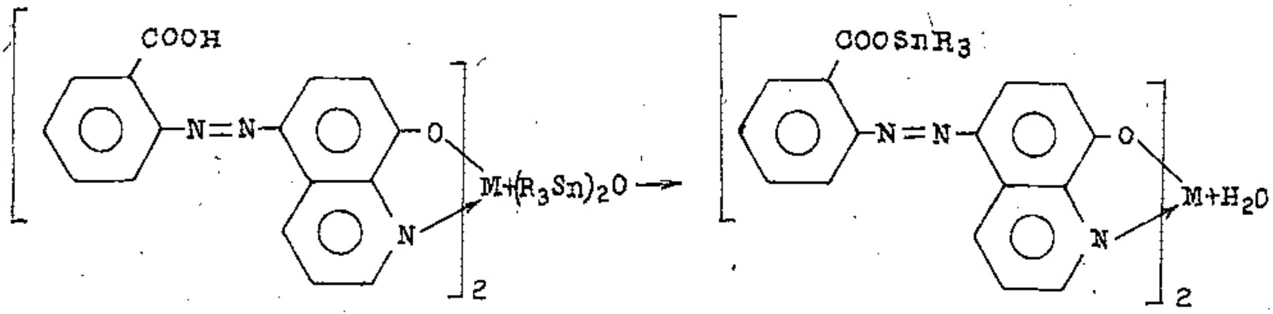
However, even with prolonged refluxing this reaction did not take place although this is a standard method for the preparation of organotin carboxylates.

(ii) Reaction of the Ag - Salt of the transition metal complex with R_3SnCl :



when refluxed in benzene for a very long period, only small amounts of the desired products are formed. This reaction was also found unsuitable as a practical method of preparation.

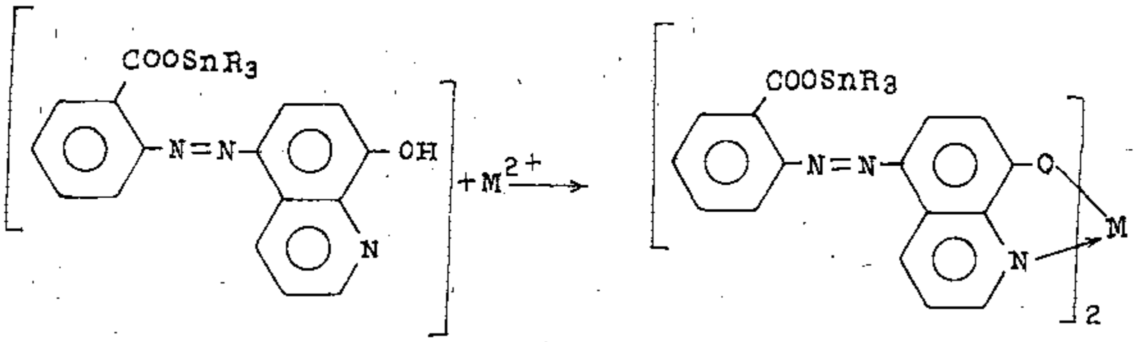
(iii) Reaction of the transition metal complex with $(R_3Sn)_2O$:



This reaction was found to be the best available route to the preparation of organotin-transition metal mixed complexes.

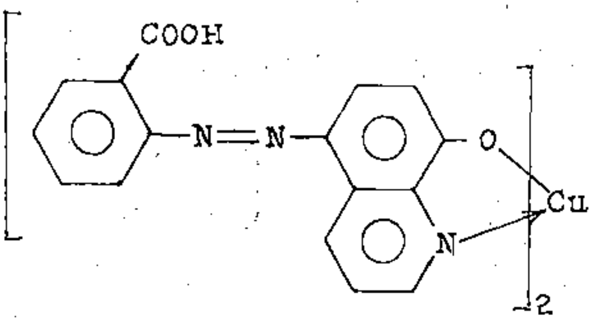
The experimental details are given in Section IVD.

Attempts were also made to prepare the transition metal-organotin complexes by the reaction of $R_3SnL'H$ type compounds with the metal ions in alcohol:

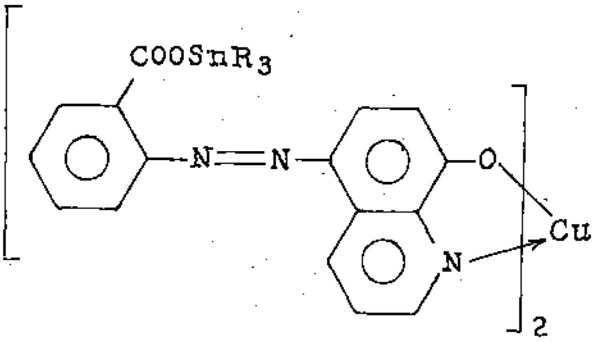


However, the organotin groups were invariably cleaved during reaction.

In the discussion that follows we shall use the abbreviation given in Chapter II and III. The corresponding metal complexes, e.g., copper [5-(2'-carboxy phenyl) azo-8-quinolinolate] (IV) is abbreviated as $(L'H')_2Cu$. The mixed complex (V) is abbreviated as $(L'SnPh_3)_2Cu$.



(IV)



(V)

IVC. Properties of the organotin-transition metal complexes:

All the complexes are red solids and are moderately soluble in common organic solvents. This contrasts sharply with the transition metal complexes of the type $(L'H')_2M$ which are very sparingly soluble in all common organic solvents except strong donor solvents like DMSO (dimethyl sulphoxide), Pyridine, DMF (dimethyl formamide) etc. The solubility in the donor solvent is presumably due to the solvation of the metal atom and/or interaction with the -COOH group through H-bonding.

(i) Electronic spectra:

The transition metal-organotin mixed complexes, $(R_3SnL')_2M$ are expected to be structurally similar to $(R_3'SnL')_2SnR_2$ type compounds. Therefore, these compounds are expected to show a single, intense absorption band in the visible region, both in protic and aprotic solvents as is the case with $(R_3'SnL')_2SnR_2$ [See chapter-III]. The data given in Table - 1 and Figures 1-6 borne out this expectation.

Table - 1

Absorption maxima of $(R_3SnL')_2M$ type compounds

Compound	Electronic spectra [λ_{max} (nm)]	
	Methanol	Benzene
$(L'SnPh_3)_2Cu$	453	460
$(L'SnBu_3)_2Cu$	452	470

Contd..

Table - 1 (Contd..)

Compound	Electronic spectra [λ_{max} (nm)]	
	Methanol	Benzene
$(L'SnPr_3)_2Cu$	453	470
$(L'SnPh_3)_2Ni$	452	440
$(L'SnPr_3)_2Ni$	450	440
$(L'SnPh_3)_2Mg$	420	420
$(L'SnBu_3)_2Mg$	410	415

Compared to the binuclear organotin complexes, $(R'_3SnL')_2SnR_2$, the transition metal-organotin mixed complexes, $(R_3SnL')_2M$ (M = Cu, Ni) show a larger bathochromic shift compared to the corresponding binuclear organotin complexes, $(R_3SnL')_2SnR_2$ for which data are given in Table - 1, Chapter-III. In order to ascertain whether or not the stability of the complexes has a role in determining the magnitude of the bathochromic shift, viz., $(R_3SnL')_2Mg$, were also prepared. Magnesium was chosen for this study since 8-hydroxyquinoline (oxine) complexes of magnesium has much lower formation constant than the corresponding complexes of copper and nickel[2]. It is interesting to note that the magnitude of the bathochromic shift in

ELECTRONIC SPECTRA

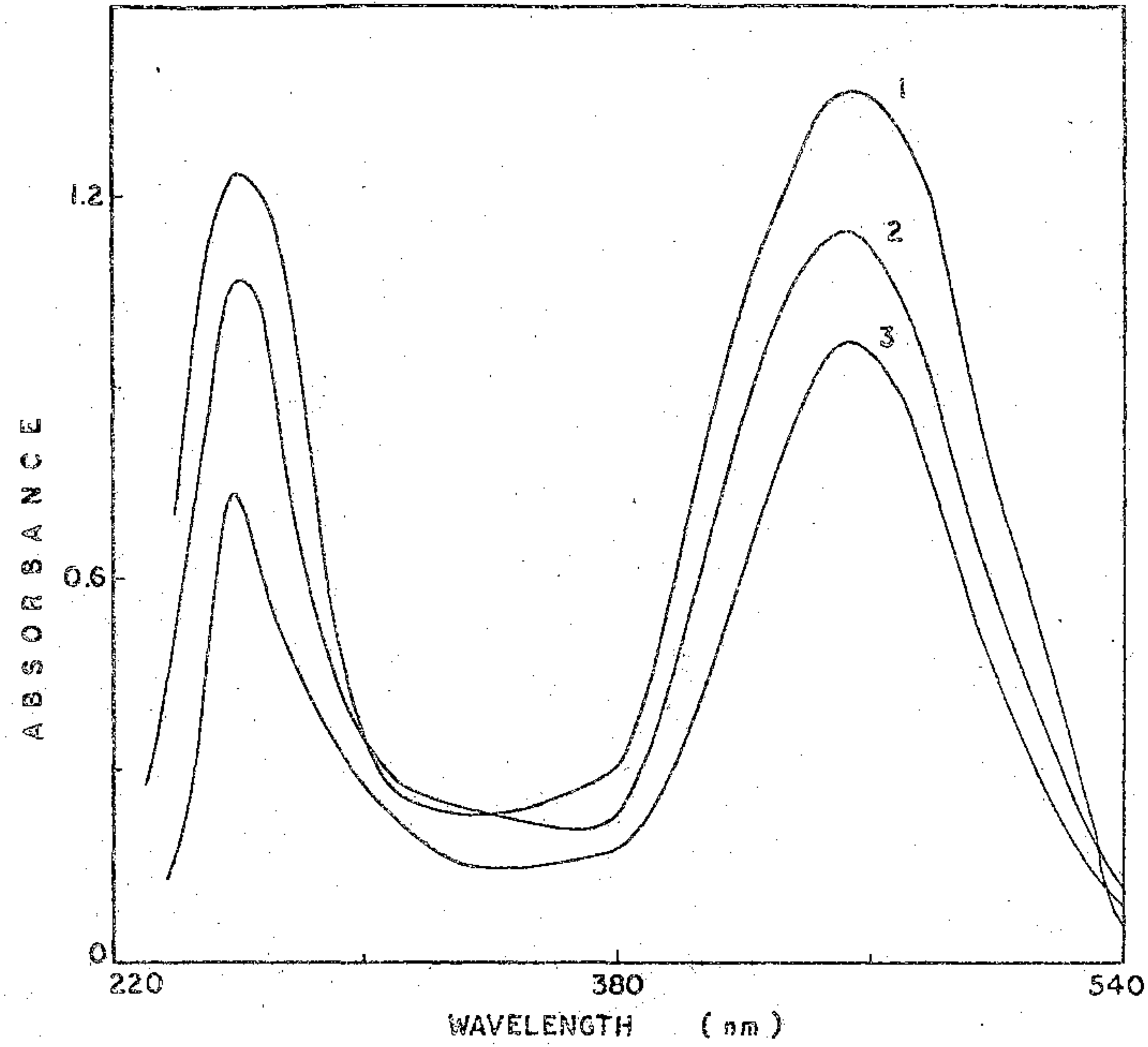


FIG. I. ABSORPTION SPECTRA IN METHANOL OF 1. $Cu(L'SnPh_3)_2$, 2. $Cu(L'SnBu_3)_2$ AND 3. $Cu(L'SnPr_3)_2$

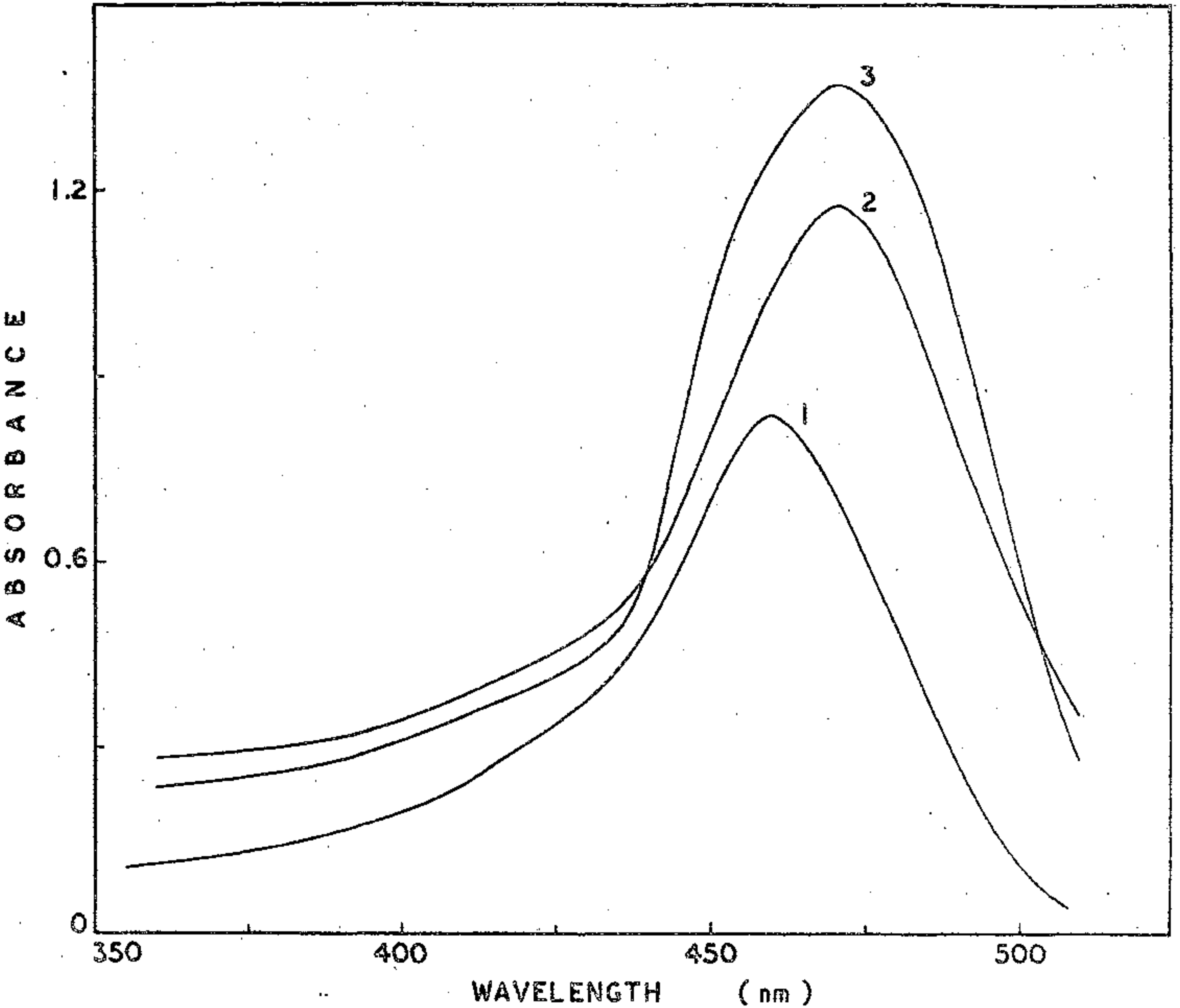


FIG. 2. ABSORPTION SPECTRA IN BENZENE OF
1. Cu(L′SnPh$_3$)$_2$, 2. Cu(L′SnBu$_3$)$_2$ AND 3. Cu(L′SnPr$_3$)$_2$

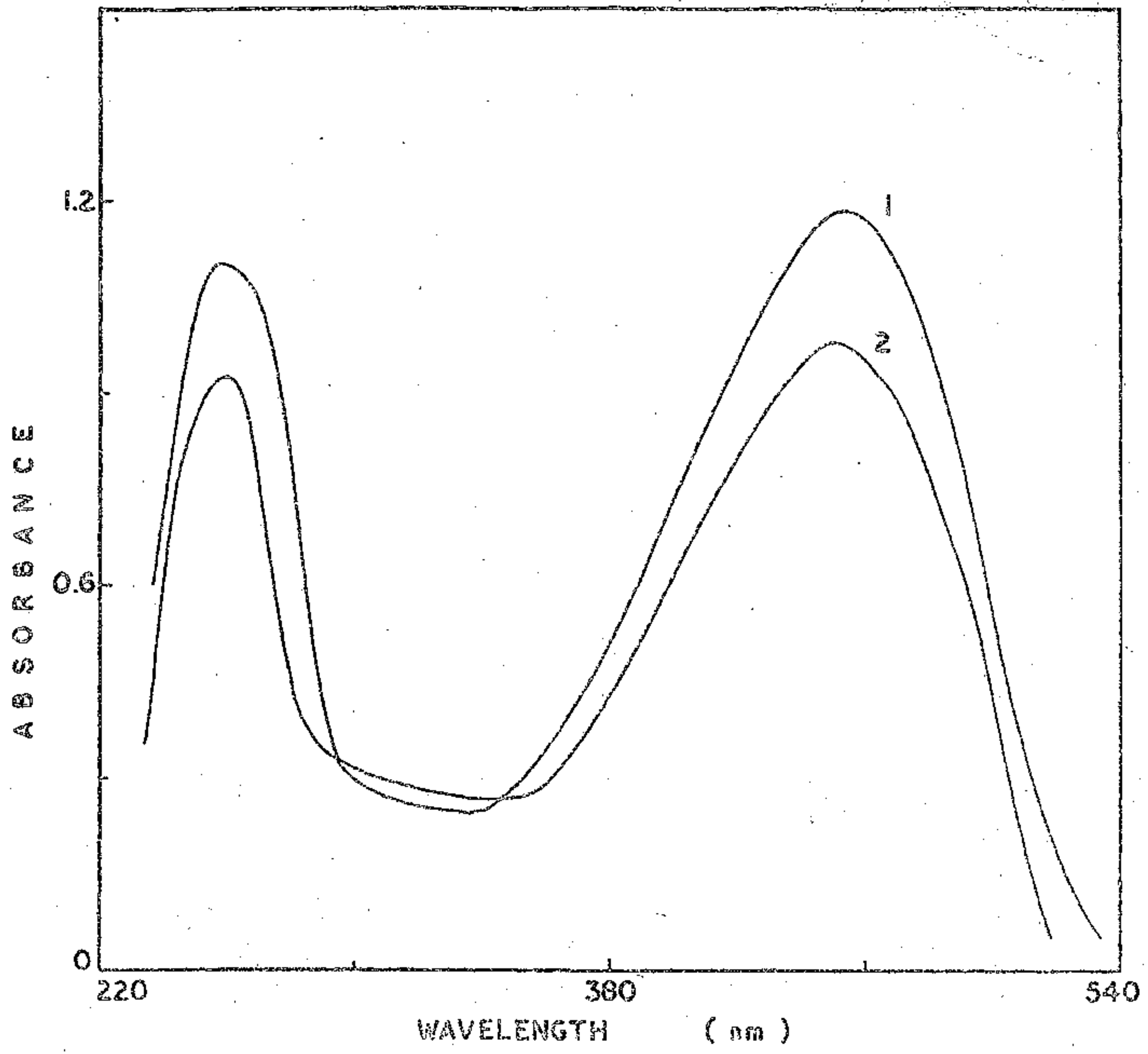


FIG. 3. ABSORPTION SPECTRA IN METHANOL OF 1. $Ni(L'SnPh_3)_2$ AND 2. $Ni(L'SnPr_3)_2$

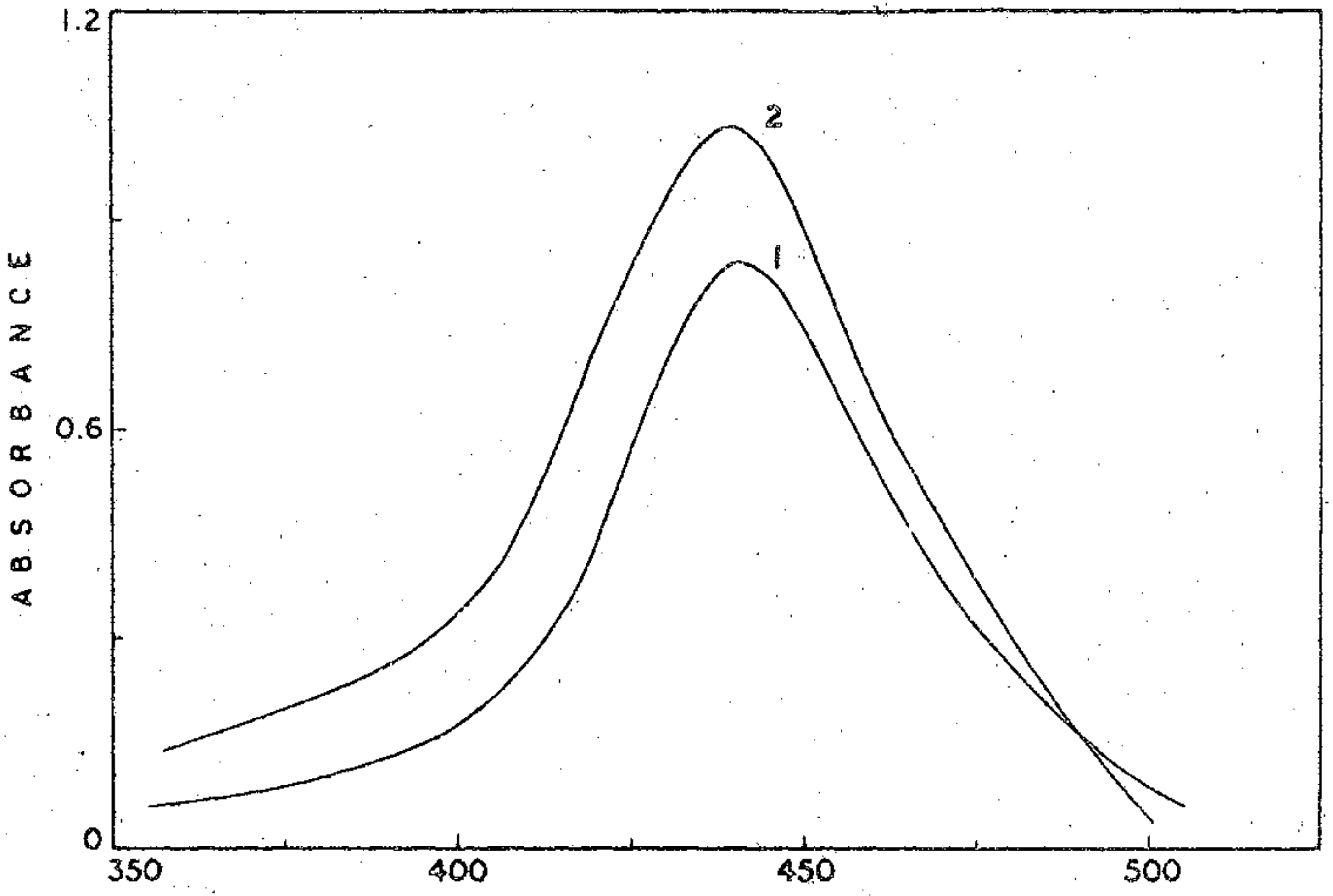
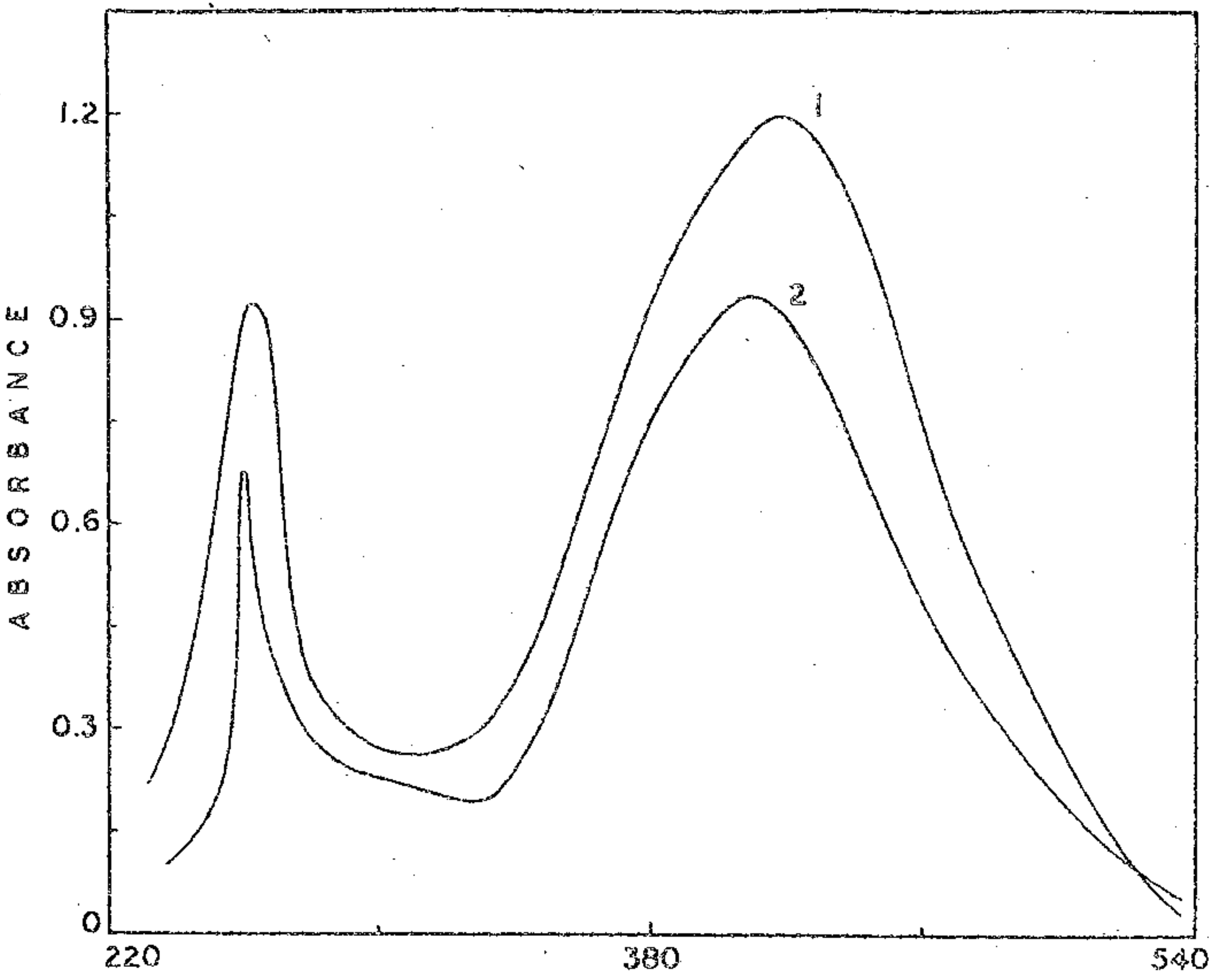


FIG. 4. ABSORPTION SPECTRA IN BENZENE OF 1. $Ni(L'SnPh_3)_2$ AND 2. $Ni(L'SnPr_3)_2$



WAVELENGTH (nm)

FIG. 5. ABSORPTION SPECTRA IN METHANOL OF
1. Mg(L'SnPh$_3$)$_2$ AND 2. Mg(L'SnBu$_3$)$_2$

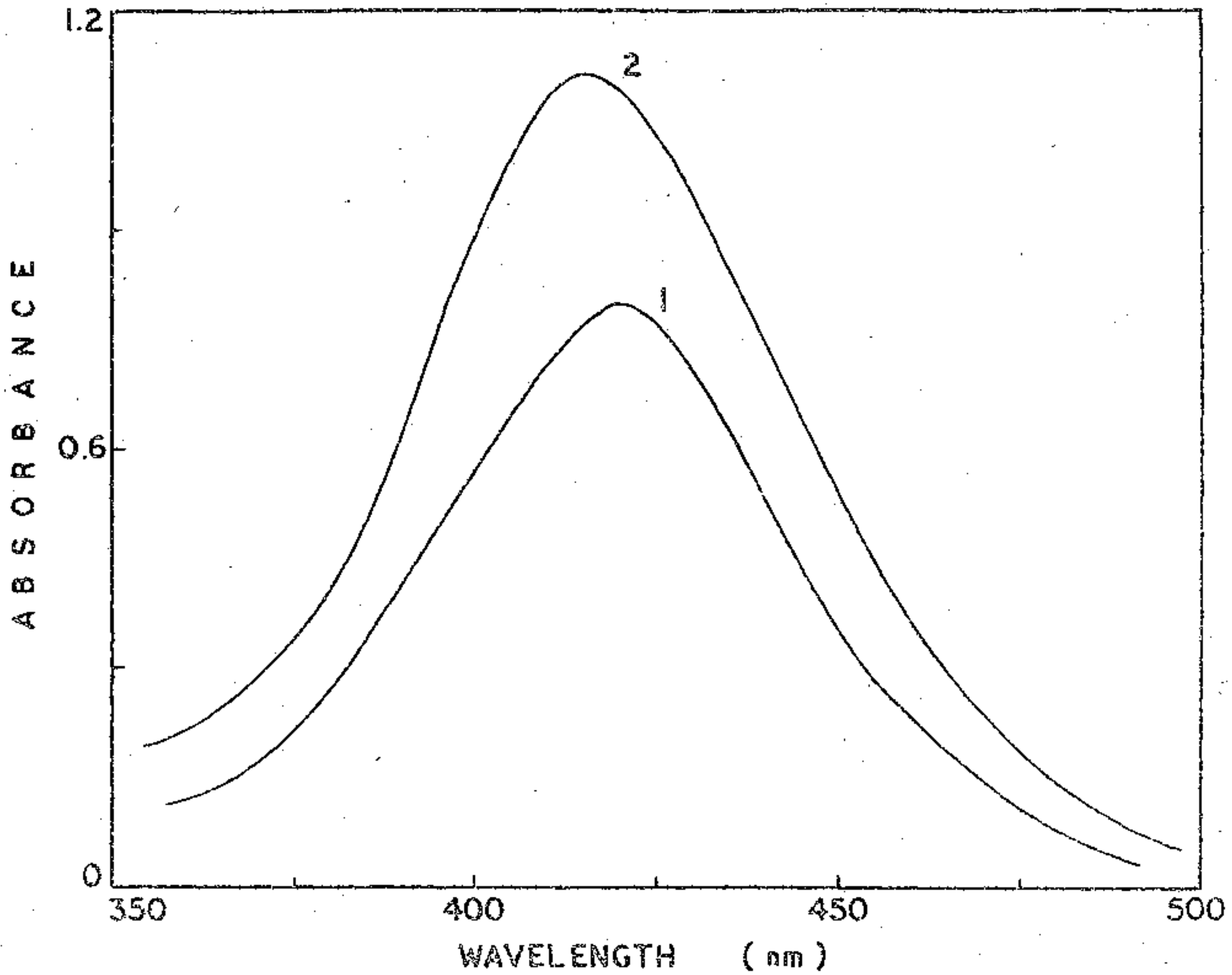


FIG. 6. ABSORPTION SPECTRA IN BENZENE OF

1. $Mg(L'SnPh_3)_2$, 2. $Mg(L'SnBu_3)_2$

$(R_2SnL')_2M$ (M = Cu, Ni and Mg) follows the order of the stability of their oxine complexes which decrease in the sequence M = Cu $<$ Ni $\ll$ Mg. A very plausible reason for this behaviour is that d-orbitals on Cu^{2+} and Ni^{2+} are more favourable for $d_\pi - p_\pi$ interaction with the ligand π-MO's. The $d_\pi - p_\pi$ overlap between the metal 'd' orbitals and the ligand π-orbitals will result in a mixing of the electronic states of the ligands with charge transfer states. This will stabilise the ground state as well as the first excited state of the complex. Such interaction normally stabilises the excited state to a greater extent relative to the ground state resulting in a bathochromic shift of the first $\pi-\pi^*$ transition[14,15]. On the other hand, energetically favourable d-orbitals are not available either in the diorganotin or magnesium complexes and as such the interaction of the metal atom with the ligand can not be strong as that in the case of Copper or Nickel. Since the stabilities of the complexes will depend partly on the magnitude of the metal-ligand interaction through $d_\pi - p_\pi$ interaction, the magnitude of the bathochromic shift of the $\pi-\pi^*$ transition of the ligand is expected to follow the order of the stability of the corresponding metal complexes.

(iii) IR spectra:

The infra red spectra of the transition metal complexes, $(L'H')_2M$, are characterised by a strong absorption at 1700-

1720 cm^{-1} due to asymmetric carboxylate stretch. In addition, a new absorption occurs at ~ 500 cm^{-1} as a doublet in some compounds and as a broad band in others. This is presumably due to the M-O stretch, the doublet probably arises from the symmetric and asymmetric combination of the vibration of the two M-O bonds present in $(L'H')_2M$ type compounds. Undoubtedly, this vibration will be mixed with the chelate ring modes including the M ← N stretch. However, absorption in this region in transition metal complexes of chelating ligands, e.g., oxalic acid, acetyl acetone etc has been attributed to a mode which is predominantly M-O stretch[3,4].

Stannylation of the carboxylic group to form the mixed complexes, $(R_3SnL')_2M$ results in the disappearance of the strong carboxylic stretch band at ~1700-1720 cm^{-1} in the transition metal complexes, $(L'H')_2M$. Instead, the carboxylate stretch is lowered to 1550-1630 cm^{-1} region which is common in organotin carboxylates[5-8]. A broad absorption band at 430-450 cm^{-1} which is found in the IR spectra of the mixed complexes, but not in that of the transition metal complexes, is presumably due to ν(Sn-O) which is known to occur in ~400-600 cm^{-1} region in most organotin compounds[5-8,9]. Some typical spectra are shown in Figs. 1-6.

Table - 2

Frequencies of important vibrational modes in $(L'H')_2M$ and $(R_3SnL')_2M$ type compounds.

Compound	Frequencies (in cm^{-1}) of[a]		
	$\nu_{as}(COO)$	$\nu(M-O)$	$\nu(Sn-O)$
$(L'H')_2Cu$	1720	525,510	-
$(Ph_3SnL')_2Cu$	1620	510[c]	450
$(Bu_3SnL')_2Cu$	1545	510,500	d
$(Pr_3SnL')_2Cu$	1545	510,500	430
$(L'H')_2Ni$	~1600 (br)	490[c]	d
$(Ph_3SnL')_2Ni$	1610[b]	485[c]	445
$(Pr_3SnL')_2Ni$	1610	495[c]	445
$(Ph_3SnL')_2Mg$	1625[b]	500[c]	d
$(Bu_3SnL')_2Mg$	1625	500[c]	d

a) This absorption band overlaps with the strong ring vibration modes appearing in this region. As such the position of the band maximum may be in error by as much as 10 cm^{-1}.

b) Appears as a shoulder of the strong ring vibration modes at ~1600 cm^{-1}.

c) The doublet is not resolved, appears as a broadened absorption band.

d) $\nu(Sn-O)$ could not be identified with reasonable certainity.

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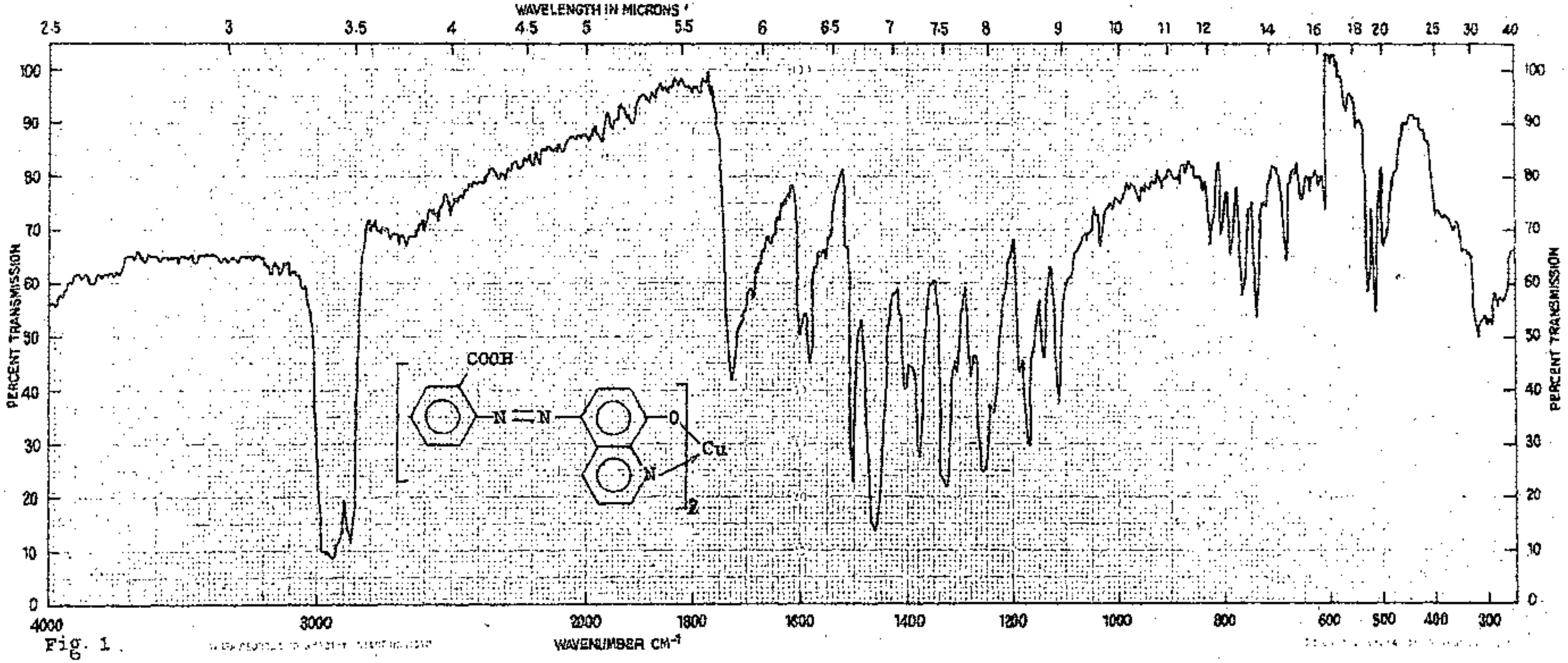
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WAVENUMBER CM⁻¹
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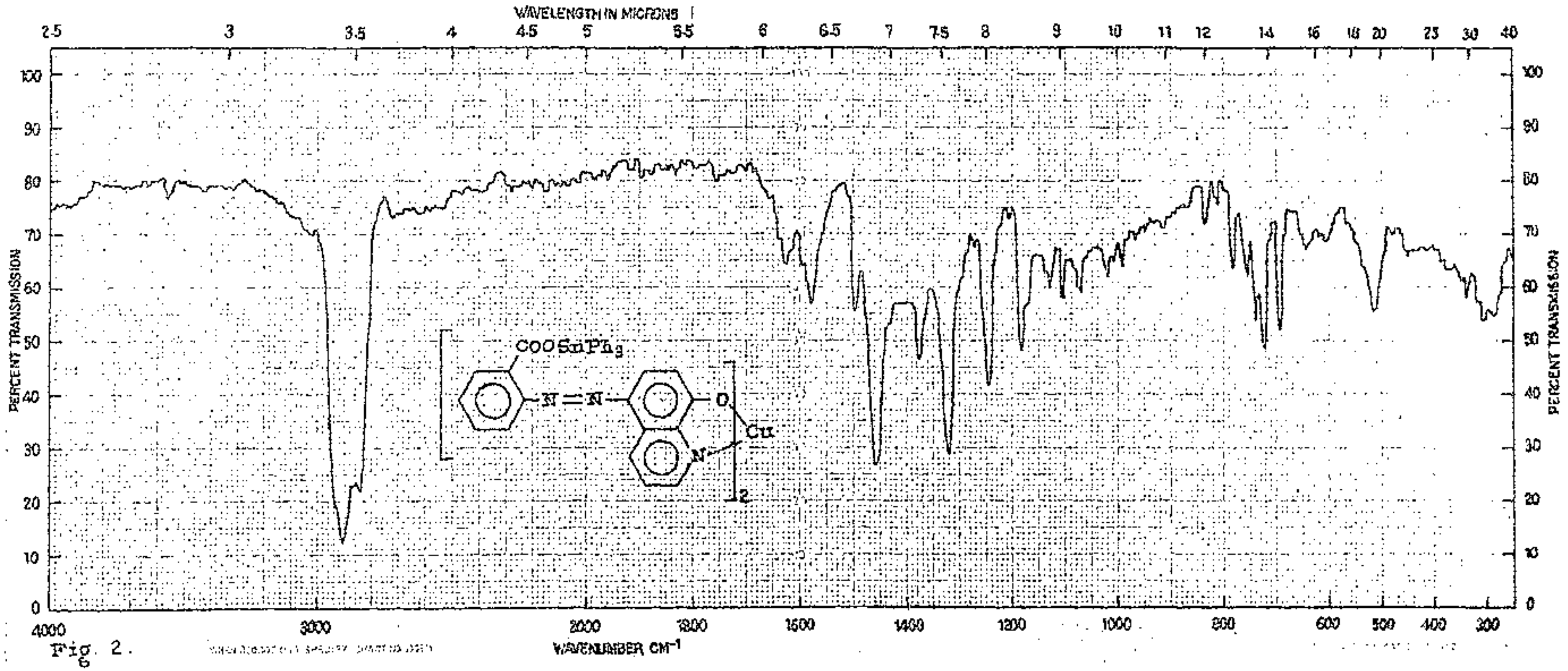
Fig. 1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WAVENUMBER CM⁻¹
COOSnPh$_3$
N=N
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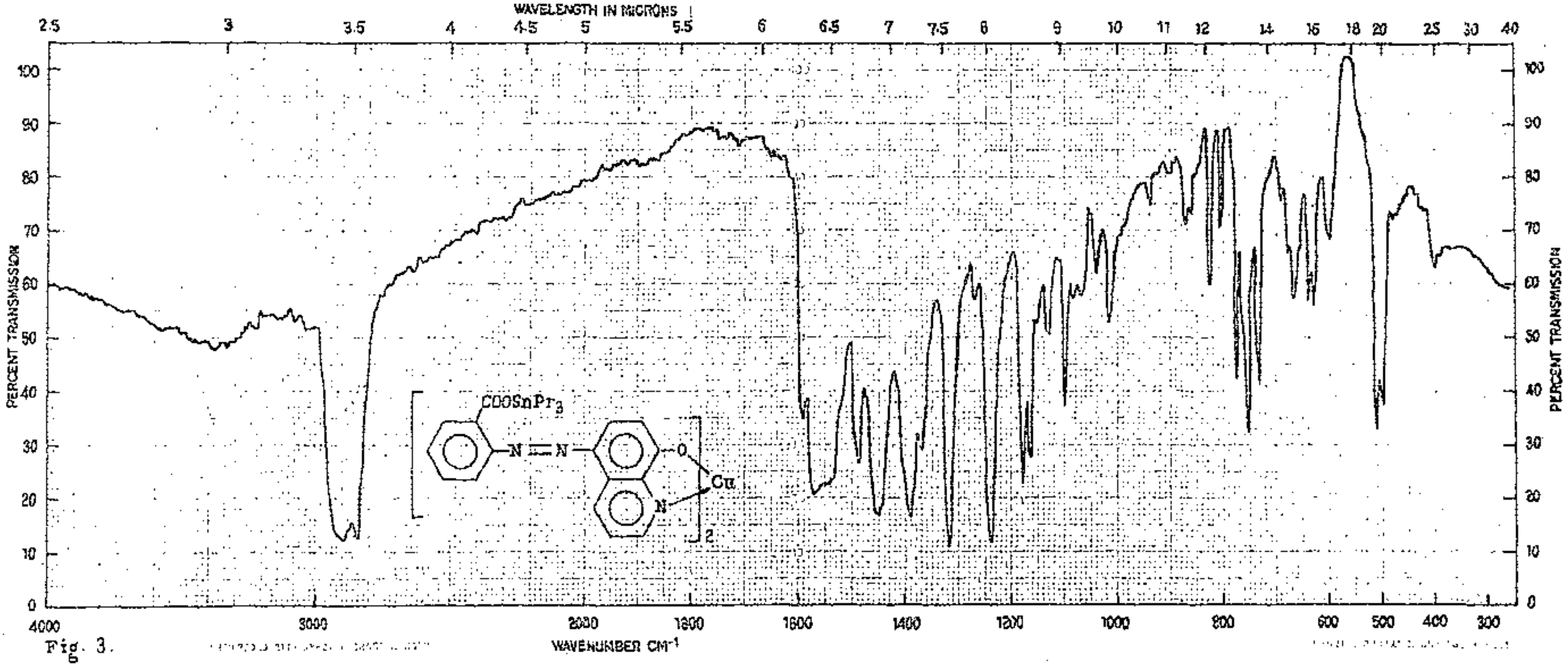
Fig. 2.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WAVENUMBER CM⁻¹
COOSnPr3
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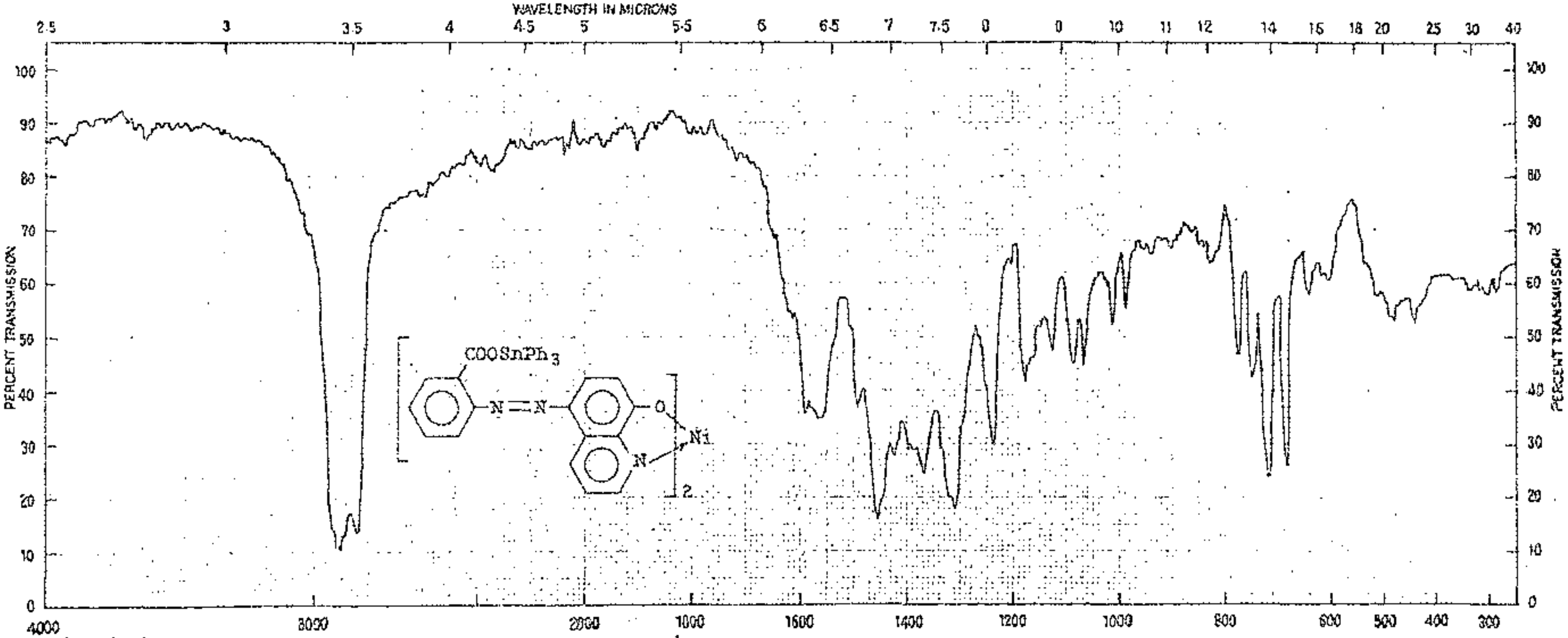
Fig. 3.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WAVENUMBER CM⁻¹
COOSnPh₃
N=N
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Ni
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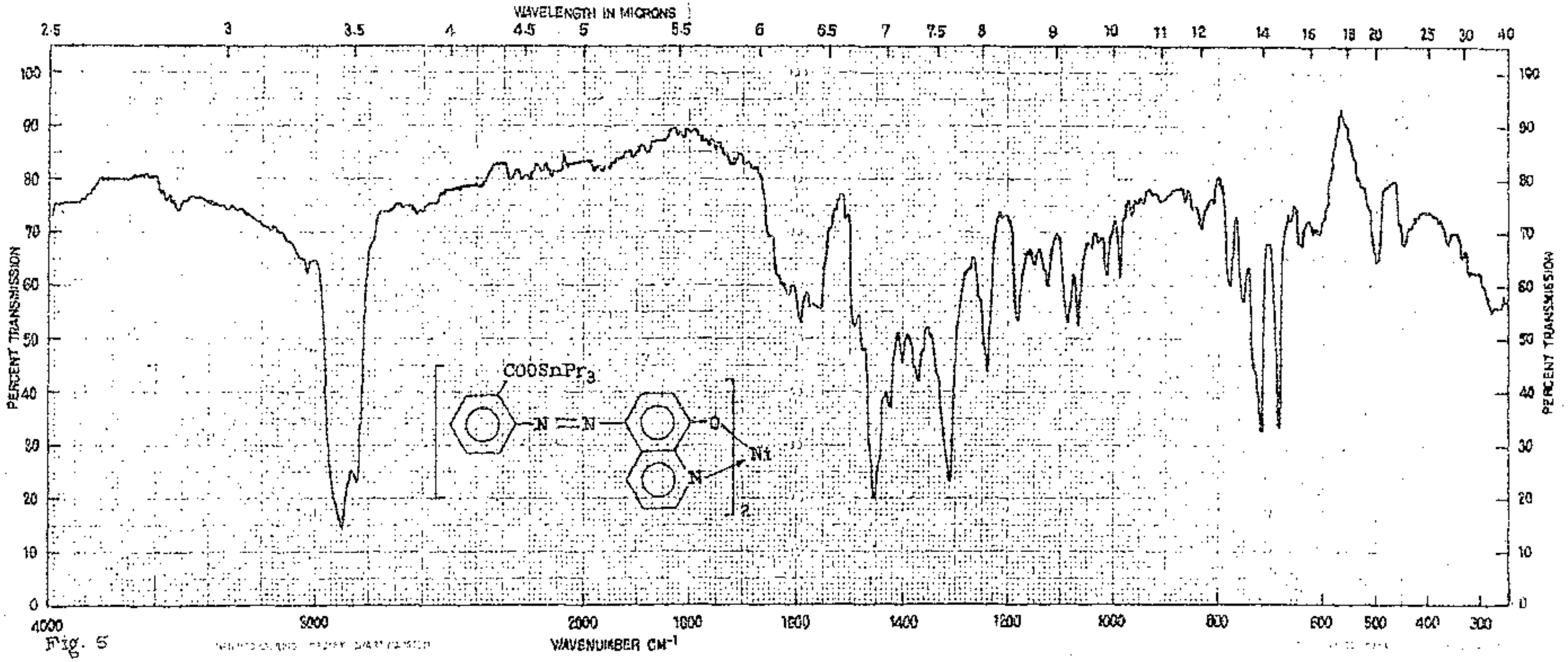
Fig. 4.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WAVENUMBER CM⁻¹
COOSnPr₃
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Ni
N
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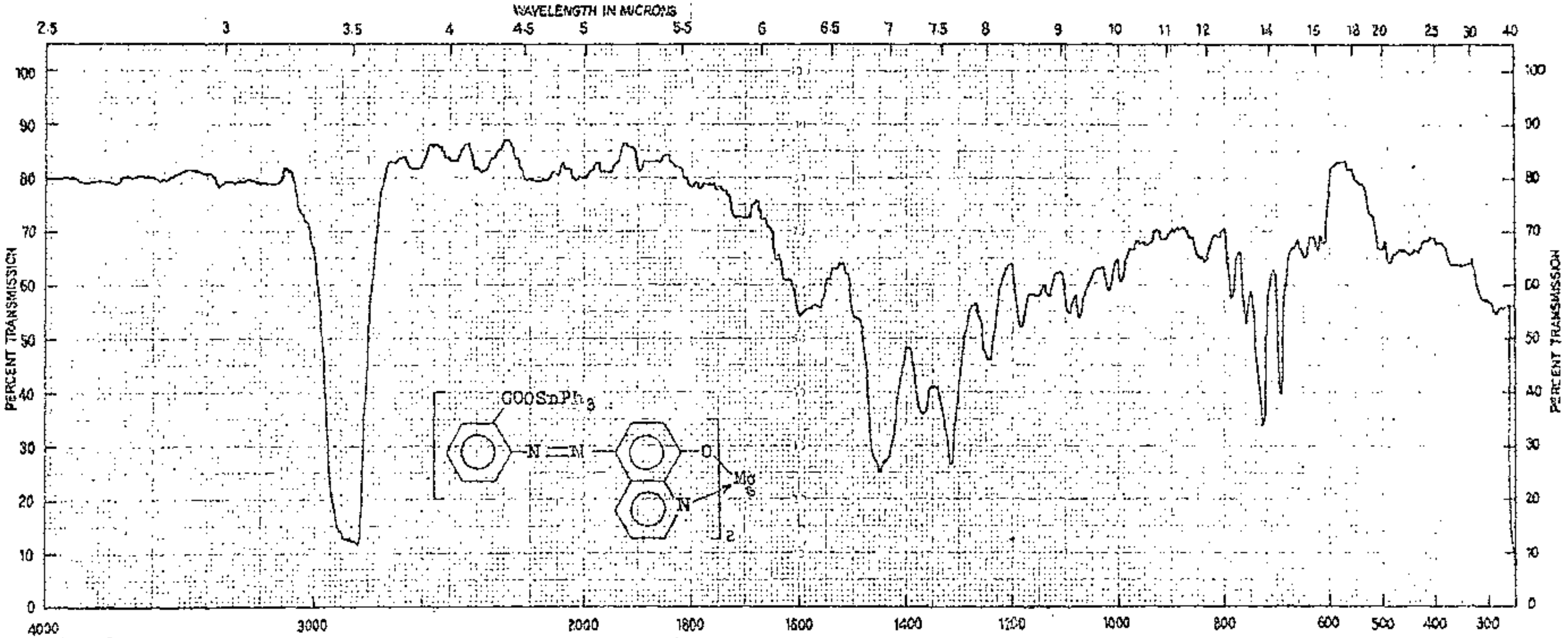
Fig. 5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PERCENT TRANSMISSION
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1600
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1000
800
600
500
400
300
WAVENUMBER CM⁻¹
COOSnPh3
N=N
O
Mg
N
2

Fig. 6

(iii) Magnetic moments of the organotin-transition metal mixed complexes:

The observed magnetic moment of the Cu^{+2} ion in its complexes is generally about 1.9 B.M. at room temperature which is close to the spin only value for one unpaired electron, irrespective of the stereochemical environment of the ion[10]. The complexes usually have a distorted octahedral stereochemistry, although a few are known which are square planar or approximate to a tetrahedral stereochemistry[10]. For tetrahedrally coordinated Cu^{+2} ion, a moment of 2.2 B.M. is anticipated at room temperature[10], but this value has not been observed in any compounds, though the moments are generally higher than normally observed for octahedral complexes. For example, the magnetic moments of the tetrahedral complexes, $(R_3P)_2CuX_2$ ($X = Cl, Br$), lie in the range $\sim 2.0 - 2.1$ B.M.

The moment of Ni^{+2} ion is however stereochemically dependent. In a ligand field of tetrahedral symmetry, the moment at room temperature lies between 3.6 and 4.0 B.M. If the ligand field departs from tetrahedral symmetry or electron delocalisation occurs, the moment tends to be closer to the spin-only value of 2.83 B.M[10]. In the square plannar geometry, Ni^{+2} ion is diamagnetic while octahedral complexes of Ni^{+2}, generally have moments between 2.9 and 3.3 B.M.[10]

Experimental magnetic moment data given in Table -3 which have been corrected for the diamagnetic contributions show that the Ni(II) complexes and mixed organotin - Ni(II) complexes have a tetrahedral stereochemistry around Ni(II). The slightly lower value may be due to a slight departure from perfect tetrahedral symmetry. In view of the higher magnetic moments, the analogous complexes of Cu(II) are also expected to have tetrahedral stereochemical environment around Cu(II).

Table - 3

Magnetic moment data:

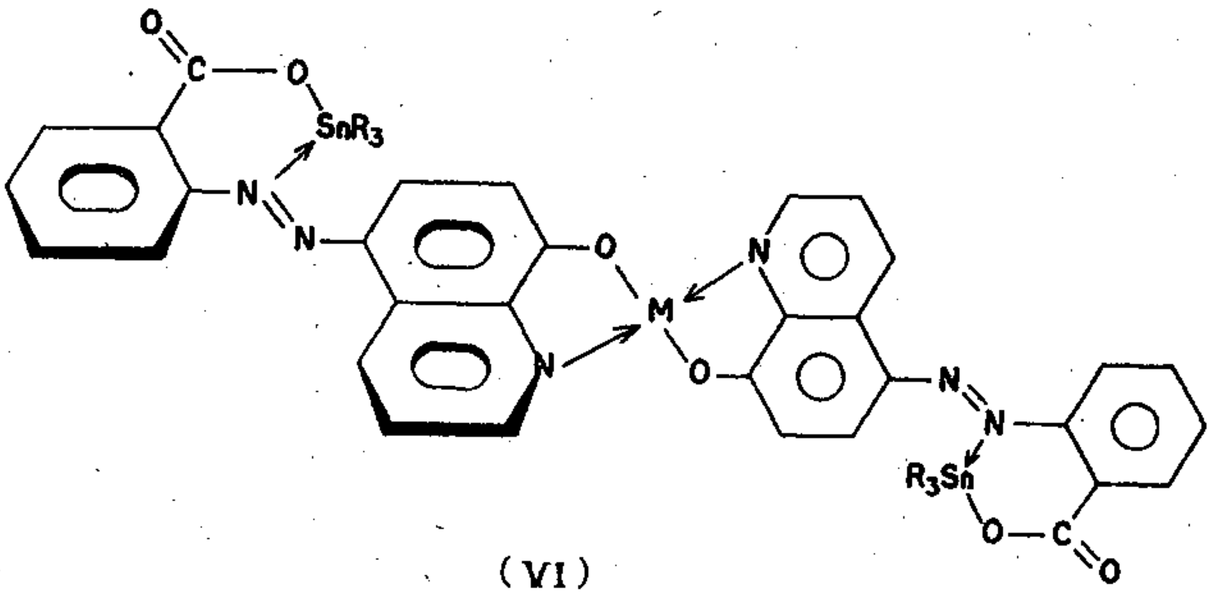
Compound	Magnetic moment[a] μeff (B. M.)
$(L'H')_2Cu$	1.79
$(L'Me)_2Cu$	1.95
$(L'SnBu_3)_2Cu$	2.06
$(L'SnPr_3)_2Cu$	1.94
$(L'H')_2Ni$	3.04
$(L'SnPr_3)_2Ni$	3.52

a) Temperature, 19.5°C

It is interesting to note that the substitution of the carboxylic proton in the transition metal (arylazo)-quinolinolates by R_3Sn group results in an increase of the magnetic moment. The increase is 0.48 B.M. in the Ni(II) complexes and 0.11-0.15 B.M.

in the Cu(II) complexes. The increase in μ_{eff}s is presumably due to the increase in the dihedral angles between the planes of the two ligand molecules towards tetrahedral orientation to avoid steric crowding of the bulky triorganotin groups.

The foregoing discussion on the physicochemical properties of the organotin-transition metal complexes and the discussion on the organotin complexes presented in chapter - II and III suggest that these complexes should be formulated as in (VI), the geometry around the metal M being tetrahedral.



(VI)

IVD. Experimental:

Organotin compounds used in this work were prepared and purified as described in Chapter -II (Section II F). Bis-(tripropyl tin) oxide was prepared from tripropyl tin chloride as described by Sasin et al[11].

Unless otherwise stated, petroleum ether used in the present investigation refers to the fraction with the boiling range 60-80°C when necessary, solvents used were purified and dried by the standard methods[12]. A.R. (BDH) Copper acetate, Nickel acetate and Magnesium acetate were used for the preparation of the transition metal complexes.

Preparation of the ligand, 5-(2'-carboxyphenyl) azo-8-quinolinol (L'HH'), is given in Chapter - II, Section F. All melting points are uncorrected.

The UV - Visible spectra were obtained with the Beckman DU-2 spectrophotometer using 1 cm quartz cells. All solvents used were of Uvasol (E. Merck) grade.

Infra red spectra reported in this work were obtained with Beckman IR-20 infrared spectrophotometer using Nujol mull.

Magnetic moment data were obtained with PAR, Vibrating sample magnetrometer, Model - 155 at room temperature.

Estimation of Metals:

A known weight of the compound was decomposed with conc. HNO_3. For complete oxidation of the organic matter, a few drops of perchloric acid were added. When tin was present, it separated out as tin dioxide on dilution and digestion. This was filtered off and the tin was estimated by the usual procedure[13].

The filtrate was evaporated with a few ml of conc. H_2SO_4 to remove the nitric acid and then diluted with water to appropriate volume.

Copper, when present, was estimated volumetrically by iodometry. Nickel was estimated gravimetrically with dimethyl glyoxime and Magnesium was estimated volumetrically with EDTA. The procedures described by Vogel[13] were adopted.

(i) Synthesis of the transition metal complexes:

1. Preparation of $(L'H')_2Cu$:

4.0 gms of L'H'' was dissolved in 136 ml of N/5 aqueous sodium hydroxide solution with constant stirring. To complete the dissolution of the ligand it was digested on water bath for 45 minutes. 1.3 gms of copper-acetate was dissolved in 20 ml of water containing a few drops of acetic acid. This copper solution was added dropwise with constant stirring to the hot solution of L'HH'. Then the mixture was warmed on water bath for 30 minutes. On acidification with acetic acid, the metal complex was readily obtained as a precipitate. The precipitate was digested on water bath and filtered while hot. The solid was washed several times with water to remove excess acid. The solid was digested with methanol, filtered and finally washed with ether.

m.p. : > 255°C

yield : 90%

Analytical data :	C	H	N	Cu (%)
Found:	58.90	3.12	12.92	9.87
Calculated for $C_{32}H_{20}N_6O_6Cu$	59.30	3.09	12.97	9.80

IR : ν_{as}(COO) : 1720 cm^{-1}

μ_{eff} : 1.79 B.M.

2. Preparation of $(L'H')_2Ni$:

5.0 gms L'HH' was dissolved in 163.8 ml of N/5 aqueous sodium hydroxide solution with constant stirring followed by digestion on water bath for about 30 minutes. A solution containing 2.13 gm of Nickel acetate in 30 ml water with a few drops of acetic acid was added dropwise with continuous stirring to the hot solution of the ligand. The reaction mixture was warmed on water bath for another 1/2 hour. It was slightly acidified with acetic acid. The metal complex was readily precipitated as a brown coloured solid was filtered and thoroughly washed with water to remove excess acid. The solid was redissolved in aqueous sodium bicarbonate and then reprecipitated by acidification. The product was thoroughly washed with water, followed by hot methanol, and finally with ether. The product was dried for several days under vacuum.

m.p. : $> 270^\circ C$

yield : 90%

Analytical data :	C	H	N	Ni (%)
Found :	58.72	3.09	12.96	9.23
Calculated for $C_{32}H_{20}N_6O_6Ni$	59.75	3.11	13.07	9.13

IR : ν_{as}(COO) : 1600 (br) cm^{-1}

μ_{eff} : 3.04 B.M.

3. Preparation of $(L'Na)_2Cu$:

2.5 gms of the copper complex, $(L'H')_2Cu$ was dissolved in 250 ml aqueous solution containing 0.66 gms of sodium bicarbonate by warming the mixture on water bath for 30-40 minutes. The filtrate was then evaporated to dryness and the residue was extracted with hot methanol. Upon concentration by evaporation, the methanolic solution yielded crystal of $(L'Na)_2Cu$ which was dried and kept in vacuum.

4. Preparation of $(L'Ag)_2Cu$:

1.9 gms of sodium salt of the copper complex, $(L'Na)_2Cu$ was dissolved in 150 ml of methanol. 1.40 gms of silver nitrate in 50 ml of water was slowly added with stirring to the methanolic solution. The silver salt of the metal complex readily separated as a solid which was filtered and thoroughly washed with hot water followed by hot methanol and finally ether. The solid was dried in vacuum.

5. Preparation of $(L'Na)_2Ni$:

2 gms of the nickel complex, $(L'H')_2Ni$ was dissolved in 200 ml of water containing 0.53 gms of sodium bicarbonate by warming on water bath for about 30 minutes and filtered hot. The filtrate was evaporated to dryness. The residue was extracted with hot methanol. The crystals of the desired product were obtained by concentration of the methanolic solution. The product was dried in vacuum.

6. Preparation of $(L'Ag)_2Ni$:

2.5 gms of corresponding sodium salt, $(L'Na)_2Ni$ was dissolved in 250 ml of methanol. 1.65 gms of silver nitrate in 50 ml water was added dropwise with constant stirring to the hot methanolic solution. The silver salt separated as a solid which was filtered hot. The solid was thoroughly washed successively with hot water, hot methanol and ether. The complex so obtained was dried in vacuum.

7. Preparation of $(L'H')_2Mg$:

4.0 gms of L'H'' was dissolved in 140 ml of N/5 sodium hydroxide solution. 1.15 gms of Magnesium - acetate dissolved in 25 ml of water was then added slowly to the hot solution of the ligand. The mixture was warmed on water bath for another 30 minutes and the solution was slightly acidified with acetic acid. The metal complex was immediately obtained as a coloured solid which was filtered hot. The solid was washed several times first with hot water and then with cold water. Finally the solid was washed with methanol, ether and then dried in vacuum.

m.p. : > 270°C

yield : 90%

Analytical data:	<u>C</u>	<u>H</u>	<u>N</u>	<u>Mg</u> (%)
Found :	62.97	3.09	12.97	4.3
Calculated for $C_{32}H_{20}N_8O_8Mg$	63.12	3.29	13.81	4.0

3. <u>Preparation of $(L'Me)_2Cu$:</u>

2.0 gms of L'MeH was dissolved in 20 ml of hot methanol. 5.96 gms of Cu $(COOCH_3)_2$ in 30 ml of hot methanol containing a few drops of acetic acid was added slowly to the solution of L'MeH. Then the reaction mixture was digested for 15 minutes on water bath and filtered hot. The solid was washed successively with water, methanol and finally with benzene to remove traces of the unreacted L'MeH that may be present. The orange coloured solid was dried in vacuum.

m.p. : > 255°C

yield : 85%

Analytical data :	C	H	N	Cu (%)
Found :	60.27	3.49	12.42	9.43
Calculated for $C_{34}H_{24}N_6O_6Cu$:	60.39	3.55	12.43	9.40

IR : $\nu_{as}(OCO)$: 1720 cm^{-1}

μ_{eff} : 1.95 B.M.

(ii) Synthesis of Transition metal-organotin mixed complexes of the ligand:

1(a) Preparation of $(L'SnPh_3)_2Cu$:

A mixture of 2.0 gms of $(L'H')_2Cu$ and 2.20 gms of $(Ph_3Sn)_2O$ in 200 ml of dry benzene was refluxed for about 15 hours. Then the reaction mixture was cooled and filtered. Upon concentration the filtrate yielded crystals of the desired product. This was washed several times with hot petroleum ether. Then the solid was washed with 2% sodium bicarbonate solution to remove the unreacted $(L'H')_2Cu$ and finally with water. The solid was then extracted with hot benzene and recrystallised and dried in vacuum.

decomposition point : 235°C

yield : 50%

Analytical data :	C	H	N	Sn	Cu (%)
Found :	60.25	3.44	6.20	17.72	4.38
Calculated for $C_{68}H_{48}N_6O_6Sn_2Cu$:	60.67	3.56	6.24	17.65	4.72

IR : $\nu_{as}(COO)$: 1620 cm^{-1}

(b) Preparation of $(L'SnPh_3)_2Cu$:

A mixture of 2.0 gms of the $(L'Ag)_2Cu$ and 1.79 gms of the Ph_3SnCl in 200 ml dry benzene was refluxed for 25 hours. It was cooled and filtered. The filtrate was concentrated and petroleum ether was slowly added when the desired product separated out. The product was washed several times with hot petroleum ether, followed by 2% $NaHCO_3$ solution and then water. The solid was extracted with hot benzene and the product was crystallised from benzene-petroleum ether mixture.

decomposition point : 235°C

Yield : 10%

Analytical data :	C	H	N	Sn	Cu (%)
Found :	60.66	3.40	6.12	17.43	4.58
Calculated for $C_{68}H_{48}N_6O_6Sn_2Cu$:	60.67	3.56	6.24	17.65	4.72

IR : $\nu_{as}(COO)$: 1625 cm^{-1}

(c) Preparation of $(L'SnPh_3)_2Cu$:

2.0 gms of sodium salt of the copper complex, $(L'Na)_2Cu$ and 2.22 gms of Ph_3SnCl were dissolved in dry methanol and refluxed for 10 hours. It was filtered and the filtrate was evaporated to dryness. The residue was extracted with cold benzene and concentrated. Petroleum ether was gradually added till a solid separated out. This was washed with 2% aqueous sodium bicarbonate solution followed by water. The solid was recrystallised from benzene and petroleum ether mixture.

decomposition point : 234°C

Yield : 15%

Analytical data:	C	H	N	Sn	Cu (%)
Found :	60.32	3.68	6.20	17.66	4.98
Calculated for $C_{68}H_{48}N_6O_6Sn_2Cu$:	60.67	3.56	6.24	17.65	4.72

IR : $\nu_{as}(COO)$: 1620 cm^{-1}

2. Preparation of $(L'SnBu_3)_2Cu$:

A mixture of $(L'H')_2Cu$ and 1.84 gms of $(Bu_3Sn)_2O$ was refluxed in about 250 ml of dry benzene for 18 hours. Then it was cooled and filtered. The filtrate was concentrated and cooled when a solid separated out which was washed successively with hot petroleum ether, 2% aqueous sodium bicarbonate solution and final with water. The solid was extracted with benzene and recrystallis from benzene-petroleum ether mixture.

m.p. : 215°C

Yield : 80%

Analytical data :	<u>C</u>	<u>H</u>	<u>N</u>	<u>Sn</u>	<u>Cu</u> (%)
Found :	54.97	5.69	6.42	19.40	5.21
Calculated for $C_{56}H_{72}N_6O_6Sn_2Cu$:	54.86	5.87	6.85	19.38	5.18

IR : $\nu_{as}(COO)$: 1545 cm^{-1}

μ_{eff} : 2.06 B.M.

3. <u>Preparation of $(L'SnPr_3)_2Cu$</u> :

A solution of 2.0 gms of $(L'H')_2Cu$ and 1.57 gms of $(Pr_3Sn)_2O$ in 120 ml of dry benzene was refluxed for 15 hours. It was cooled and filtered. The filtrate was concentrated and cooled when a brown coloured crystalline product separated out. The solid was filtered off and washed with hot petroleum ether. The solid was then washed with 2% $NaHCO_3$ solution and finally with water. The solid was extracted with hot benzene and recrystallised from benzene-petroleum ether mixture and dried in vacuum.

m.p. : 222°C

Yield : 80%

Analytical data:	<u>C</u>	<u>H</u>	<u>N</u>	<u>Sn</u>	<u>Cu</u> (%)
Found:	52.60	5.28	7.35	21.20	5.62
Calculated for $C_{50}H_{60}N_6O_6Sn_2Cu$:	52.58	5.25	7.36	20.80	5.56

IR : $\nu_{as}(COO)$: 1545 cm^{-1}

μ_{eff} : 1.94 B.M.

4. Preparation of $(L'SnPh_3)_2Ni$:

2.0 gms of $(L'H')_2Ni$ and 2.22 gms of $(Ph_3Sn)_2O$ was refluxed in 150 ml of dry benzene for 12 hours. Then the reaction mixture was cooled and filtered. Filtrate was concentrated. On cooling solid separated as a crystal which was washed with hot petroleum ether. The solid was further purified by washing successively with 2% $NaHCO_3$ solution and water. The solid was extracted with hot benzene and recrystallised from benzene-petroleum ether.

m.p. : $> 255^\circ C$

Yield : 40%

Analytical data:	C	H	N	Sn	Ni (%)
Found :	60.79	3.56	6.16	17.79	4.38
Calculated for $C_{63}H_{48}N_6O_6Sn_2Ni$:	60.89	3.58	6.26	17.71	4.37

IR : $\nu_{as}(COO)$: 1610 cm^{-1}

5. Preparation of $(L'SnPr_3)_2Ni$:

A solution of 2.0 gms of $(L'H')_2Ni$ and 1.59 gms of $(Pr_3Sn)_2O$ in 200 ml of dry benzene was refluxed for about 12 hours. It was cooled and filtered. The filtrate was concentrated and cooled when a solid separated. It was filtered and washed successively with hot petroleum ether, 2% $NaHCO_3$ solution and finally with water. The solid was then extracted with hot benzene and crystallised from benzene-petroleum ether mixture and dried in vacuum.

decomposition point : 280 °C

Yield : 80%

Analytical data :	C	H	N	Sn	Ni (%)
Found :	52.72	5.19	7.28	20.83	5.21
Calculated for $C_{50}H_{60}N_6O_6Sn_2Ni$:	52.80	5.20	7.30	20.90	5.10

IR : $\nu_{as}(COO)$: 1610 cm^{-1}

μ_{eff} : 3.52 B.M.

6. Preparation of $(L'SnPh_3)_2Mg$:

A mixture of 2.0 gms of the $(L'H')_2Mg$ and 2.35 gms of $(Ph_3Sn)_2O$ in 200 ml dry benzene was refluxed for 15 hours. It was cooled and filtered. The filtrate was concentrated and cooled. The solid that seperated was filtered and washed several times with hot petroleum ether. It was then washed with 2% $NaHCO_3$ solution and finally with water. The product was extracted with benzene and crystallised from benzene-petroleum ether mixture and dried in vacuum.

m.p. : 185°C

Yield : 50%

Analytical data :	C	H	N	Sn	Mg (%)
Found :	62.28	3.52	6.48	18.31	1.85
Calculated for $C_{68}H_{48}N_6O_6Sn_2Mg$:	62.50	3.67	6.43	18.18	1.83

IR : $\nu_{as}(COO)$: 1625 cm^{-1}

7. Preparation of $(L'SnBu_3)_2Mg$:

A mixture of 2.0 gms of the $(L'H')_2Mg$ and 1.36 gms of $(Bu_3Sn)_2O$ in 175 ml of dry benzene was refluxed for about 17 hours. It was then cooled and filtered. The filtrate was concentrated, cooled and the orange crystals that separated was filtered. It was washed with hot petroleum ether and then with 2% $NaHCO_3$ solution and finally with water. The solid was extracted with hot benzene and crystallised as before. The product was dried in vacuum.

m.p. : 173°C

Yield : 60%

Analytical data:	C	H	N	Sn	Mg (%)
Found:	57.02	6.03	7.12	20.10	2.05
Calculated for $C_{56}H_{72}N_6O_6Sn_2Mg$	56.68	6.07	7.08	20.02	2.02

IR : $\nu_{as}(COO)$: 1625 cm^{-1}.

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