

**ARYLAZO PHENOXY DERIVATIVES OF  
ORGANOTIN COMPOUNDS**

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**Thesis**  
**Submitted for the Degree of Doctor of Philosophy (Science)**  
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## A C K N O W L E D G E M E N T

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1990

D.K. CHATTERJEE

## AIMS AND OBJECTIVES

The Lewis acidity of organotin compounds which increases in the sequence;  $R_4Sn < R_3SnX < R_2SnX_2 < RSnX_3$  (where X = halogen or other electronegative groups) has been utilised to prepare a variety of organotin complexes. In conformity with this trend of Lewis acidity, numerous examples of 6 and 7 co-ordinated mono organotin complexes, 5, as well as 6- co-ordinated di- organotin complexes are known, while triorganotin complexes are almost invariably 5-coordinated.

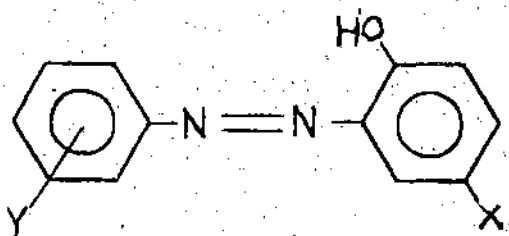
The biocidal properties of organotin compounds and their consequent application in pest control, environmental problems, veterinary medicines and human medicine have led to very rapid increase in the preparation of organotin derivatives of diverse types of ligands. The organotin chemistry, particularly the coordination chemistry, has thus become very rich during the last two decades or so.

Surprisingly, however no example of organotin complexes of arylazo phenoxy compounds have yet been reported, though a great variety of organotin complexes of arylazo carboxylic acids are already known. As organotin phenoxides are well known, it will be of great interest to ascertain the effect of the arylazo group on the preparation and properties of the phenoxy derivatives of organotin compounds.

The present study was, therefore, planned to investigate the reactions of azo-phenoxy compounds with organotin compounds

with a view to preparing<sup>e</sup> their organotin derivatives. Consideration of the steric and other requirements show that a reasonably favourable situation for the formation of arylazophenoxy derivatives of tri-organotin compounds may be expected in the following ligands.

I.



where X =  $-\text{CH}_3$ ,  $-\text{Cl}$

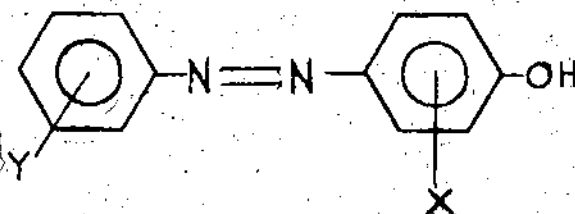
$-\text{N}(\text{CH}_3)_2$

Y = o- or p-

$-\text{OH}$ ,  $-\text{NO}_2$ ,

$-\text{F}$ ,  $-\text{H}$  etc.

II.



where X = o- or m-

$-\text{CH}_3$ ,  $-\text{Cl}$ ,  $-\text{N}(\text{CH}_3)_2$

X = o- or m-  $\text{CH}_3$ ,  $-\text{Cl}$ ,

$-\text{N}(\text{CH}_3)_2$ ;

Y = o- or p-

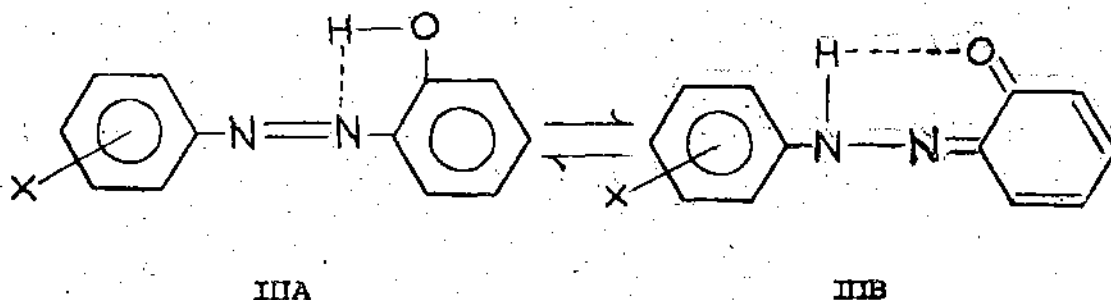
$-\text{OH}$ ,  $-\text{NO}_2$ ,  $-\text{F}$ ,  $-\text{H}$  etc.

At a first glance the above ligands appeared to be well suited for the preparation of a variety of interesting organotin complexes because,

- (1) arylazophenoxy compounds with a wide variety of nuclear substituents can be prepared by diazotisation of amines, nitroanilines and aminophenols followed by coupling with suitable aryl moiety,

(ii) the ligands have a very favourable steric arrangements for the formation of tin complexes as a large number of transition metal complexes of these ligands are well known.

Ligands of type I are of considerable interest since the organotin derivative may involve  $N(azo) \rightarrow Sn$  co-ordinate bond. However, azo compounds of type I are well known to exhibit azo-hydrazone tautomerism of the type:



In addition, both the forms IIIA, IIIB are expected to be intramolecularly hydrogen bonded. In accordance with this expectation, all attempts to prepare simple triorganotin derivatives of this type of ligands failed.

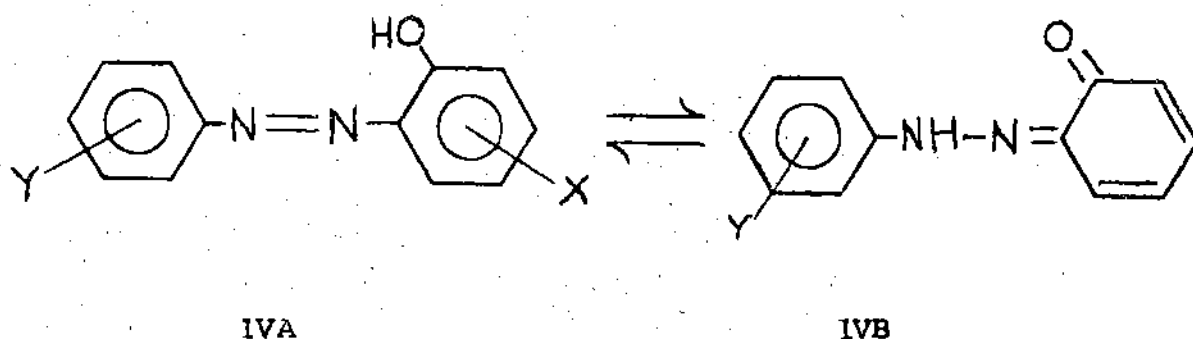
Ligands of type II were found to be comparatively more acidic and the sodium salt could be obtained easily. This gave the desired triorganotin derivatives on reaction with the organotin halides. However, the presence of a substituent at ortho position to the -OH group inhibited formation of any organotin derivative, presumably due to the steric hindrance by the ortho-substituent. The ortho-



substituted ligands of the type II also failed to react with organotin compounds, presumably due to the steric hindrance of the substituent.

The reactions of different ligands are summarised below:

In addition, ligands of type I often show azo-hydrazone tautomerism.



It is, therefore, of considerable interest to investigate the effect of  $R_3Sn$  group on tautomeric equilibrium.

The present study, therefore, aimed at

- (i) preparation of suitable Arylazo phenols,
- (ii) investigating the reactions of the aryl azo phenols with organotin oxides of the type  $(R_3Sn)_2O$  with a view to ascertaining the relative reactivity of the aryl azo phenols towards the organotin oxides,
- (iii) preparation of the derivatives of the type  $R_3SnL$  ( $LH$  = aryl azo phenol), and
- (iv) to study the physico chemical properties of the organotin derivatives.

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DEDICATED TO MY MOTHER,

SMT. SARASWATI DEBI

## CHAPTER - I

### A SHORT REVIEW OF ORGANOTIN CHEMISTRY

IA. INTRODUCTION

IB. BONDING IN ORGANOTIN COMPOUNDS

IC. ORGANOTIN COMPLEXES

REFERENCES

## I.A. Introduction

Organotin compounds are those which contain at least one tin-carbon bond. The first chemist to report an organotin compound seems to have been E. Frankland<sup>1,2</sup>. But his work appears to remain unknown to most of his contemporaries as well as to later authors. The work of C. Lowig<sup>3</sup> in 1852 has unusually been considered to represent the beginning of organotin chemistry. Apart from the compounds described by Lowig, many significant contributions were made in this field during the next few decades.

The vast majority of organotin compounds fall within the four classes:



R can be identical or different, substituted or unsubstituted, aliphatic or aromatic groups. X can be negative groups such as -OR, -SR, -OCOR, -OSnR<sub>3</sub>, -NR<sub>2</sub> or halogens or some other acid radicals or neutral ligands such as -H or electropositive one such as Li or Na. The three series of organotin hydrides R<sub>3</sub>SnH, R<sub>2</sub>SnH<sub>2</sub>, RSnH<sub>3</sub> have assumed considerable importance<sup>4-7</sup>. The acceptor strength of the organotin compounds generally follows the sequence;  $R_3SnX < R_2SnX_2 < RSnX_3$ .

Stannyl metal compounds of the type R<sub>3</sub>SnM, R<sub>2</sub>SnM<sub>2</sub><sup>8,9</sup>,  $Ph_3SnSiPh_3$ ,  $Ph_3SnSi(GePh_3)$ ,  $R_3Sn-SnR_3$ <sup>8</sup>,  $Me_3Si-Hg-SnR_3$ ,  $R_3Sn-Hg-SnR_3$ <sup>10</sup>,  $Ph_3Sn-ZnSnPh_3$ ,  $Ph_3SnCdSnPh_3$ , are also known where R may be aliphatic or aromatic, M may be Li, Na or K.

The discovery of industrial applications of organotin compounds as rubber anti-oxidants, Ziegler type catalysts in the polymerization of olefins, food preservatives, agricultural fungicides and as active ingredients in certain veterinary medicine<sup>11</sup> and also an increased general scientific interest produced a striking renaissance of organotin chemistry starting about 1949 continuing to the present day.

The biocidal properties of organotin compounds have led, over the past decade, to a rapid increase in the commercial utilization of these species. Organotins are currently in use as agricultural fungicides and miticides, surface disinfectants, anthelmintics and marine antifouling agents<sup>12</sup>.

One intriguing development is the synthesis of compounds in which the organotin is bonded to ligands that exhibit biocidal activity, the effectiveness of the product being potentially greater than the sum of the components. Although several ligand systems suggest themselves for study, the oxy and thio phosphorus acids are particularly amenable. Esters of dithiophosphoric acids have, for example, found widespread use in the post war years as pesticides, being marketed under such trade names Ethion, Malathion and Thimet<sup>13</sup>, while the importance of phosphates in in-vivo systems is well documented.<sup>14</sup> Moreover, specific evidence for the activity of miscellaneous organotin derivatives of the phosphorus acids is available<sup>15,16</sup> and provides encouragement for more detailed studies. In particular, answers to the important structure — activity questions demand the availability of

reliable structural data, the collection of which has formed the basis of many recent research efforts.

Application of fungitoxic organotin phenoxy-acetates for controlling human dermatomycosis have also been reported<sup>17</sup>.

Diorganotin dicarboxylates are widely used in industry as homogenous catalysts for polyurethane and RTV Silicone polymerizations and for trans esterification reactions<sup>125</sup>.

### I.B. Bonding in organotin compounds

The electronic configuration of tin atom is :  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^2$ , the ground state being 3p state derived from  $s^2 p^2$  configuration<sup>18</sup>. The tetravalent state is derived from the  $sp^3$  hybridisation by promoting one of the 5s electrons to the 5p level. A large number of organotin compounds consist of tetravalent tin atom because of its much more frequent occurrence than the divalent atom. The metals of Gr. IVA form organometallic compounds which are more stable and less reactive than those of Gr. III or IVB metals. The increased stability may be partly due to  $sp^3$  hybridisation. Thus, tetravalent tin is unreactive towards air and water but trimethyl indium and trimethyl antimony have a strong affinity towards these reagents. The significant increase in stabilities of  $R_4Sn$  compounds over  $R_2Sn$  types also show the effect of increased hybridisation on the stability. Metal-carbon bond strengths have been



reviewed by Skinner<sup>19</sup> who observed that mean bond dissociation energies ( $\bar{D}$ ) fall as the sub group is descended so that  $\bar{D}(\text{C-R}) > \bar{D}(\text{Si-R}) > \bar{D}(\text{Ge-R}) > \bar{D}(\text{Sn-R}) > \bar{D}(\text{Pb-R})$ . The mean values of the bond dissociation energies are C-C : 87, C-Si : 70, C-Ge : 60, C-Sn : 50, C-Pb : 31-37 K.Cal/mole. Moreover, these values are dependent on the nature of the alkyl group i.e., on the stabilisation of the corresponding alkyl radical by hyperconjugation etc.

The tin atom has covalent radius of  $1.4\text{\AA}$  and is independent of the nature of the ligands. There is some sort of decrease in bond lengths only when strongly negative ligands are accumulated around the tin. The bonding of the tin would thus appear to be almost entirely covalent at least in crystalline solids, in the vapour and in non-polar media. However, the electronegativity of tin being less than most of the common ligands, e.g. carbon, nitrogen, oxygen, halogen and even hydrogen, the bonds are expected to be sufficiently polar in the sense  $\overset{+\delta}{\text{Sn}} - \overset{-\delta}{\text{X}}$  and dipole moments of various Sn-X bonds have also been estimated. The dipole moment of the alkyl tin bond, mostly estimated as 0.45-0.6D<sup>20-22</sup> depends both in direction and magnitude on the nature of the alkyl group<sup>23</sup>.

The electronegativities of Gr. IV elements have been investigated by several workers<sup>24a-d</sup>. The results always vary with the method of measurement and the compounds selected. It is not surprising since the electronegativity, not being a uniquely defined parameter, depends on the method of measurement and the environment of the atom in

question. In fact, one always works not with an electronegativity of tin but with a value for tin in a particular combination and allowance will have to be made for the influence of all ligands.

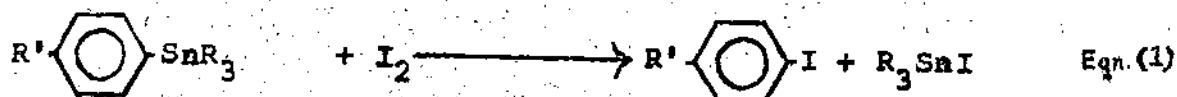
Table - 1

Electronegativities of Gr. IVA elements

	Pauling	Sanderson	Fineman Daignault	Allred-Rochow
C	2.5	2.47	2.57	2.60
Si	1.8	1.74	1.90	1.90
Ge	1.8	2.31	2.02	2.00
Sn	1.8	2.02	2.47	1.93
Pb	1.8	-	-	2.45

Closely related with this is the inductive effect which the tin atoms or stannyl groups exert on their surroundings. The bond polarisation  $\overset{-\delta}{\text{C}} - \overset{+\delta}{\text{Sn}}$ , which is there in principle, may be changed by substitution at C as well as at Sn. NMR data on organotin compounds<sup>25,26</sup> and semiempirical calculations of Majee and Gupta<sup>27</sup> emphasise this. According to Eaborn et al<sup>28</sup>, polarisation is increased by electron donor substituents R' in the p-position in a phenyl group, as demonstrated by the increase in the rate of cleavage of C-Sn bond by iodine according to the reaction (1). Thus, this reaction may be

marked as electrophillic aromatic substitution.



The electron attracting groups  $R'$  diminish the rate by lowering the nucleophilicity of the ring carbon attached to tin. The sequence of relative reaction rates is for  $R' = \text{OMe} > \text{-Bu} > \text{1-Pr} > \text{Rt} > \text{Me} > \text{H} > \text{Br} > \text{F} > \text{Cl} > \text{COOH}$ .

Electron donor properties increase in the series ( $R = \text{Me}$ ) :  $\text{SiR}_3 < \text{GeR}_3 < \text{SnR}_3$ , as may be seen from the relative rates of acidolysis of  $p\text{-R}_3\text{MCH}_2\text{CH}_4\text{-SnR}_3$ . These are :  $M = \text{Si } 1.00, \text{Ge } 1.36, \text{Sn } 3.21^{29}$ . A similar sequence emerges from IR and NMR measurements<sup>30</sup> and also from IR studies on esters of the  $\text{MeCOOMe}_3$  ( $M = \text{C, Si, Ge}$ )<sup>31</sup>.

A problem which often arises in the investigations to measure relative inductive effects is that there may be some  $\pi$ -character in a bond between tin and an element possessing p-electrons<sup>32-34</sup>. Thus in a  $\text{Sn-X}$  bond where  $X$  is  $\text{C} (sp^2)$ ,  $\text{N}$ ,  $\text{O}$ ,  $\text{S}$  or halogen, it is possible that, opposing the inductive electron drift  $\text{Sn} \xrightarrow{+\delta} \text{X} \xleftarrow{-\delta}$ , there may be some overlap between an empty 5d orbital on Sn and a filled p-orbital on X causing a transfer of electron density in the opposite direction.

Inspite of many disputes<sup>34-37</sup> it is widely accepted that there are significant ( $p\pi \rightarrow d\pi$ ) contributions to the  $\text{Sn-N}$  bonds in compounds

such as the planar triethylamine<sup>38</sup>. There is some evidence that in phenyl tin compounds, interaction occurs between the electrons of the phenyl group and the 5d orbitals of tin. This conclusion is based on the interpretation of NMR<sup>39,40</sup>, IR<sup>41</sup>, UV<sup>41</sup> and dipole moments<sup>42</sup> of  $\text{Ph}_3\text{Sn}$  compounds and the acid strengths of the substituted benzoic acids  $p\text{-Me}_3\text{MC}_6\text{H}_4\text{COOH}$  ( $\text{M} = \text{C}, \text{Si}, \text{Ge}, \text{Sn}$ ). It can not be assumed that other aromatic groups behave similarly since the  $\text{pK}_a$  values for a series of pyridine having  $\text{Me}_3\text{M}$  ( $\text{M} = \text{C}, \text{Si}, \text{Ge}, \text{Sn}$ ). Substituents in the 2-position indicated the absence of  $p\pi - d\pi$  bonding in the tin-pyridine link<sup>43</sup>. Calculation based upon nuclear quadrupole resonance measurements indicated  $\pi$ -character in the  $\text{Sn-I}$  bonds of diethyl tin diiodide whereas it was concluded from the dipole moments of organotin chlorides that the  $\text{Sn-Cl}$  bond order is close to unity<sup>42</sup>. There is evidence for  $d\pi - d\pi$  interaction in the bonds formed between tin and certain transition metals<sup>44,45</sup>. On the other hand Majee and Gupta has shown in a series of paper<sup>27</sup> that most of the properties of organotin compounds may be interpreted without assuming any  $d\pi - p\pi$  interaction.

Such apparently contradictory observations and interpretations probably originate from the fact that the overall behaviour of tin compounds is a complex function of many factors, e.g., atoms or groups to which it is joined, its coordination number, its oxidation state, the phase in which the molecule is found and even temperature and external pressure may often change the behaviour dramatically. Since tin forms a very large variety of compounds with many different atoms, groups and ligands, any attempt to interpret the properties of all

groups of tin compounds in terms of a particular criteria is fraught with grave danger of creating confusion, rather than systematisation.

Notwithstanding such wide variations, one may, however, classify tin (IV) compounds, which constitute the overwhelmingly major part of organotin literature, into the following categories<sup>46</sup>:

1. Ionic compounds in which tin may be considered to be in +4 oxidation state with electronic configuration  $[\text{Kr}] 4d^{10} 5s^0 5p^0$ .
2. Covalent tetrahedral compounds in which tin may be considered to be  $sp^3$  hybridized.
3. Tin (IV) complexes where the 5d orbitals may be included in hybridisation scheme to form organotin compounds with coordination number of 5 to 8.

All compounds of the type  $R_{4-n}\text{SnX}_n$  (R = organic group, X = monodentate atom, group or liand) usually belong to category 2 and characterised by tetrahedral geometry around the tin atom except when the group X is capable of forming intra or intermolecular coordination bond.

In general the X group (s) play the most dominant role in determining the bonding and structure of organotin compounds. Because of this, there has been a tremendous spurt of activity on the synthesis and structural studies of organotin complexes. In the following section a brief discussion on the organotin complexes is therefore presented.

## I.C. Organotin Complexes

Organotin compounds can form various types of complexes with ligands. The structural aspect of these compounds has been exhaustively reviewed by Ingham et al<sup>8</sup>, Poller<sup>47</sup>, Gielen and Sprecher<sup>48</sup> and by Ho, Zuckerman<sup>49</sup>, P.G. Harrison<sup>75</sup>, Koten<sup>51</sup>, Pelizzi<sup>52</sup> and latter by Zubieta and Zuckerman<sup>53</sup>.

The structural aspects, viz., coordination number and geometry around the tin atom, of organotin complexes derived from  $R_nSnX_{4-n}$  type compounds, depend both on the number of the organic groups (R) around the tin atom and the ligand. As a general rule,  $R_3SnX$  type compounds tend to form penta coordinated complexes, while higher coordination number can be realised with  $R_2SnX_2$  and  $RSnX_3$  type compounds.

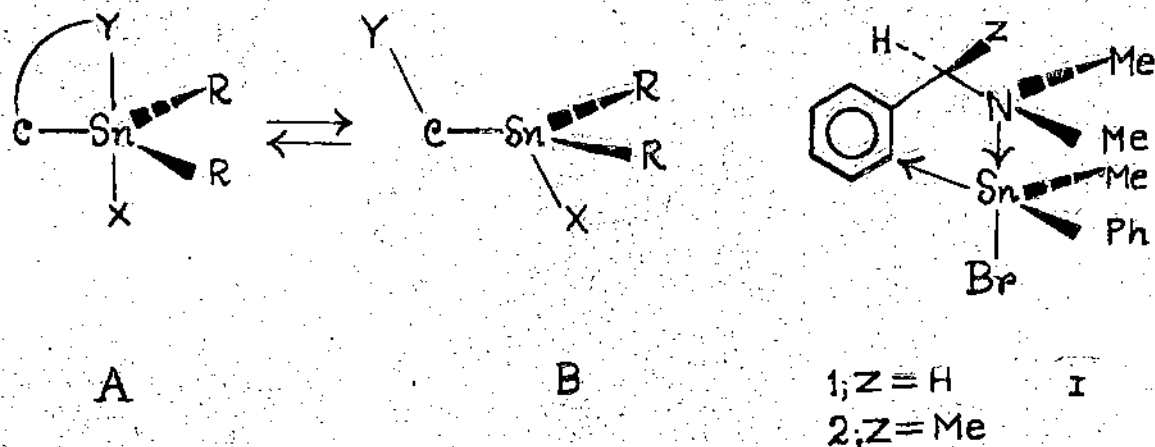
The most interesting example is afforded by  $R_3SnX$  type compounds which form various type of adducts with Lewis bases<sup>8</sup>. These compounds are generally penta co-ordinated<sup>54,55</sup>. For  $X = Cl, Br, I, Me_3SnX$  type are usually tetrahedral but for  $X = ClO_4^-, F^-, CO_3^{2-}, BF_4^-, NO_3^-$ ,  $AsF_6^-$ ,  $-OCOR$ , the compounds are five co-ordinate about tin where the anions are probably either bridging or chelate type<sup>56,57</sup>.  $R_3SnX$  and  $R_2SnX_2$  compounds can form organotin chelates with chelating agents, viz. 8-hydroxy quinoline<sup>58,59</sup>, acetyl acetone<sup>60,61</sup>, 1, 10-phenanthroline<sup>51,61</sup> etc, which may be five or six co-ordinated compounds.

N-substituted salicylidineiminato trialkyl tin derivatives have been prepared by the reaction of the trialkyl tin chloride or

alkoxides with the corresponding Schiff<sup>62</sup> bases. These complexes are believed to contain 5-co-ordinate tin atom. Trimethyl tin derivatives of sulphur containing Schiff bases are also known<sup>63</sup>. Several triorganotin dithiocarbamates of the formula  $R_3SnDtc$  ( $R = Ph, n-Bu, Bz, Dtc = n-pr, n-Bu, 2-phenyl, dibenzyl$  etc - dithiocarbamates) have been reported by Srivastava<sup>64</sup>. The quaternary phosphonium cations  $[>PCH_2SnMe_3]^+$  is also known<sup>65</sup>. Nitrate complex of organotin (IV) containing triphenyl phosphine oxide has been reported<sup>66</sup>.

A series of triorganotin halides,  $RR'SnBr(C-N)$ , and a series of tetraorganotin compounds  $R_3Sn(C-N)$  have been synthesized<sup>88</sup> in which C-N is either monoanionic  $2-Me_2NC_6H_4CH_2^-$  or novel monoanionic  $2-Me_2N.C_6H_4CH(SiMe_3)^-$ .  $^1H$  and  $^{13}C$  NMR data indicate that the tin center in the  $R_3Sn(C-N)$  compounds is tetra coordinate whereas the tin atom in the  $RR'SnBr(C-N)$  derivatives is penta coordinate as a result of intramolecular Sn-N coordination. Penta coordination in a trigonal bipyramidal manner with axial N and Br atoms has also been established by the X-ray structure determination of  $[2-Me_2NC_6H_4CH(SiMe_3)]SnMePhBr$ .

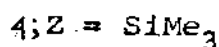
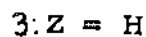
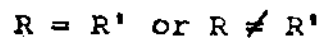
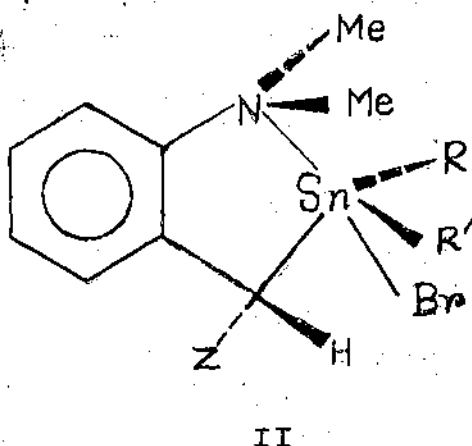
The existence of an equilibrium in solution between two possible situations i.e. with and without intramolecular Sn-Y coordination (A and B respectively) could be monitored in many cases by following the temperature dependence of the  $^1H$  NMR patterns of prochiral groupings present in the compounds e.g. the  $CH_2$  and  $NMe_2$  groups.



The influence of intramolecular co-ordination (cf A) on the configurational stability of triorganotin halides is the steric bulkiness, the heteroatom-containing group represents when it is not coordinated has been explained. If one compares the stereochemistry of the coordinated and non coordinated situations A and B respectively for compounds 1 and 2, both having two  $sp^2$  C-atoms in the five membered chelate ring, one comes to the conclusion that the non coordinated  $O-CH(Z)NMe_2$  substituent represents a group with considerable steric bulkiness. This bulkiness destabilizes situation B with respect to the five-coordinate situation A. In the latter situation this bulkiness has been completely removed by the Sn-N coordination.

An X-ray crystal structure determination of one diastereomer, i.e.  $[2-Me_2NC_6H_4CH(SiMe_3)SnMePhBr]$  has been described.



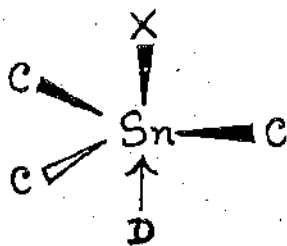


The structure shows that the chelate ring conformation is such that it places the bulky  $\text{Me}_3\text{Si}$  substituent both out of the plane of the aryl ring and furthermore, at the side of the less bulky methyl ligand. It is suggested that the unusual high configurational stability of the  $\text{RR}'\text{SnBr}(\text{C}-\text{N})$  compounds arises from the rigidity of the  $2\text{-Me}_2\text{NC}_6\text{H}_4\text{CH}(\text{Z})^-$  ligand which holds the  $2\text{-Me}_2\text{N}$  group in close proximity of the tin centre. If Z is the bulky  $\text{SiMe}_3$  group also, the  $\text{SnR}_2\text{Br}$  grouping is locked in a fixed position with respect to the N donor site.

The penta co-ordinated organotin complexes may be classified into three groups:

1) Type - I

Addition complexes, in which a donor molecule is coordinated to  $\text{R}_3\text{SnX}$  molecule to give a trigonal bipyramidal arrangement.

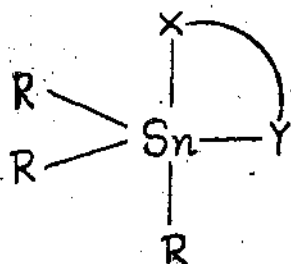


Type - I

In these complexes, R-groups occupy the equatorial positions while the electronegative group X and the ligand occupy the axial position as would be expected from the isovalent hybridisation principle. A well known example of this structure is the 1:1 addition compound of  $(\text{CH}_3)_3\text{SnCl}$  and pyridine.

#### ii) Type - II

Organotin complexes derived from chelating agents, e.g., 8-hydroxy quinoline, acetylacetone, 1,10-phenanthroline etc., are generally intramolecularly coordinated (II)



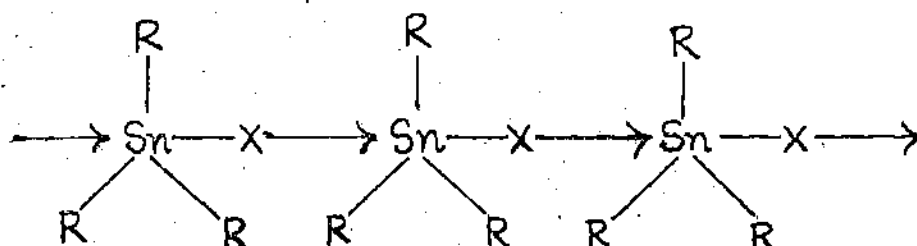
Type - II

Large number of such complexes have been synthesised and studied. Structural studies using X-ray crystallography have also been reported in many cases.

An X-ray study was reported for (triphenyltin 1,3-diphenylpropionate) triphenyltin which established the occurrence of penta co-ordination as a result of intramolecular co-ordination with the ligand spanning axial equatorial sets<sup>100</sup>.

## iii) Type - III

In contrast to the intramolecularly coordinated organotin complexes (type II), the intermolecularly coordinated compounds are more abundant in organotin chemistry. In this case, a polymeric structure ~~is~~ formed by bridging of an anionic group to the tin atom from either side of the plane of R groups (III).



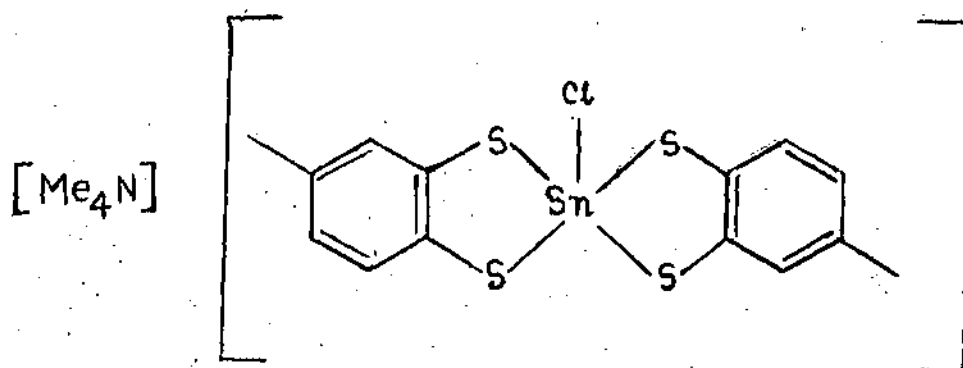
Type - III

The intermolecular associated form of 2-(tri-*n*-butyl stannyl) tetrazoles<sup>67</sup> in benzene and chloroform is well known.

The first anionic five co-ordinated tin compounds containing saturated rings has been reported<sup>68</sup> to be formed from the reaction of  $\text{RSnCl}_3$  and  $\text{Et}_4\text{N}^+\text{Cl}^-$  with sodium ethane-1, 2-dithiolate and from the partial hydrolysis of bis (ethane-1, 2-dithiolate) tin in the presence of an amine base. X-ray analysis of the new stannates and the distannates showed that the geometry of the former in terms of distortions from a square or rectangular pyramid, while geometry of the latter more closely approaches a trigonal bipyramid.

The authors<sup>68</sup> <sup>ve</sup> has reported earlier the synthesis and X-ray study of the first tin compound having a discrete square-pyramidal

geometry. The compound was a spirocyclic derivative that resulted from the reaction of bis(toluene-3, 4-dithiolato) tin (IV) with  $(\text{CH}_3)_4\text{N}^+\text{Cl}^-$  at room temperature.



III

The first example of polytopal dominance of square pyramidal geometry in organotin penta coordination : crystal structure of tribenzyl (2-thiolato pyridine-N-oxide) tin (IV) has been reported<sup>118</sup>.

The coordination geometry about the central atom in monomeric tribenzyl (2-thiolato pyridine-N-oxide) tin (IV) is a unique square pyramid, with one benzyl carbon atom occupying the apical position and the base plane containing the other two benzyl carbon atoms along with the oxygen and sulfur atoms of the chelating ligand; the tin atom is displaced out of the basal plane in the direction of the apical carbon atom by 0.64(1) Å.

Many N-substituted N-(triphenyl stannyl) cyanamides have been reported and the tin in these complexes is shown to have a co-ordination No. > 4 by means of IR and Mossbauer Spectroscopy<sup>69</sup>.

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Several organotin (IV) complexes with quadri and tetradentate anionic Schiff base ligands have been prepared and investigated in the solid state<sup>70,71</sup>. Mossbauer parameters derived from both zero field and magnetically perturbed spectra suggest that the  $R_2Sn(Salen)^*$ ,  $R = Me, Et, Ph$  and  $Me_2Sn(Saldap-2-OH)^{**}$  complexes have distorted trans octahedral structures. However in  $Ph_2Sn(H-Saldap-2-O)$  the ligand appear to be only terdentate leading to a penta- co-ordinate structure similar to those of the  $R_2Sn(Sal-N-2-OC_6H_4)$  derivatives ( $R = Ph, Me$ ).

The Mossbauer parameters are given in table 2.

Table 2

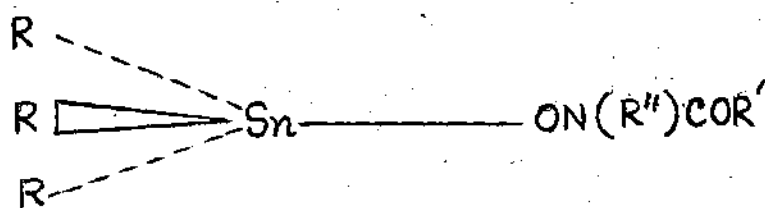
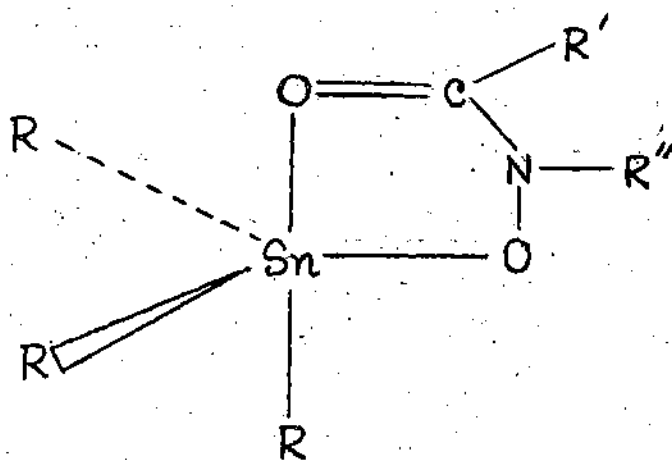
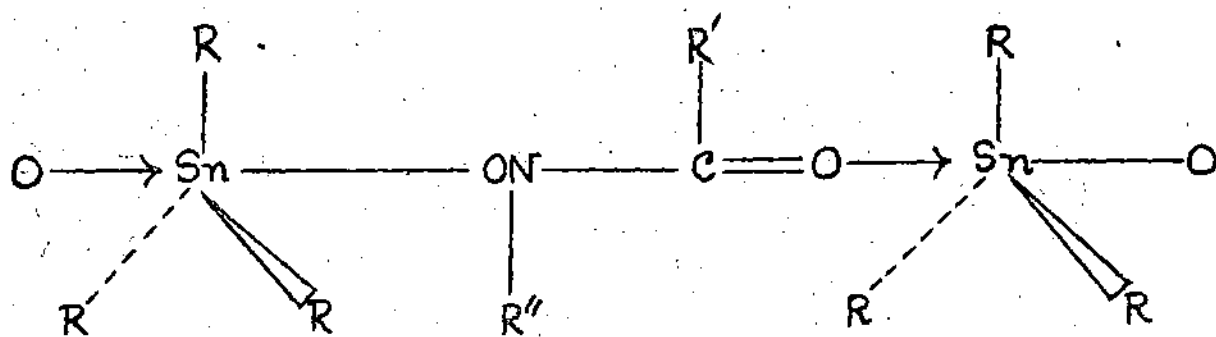
Compound	$\delta$	$\Delta E$	$\Delta E/\delta$
$CF_3C(CO)(CN)NSnPh_3$	1.07	4.54	4.24
$CH_3OC(O)(CN)NSnPh_3$	1.55	4.23	2.73
$PhSO_2(CN)NSnPh_3$	1.07	4.54	4.24
$MeC(O)(CN)NSnPh_3$	1.55	4.23	2.73

\*  $H_2Salen-N,N'$  ethylene bis(Salicylaldimine)

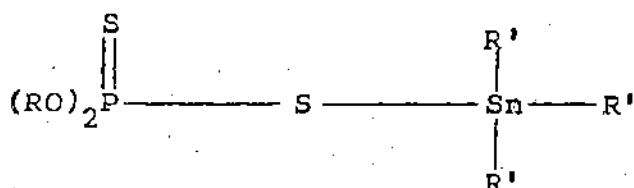
\*\*  $H_2Saldap-2-OH-N,N'$  (2-hydroxy trimethylene)bis(salicylaldimine).

Organotin complexes of strong  $\pi$ -acids of the type  $\text{Me}_3\text{SnTCNQ}$ ,  $\text{MeCP}_2\text{Sn.TCNQ}$ ,  $\text{MeCP}_2\text{Sn.nTCNE}$  ( $n = 1, 2$ ) and  $\text{SnX}_4\text{TCNE.THF}$  ( $X = \text{Cl}, \text{Br}$ )<sup>72</sup> have been prepared (TCNQ = Tetra cyano-p-quinodimethane, TCNE = tetracyano ethylene). The infrared spectra of the complex  $\text{Me}_3\text{Sn.TCNQ}$  exhibits a single band at  $555\text{ cm}^{-1}$  in the tin-carbon stretching region which is assigned to the anti-symmetric mode of a planar  $\text{Me}_3\text{Sn}$  moiety, with bridging TCNQ residues resulting in a trigonal bipyramidal configuration at the tin. The intense colouration of the compound is indicative of the formation of  $(\text{TCNQ})^-$  radical anion on complexation. The complex is therefore best represented by the canonical form  $(\text{Me}_3\text{Sn})^+ . (\text{TCNQ})^-$  and thus provides the first example of an isolable paramagnetic organotin complex.

Example of a compound containing organotin (II) and organotin (IV) in one molecule,  $(\text{Me}_3\text{Sn}^{\text{IV}}\text{C}_5\text{H}_5)_2\text{Sn}^{\text{II}}$  has also been reported<sup>73</sup>. A flat sandwich type compound, decaphenyldicyclopentadienylstannocene, involving tin (II) structure  $\left[ \eta^5 - (\text{C}_6\text{H}_5)_5\text{C}_5 - \right]_2\text{Sn}^{\text{II}}$  has been reported<sup>74</sup>. The triorganotin derivatives of N-acyl-hydroxylamine e.g.  $\text{Me}_3\text{Sn} \left[ \text{ON}(\text{Ph})\text{SO}_2\text{C}_6\text{H}_4\text{CH}_3 \right]$ ,  $(\text{CH}_3)_3\text{Sn} \left[ \text{ON}(\text{Ph})\text{COPh} \right]$ ,  $\text{Me}_3\text{Sn} \left[ \text{ON}(\text{Me})\text{COMe} \right]$  have been prepared. The presence of a second donor site in the N-acylhydroxylamine ligand permits its potential function as a unidentate or a chelating bidentate ligand; thus giving rise to the possible four co-ordinated structure (IV) or the two 5-co-ordinated structure (V) and (VI)<sup>75</sup>.

Type -IVType -VType -VI

Triorganotin dialkyl thiophosphates,  $(RO)_2P(=S)SSnR'_3$  ( $R = Et, i\text{-}Pr, n\text{-}Pr$  or  $Ph$  and  $R' = Me, Et, Bu$  or  $Ph$ ) have been prepared<sup>76</sup>. An ester type structure has been proposed for these compounds.



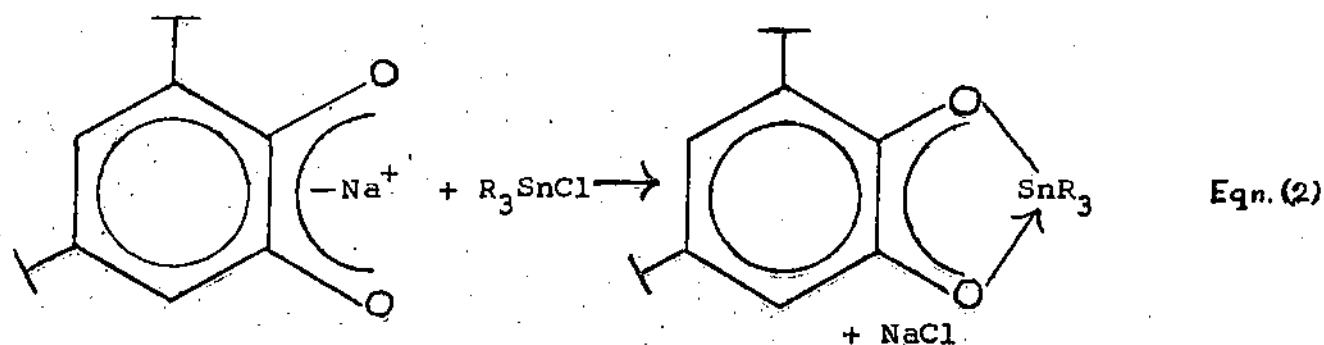
#### Type- VII

Works on oxy and thio phosphorous acid derivatives of tin-structural contrasts has been reported by Molloy et al<sup>77</sup>.

The contrast between the chelating of the dithiophosphorus acid groups and the bridging of the corresponding oxygenated ligands has been reported<sup>77</sup>, where it has been rationalized on two counts. Firstly the  $Sn-O$  bond is at least  $0.2\text{\AA}$  shorter than the corresponding  $Sn-S$  bond. Thus when chelation occurs, the angular strain within the resulting four-membered  $SnE_2P$  ( $E = O, S$ ) heterocycle is greater for oxygen, rendering chelation less favourable. The relative electronegativities of  $C(2.50)$ ,  $S(2.44)$  and  $O(3.50)$  underlie the second rationale. In a trigonal bipyramid, for example, competition between carbon and sulfur for p- or s-dominated orbitals on tin will be negligible. Conversely, the increased electronegativity of oxygen over carbon directs it into the axial position of the trigonal bipyramid with the ligand unable to span both axial sites in the same molecule, bridging was observed.

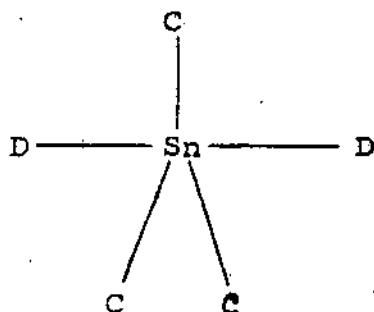


The initial ESR spectra observed for the reactions of O-quinone with  $R_3SnSnR_3$  are analogous to the signals of tin containing semiquinones formed according to the reaction.

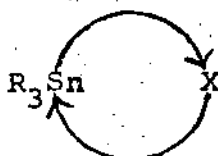


From the reaction of pyridine N-oxide with nitratotriphenyl tin in dry acetone under nitrogen, two types of crystals, belonging to the monoclinic and triclinic system, respectively and having same  $[Sn(C_6H_5)_3(NO_3)(C_5H_5NO)]$  stoichiometry has been reported<sup>78</sup>. Moreover, a molecular adduct of Nitratophenyl tin with triphenyl arsenic oxide  $[Sn(C_6H_5)_3(NO_3)(C_6H_5)_3AsO]$  has also been synthesised. The co-ordination about tin is bipyramidal with phenyl ring in the equatorial and oxygenated ligands in the axial positions<sup>79</sup>.

In cases where the anionic groups have no co-ordinating sites e.g.  $B(C_6H_5)_4^-$ , two molecules of a mono-anionic Lewis base viz., water can occupy the co-ordination sphere, giving a planar  $SnC_3$  arrangement with a penta co-ordinated tin atom (Type VIII).

Type VIII

Intramolecular coordination often results in many interesting structural variations when the X group in  $R_3SnX$  belongs to a chelating ligand. Such structures may be schematically represented as shown below (Type IX).

Type IX

Crystal structure of tribenzyl (2-pyridinethiolato-N-oxide) tin (IV) : a rare example of square pyramidal organotin (IV) compound has been reported<sup>119</sup>.

Tribenzyl (2-pyridinethiolato-N-oxide)tin (IV),

$[(C_6H_5CH_2)_3Sn(2-SC_5H_4NO)]$ , crystallizes in space group  $P\bar{1}$ , with

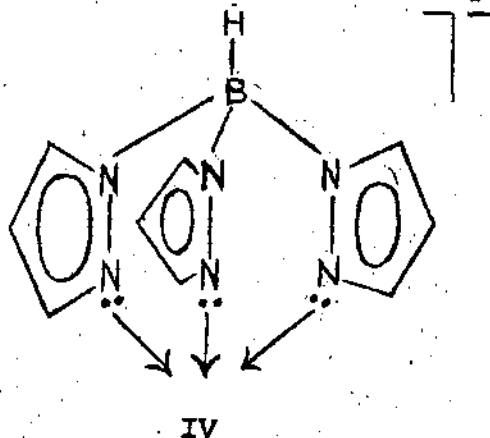
a 9.169( ), b 10.498(3), c 13.511(4) Å,  $\alpha$  91.54(2),  $\beta$  104.61(2),  $\gamma$  112.49(2)° and Z = 2. The structure has been refined to R = 0.028 using 4593 observed MO-K $\alpha$  reflections. The molecule adopts a configuration displaced 91% from trigonal bipyramid to a square pyramid along the Berry pseudorotation pathway. The basal plane is composed of the oxygen and sulfur atoms of the chelating 2-pyridinethiolato ligand and the carbon atoms of two benzyl groups [Sn-O 2.261(2), Sn-S 2.577(1), Sn-C 2.189(3), 2.196(3) Å]. The apical tin-carbon bond [Sn-C 2.167(3) Å] is shorter than the other two tin-carbon bonds. The tin atom is placed 0.64(1) Å from the basal plane in the direction of the apical carbon [sum of the basal angles = 341.7(4)° and the C apical - Sn L basal angles are in range 100.1(1)-110.1(1)°].

The unusual geometry of tribenzyl (2-pyridinethiolato-N-oxide) tin (IV) provides the first example of polytopal dominance of the square pyramidal configuration in penta coordinated organotin compounds.

In contrast to the penta co-ordinated triorganotin compounds, examples of 6-coordinate triorganotin compounds are very few. The Mossbauer recoil free fraction and structure of triorganotin aryl-azobenzoates has been reported<sup>82</sup>. Spectral and other studies indicate some of these to be 6-coordinated triorganotin compounds.

The synthesis and X-ray structures of Tris(Pyrazolyl)borate (Trimethyl)tin : A six coordinate Trialkyltin complex has been reported<sup>120</sup>.

Reaction between  $\text{Me}_3\text{SnCl}$  and  $\text{K}[\text{HB}(\text{PZ})_3]$  ( $\text{PZ} = 1\text{-pyrazolyl, C}_3\text{H}_3\text{N}_2$ ) affords  $[\text{HB}(\text{PZ})_3]^- \text{SnMe}_3^+$  which was shown by a full X-ray structure determination (Trigonal space group  $\text{P}\bar{3}$ ,  $a = b = 11.722(3)$   $\text{\AA}$ ,  $c = 8.211(2)$   $\text{\AA}$ ,  $\gamma = 120^\circ$ ,  $Z = 2$ ) to contain six coordinate tin bonded to three methyl groups and to three pyrazolyl groups.



The infrared and mass spectra of  $\text{HB}(\text{pz})_3\text{SnMe}_3$ , were fully consistent with the assumed formulation and the  $^1\text{H}$  NMR spectra showed that all three pyrazolyl rings were equivalent between  $-60$  and  $+30^\circ\text{C}$ , suggesting that all three were coordinated to the tin atom, or that rapid exchange of the rings of a partially co-ordinated ligand was occurring.

The invariance of the  $^1\text{H}$  NMR spectrum of  $\text{HB}(\text{pz})_3\text{SnMe}_3$  over the range  $-60$  to  $+30^\circ\text{C}$  suggests that a six coordinate structure with equivalent pyrazolyl rings is maintained in solution, although a lower coordination system with rapid exchange of rings cannot be ruled out.

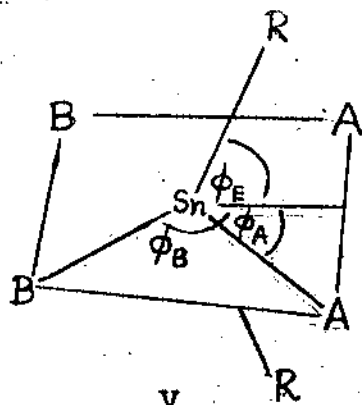
Skew-trapezoidal bipyramidal diorganotin (IV) bis chelates. Crystal structure of dimethyl-bis(2-pyridinethiolato-N-oxide)tin(IV) has been reported<sup>121</sup>.

Dimethyl bis (2-pyridinethiolato-N-oxide)tin (IV),  $\text{Me}_2\text{Sn}(\text{2-SPyO})_2$ , crystallizes in space group  $\text{P2}_1/\text{C}$  with a 9.877(3), b 11.980(4), c 13.577(3) Å,  $\beta$  109.1(2)° and  $Z = 4$ . The structure was refined to  $R_F = 0.036$  for 2263  $\text{Mo-K}\alpha$  observed reflections.

The coordination geometry at tin is a Skew-trapezoidal bipyramid, with the oxygen  $\text{[Sn-O 2.356(3), 2.410(4) Å]}$  and sulphur  $\text{[Sn-S 2.536(1), 2.566(1) Å]}$  atoms of the chelating groups occupying the trapezoidal plane and the methyl groups  $\text{[Sn-C 2.106(6), 2.128(7) Å]}$  occupying the apical positions. The methyl-tin-methyl skeleton is bent  $\text{[C-Sn-C 138.9(2)°]}$ . The S-Sn-S angle is 77.8(1)°, but the O-Sn-O angle is opened to 136.7(1)° to accommodate the intruding methyl groups. The carbon-tin-carbon angles predicted from quadrupole splitting ( $^{119}\text{mSn}$  Mossbauer) and one-bond  $^{119}\text{Sn}$   $^{13}\text{C}$  coupling constant (solution  $^{13}\text{C}$  NMR) data agree closely with the experimental value.

In the idealized case of a six coordinated diorganotin bis-chelate the carbon-tin-carbon angle is 90° for the cis and 180° for the trans isomer. The angle of 138.9(2)° found for the title compound is close to the average of the two extremes.

The geometry of the co-ordination polyhedron around the tin in  $\text{Me}_2\text{Sn}(\text{2-SPyO})_2$  is best described as a Skew-trapezoidal bipyramid (STB). A schematic representation of this is shown in Fig.



The first X-ray crystal structure of a diorganotin dicarboxylate as well as the first X-ray structural study of a 7-coordinate organotin anion, a diorganotin tricarboxylate has also been reported<sup>122</sup>.

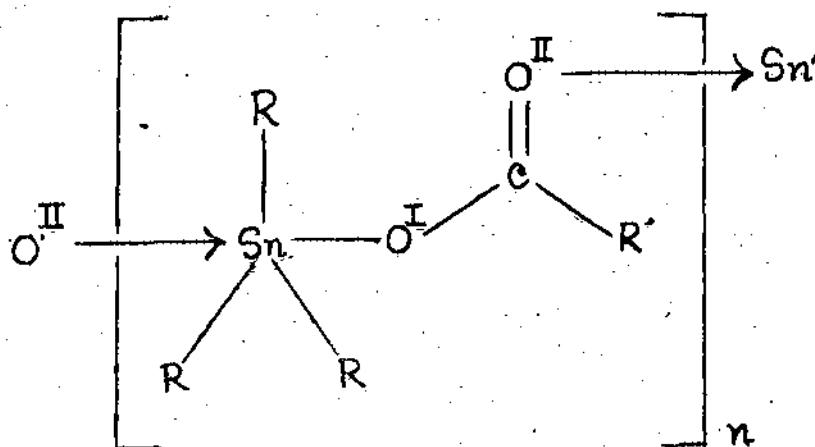
The X-ray crystal and molecular structure of  $\text{Me}_2\text{Sn}(\text{OAc})_2$  has been reported<sup>122</sup> and compared with previous predictions based on other structural methods. The molecule is found to be monomeric and 6-coordinate at tin in the solid state. The Me-Sn-Me angle of  $135.9(2)^\circ$  is in close agreement with the value predicted from solid-state and solution NMR studies.

The most striking result of this study is the discovery that 6-coordinate  $\text{Me}_2\text{Sn}(\text{OAc})_2$  is capable of adding a third acetate group, giving rise to a diorganotin (IV) anion with a coordination number of 7. Solution and solid-state NMR data for  $\text{Me}_2\text{Sn}(\text{OAc})_3^- \text{NMe}_4^+$  provide evidence that the complex is thermodynamically stable in solution relative to dissociation and indicate that, in addition to the well characterized penta substituted di- and triorganotin (IV) halide anions, organotin (IV) compounds bearing other, less strongly electron withdrawing ligands can give rise to stable, isolable anionic complexes.

A clear implication of the results obtained for the reaction of  $\text{Me}_2\text{Sn}(\text{OAc})_2$  with  $\text{NMe}_4^+\text{OAc}^-$  is that nucleophilic substitution reactions of even 5- and 6- coordinate tin compounds can, and may frequently, proceed by associative mechanisms involving anionic tin intermediates of high coordination number. Such mechanisms may in fact be the rule for many industrially important reactions catalyzed by diorganotin dicarboxylates.

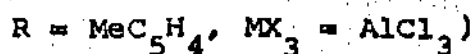
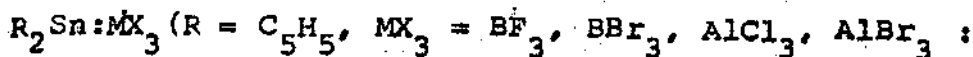
It has been reported<sup>123</sup> that an analysis of X-ray data for seventeen polymeric triorganotin (IV) carboxylates gives a repeat distance of  $5.19 \pm 0.21 \text{ \AA}$  for the carboxylate-bridged  $\text{R}_3\text{SnO}\cdot\overset{\text{O}}{\text{C}}(\text{O})\text{R}'$  unit that defines the crystal lattice. The repeat distance is insensitive to the organic substituents on either the tin or carboxylate group. Tricyclohexyltin acetate and tricyclohexyltin trifluoroacetate are reclassified as weakly associated polymers.

In the crystal lattice, the  $\text{Sn}-\overset{\text{I}}{\text{O}}-\overset{\text{I}}{\text{C}}$  angle is generally  $120^\circ$  but the  $\overset{\text{II}}{\text{C}}-\text{O}-\text{Sn}'$  angle can open up to accommodate more bulky  $\text{R}'$  groups<sup>124</sup>.



VI

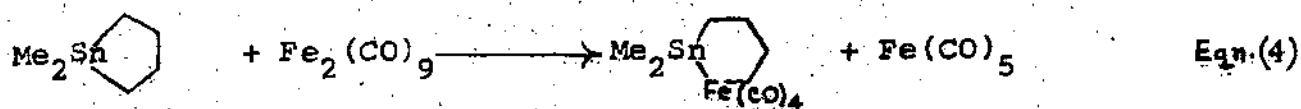
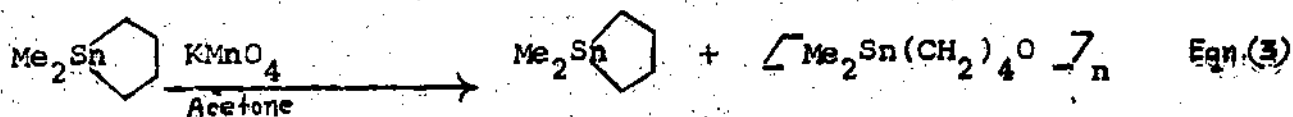
The reaction of dicyclopenta-diethyl tin and bis-(methyl cyclo-pentadienyl) tin with some boron, aluminium trihalides give complexes of the composition<sup>83</sup>.



The addition of dicyclopentadienyltin to THF solution of the complexes  $M(CO)_5THF$  ( $M = Cr, Mo, W$ ) produces complexes<sup>84</sup> :

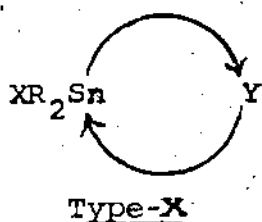
$R_2Sn : M(CO)_5$  (where  $R = C_5H_5, M = Cr, Mo, W$ ),  $R = MeC_5H_4, M = Cr, W$ . The evidence for cis-Bis(2,4-pentanedionates) dimethyl tin (IV) has been found in solution<sup>85</sup>.

As a result of the enhanced reactivity of the endocyclic tin-carbon bond, 1,1, dimethyl-1-stannacyclopentane (DMSO-5) readily undergoes ring expansion reactions with a variety of substrates to produce new organotin heterocycles. A few examples of ring expansion involving  $O_2, S, SO_2Fe_2(CO)_9$ <sup>86</sup> are given below.

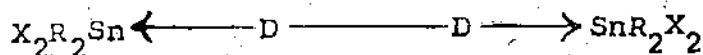




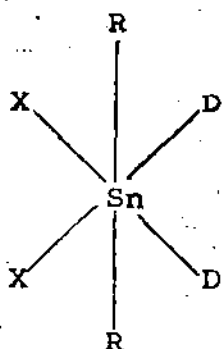
In case of diorganotin derivatives, both penta co-ordinated and hexa-coordinated tin compounds have been reported. Penta co-ordinated tin is observed in dialkyltin dihalide, carboxylates dialkyl tin halide oxinates and dimethyl (1, 3-dimethyl triorgano) tin halides<sup>87</sup> are of (type-X)



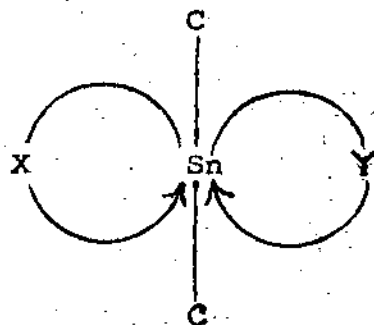
The 2:1 addition compound of  $(C_6H_5)_2Sn(NCO)_2$  and bipyridine in another type of penta-co-ordinated di-organotin structure of (type-XI).



Infrared spectroscopic investigations have shown that the addition compounds of  $R_2SnX_2$  (X = halogen) and monodentate amines in 1:2 mole ratio or bidentate amine in 1:1 mole ratio are of the (type-XII).

Type XII

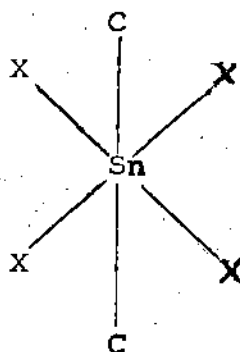
Many di-organotin bis(chelates) have been isolated<sup>54, 59, 87, 89</sup> and found to contain hexa co-ordinated tin atom. Some representative compounds are acetylacetonates, oxinates and carboxylates. The alkyl group in these compounds exists predominantly in the trans-position (Type-XIII).

Type XIII

For diorganotin dioxinates, such a conventional octahedral structure is, however, far from correct as X-ray investigation of dimethyl tin dioxinate shows this molecule may be interpreted in terms of distorted tetrahedron formed through 3-centre bonds involving  $sp^3$ -

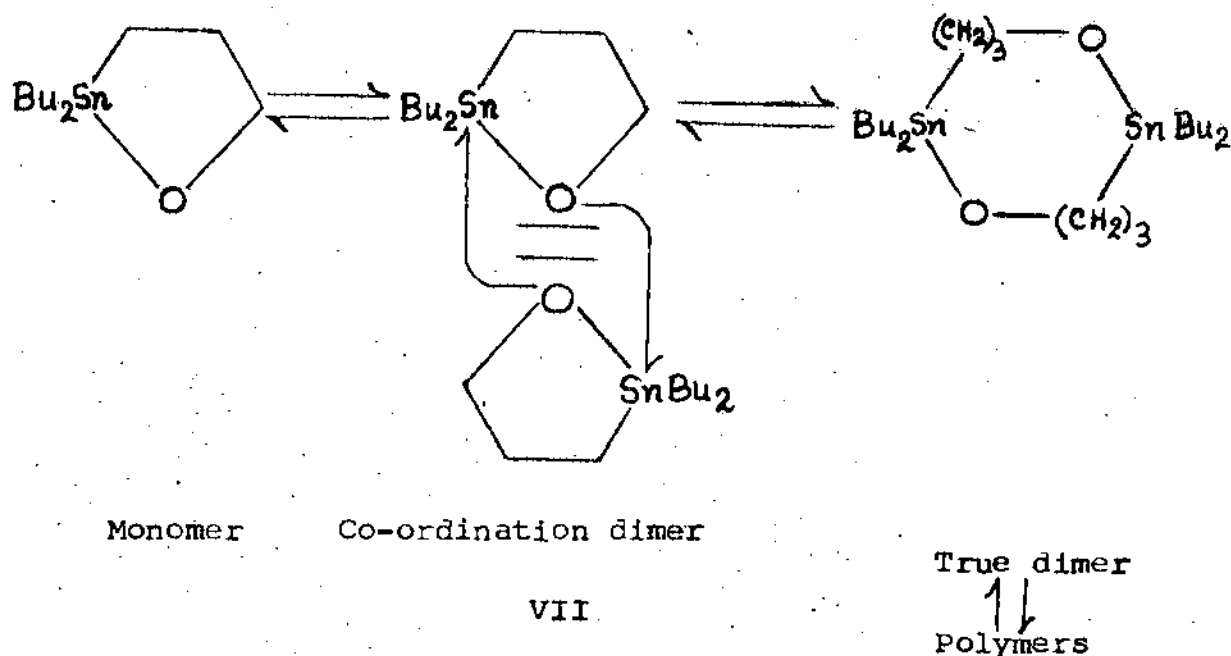
orbital of the tin atom and the valence orbitals of the donor atoms (oxygen and nitrogen) of the oxinate group<sup>90</sup>.

The most asymmetric species is the  $(\text{CH}_3)_2\text{SnX}_4^{-2}$  anion ( $\text{X} = \text{F}, \text{Cl}, \text{NCS}$ ) where the structure is represented by typeXIV. Tobias et al have shown that there are analogous species  $[(\text{CH}_3)_2\text{Sn}(\text{OH})_4]^{-2}$  as well as cationic hydrated species in aqueous solution of dimethyl tin compounds<sup>91-93</sup>.



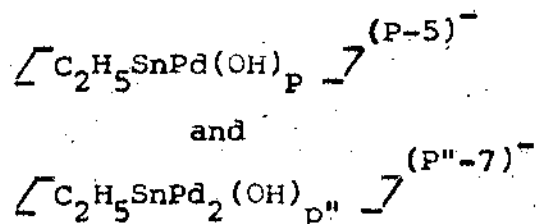
TypeXIV

An analysis of IR spectra in the  $1200-900 \text{ cm}^{-1}$  of the compounds of the type  $n\text{-Bu}_2\text{SnCH}_2\text{CHR}'\text{CHR}''\text{O}$  ( $\text{R}' = \text{R}'' = \text{H}$  or  $\text{Me}$ ) have been used to distinguish between monomers, co-ordination dimers and cyclic polymers.<sup>94</sup>

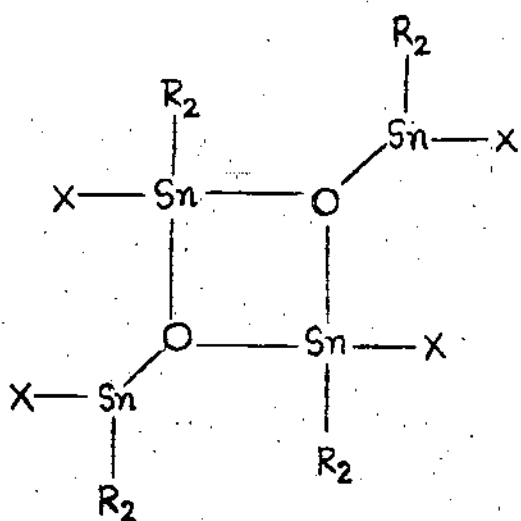


Reports on mono organotin compounds indicate that some of these might have hexa-co-ordinated and even hepta co-ordinated tin atoms. However little work has been done on their detailed configurations. Mono-organotin halide bis-acetylacetonates<sup>95</sup> and bis-oxinates<sup>96</sup> as well as the addition compounds of formula  $\text{RSnX}_2 \cdot 2\text{D}$ <sup>97</sup> are examples of 6-co-ordinated tin compounds.

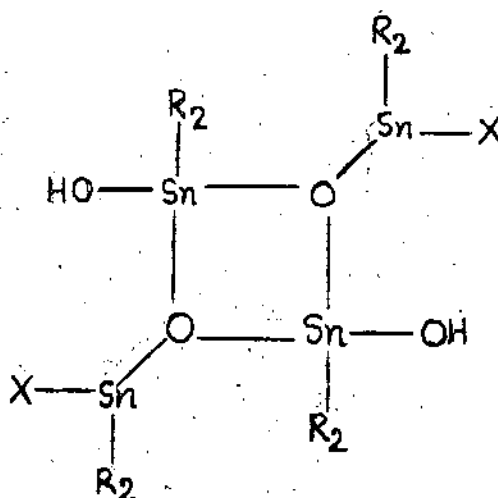
In basic aqueous media the derivatives of ethyl tin (IV) and Palladium (II) ions give two mono organotin complexes<sup>98</sup>.



T) dimeric tetraalkyl distannoxanes<sup>53</sup>  $(XR_2SnOSnR_2X)_2$  and  $(XR_2SnOSnR_2OH)_2$  are unique because they are believed to contain both tetra-co-ordinated and penta-co-ordinated tin atoms (Type-XV and XVI)



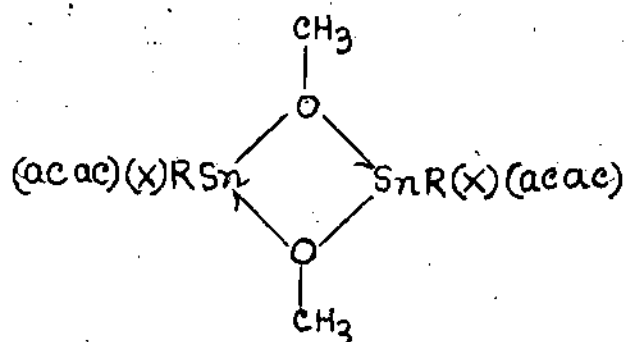
Type-XV



Type-XVI

A hepta-co-ordinated tin is observed in phenyl tin tris (tropolonate) and probably in mono organo tin tris (carboxylates).

The complex compound  $[(acac)XRSn(OCH_3)]_2$  obtained by partial alcoholysis from  $RXSn(acac)_2$ <sup>53</sup> is unique in that it contains two bridging methoxy groups forming a four membered Sn-O ring as shown in structure(XVII).



Type-XVII

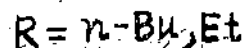
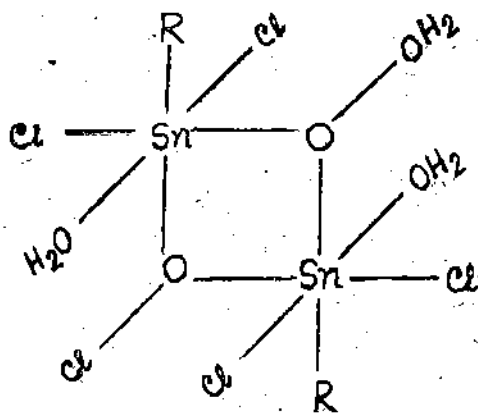
The mono-, di- and tri- organotin compounds generally exhibit a co-ordination number from 4-6. However, not many organotin compounds have been found to possess hepta-co-ordinated tin, the geometry of which is expected to be pentagonal bipyramidal one. Phenyl tin tris-tropolonate has been reported<sup>99</sup> to be monomeric in methylene chloride, suggesting a seven co-ordination around the tin. P.G. Harrison<sup>75</sup> have concluded from UV, NMR and IR data that n-butyl tin tris-oxinate may have 7-co-ordinated tin atom. Ruddick and Sams<sup>101</sup>, from Mossbauer spectroscopy, determined the co-ordination number around tin in  $\text{BuSn}(\text{OX})_3$  which is consistent with seven co-ordination, with three equivalent bidentate oxine groups. A new structural interpretation<sup>102</sup>, based on solid-state and solution  $^{13}\text{C}$  NMR data for  $\text{Me}_2\text{Sn}(\text{OAc})_2$  was put forth for diorganotin di-carboxylates. The first X-ray structural study of a 7-coordinate organotin anion, a diorganotin tri-carboxylate has been reported<sup>122</sup>.

The structure of polymeric mono-organo-stannoic acids and the crystal structures of their carboxylate derivatives has<sup>ve</sup> been reported<sup>103,104</sup> where it has been shown that polymeric tin compounds are most likely to show a Mossbauer effect at ambient temperature.

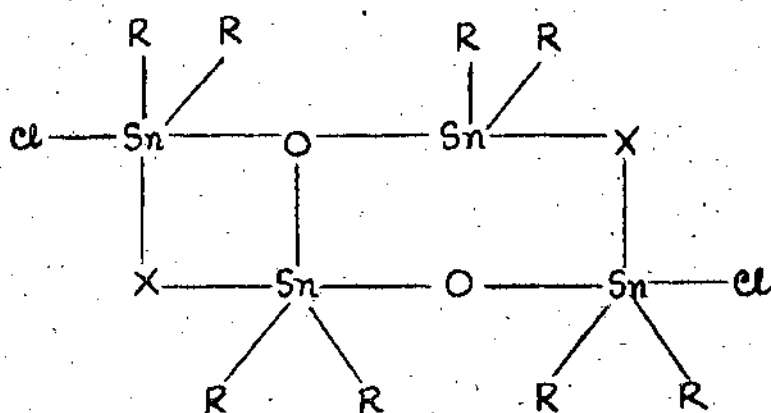
The synthesis and X-ray crystal structure of hexameric phenyltin oxycyclohexanecarboxylate,  $[\text{PhSn}(\text{O})\text{O}_2\text{CC}_6\text{H}_{11}]_6$  has been reported<sup>105</sup>. The x-ray characterisation shows tin (IV) present in a new structural environment appearing as a drum shaped molecule containing hexa coordinated tin atoms.

The synthesis of hexameric n-butyloxotin benzoate  $[\text{n-BuSn}(\text{O})\text{O}_2\text{CC}_6\text{H}_4\text{NO}_2-2]_6 \cdot 3\text{C}_6\text{H}_6$  and the dimeric methyloxotin cyclohexanoate,  $[(\text{MeSn}(\text{O})\text{O}_2\text{CC}_6\text{H}_{11})_2\text{MeSn}(\text{O}_2\text{CC}_6\text{H}_{11})_3]$  by condensing the stannic acid with the respective carboxylic acid as well as synthesis of dimeric n-butyloxotin carboxylate, by reacting n-butylin trichloride with the silver salt of the respective carboxylic acid have been reported<sup>106</sup>. These substances, as found by X-ray analysis, form a new structural class of organotin compounds having "unfolded drum" or "ladder" structures.

Formation of distannoxane rings seems to be an integral component of hydrolysis products of many organotin compound<sup>107</sup>. For example, monoalkyltin halides hydrolyze to give distannoxanes- of the type



whereas diorganotin halides give dimeric distannoxanes as end products. These possess "ladder"<sup>107-109</sup> or "stair case"<sup>110,111</sup> structures. Here the tin atoms are penta-coordinated.



IX

where X = Cl, OH

R = Ph, alkyl

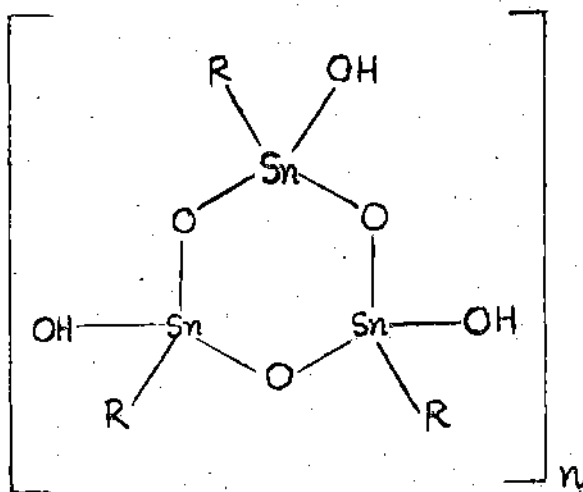
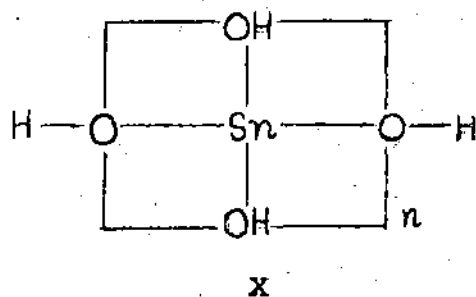
The synthesis of a soluble drum compound, containing cyclopentane units,  $\left[ n\text{-BuSn}(\text{O})\text{O}_2\text{CC}_5\text{H}_9 \right]_6 \cdot \text{C}_6\text{H}_6$  and the formation of a novel chloro derivative  $\left[ (n\text{-BuSn}(\text{O})\text{O}_2\text{CPh})_2 (n\text{-BuSn}(\text{Cl})(\text{O}_2\text{CPh})_2) \right]_2$  having "ladder" or "open drum" structures has been reported<sup>112</sup>. Interconversion of the drum and ladder structures has been established



in solution by  $^{119}\text{Sn}$  NMR along with a possible mechanism of hydrolysis of a ladder to a drum formulation has been reported<sup>112</sup>.

Chandrasekhar et al<sup>112</sup> employed a variation of the original reaction by Lambourne<sup>113</sup> in exploring condensation products leading to the drum composition as well as to a mixed oxocarboxylate-tricarboxylate formulation,  $\left[ (\text{R}'\text{Sn})(\text{O})\text{O}_2\text{CR} \right]_2 \text{R}'\text{Sn}(\text{O}_2\text{CR})_3 \right]_2$ . The latter was identified as having an unfolded drum or ladder structure<sup>106</sup>. The reaction consists of a condensation of an organostannanoic acid with a carboxylic acid.

The stannous acids are infusible powders for which a polymeric structure (X) have been proposed<sup>114,115</sup>. For the partially dehydrated material structure (XI) has been proposed by Platt et al<sup>116</sup>.



In both (X) and (XI), tin atom is 4-co-ordinated and is enclosed within the tetrahedra formed by the three oxygen atoms and the organic group R.

From the values of quadrupole splitting ( $EQ = 1.29-1.83$  mm/sec) in organo stannic acids Davies et al<sup>117</sup> have suggested a tetrahedral geometry at tin, though the possibility of association has not been completely excluded. The isomer shift value ( $\delta = 0.40-0.78$  mm/sec) are very small because of the very low 's' electron density at the tin atom resulting from electron attraction by the surrounding oxygens.

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## CHAPTER - II

### A SHORT REVIEW OF ORGANOTIN ALKOXIDES AND RELATED COMPOUNDS.

IIA. INTRODUCTION

IIB. ORGANOTIN ALKOXIDES

IIC. ORGANOTIN ENOLATES

IID. ORGANOTIN PHENOXIDES

IIIE. ORGANOTIN DERIVATIVES OF SOME (ARYLAZO)PHENOLS

IIIF. STANNOXIDES OF OTHER ELEMENTS

REFERENCES

## IIA. Introduction

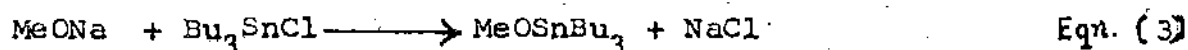
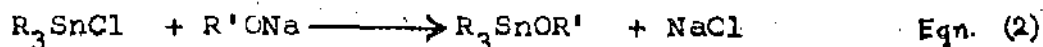
As the present work is a study on the reactions of azo-phenoxy compounds with organotin compounds, it is desirable that a brief review of the chemistry of organotin alkoxides and related compounds be presented to make the reader familiar with the wide variety of alkoxides, phenoxides and related compounds and their reactions and structures so that a proper assessment of the present work may be made.

## IIB. Organotin alkoxides.

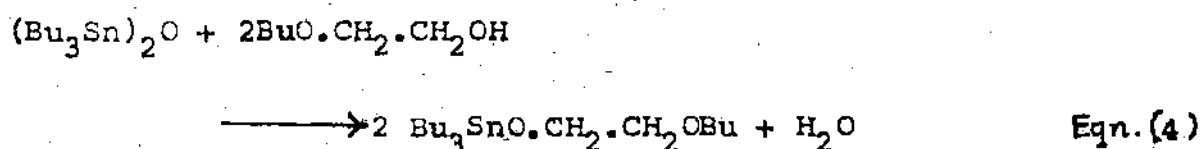
The simple organotin alkoxides and phenoxides are usually prepared by nucleophilic substitution by an alcohol or its metal derivatives at a tin centre [equation (1) ( $M = H, Na$  etc. )]. The best established method is that in which an organotin halide is treated with the sodium alkoxide, often in the parent alcohol as solvent. The sodium chloride which is formed is filtered or centrifuged off and the alkoxide is recovered by distillation or crystallisation [e.g. eqn. (3)].



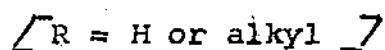
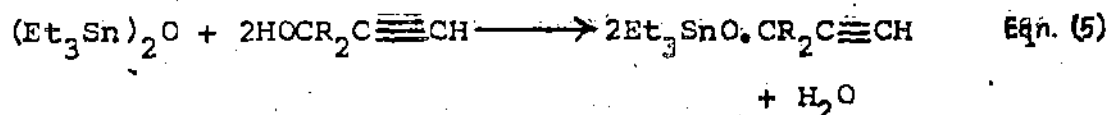
Alkoxides can be prepared by reaction between an alcohol and an organotin halide in the presence of a base<sup>1</sup> or by a metathetical reaction from an alkali-metal alkoxide<sup>2,3</sup>.



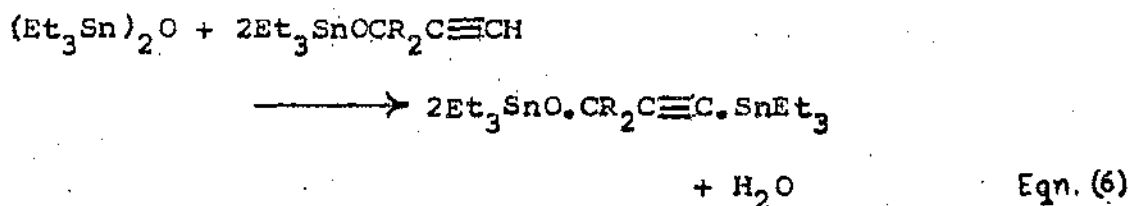
The alkoxides are sensitive to moisture and carbon dioxide, and the filtration has to be carried out in the absence of air, which may be tedious if the sodium chloride is finely divided. A more convenient route to the trialkyltin alkoxides, when the alcohol or phenol boils above about 90°C, is the azeotropic dehydration of a mixture of the appropriate alcohol and bis-(trialkyltin) oxide in benzene or toluene<sup>4</sup>.



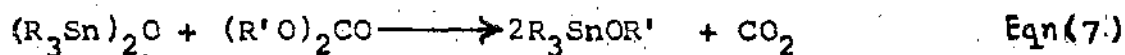
The water formed can be collected in a Dean and Stark Separator and good yields are obtained after one hour's boiling under reflux<sup>5</sup>. Triethyltin oxide reacts with acetylenic alcohols at room temperature .



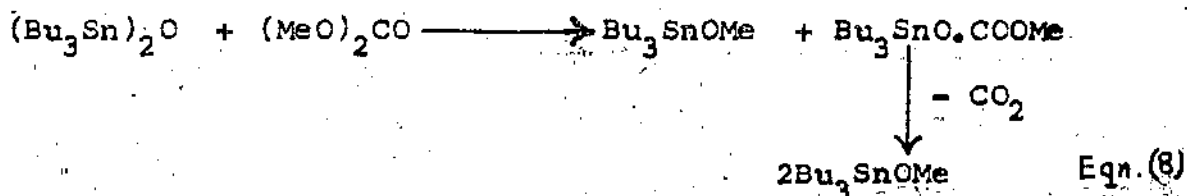
If the mixture is heated and water is removed azeotropically the product reacts further<sup>6,7</sup>.



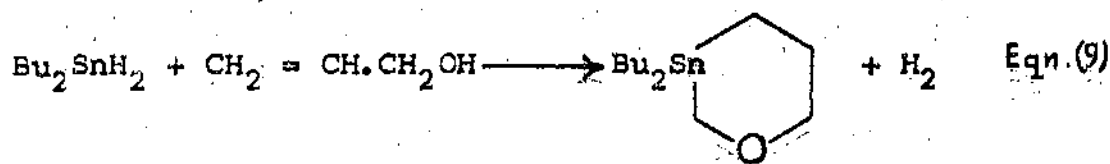
Trialkyltin alkoxides can be obtained in good yields by heating together an oxide and a dialkyl carbonate<sup>5</sup>



If the alcohol is more volatile, for example if it is methanol then trialkyltin alkoxide can be obtained conveniently<sup>4</sup> by using dialkyl carbonate.



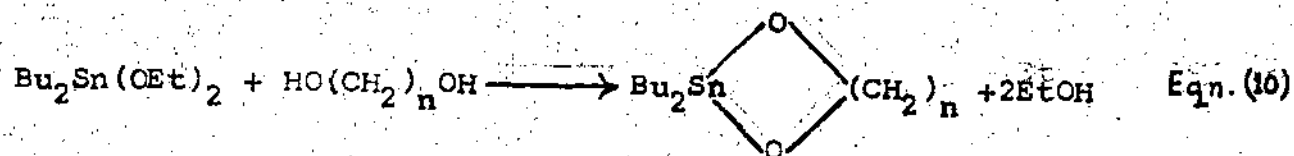
A further process which avoids filtration is the reaction between alkyltin hydrides and alcohols to give alkoxides and molecular hydrogen. This route has been used particularly for preparing cyclic alkoxides<sup>8</sup>.





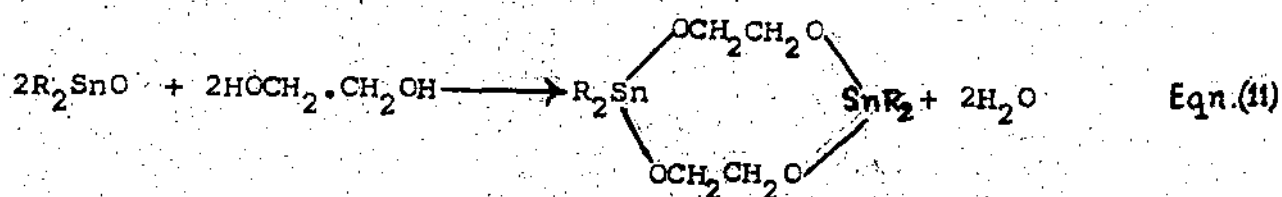
Suitable dialkyltin compounds with glycols give cyclic alkoxides<sup>9</sup>

[Mercaptoalcohols such as  $\text{HSCH}_2\text{CH}_2\text{OH}$  react similarly]



( $n = 4, 5, 6$ )

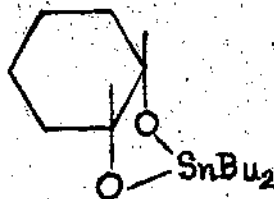
(Ref. 10)



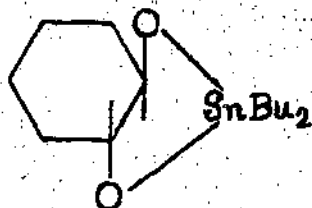
I

(Refs. 11, 12)

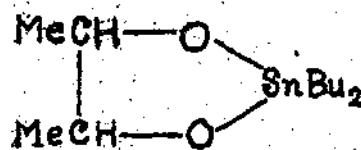
Although compound I, ( $\text{R} = \text{Bu}$ ) has a molecular weight corresponding to the dimeric structure shown, a number of 1,2-glycols can give monomeric cyclic alkoxides, for example, compounds II-IV<sup>10,11</sup>



II

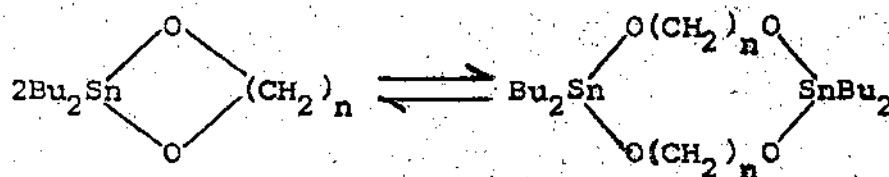


III

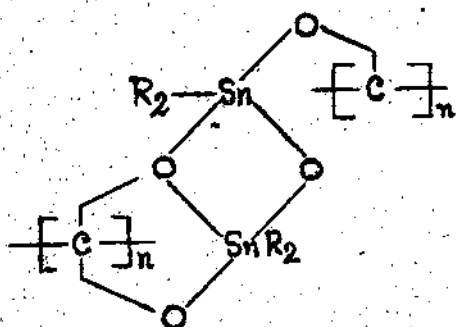


IV

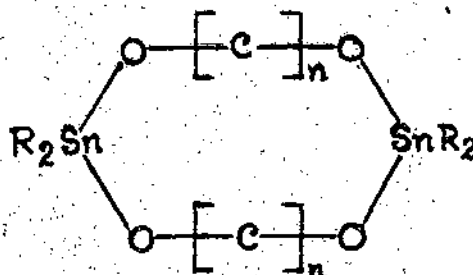
other workers have suggested that in solution, these cyclic compounds exist as an equilibrium mixture of monomer and dimer<sup>10</sup>



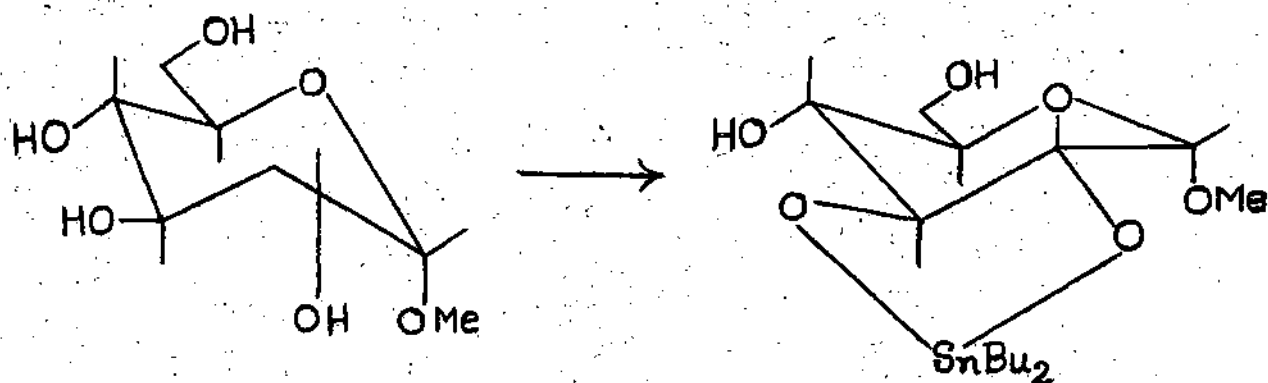
Diols are more reactive towards dialkyltin oxides and triols towards alkyl stannic acids, than are monohydric alcohols and the cyclic dialkyltin dialkoxides and mono alkyltin trialkoxides can be prepared by azeotropic dehydration. Sometimes the products from diols may exist as both monomers or dimers<sup>13</sup>. IR and NMR data<sup>13</sup> support the structure (V) and the nature of some reaction products<sup>14,15</sup> favours the larger ring (VI). Carbohydrates react in this way to form cyclic dialkoxides, which are useful in organic synthesis. For example methyl- $\alpha$ -D-glucopyranoside gives methyl 2, 3, -O-dibutylstannylene- $\alpha$ -D-glucopyranoside (VII)<sup>16</sup>.



V

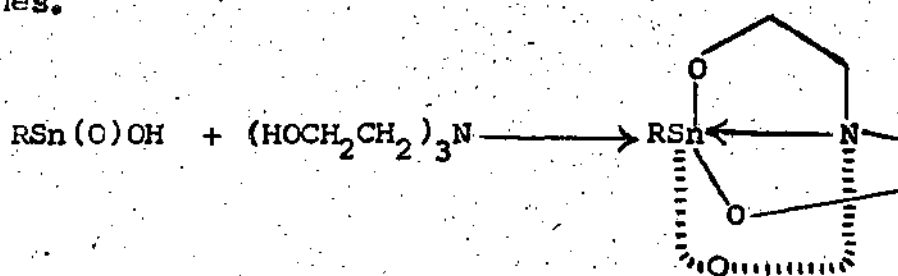


VI



VII

The stannatranes (VIII) which can be formed by azeotropic dehydration of a mixture of stannous acid and triethanolamine<sup>17</sup> have attracted a lot of attention because of their triptych structures<sup>18</sup> and their analogy with the physiologically active silatranes.

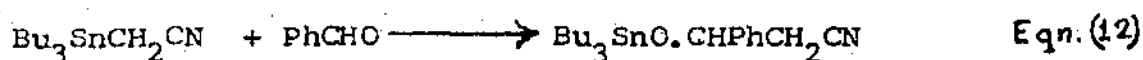


VIII

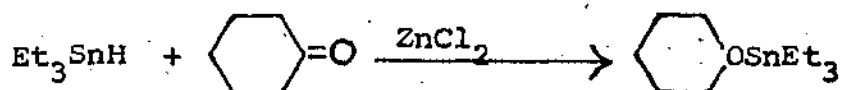
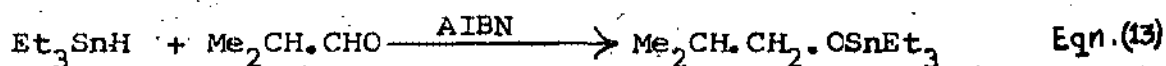
Reactions (4) and (7) are the best for preparing trialkyltin alkoxides. Under the same conditions, dialkyltin oxides react only to the stage of the dialkoxy-tetraalkyldistannoxanes  $R' - OR_2SnOSnR_2OR'$  and though these decompose thermally to give  $R_2SnO$  and  $R_2Sn(OR')_2$ , the reaction between sodium alkoxides and dihalides still provides

the best route to the dialkoxides. In tetralin however, phenols react with dialkyltin oxides to give the diphenoxides  $R_2Sn(OAr)_2$  directly<sup>19</sup> and it is possible that the higher boiling alcohols might show a similar reaction.

A number of  $\alpha$ -substituted organotin compounds add to the carbonyl groups of aldehydes and ketones to give substituted alkoxides for example<sup>26</sup>

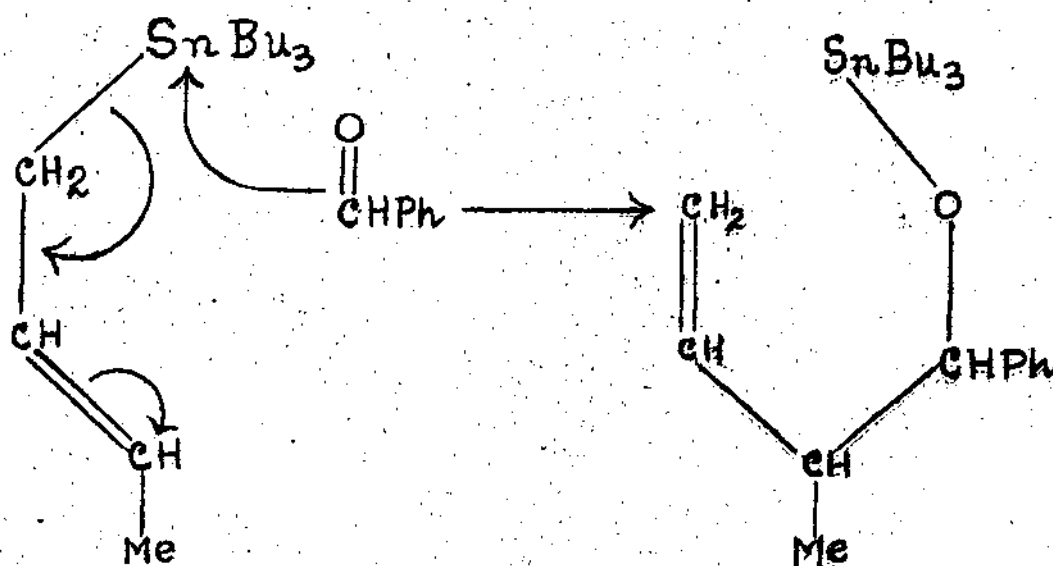


Organotin alkoxides can also be formed by the addition of the Sn-H bond or activated Sn-C, Sn-O or Sn-N bonds to the carbonyl groups of aldehydes and ketones. The Sn-H additions can be catalysed by azobisisobutyronitrile (AIBN) or by zinc chloride, involving attack at oxygen by a radical or an electrophilic tin species respectively<sup>27</sup>.



Activated  $Sn-CH_2X$  bonds ( $X = CN, COMe, COOEt, CONMe_2, CH_2 = CH_2$  (etc)) will add to certain aldehydes and ketones<sup>37,38</sup>.

Substituted allyl compounds react with aldehydes, probably through a cyclic transition state (IX)<sup>37</sup>.

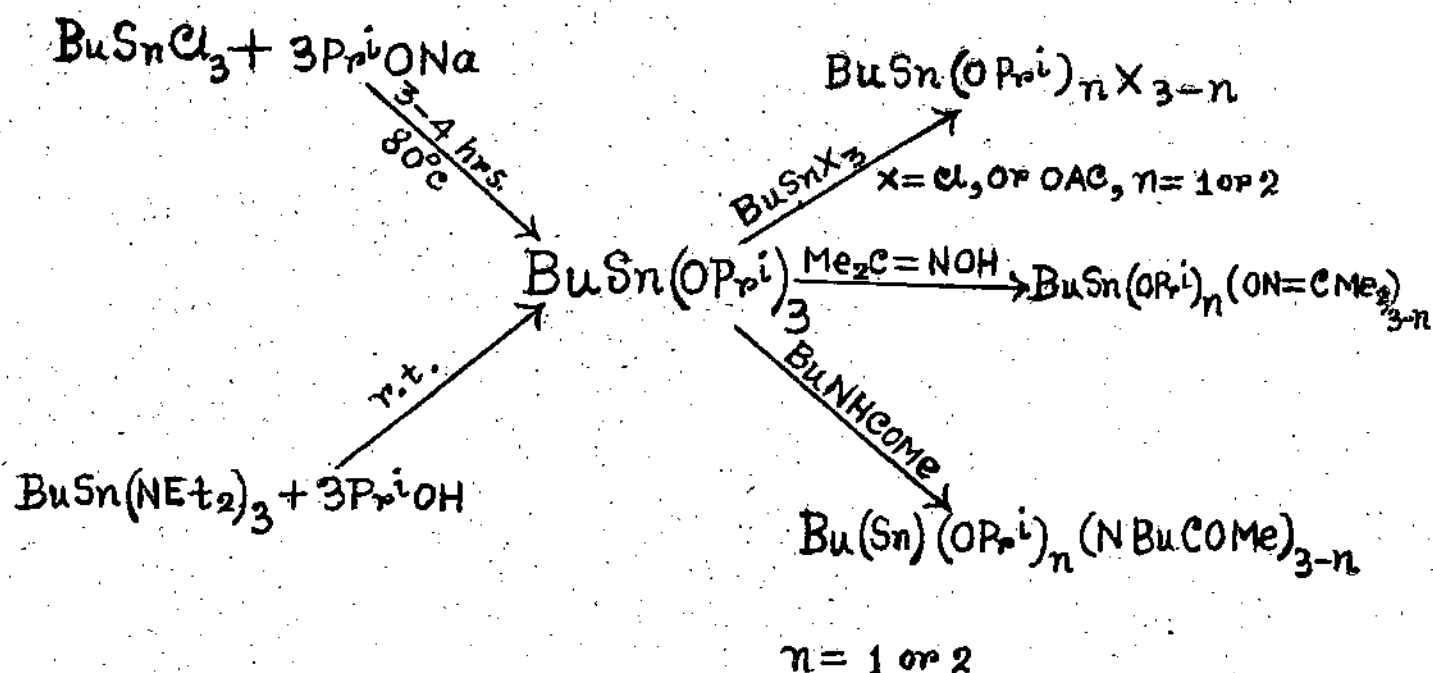


IX

Alkyltin trialkoxides can be formed by heating together the sodium alkoxide and alkyltin trichloride in benzene for 3 or 4 hours<sup>20</sup>. Alternatively the alkyltin tris-(diethylamides) may be subjected to alcoholysis which is rapid and exothermic at room temperature<sup>21,22</sup>.

Some reactions by which the trialkoxides may be converted into other alkoxy derivatives are shown in the scheme-1<sup>22</sup>.

Scheme - 1



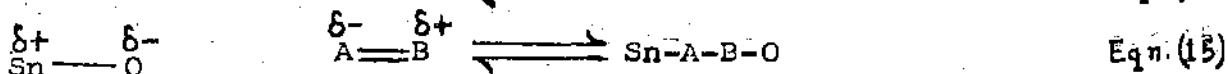
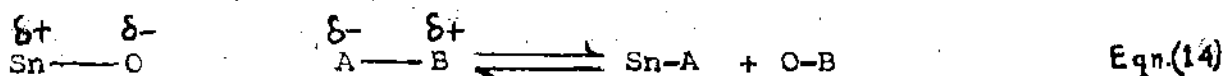
Physical properties of some typical organotin alkoxydes are given in Table-1.

Table - 1

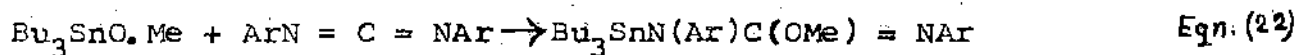
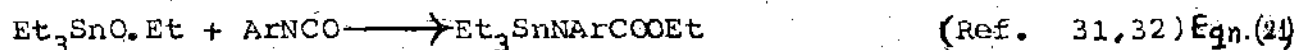
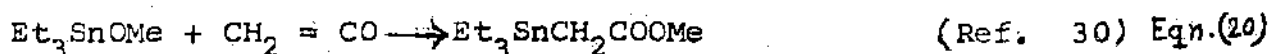
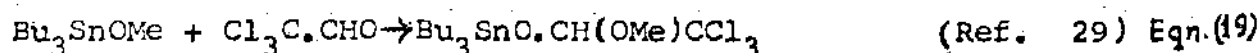
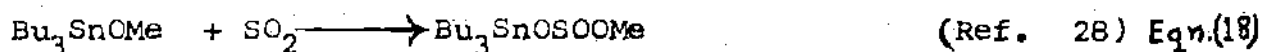
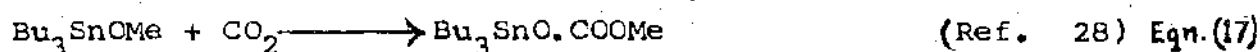
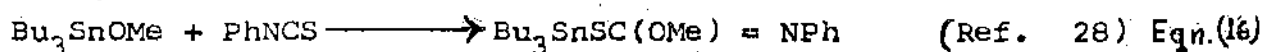
Physical properties of some organotin alkoxides and phenoxides<sup>79</sup>

Compound	m.p	b.p	$n_D^{20}$	$d^{20}$
$\text{Me}_3\text{SnO.Bu}$	-	175-6°	1.4575	1.2656
$\text{Et}_3\text{SnOCH}_2\text{.CH}_2\text{OCH}=\text{CH}_2$	-	90-90.5°/3 mm	1.4810	1.2560
$\text{Pr}_3\text{SnO.Me}$	-	87-88°/3 mm	-	-
$\text{Pr}_3\text{SnOPh}$	-	145-147°/1 mm	1.5284	1.2167
$\text{Bu}_3\text{SnOMe}$	-	97-97.5°/0.06 mm	1.4710(25°)	1.1294(1.1690)
$\text{Bu}_3\text{SnOBu}$	-	124-128°/3 mm	1.4690	1.0189
$\text{Bu}_3\text{SnOPh}$	-	152°/1 mm	1.5171	1.1666
$\text{Bu}_2\text{Sn(OMe)}_2$	-	126-128°/0.05 mm	1.4852(25°)	-
$\text{Ph}_3\text{SnOMe}$	65-66°	-	-	-

Most of the reactions of the organotin oxides and alkoxides involve heterolytic substitution or addition reactions. The utility of these reactions in organic synthesis depends on the modulation of the nucleophilicity of the oxygen by the tin atom : the substitution and addition process often occur in various combinations and these applications have been reviewed<sup>23,24,25</sup>.

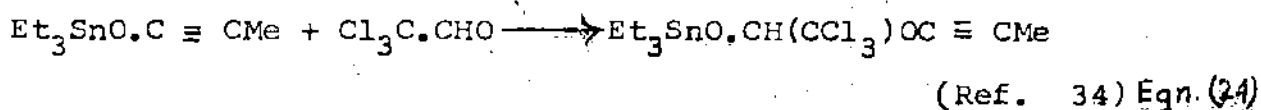
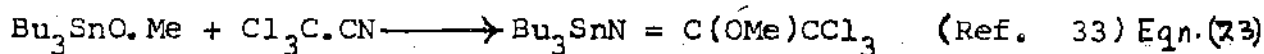


The alkoxides must be protected from moisture which causes rapid hydrolysis and the readiness with which these compounds participate in both substitution and addition reaction is being increasingly exploited. The versatility of organotin alkoxides to add across unsaturated linkages are provided by the following examples:



(Ref. 28)



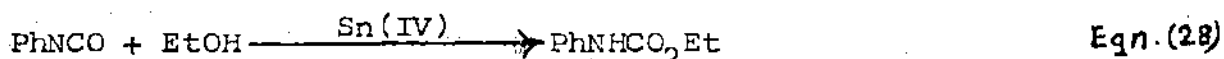
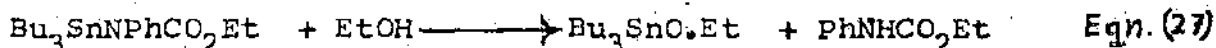
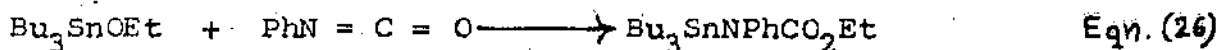


The product from addition to the isocyanate will undergo protolysis with an alcohol to give the urethan and the regenerated organotin alkoxide.

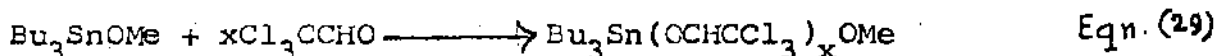


It can be thus seen that a small amount of an organotin compound can catalyse the reaction between alcohols and isocyanates and this explains the known efficacy of organotin catalysts for the production of polyurethans<sup>31</sup>.

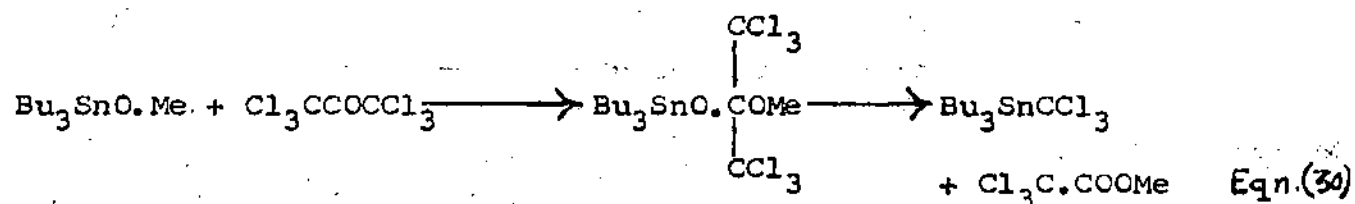
The reaction probably involves combination of an addition followed by a substitution reaction.



Addition to carbonyl compounds occurs with a number of aldehydes and with reactive ketones such as hexachloroacetone. Since the products are themselves alkoxides further additions may occur and in the case of chloral, a polymeric product was obtained<sup>29,35</sup>.



The product from addition of tributyltin methoxide to hexachloroacetone is unstable and decomposes to give the trichloromethyltin derivative<sup>36</sup>.



<sup>119</sup>Sn NMR chemical shift in some butyltin alkoxides shown in Table - 2, provide some insight into the nature of these alkoxides.

Table - 2

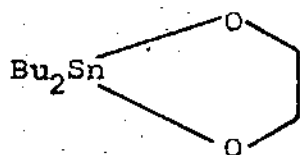
<sup>119</sup>Sn Chemical Shifts (p.p.m) of Butyltin Alkoxides<sup>a</sup>

R	Bu <sub>3</sub> SnOR	Bu <sub>2</sub> Sn(OR) <sub>2</sub>	BuSn(OR) <sub>3</sub>
Me	+83	-165	-
Et	+86	-161	-428
Pr <sup>n</sup>	+87	-159	-414
Pr <sup>i</sup>	+76	- 90	-333
Bu <sup>n</sup>	+91	-161	-428 <sup>b</sup>
Bu <sup>i</sup>	+82	-150	-401 <sup>c</sup>
Bu <sup>s</sup>	+80	- 34	-321
Bu <sup>t</sup>	+60	- 34	-200

<sup>a</sup> Neat liquids at 25°C, <sup>b</sup> at 38°C, <sup>c</sup> at 66°C

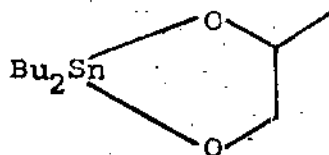
The tributyltin alkoxides all show a high frequency shift and are believed to exist as tetrahedral monomers at room temperature. The dibutyltin dialkoxides are monomeric only when a butyl alkyl group ( $R = Bu^s$  or  $Bu^t$ ) prevents dimerization and the enthalpy of dissociation of the dimers in solution is found to be  $60-100 \text{ kJ mol}^{-1}$ <sup>39</sup>. The butyltin trialkoxides exhibit a wider range of chemical shifts<sup>22</sup>. Butyltin tributoxide again appears to be monomeric, for steric reasons, but the compounds with similar alkyl groups, showing chemical shifts of about  $-425 \text{ p.p.m.}$ , are probably octahedrally six coordinated.

By this chemical shift criterion, the dibutyltin derivatives of the 1,2-diols shown in structure X to XII appears to contain five coordinated tin as in VI<sup>39</sup>.



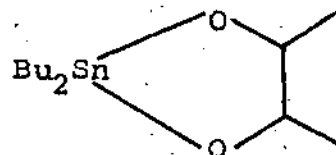
X

<sup>119</sup>Sn chemical  
shift (p.p.m.) -189



XI

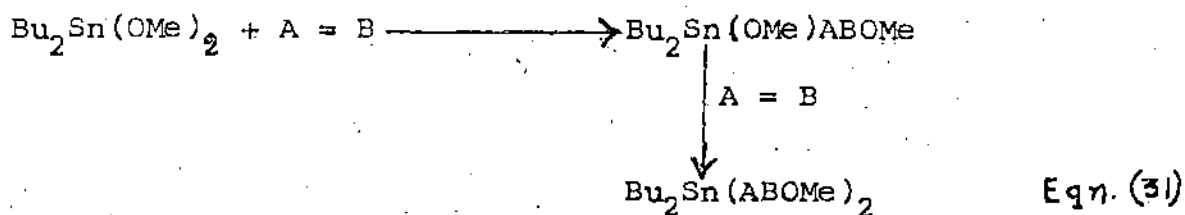
-164



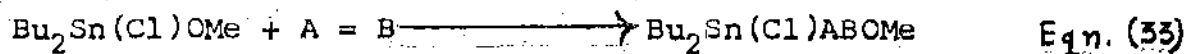
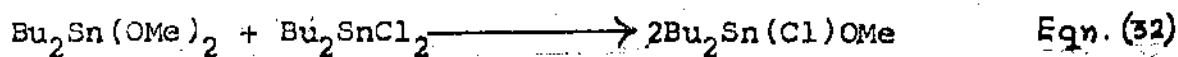
XII

-155 (in  $\text{CDCl}_3$ )

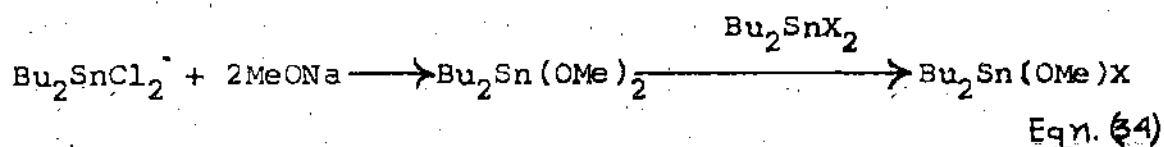
Dialkoxides undergo similar addition reactions to those already discussed for the monoalkoxides and in most cases, 1:1 and 1:2 adducts can be isolated<sup>40</sup>.



(A = B = isocyanate, isothiocyanate, aldehyde, sulphur dioxide, carbon dioxide, cyanide, carbodiimide). Dibutyltin dimethoxide undergoes a redistribution reaction with a dibutyltin dihalide and the resulting halomethoxide also participates in addition reactions<sup>40,41</sup>.

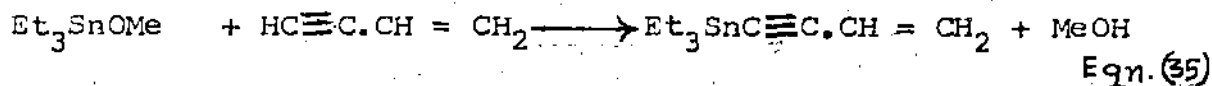


The dialkoxides react with a variety of compounds,  $\text{R}_2\text{SnX}_2$  in solution, in a process analogous to the Schlenk equilibrium involving Grignard reagents to give the monoalkoxy compounds<sup>41</sup>. The  $^{119}\text{Sn}$  NMR spectra show that the methoxide chlorides  $\text{R}_2\text{Sn}(\text{OMe})\text{Cl}$  (R = Me or Bu) exist as monomers in dilute solution, but as methoxide-bridged dimers in more concentrated solutions<sup>42</sup>.

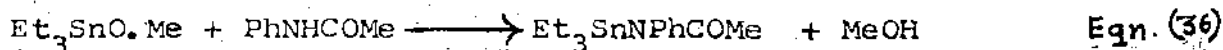


(X = F, Cl, Br, I, SNC, OAc, OSO<sub>2</sub>R)

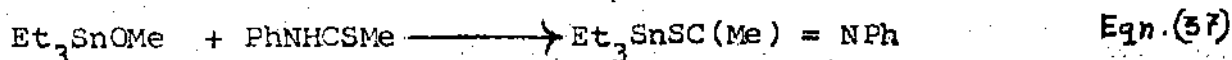
Turning next to substitution reactions, the alkoxides are sensitive to a wide range of protic species; reaction with water has already been mentioned and acetylenes readily displace alkoxyl groups<sup>43</sup>.



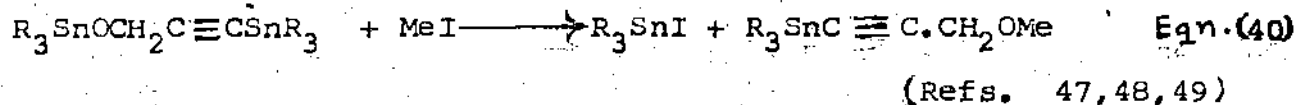
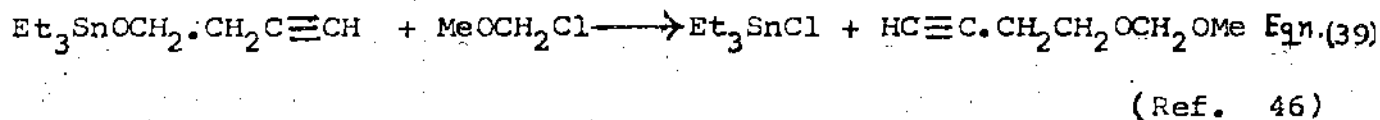
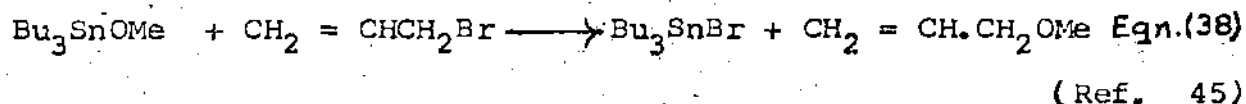
N-Stannylamides are conveniently prepared from alkoxides



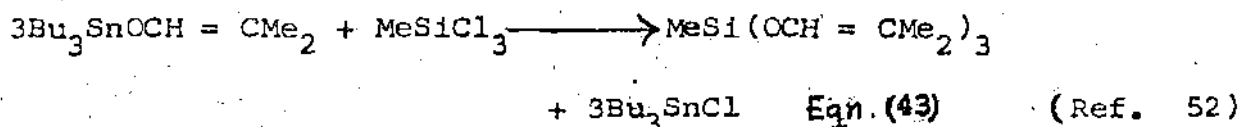
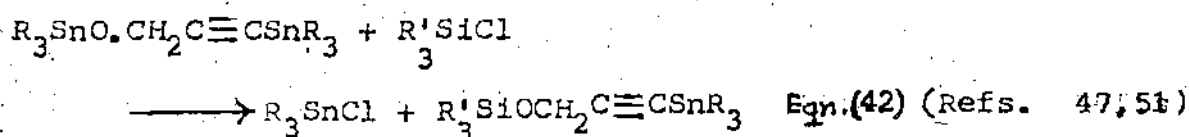
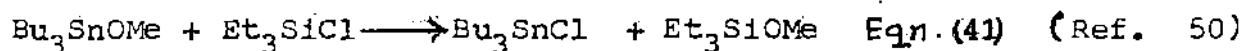
However when the corresponding thioamides are used the products have Sn-S rather than Sn-N bonds<sup>44</sup>.



Alkyl halides and alkoxides react to give ethers and organotin halides.

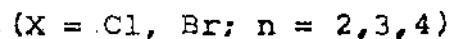


Irradiation with ultraviolet light and the addition of Lewis acids did not increase the yields in these reactions<sup>45</sup>. In a similar manner alkoxyl groups can be transferred to silicon by the use of silyl halides.

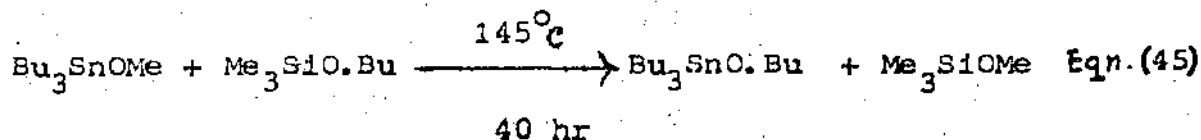


The silyl halides react more readily than the alkyl halides and cooling is often necessary.

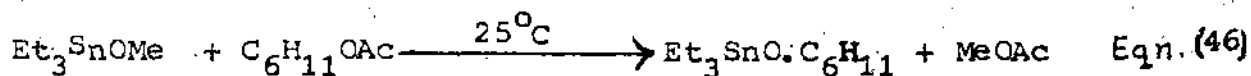
Trans-alkoxylations can be effected by heating an alkoxide with excess of another alcohol<sup>53</sup>.



An alkoxysilane may also be used<sup>54</sup>.



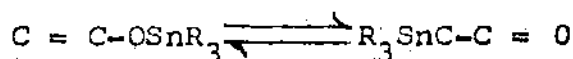
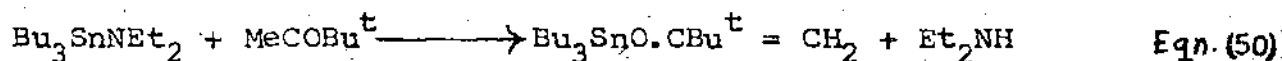
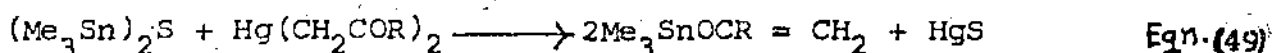
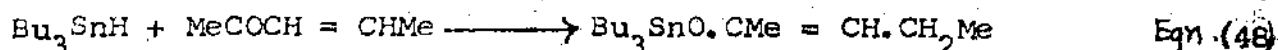
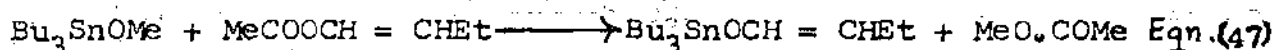
A similar reaction occurs under milder condition when an alkoxide is treated with an ester<sup>55</sup>.



### IIC. Organotin Enolates

Organotin derivatives of simple enols are usually prepared by treating the acetate of the appropriate enol with a trialkyltin methoxide but the alternative routes have also been used<sup>56-59</sup>.

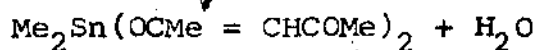
The keto and enol forms exist in metallotropic equilibrium which usually favours the C-isomer.



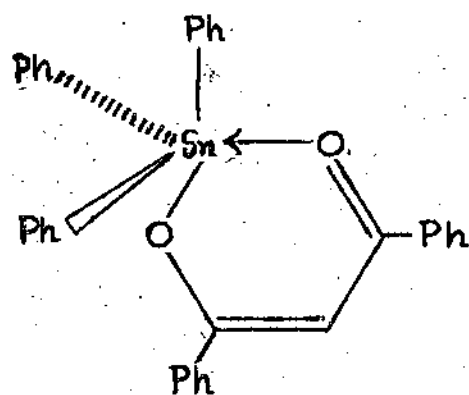
O-isomer

C-isomer

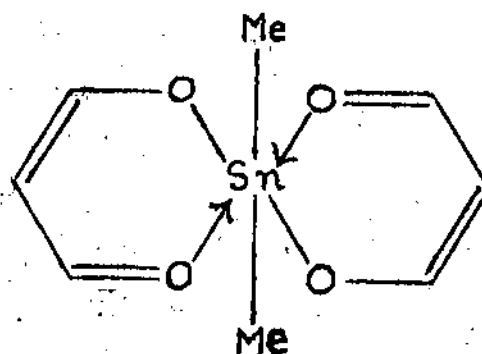
The derivatives of 1,3-diones can be prepared from the organotin oxides<sup>60</sup> in a reaction analogous to the preparation of alkoxides. These diones act as bidentate ligands and the structures shown in XIII<sup>61</sup> and XIV<sup>62</sup> have been established by X-ray crystallography.



Eqn. (51)



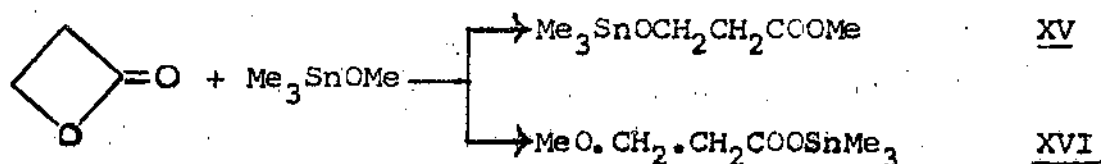
XIII



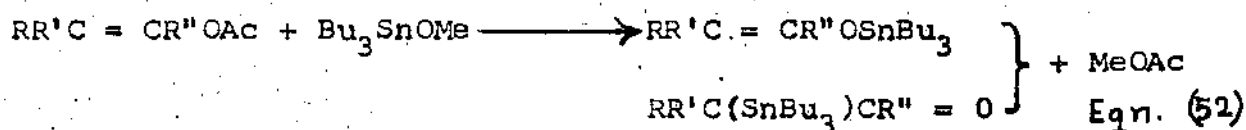
XIV

The reaction of  $\beta$ -propiolactone with trimethyltin methoxide (and other  $\text{Me}_3\text{SnX}$  compounds) has been studied in detail<sup>63,64</sup>. The dominant product is that resulting from acyl-oxygen bond cleavage XV but the product obtained from alkyl-oxygen bond cleavage XVI can also be detected, the ratio of the products depending upon the polarity of the solvent used

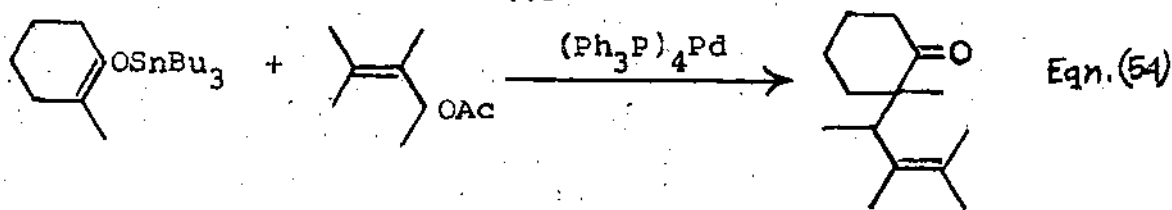
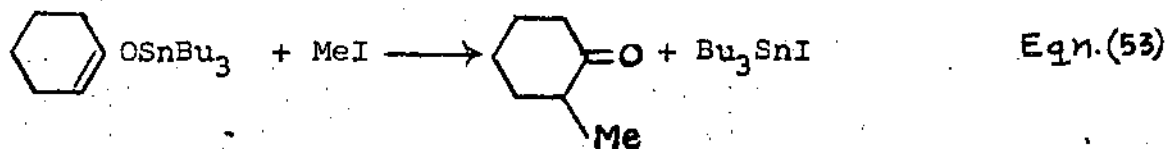




Stannylated celluloses are prepared by reaction between cellulose (or a derivative) and an organotin alkoxides<sup>65</sup>. When an alkoxide reacts with an enol ester then the O-stannyl derivative of the enol form and/or the C-stannyl derivatives of the keto form is obtained<sup>57,66</sup>.

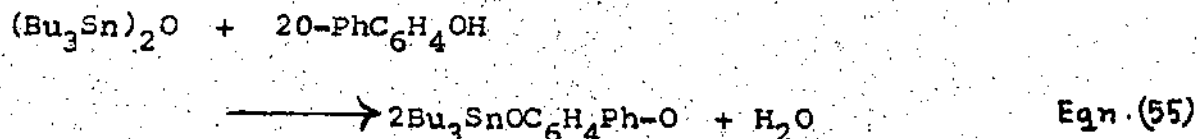


Organotin enolates in which the O- and C- bonded isomers are in metallotropic equilibrium react with alkyl halides by C-alkylation<sup>67</sup> and C-allylation can be brought about by allylic acetates in the presence of tetrakis - (triphenylphosphine) palladium (0)<sup>68</sup>.

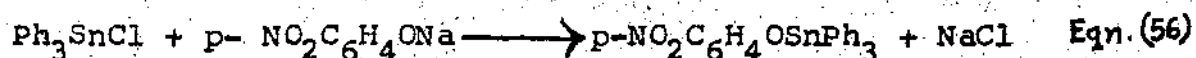


### IID. Organotin Phenoxides

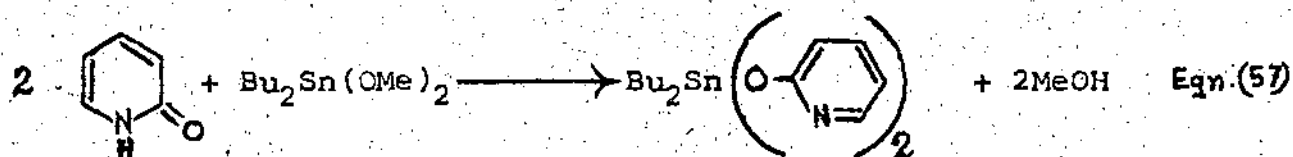
The organotin phenoxides,  $R_n\text{Sn}(\text{OAr})_{4-n}$ , are conveniently prepared by reaction between an oxide and a phenol in the same manner as the alkoxides<sup>69</sup>.



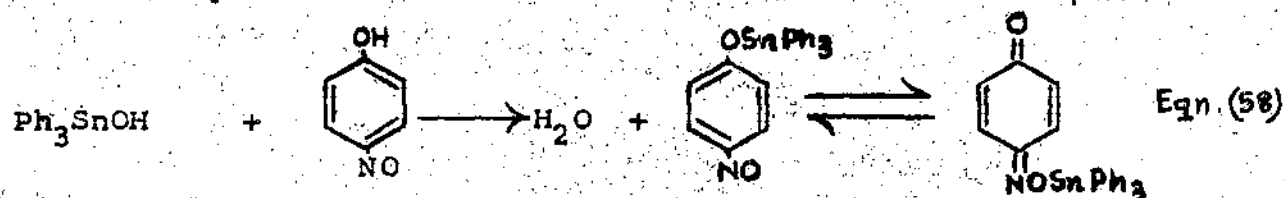
Among other methods, treatment of an organotin chloride with a phenoxide may be used<sup>70</sup>.



Dibutyltin dimethoxide reacts with 2-pyridone as follows<sup>71</sup>

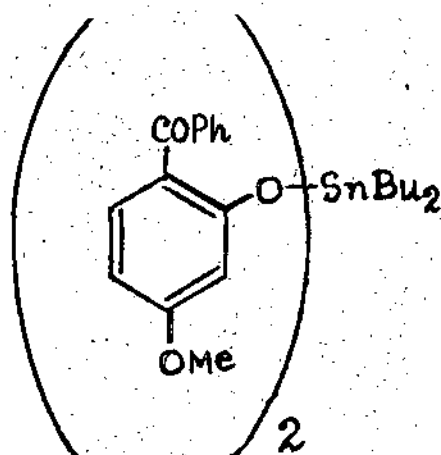


Reaction between triphenyltin hydroxide and p-nitrosophenol gave the p-nitrosophenoxide which, from the infrared and visible spectra of its solutions, was considered to be in equilibrium with the tautomeric quinoxime<sup>72</sup>.

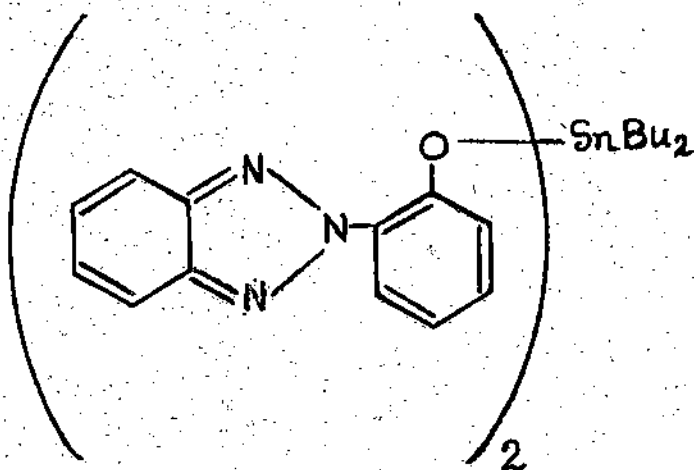


The crystalline product consisted solely of the quinoxime form.

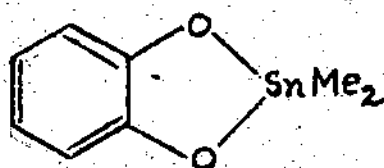
The phenoxides like the alkoxides are generally sensitive to moisture but compounds derived from more acidic phenols (e.g. nitrophenols) are less readily hydrolysed<sup>70,73</sup>. High thermal stability is a property of a number of phenoxides for example compounds XVII<sup>74</sup> and XVIII<sup>75</sup> and also of compounds derived from dihydric phenols such as XIX and XX<sup>76</sup>.



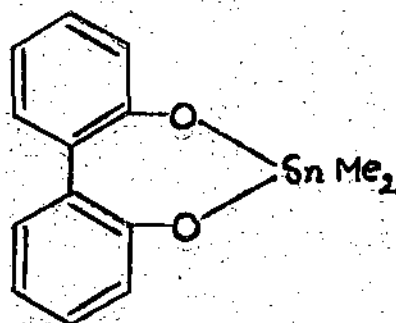
XVII



XVIII

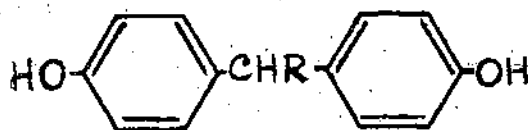


XIX



XX

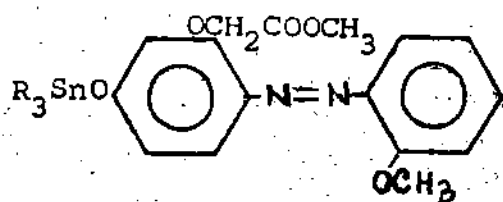
A polymeric phenoxide, having repeating unit  $-\text{OSnPh}_2\text{OC}_6\text{H}_4-$  - was prepared from diphenyltin dichloride and the dipotassium salt of hydroquinone<sup>77</sup>. A number of polymeric products have also been made by heating together in toluene, dialkyl tin oxides and dihydric phenols of the type XXI<sup>78</sup>.



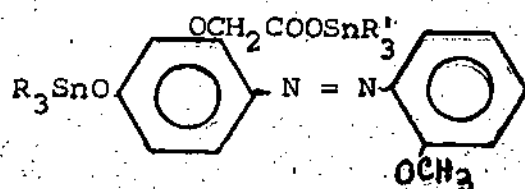
XXI

#### III. Organotin derivative of some (Arylazo) phenols

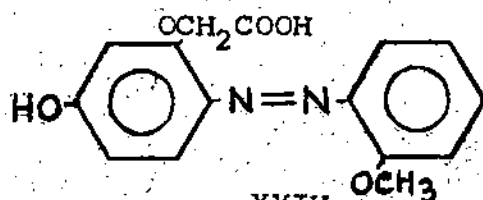
Although no attempt on the synthesis of organotin derivatives of (arylazo) phenols has been yet reported, Sengupta<sup>80</sup> reported the stannylation of the  $-\text{OH}$  group in 2-(2'-methoxy benzene azo)5-hydroxy phenoxy methyl acetate and the corresponding acid leading to the formation of the compounds XXII and XXIII. Interestingly, stannylation of the  $-\text{OH}$  group invariably occurred whenever any attempt to substitute the proton of the  $-\text{COOH}$  group in XXIV by organotin group was made.



XXII

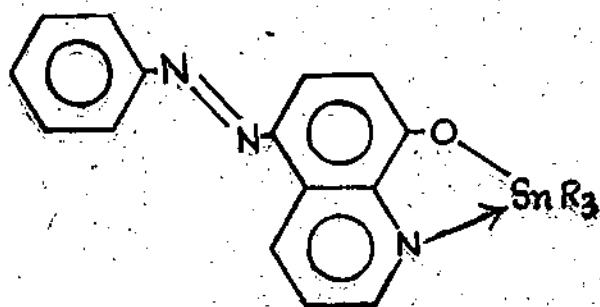


XXIII

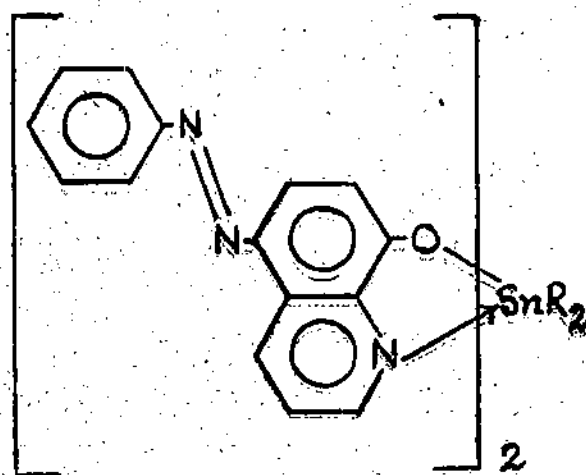


XXIV

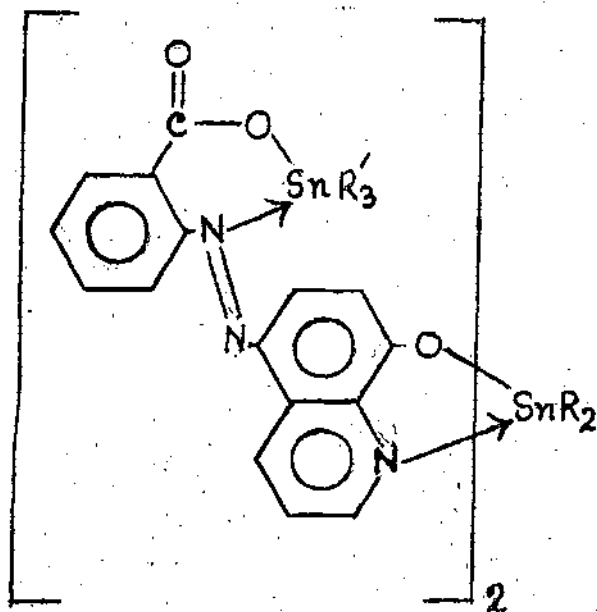
Another group of organotin compounds involving Aryl-O-Sn bond is the organotin derivatives of 5-phenylazo-8-quinolinol and 5-(2'-carboxy phenyl) azo-8-quinolinol XXV, XXVI, XXVII, XXVIII have been reported<sup>81</sup>.



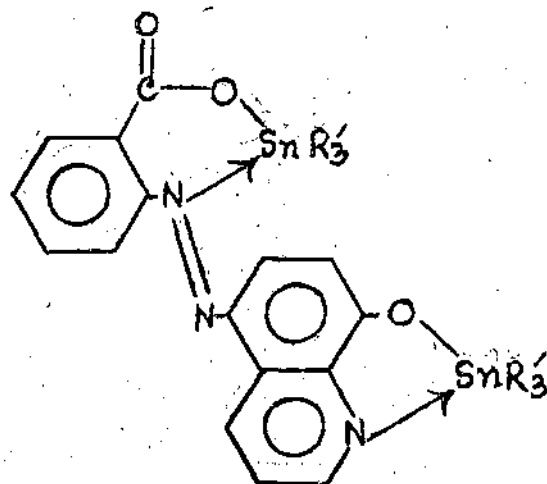
XXV



XXVI



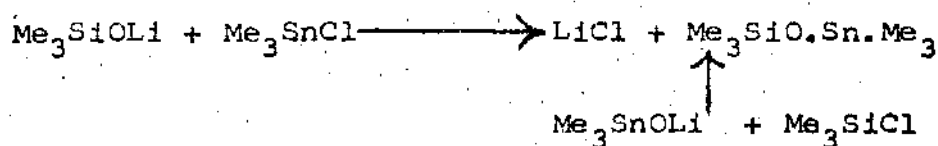
XXVII



XXVIII

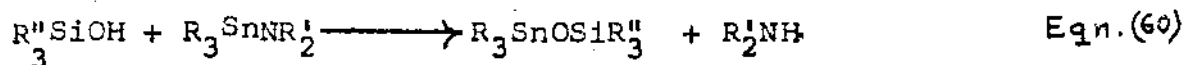
### III. Stannoxides of other elements

The Chemistry of the metallostannoxanes has been reviewed<sup>82</sup>, the most important compounds in this class are the stannosiloxanes containing the grouping  $\text{>Sn} - \text{O-Si} \leq$ . Although a number of compounds for example  $\text{Me}_3\text{SiOSnR}_3$  ( $\text{R} = \text{Pr}, \text{Bu}$ ) have been prepared by cohydrolysis of the mixed halides<sup>83,84</sup>, the alkali metal oxides are more generally used for laboratory synthesis<sup>85</sup>.

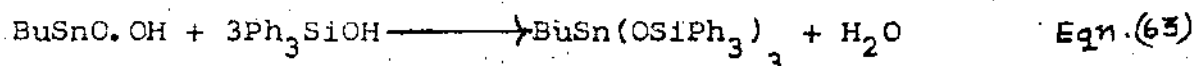
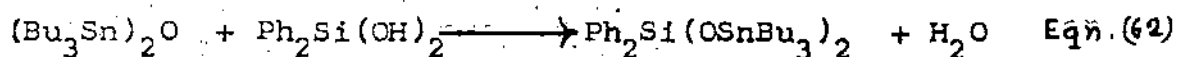
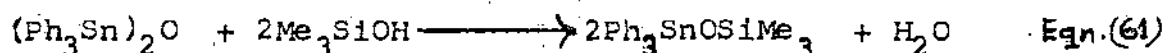


Eqn. (59)

The reaction of stannylamines with protic species is the basis of many preparative procedures and can be applied to the preparation of Stannosiloxanes<sup>86</sup>.



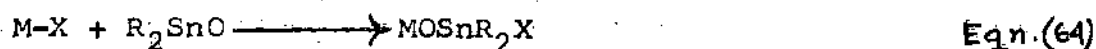
Benzene, toluene or ligroin solutions of organotin oxides and hydroxides react with hydroxy-silanes and germanes to give water and the stannosiloxanes or stannogermoxanes<sup>87</sup>.



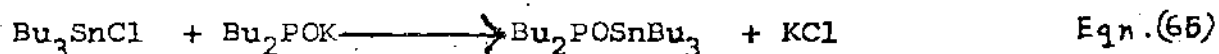
On treatment with a Grignard reagent the stannosiloxanes are alkylated at the tin atom, for example  $Et_3SnO.SiEt_3$  on treatment with  $EtMgBr$  gives eventually,  $Et_4Sn + Et_3SiOH$ <sup>88</sup>.

Much of the work in this area has been directed at obtaining modified organopolysiloxanes in which there has been partial replacement of silicon by tin. Although such polymeric compounds have been made<sup>89</sup> their stabilities and physical properties are inferior to those of the organopolysiloxanes<sup>90</sup>.

Reaction between metallic or organometallic halides and organotin oxides is a general method of preparing organohalogeno-stannometalloxanes<sup>91</sup>.



Reaction between diethyl cadmium and triethyl tin hydroxide gave impure  $\text{Et}_3\text{SnOCdEt}^{92}$ : compounds containing Sn-O-P linkages have been made<sup>93</sup>.



Some stannoxyzirconium alkoxides have also been isolated<sup>94</sup>.

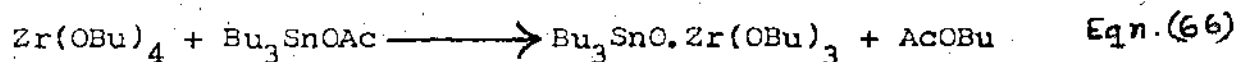


Table -3

Physical properties of some Stannoxides<sup>79</sup>

Compound	m.p.	b.p.	$n_D^{20}$	$d^{20}$
$\text{Me}_3\text{SnOSiMe}_3$	-	144°	-	-
$\text{Me}_3\text{SnOSiEt}_3$	-	49°/1 mm	-	-
$\text{Et}_3\text{SnOSiMe}_3$	-	99°/20 mm	-	-
$\text{Et}_3\text{SnOSiEt}_3$	-	114-115°/4 mm	1.4635	1.1149
$\text{Et}_3\text{SnO} \cdot \text{GePh}_3$	-	167-169°/0.04 mm	-	-
$\text{Bu}_3\text{SnOPBu}_2$	-	165-167°/1 mm	-	-
$\text{Bu}_3\text{SnOZr}(\text{OBu})_3$	-	-	1.4892	1.2020(24°)
$\text{Et}_2\text{Si}(\text{OSnBu-}i_3)_2$	-	203°/3 mm	1.4800	1.1443
$\text{Ph}_3\text{SnO} \cdot \text{SiMe}_3$	-	140°/0.1 mm	-	-
$\text{Ph}_3\text{SnO} \cdot \text{SiPh}_3$	139-140°	-	-	-
$\text{Ph}_2\text{Si}(\text{OSnPh}_3)_2$	94.5-96.5°	-	-	-



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50618.



## CHAPTER III

ARYLAZO PHENOLS : PREPARATION AND REACTION WITH  
STANNOXANES AND TRIORGANOTIN HALIDES.

IIIA. INTRODUCTION

IIIB. LIGANDS : ABBREVIATIONS AND ANALYTICAL DATA

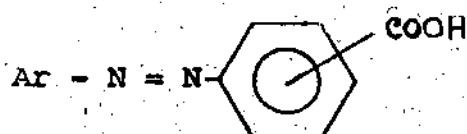
IIIC. REACTIONS WITH ORGANOTIN COMPOUNDS

IIID. EXPERIMENTAL : PREPARATION OF THE LIGANDS AND  
REACTION OF THE LIGANDS WITH STANNOXANES AND  
TRIORGANOTIN HALIDES.

REFERENCES

### IIIA. Introduction

Studies on the arylazo derivatives of carboxylic acids (I) has shown the possibility of realisation of a number of structurally interesting organo tin derivatives<sup>1,3,11,12,13</sup>.

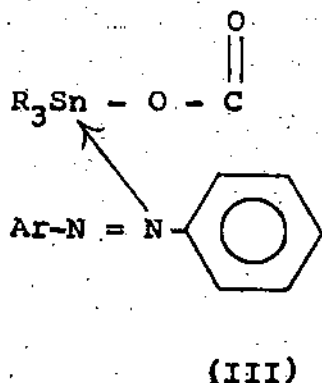


(I)

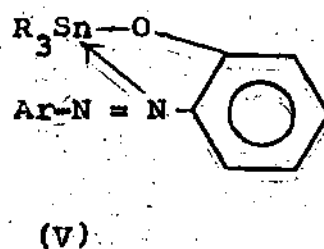
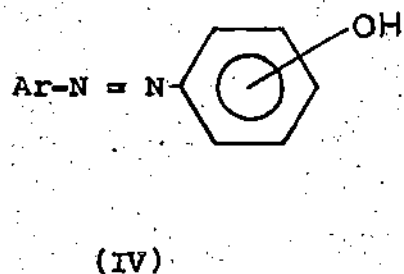
The arylazo group may affect the structure of the organotin derivatives (II) through (i) the electronic effects of the azo group (inductive as well as mesomeric) which tends to oppose the tendency of carboxyl group to polarise in the sense  $-C \overset{\curvearrowright}{=} O$  which is expected to lead to a decrease in the tendency of the carboxyl group to form intermolecularly co-ordinated polymeric carboxylates and (ii) the donor properties of the azo group which is expected to lead to a co-ordination with the Sn atom in ortho substituted compounds (III).



(II)



Both the effects are expected favour intramolecularly co-ordinated organotin compounds. These theoretical considerations led to an extensive studies on the organotin derivatives of arylzo carboxylic acids. Apparently, the same considerations should apply to the 'Hydroxy' compounds (IV) and the corresponding organotin derivatives (V).



The present study was therefore motivated by the possibility of preparing both simple phenoxy derivatives (IV) and intramolecularly coordinated derivatives (V) with a view to making a comparative studies on the physico-chemical properties of these two possibilities.

In this chapter the preparation of the ligands and their reactions with the organotin compounds and the analytical data are described.

### IIIB. Ligands : Abbreviations & Analytical data

The ligands used for the present study were prepared by coupling appropriate phenols with different types of diazotised components. All the ligands belong to the type (IV) in which -OH group may be in o-, m- or p- position with respect to the azo group. The ligands and their abbreviations used in this work are shown in Table - 1. The analytical data on the ligands are given in Table-2.

Table - 1

Ligands and their abbreviations used in this work

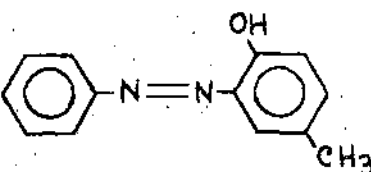
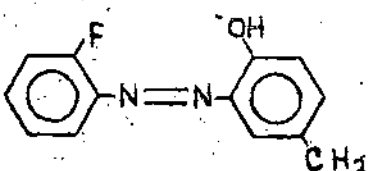
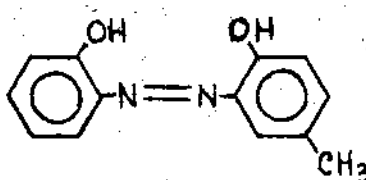
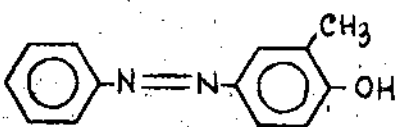
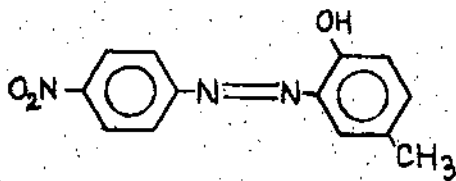
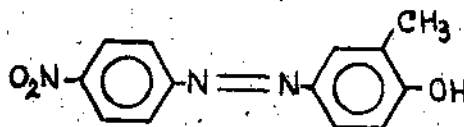
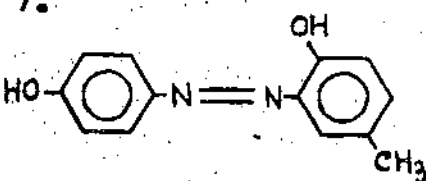
Structure	Name	Abbreviation used
1. 	2-hydroxy-5-methyl- azo benzene	$L^1H$
2. 	2'-(2-hydroxy-5- methyl benzene azo)- fluoro benzene	$L^2H$

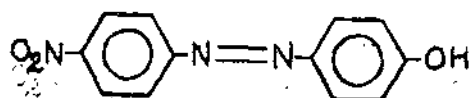
Table - 1 (Contd..)

3.		2'-(2-hydroxy-5-methyl benzeneazo) hydroxy benzene	L <sup>3</sup> H
4.		3-methyl-4-hydroxy (benzeneazo) benzene	L <sup>4</sup> H
5.		4'-(2-hydroxy-5-methyl benzeneazo)-nitrobenzene	L <sup>5</sup> H
6.		4'-(3-methyl-4-hydroxy-benzeneazo)-nitrobenzene	L <sup>6</sup> H
7.		4'-(2-hydroxy-5-methyl benzeneazoe) hydroxy benzene	L <sup>7</sup> H

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Table - 1 (Contd..)

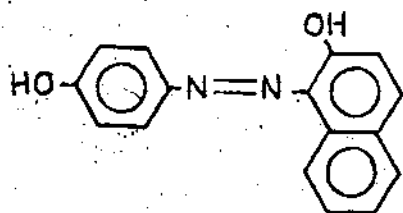
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4'-(4-hydroxy-  
benzeneazo)-  
nitrobenzene

 $L^8_H$ 

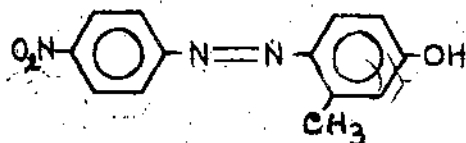
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4'-(2-hydroxy-  
naphthylazo)-  
hydroxy benzene

 $L^9_H$ 

10.



4'-(2-methyl-4  
hydroxy-benzeneazo)-  
nitrobenzene

 $L^{10}_H$

Table - 2

Analytical data on 'Ligands'

Formula	Found (Calculated) (%)		
	C	H	N
1. $C_{13}H_{12}N_2O$ [L <sup>1</sup> H]	74.7 (73.58)	5.36 (5.66)	13.18 (13.20)
2. $C_{13}H_{11}N_2O^F$ [L <sup>2</sup> H]	68.7 (67.82)	5.04 (4.78)	11.45 (12.17)
3. $C_{13}H_{12}O_2N_2$ [L <sup>3</sup> H]	67.45 (68.42)	4.11 (5.26)	13.10 (12.28)
4. $C_{13}H_{12}N_2O$ [L <sup>4</sup> H]	69.27 (73.58)	5.39 (5.66)	14.84 (13.20)
5. $C_{13}H_{11}N_3O_3$ [L <sup>5</sup> H]	59.07 (60.70)	4.05 (4.28)	15.60 (16.34)
6. $C_{13}H_{11}N_3O_3$ [L <sup>6</sup> H]	61.0 (60.70)	4.63 (4.28)	15.92 (16.34)
7. $C_{13}H_{12}O_2N_2$ [L <sup>7</sup> H]	69.2 (68.42)	4.94 (5.26)	13.11 (12.28)
8. $C_{12}H_9O_3N_3$ [L <sup>8</sup> H]	59.46 (59.25)	3.70 (3.70)	17.82 (17.28)

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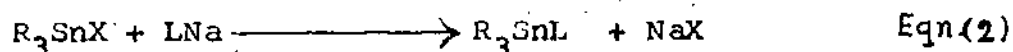
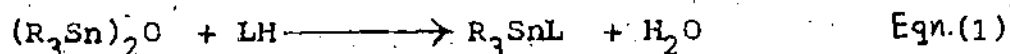
Table - 2 (Contd..)

9. $C_{16}H_{12}O_2N_2$ [L <sup>9</sup> H]	73.84 (72.72)	4.17 (4.54)	10.70 (10.60)
10. $C_{13}H_{11}O_3N_3$ [L <sup>10</sup> H]	61.02 (60.70)	4.49 (4.28)	15.95 (16.34)

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IIIC. Reactions with Organotin Compounds

The preparation of the triorganotin derivatives of the phenoxy azo benzenes was attempted using (i) the reaction between the distannoxanes and the ligand LH (eqn. 1) and (ii) the reaction of the Na/K derivatives of the ligand with the triorganotin halides (Eqn. 2).



The first method was attempted with all the ligands by refluxing the ligands in appropriate mole ratio. The second method was limited to only a few nitro substituted ligands, viz., L<sup>8</sup>H and L<sup>10</sup>H as the Na/K salt of the ligands could be prepared only for these two ligands.

A summary of the reactions studied is given in Table - 3 and the analytical data on the products isolated are given in Table - 4.



Table - 3

## SUMMARY OF REACTION CONDITIONS AND PRODUCTS

Reactants (mole ratio)	Expt. conditions <sup>a, b, c</sup>	Product (m.p./D.P. yield %)
1. $L^1H$ (2:1) + $(Ph_3Sn)_2O$	a. Refluxing for 30 hours in dry benzene and removing the water azeotropically, the product was extracted with benzene pet-ether mixture	$PhL^1Sn(OH)_2$ ( $> 300^\circ C$ , 30)
2. $L^2H$ (2:1) + $(Ph_3Sn)_2O$	a. 50 hours	$PhL^2Sn(OH)_2$ ( $> 300^\circ C$ , 30)
3. $L^3H$ (2:1) + $(Ph_3Sn)_2O$	a. 28 hours	$PhL^3Sn(OH)_2$ ( $> 300^\circ C$ , 40)
4. $L^4H + (Ph_3Sn)_2O$ (2:1)	a. 40 hours	No reaction
5. $L^5H$ (2:1) + $(Ph_3Sn)_2O$	a. 36 hours	$PhL^5Sn(OH)_2$ ( $> 300^\circ C$ , 40)
6. $L^6H + (Ph_3Sn)_2O$ (2:1)	a. 24 hours	No reaction
7. $L^7H$ (2:1) + $(Ph_3Sn)_2O$	a. 30 hours	$PhL^7Sn(OH)_2$ ( $> 300^\circ C$ , 30)

Contd..

Table - 3 (Contd..)

8. $L^7H$ (2:1) + $(Bu_3Sn)_2O$	a. 48 hours	$BuL^7Sn(OH)_2$ ( $> 300^\circ C$ , 30)
9. $L^8H + (Ph_3Sn)_2O$ (2:1)	a. 24 hours	No reaction
10. $L^9H$ (2:1) + $(Ph_3Sn)_2O$	a. 28 hours	$PhL^9Sn(OH)_2$ ( $> 300^\circ C$ , 40)
11. $L^9H$ (2:1) + $(Bu_3Sn)_2O$	a. 42 hours	$BuL^9Sn(OH)_2$ ( $> 300^\circ C$ , 30)
12. $L^8 - Na$ (1:1) + $Ph_3SnCl$ *	b. Refluxing for 12 hours in dry MeOH, the product was crystallised from benzene-pet ether mixture	$Ph_3SnL^8$ ( $160^\circ C$ , 80)
13. $L^8 - Na$ (1:1) + $Cy_3SnCl$	b. 12 hours	$Cy_3SnL^8$ ( $140^\circ C$ , 70)
14. $L^8 - Na$ (1:1) + $Bu_3SnCl$	c. Refluxing for 36 hours in dry benzene, the product was crystallised from benzene-pet ether mixture	$Bu_3SnL^8$ ( $171^\circ C$ , 40)

Contd..

Table - 3 (Contd..)

15.  $L^{10}$  - Na (1:1) b. 12 hours  
+  
 $Ph_3SnCl$

$Ph_3SnL^{10}$   
(138°C, 60)

16.  $L^{10}$  - Na (1:1) b. 12 hours  
+  
 $Cy_3SnCl$

$Cy_3SnL^{10}$   
(130°C, 50)

17.  $L^{10}$  - Na (1:1) c. 40 hours  
+  
 $Bu_3SnCl$

$Bu_3SnL^{10}$   
(147°C, 40)

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(a)(b)(c) Given in order : method, time and solvent used.

(a) Refluxing azeotropically in dry benzene

(b) Refluxing in dry MeOH

(c) Refluxing in dry benzene.

Table - 4

Analytical data on organotin derivatives

Compound	Found (Calculated)(%)			
	C	H	N	Sn
1. $C_{19}H_{18}O_3N_2Sn$ PhL <sup>1</sup> Sn(OH) <sub>2</sub>	52.06 (51.73)	4.72 (4.08)	7.11 (6.35)	27.06 (26.93)
2. $C_{19}H_{17}O_3N_2FSn$ PhL <sup>2</sup> Sn(OH) <sub>2</sub>	50.88 (49.70)	3.97 (3.70)	6.38 (6.10)	25.32 (25.87)
3. $C_{19}H_{18}N_2O_4Sn$ PhL <sup>3</sup> Sn(OH) <sub>2</sub>	48.98 (49.92)	3.87 (3.94)	5.98 (6.13)	26.01 (25.99)
4. $C_{19}H_{17}O_5N_3Sn$ PhL <sup>5</sup> Sn(OH) <sub>2</sub>	47.02 (46.94)	3.37 (3.50)	7.98 (8.64)	24.87 (24.43)
5. $C_{19}H_{18}O_4N_2Sn$ PhL <sup>7</sup> Sn(OH) <sub>2</sub>	50.54 (49.92)	4.02 (3.94)	5.97 (6.13)	26.32 (25.99)
6. $C_{17}H_{22}O_4N_2Sn$ BuL <sup>7</sup> Sn(OH) <sub>2</sub>	46.78 (46.71)	4.98 (5.03)	6.05 (6.41)	26.92 (27.18)
7. $C_{22}H_{18}O_4N_2Sn$ PhL <sup>9</sup> Sn(OH) <sub>2</sub>	52.89 (53.58)	3.80 (3.65)	5.97 (5.68)	23.89 (24.09)
8. $C_{20}H_{22}O_4N_2Sn$ BuL <sup>9</sup> Sn(OH) <sub>2</sub>	49.72 (50.77)	4.30 (4.65)	6.13 (5.92)	25.01 (25.11)

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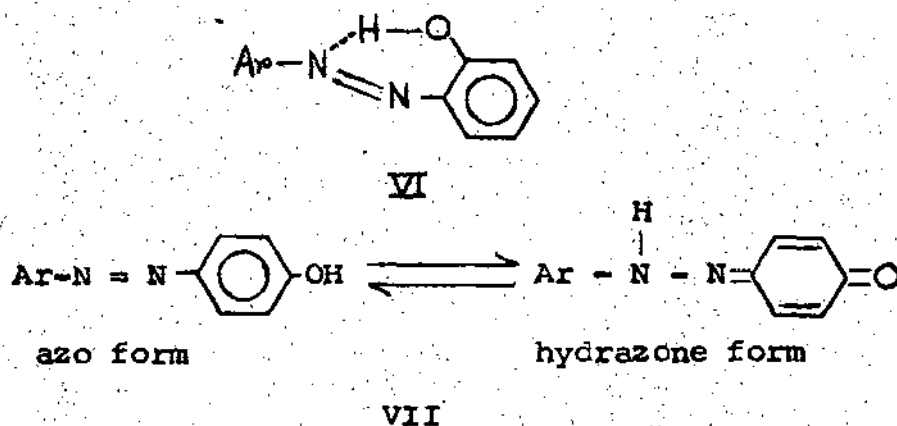
Table - 4 (Contd..)

9. $C_{30}H_{23}O_3N_3Sn$ $Ph_3SnL^8$	60.84 (60.84)	3.89 (3.88)	7.23 (7.09)	19.97 (20.06)
10. $C_{30}H_{41}O_3N_3Sn$ $Cy_3SnL^8$	59.54 (59.04)	6.46 (6.72)	6.29 (6.88)	20.03 (19.46)
11. $C_{24}H_{35}O_3N_3Sn$ $Bu_3SnL^8$	54.86 (54.16)	6.98 (6.58)	8.02 (7.89)	21.82 (22.32)
12. $C_{31}H_{25}O_3N_3Sn$ $Ph_3SnL^{10}$	61.65 (61.41)	4.26 (4.12)	6.29 (6.93)	20.01 (19.59)
13. $C_{31}H_{43}O_3N_3Sn$ $Cy_3SnL^{10}$	60.02 (59.64)	6.81 (6.89)	5.99 (6.73)	19.97 (19.03)
14. $C_{25}H_{37}O_3N_3Sn$ $Bu_3SnL^{10}$	54.01 (54.97)	6.97 (6.78)	7.49 (7.69)	20.99 (21.75)

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An examination of the results given in table-3 shows that the triorganotin derivative of the type  $R_3SnL$  could be isolated only through the displacement of the halide group in  $R_3SnX$  by the Na/K salt of the ligand. On the other hand, the ligands show little reactivity towards the stannoxanes. On prolonged refluxing with dry benzene azeotropically, polymeric products formed through extensive cleavage of the R-Sn bonds are obtained<sup>6-10</sup>. Use of desiccants to accomplish dehydration to push the reaction forward has no effect. Attempts to obtain  $R_3SnL$  type derivatives by stirring freshly prepared  $R_3SnOH$  with the ligand in alcohol also failed.

The reaction of the organotin oxides/hydroxides with phenols / alcohols is a consequence of the basicity of the organotin oxides, hydroxides and the acidic nature of the hydroxylic H-atom in phenols / alcohols. Consequently, the presence of hydrogen bonding (VI) or intramolecular rearrangement involving the H-atom of the -OH group, e.g., azo-hydrazone tautomerism (VII)<sup>15-18</sup> greatly reduces the reactivity of the phenols towards the organotin oxides or hydroxides. The possible reasons for the low reactivity of the arylazo phenols towards the organotin oxides will be examined in Chapter IV.



### IIID. Experimental

Triorganotin (Phenyl, Butyl, Cyclohexyl) derivatives of arylazo phenoxy compounds have been prepared by reaction between  $(R_3Sn)_2O$  or  $R_3SnCl$  in stoichiometric ratios by refluxing and/or stirring in dry benzene/methanol and removing water azeotropically wherever necessary.

Triphenyl tin chloride (Fluka, Switzerland) was used after recrystallisation from petroleum ether m.p.  $106^\circ$  (lit.  $105^\circ-107^\circ$ ). When necessary, triphenyl tin chloride was prepared by the method of Gilan et al from tetraphenyl tin. Tri-cyclohexyl tin chloride (Aldrich, W. Germany) m.p.  $126^\circ C$ , tributyl tin chloride (Fluka, Switzerland) b.p.  $152^\circ/10$  mm, bis-tributyl tin oxide (Fluka, Switzerland) b.p.  $210^\circ-4^\circ/10$  mm were used without further purification. Bis-triphenyl tin oxide, m.p.  $122^\circ$  (lit. m.p.  $122^\circ-124^\circ$ ) was prepared by the reaction of triphenyl tin chloride with sodium hydroxide<sup>14</sup>.

Unless otherwise stated petroleum ether used in the present investigation refers to the fraction with the boiling range  $60-80^\circ C$ . All melting points are uncorrected.

#### Preparation of the ligands

##### 1. Preparation of 2-hydroxy-5-methyl azo benzene ( $L^1H$ )

9.3 gms of aniline was diazotised by the usual procedure<sup>2</sup>. 10.8 gms of p-cresol was dissolved in 80 ml of 20% sodium hydroxide

solution and cooled to 5°C in an ice-bath, which was then added to the cold diazonium salt solution with vigorous stirring, when a yellow coloured dye separated out. The mixture was kept overnight in a refrigerator followed by 1 hour at room temperature. It was filtered, washed several times with water, dried in air and finally in vacuum at room temperature. Crystallisation from acetone-pet ether mixture yielded yellow dye  $L^1H$  (m.p. 105°C. Yield 60%).

Analytical data:

	<u>C</u>	<u>H</u>	<u>N</u>
$C_{13}H_{12}N_2O$			
Found (Calcd)(%)	74.70 (73.58)	5.36 (5.66)	13.18 (13.20)

2. Preparation of 2'-(2-hydroxy-5-methyl-benzeneazo)-  
fluorobenzene ( $L^2H$ )

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9.6 gm of o-fluoroaniline was diazotised to which 9.9 gm of p-cresol in 80 ml of 20% NaOH was added using the procedure already described. A dye was obtained which on crystallisation from acetone-pet ether mixture yielded bright red dye  $L^2H$  (m.p. 77°C, yield 60%).

Analytical data

	<u>C</u>	<u>H</u>	<u>N</u>
$C_{13}H_{11}N_2OF$			
Found (Calcd)(%)	68.7 (67.82)	5.04 (4.78)	11.45 (12.17)



3. Preparation of 2'-(2-hydroxy-5-methyl benzeneazo)-hydroxy benzene (L<sup>3</sup>H)

9.6 gm of o-aminophenol was taken in a mortar and a fine paste of the same was prepared by adding minimum quantity of water and thoroughly grinding it with pestle. The paste of o-aminophenol was then transferred <sup>to</sup> ~~in~~ a beaker and was diazotised<sup>4,5</sup> very slowly for 5 hours by adding sodium nitrite solution containing CuSO<sub>4</sub> (0.3% of o-aminophenol by weight) and the temperature was maintained between 10°C - 15°C. 9.5 gm of p-cresol was dissolved in 70 ml of 10% sodium hydroxide solution and was cooled to 15°C in a cold water bath, which was then added to the diazonium salt solution with vigorous stirring for 2 hours at 15°C when a reddish brown colour developed. It was kept overnight in a refrigerator followed by 2 hours at room temperature and then acidified with excess 2(N)H<sub>2</sub>SO<sub>4</sub>. A brownish solid separated out. It was filtered and the residue was washed several times with water, till free from acid and then dried in air.

The solid product was thoroughly dried, powdered and treated with hot benzene when a deep red coloured solution was obtained along with some solid impurities. It was then filtered, concentrated and crystallised from benzene-pet ether mixture, yielded brownish dye L<sup>3</sup>H (decomposition point 196°C, yield 50%).

Analytical data

$C_{13}H_{12}N_2O_2$	<u>C</u>	<u>H</u>	<u>N</u>
Found (Calcd)(%)	67.45 (68.42)	4.11 (5.26)	13.10 (12.28)

4. Preparation of 3-methyl-4-hydroxy (benzeneazo)benzene ( $L^4H$ )

9.3 gm of aniline was diazotised as described in 1, to which 10.8 gm of o-cresol in 80 ml of 20% NaOH solution was added. An yellow coloured dye was obtained following the procedure described in 1, which on crystallisation from acetone-pet ether mixture yielded bright yellow dye,  $L^4H$  (m.p.  $128^\circ C$ , yield 65%).

Analytical data

$C_{13}H_{12}N_2O$	<u>C</u>	<u>H</u>	<u>N</u>
Found (Calcd)(%)	69.27 (73.58)	5.39 (5.66)	14.84 (13.20)

5. Preparation of 4'-(2-hydroxy-5-methyl benzeneazo)-nitrobenzene ( $L^5H$ )

Using 11.5 gm of p-nitroaniline in 18 ml of conc. HCl for diazotisation and 11.9 gm of p-cresol in 75 ml of 20% NaOH solution as the coupling component, a brick-red coloured dye was obtained using the procedure described in 4. Crystallisation from acetone-pet ether mixture yielded brick-red dye  $L^5H$  (m.p.  $186^\circ C$ , yield 65%).

Analytical data

$C_{13}H_{11}N_3O_3$	<u>C</u>	<u>H</u>	<u>N</u>
Found (Calcd)(%)	59.07 (60.70)	4.05 (4.28)	15.60 (16.34)

6. Preparation of 4'-(3-methyl-4-hydroxy benzeneazo)-nitrobenzene (L<sup>6</sup>H)

11.5 gm of p-nitroaniline was dissolved in 18 ml of conc. HCl and was diazotised by usual procedure<sup>2</sup> at room temperature. 11.9 gm of ortho-cresol was dissolved in 75 ml of 20% sodium hydroxide solution at room temperature, which was then added to the diazonium salt solution with vigorous stirring for 2 hours at room temperature when a red coloured dye separated out. It was kept overnight at room temperature, filtered, washed several times with water, dried in air and finally in vacuum at room temperature. Crystallisation from acetone-pet ether mixture yielded the red dye L<sup>6</sup>H (m.p. 205°C, yield 65%).

Analytical data

$C_{13}H_{11}N_3O_3$	<u>C</u>	<u>H</u>	<u>N</u>
Found (Calcd)(%)	61.0 (60.70)	4.63 (4.28)	15.92 (16.34)

7. Preparation of 4'-(2-hydroxy-5-methyl-benzeneazo)-hydroxy benzene (L<sup>7</sup>H)

9.6 gm of p-aminophenol was diazotised using the procedure described in 3. To the diazotised solution, 9.5 gm of p-cresol in 70 ml of 10% NaOH solution was added with stirring. A red coloured dye (L<sup>7</sup>H) was finally obtained following the procedure described in 3, which on crystallisation from benzene-pet ether mixture yielded greyish-brown dye, L<sup>7</sup>H (decomposition point 192°C, yield 50%).

Analytical data

$C_{13}H_{12}N_2O_2$	<u>C</u>	<u>H</u>	<u>N</u>
Found (Calcd)(%)	69.2 (68.42)	4.94 (5.26)	13.11 (12.28)

8. Preparation of 4'-(4-hydroxy-benzeneazo)-nitrobenzene ( $L^8H$ ) and its Na-salt.

11.5 gm of p-nitroaniline was dissolved in 18 ml of conc. HCl and was diazotised at room temperature as described by Vogel<sup>2</sup>.

10.3 gms of phenol was dissolved in 90 ml of 7% sodium hydroxide solution at room temperature, which was then added to the diazotised solution with vigorous stirring for 2 hours at room temperature. The Na-salt separated out as a chocolate brown product. The mixture was kept overnight at room temperature. The residue was filtered, washed repeatedly with cold water. The filtrate was treated with 5(N) acetic acid when deep yellow coloured dye separated out. It was filtered, washed several times with cold water, dried in air and finally in vacuum. Crystallisation from acetone-pet ether mixture, yielded deep yellow coloured dye  $L^8H$  (m.p.  $220^{\circ}C$ , yield 50%).

The residue (sodium salt of  $L^8H$ ) was dried in air for several days and finally dried in vacuum. Yield 50%.

Free ligand ( $L^8H$ ) was obtained by precipitation from aqueous solution of the sodium salt upon acidification.

Analytical data

$C_{12}H_9N_3O_3$	<u>C</u>	<u>H</u>	<u>N</u>
Found (Calcd)(%)	59.46 (59.25)	3.70 (3.70)	17.82 (17.28)

9. Preparation of 4'-(2-hydroxy-naphthylazo)-hydroxybenzene ( $L^9H$ )

9.6 gm of p-aminophenol was diazotised using the procedure described in 3. 12.6 gm of  $\beta$ -naphthol in 70 ml of 10% NaOH solution was coupled with the diazotised solution using the same procedure, when a brown coloured dye was obtained, which on crystallisation from benzene-pet ether mixture yielded a brownish dye  $L^9H$  (D.P.  $127^\circ C$ , yield 40%).

Analytical data

$C_{16}H_{12}N_2O_2$	<u>C</u>	<u>H</u>	<u>N</u>
Found (Calcd)(%)	73.84 (72.72)	4.17 (4.54)	10.70 (10.60)

10. Preparation of 4'-(2-methyl-4-hydroxy-benzeneazo)-nitrobenzene ( $L^{10}H$ ) and its Na-Salt.

11.5 gm of p-nitroaniline was dissolved in 18 ml of conc. HCl and was diazotised by usual method<sup>2</sup> at room temperature. 11.9 gm of m-cresol was dissolved in 8% sodium hydroxide solution at room temperature, which was then added to the diazonium salt solution with vigorous stirring for 2 hours at room temperature. The Na-salt separated out as deep brown product. The mixture was kept overnight at room temperature and the residue was filtered, washed repeatedly with cold water till the product was free from NaOH (tested with indicator paper). The filtrate was treated with 5(N) acetic acid

when brick-red coloured dye separated out. It was filtered, washed several times with cold water, dried in air and finally in vacuum. Crystallisation from acetone-pet ether mixture yielded brick-red coloured dye  $L^{10}H$  (m.p.  $180^{\circ}C$ , yield 40%).

The sodium salt which separated as residue was dried in air for several days and finally dried in vacuum (yield 40%) and was used as such.

The free ligand ( $L^{10}H$ ) was obtained when necessary by precipitation from aqueous solution of the sodium salt upon acidification.

#### Analytical data

$C_{13}H_{11}N_3O_3$	<u>C</u>	<u>H</u>	<u>N</u>
Found (Calcd)(%)	61.02 (60.70)	4.49 (4.28)	15.95 (16.34)

#### IIID. Reaction of the ligands with organotin compounds

##### 1. Reaction of triphenyl tin oxide with 2-hydroxy-5-methyl-azo benzene ( $L^1H$ )

A mixture of 1.18 gm of ligand,  $L^1H$  and 2 gm of triphenyl tin oxide in 75 ml of dry benzene was refluxed using water separator for 30 hours and filtered. The filtrate was concentrated to a small volume and pet ether was then added dropwise till a slight precipitate appeared and then allowed to cool for few hours, when a chocolate coloured solid separated out. It was filtered off.

The residue was washed thoroughly with pet ether and the chocolate coloured compound, m.p.  $> 300^{\circ}C$ , was obtained (yield 30%).

The filtrate on concentration and fractional crystallisation yielded unreacted ligand ( $L^1H$ ) and the triphenyl tin oxide.

Analytical data

$C_{19}H_{18}O_3N_2Sn$	<u>C</u>	<u>H</u>	<u>N</u>	<u>Sn</u>
Found (Calcd) (%)	52.06 (51.73)	4.72 (4.08)	7.11 (6.35)	27.06 (26.93)

2. Reaction of triphenyl tin oxide with 2'-(2-hydroxy-5-methyl-benzeneazo)fluorobenzene ( $L^2H$ )

A mixture of 1.28 gm of ligand ( $L^2H$ ) and 2 gm of triphenyl tin oxide in 75 ml of dry benzene was refluxed using water separator for 50 hours and filtered. The filtrate was concentrated to a small volume and pet ether was then added dropwise till a slight precipitate appeared and then allowed to cool for few hours, when a deep red coloured solid separated out. It was filtered off.

The residue was washed thoroughly with pet ether and deep red coloured compound m.p.  $> 300^\circ C$  was obtained (yield 30%).

The filtrate on concentration and fractional crystallisation yielded unreacted ligand ( $L^2H$ ) and the triphenyl tin oxide.

Analytical data

$C_{19}H_{17}O_3N_2FSn$	<u>C</u>	<u>H</u>	<u>N</u>	<u>Sn</u>
Found (Calcd) (%)	50.88 (49.70)	3.97 (3.70)	6.38 (6.10)	25.32 (25.87)

3. Reaction of triphenyl tin oxide with 2'-(2-hydroxy-5-methyl-benzeneazo) hydroxy benzene ( $L^3H$ )

A mixture of 1.5 gm of free ligand ( $L^3H$ ) and 2.35 gm of triphenyl tin oxide in 75 ml of dry benzene was refluxed using water separator for 28 hours and filtered. The filtrate was concentrated to a small volume and pet ether was then added dropwise to the concentrated filtrate till faint ppt. appeared and allowed to cool for few hours, when a dark brown coloured solid separated out. It was filtered off.

The residue was washed thoroughly with pet ether and the dark brown coloured compound m.p.  $> 300^\circ C$ , was obtained (yield 40%).

The filtrate on concentration and fractional crystallisation yielded unreacted ligand ( $L^3H$ ) and the triphenyl tin oxide.

Analytical data

$C_{19}H_{18}N_2O_4Sn$	<u>C</u>	<u>H</u>	<u>N</u>	<u>Sn</u>
Found (Calcd)(%)	48.98 (49.92)	3.87 (3.94)	5.98 (6.13)	26.01 (25.99)

4. Reaction of Triphenyl tin oxide with 4'-(2-hydroxy-5-methyl benzeneazo) nitrobenzene ( $L^5H$ )

A mixture of 1.5 gm of the ligand,  $L^5H$  and 2.09 gm of triphenyl tin oxide in 75 ml of dry benzene was refluxed using water separator for 36 hours and filtered. The filtrate was concentrated to a small volume and pet ether was then added dropwise to the concentrated filtrate till faint ppt appeared and allowed to cool for few hours, when a deep red coloured solid separated out. It was filtered off.



The residue was washed thoroughly with pet ether and the deep red coloured compound m.p.  $> 300^{\circ}\text{C}$ , was obtained (yield 40%).

The filtrate on concentration and fractional crystallisation yielded unreacted ligand ( $\text{L}^5\text{H}$ ) and the triphenyl tin oxide.

#### Analytical data

$\text{C}_{19}\text{H}_{17}\text{O}_5\text{N}_3\text{Sn}$	<u>C</u>	<u>H</u>	<u>N</u>	<u>Sn</u>
Found (Calcd) (%)	47.02 (46.94)	3.37 (3.50)	7.98 (8.64)	24.87 (24.43)

#### 5. Reaction of triphenyl tin oxide with 4'-(2-hydroxy-5-methyl benzeneazo) hydroxy benzene ( $\text{L}^7\text{H}$ )

A mixture of 1.5 gm of the ligand,  $\text{L}^7\text{H}$  and 2.35 gm of triphenyl tin oxide in 75 ml of dry benzene was refluxed using water separator for 30 hours and filtered. The filtrate was concentrated to a small volume and pet ether was then added dropwise to the concentrated filtrate till faint turbidity appeared and allowed to cool for few hours when brown coloured solid separated out. It was filtered off.

The residue was washed thoroughly with pet ether and the brown coloured compound m.p.  $> 300^{\circ}\text{C}$  was obtained (yield 30%).

The filtrate on concentration and fractional crystallisation yielded unreacted ligand ( $\text{L}^7\text{H}$ ) and the triphenyl tin oxide.

Analytical data

$C_{19}H_{18}O_4N_2Sn$	<u>C</u>	<u>H</u>	<u>N</u>	<u>Sn</u>
Found (Calcd)(%)	50.54 (49.92)	4.02 (3.94)	5.97 (6.13)	26.32 (25.99)

6. Reaction of tributyl tin oxide with 4'-(2-hydroxy-5-methyl benzeneazo) hydroxy benzene ( $L^7H$ )

A mixture of 1.5 gm of the ligand  $L^7H$  and 1.96 gm of tributyl tin oxide in 75 ml of dry benzene was refluxed using water separator for 48 hours and filtered. The filtrate was concentrated to a small volume and pet ether was then added dropwise to the concentrated filtrate till slight ppt appeared and allowed to cool for 2 days, when a brown coloured solid separated out. It was filtered off.

The residue was washed thoroughly with pet ether and the brown coloured compound m.p.  $> 300^\circ C$  was obtained (Yield 30%).

The filtrate on concentration and fractional crystallisation yielded unreacted ligand ( $L^7H$ ) and the tributyl tin oxide.

Analytical data

$C_{17}H_{22}O_4N_2Sn$	<u>C</u>	<u>H</u>	<u>N</u>	<u>Sn</u>
Found (Calcd)(%)	46.78 (46.71)	4.98 (5.03)	6.05 (6.41)	26.92 (27.18)

7. Reaction of triphenyl tin oxide with 4'-(2-hydroxy-naphthylazo) hydroxy benzene ( $L^9H$ )

A mixture of 1.5 gm of the ligand  $L^9H$  and 2.03 gm of triphenyl tin oxide in 75 ml of dry benzene was refluxed using water separator for 28 hours and filtered. The filtrate was concentrated to a small volume and pet ether was then added dropwise to the concentrated filtrate till slight ppt appeared and allowed to cool for few hours when a deep brown coloured solid separated out. It was filtered off.

The residue was washed thoroughly with pet ether and the deep brown coloured compound m.p.  $> 300^\circ C$  was obtained. (Yield 40%).

The filtrate on concentration and fractional crystallisation yielded unreacted ligand ( $L^9H$ ) and the triphenyl tin oxide.

Analytical data

$C_{22}H_{18}O_4N_2Sn$	<u>C</u>	<u>H</u>	<u>N</u>	<u>Sn</u>
Found (Calcd) (%)	52.89 (53.58)	3.80 (3.65)	5.97 (5.68)	23.89 (24.09)

8. Reaction of tributyl tin oxide with 4'-(2-hydroxy-naphthylazo) hydroxy benzene ( $L^9H$ )

A mixture of 2 gm of ligand ( $L^9H$ ) and 2.26 gm of tributyl tin oxide in 75 ml of dry benzene was refluxed using water separator for 42 hours and then filtered. The filtrate was concentrated to a small volume and pet ether was then added dropwise to the concentrated filtrate till a faint ppt. appeared and allowed to

cool for 2 days when deep brown coloured solid separated out. It was filtered off.

The residue was washed thoroughly with pet ether and the deep brown coloured compound, m.p.  $> 300^{\circ}\text{C}$  was obtained (Yield 30%).

The filtrate on concentration and fractional crystallisation yielded unreacted ligand ( $\text{L}^9\text{H}$ ) and the tributyl tin oxide.

#### Analytical data

$\text{C}_{20}\text{H}_{22}\text{O}_4\text{N}_2\text{Sn}$	<u>C</u>	<u>H</u>	<u>N</u>	<u>Sn</u>
Found (Calcd) (%)	49.92 (50.77)	4.30 (4.65)	6.13 (5.92)	25.01 (25.11)

#### 9. Reaction of triphenyl tin chloride with Na-salt of 4'-

(4-hydroxy-benzeneazo) nitrobenzene ( $\text{L}^8\text{H}$ )

A mixture of 1 gm of Na-salt and 1.45 gm of triphenyl tin chloride in 75 ml of dry methanol was refluxed for 12 hours and filtered. The alcohol was removed completely from the filtrate and the residue was treated with cold, dry benzene. The benzene extract was concentrated to a very small volume and pet ether was then added and kept overnight at room temperature when needled shaped orange coloured crystals separated out, which on several recrystallisation from benzene-pet ether mixture yielded the bright orange-coloured crystals of organotin derivatives having m.p.  $160^{\circ}\text{C}$ , yield 80%.

#### Analytical data

$\text{C}_{30}\text{H}_{23}\text{O}_3\text{N}_3\text{Sn}$	<u>C</u>	<u>H</u>	<u>N</u>	<u>Sn</u>
Found (Calcd) (%)	60.84 (60.84)	3.89 (3.88)	7.23 (7.09)	19.97 (20.06)

10. Reaction of tri-cyclohexyl tin chloride with Na-Salt of 4'-(4-hydroxy benzeneazo)-nitrobenzene ( $L^8H$ )

A mixture of 1 gm of Na-salt and 1.52 gm of tri-cyclohexyl tin chloride in 75 ml of dry methanol was refluxed for 12 hours and was filtered. The alcohol was removed completely from the filtrate and the residue was treated with cold, dry benzene. The benzene extract was concentrated to a very small volume and pet ether was then added and kept overnight at room temperature, when needle shaped orange-red coloured crystals separated out, which on several recrystallisation from benzene-pet ether mixture yielded the bright orange-red coloured crystals of organotin derivatives having m.p.  $140^{\circ}C$  (Yield 70%).

Analytical data

$C_{30}H_{41}O_3N_3Sn$	<u>C</u>	<u>H</u>	<u>N</u>	<u>Sn</u>
Found (Calcd)(%)	59.54 (59.04)	6.46 (6.72)	6.29 (6.88)	20.03 (19.46)

11. Reaction of tributyl tin chloride with Na-Salt of 4'-(4-hydroxy-benzeneazo)-nitrobenzene ( $L^8H$ )

A mixture of 1 gm of Na-Salt and 1.23 gm of tributyl tin chloride in 75 ml of dry benzene was refluxed for 36 hours and was filtered. The benzene was removed completely from the filtrate and the residue was treated with cold, dry benzene and filtered. Then pet ether was added to the concentrated filtrate in slight excess and allowed to cool for few hours, a solid separated out which on several recrystallisation from benzene-pet ether mixture yielded the

bright orange coloured organotin derivative having m.p.  $171^{\circ}\text{C}$ ,  
yield 40%.

Analytical data

$\text{C}_{24}\text{H}_{35}\text{O}_3\text{N}_3\text{Sn}$	<u>C</u>	<u>H</u>	<u>N</u>	<u>Sn</u>
Found (Calcd)(%)	54.86 (54.16)	6.98 (6.58)	8.02 (7.89)	21.82 (22.32)

12. Reaction of triphenyl tin chloride with Na-Salt of 4'-  
(2-methyl-4-hydroxy-benzeneazo) nitrobenzene ( $\text{L}^{10}\text{H}$ )

A mixture of 1 gm of Na-Salt and 1.38 gm of triphenyl tin chloride in 75 ml of dry methanol was refluxed for 12 hours and filtered. The alcohol was removed completely from the filtrate and the residue was treated with cold, dry benzene. The benzene extract was concentrated to a very small volume and pet ether was then added and kept overnight at room temperature when needle shaped red coloured crystals separated out, which on several recrystalliation from benzene-pet ether mixture yielded the bright red coloured crystals of organotin derivatives having m.p.  $138^{\circ}\text{C}$ , yield 60%.

Analytical data

$\text{C}_{31}\text{H}_{25}\text{O}_3\text{N}_3\text{Sn}$	<u>C</u>	<u>H</u>	<u>N</u>	<u>Sn</u>
Found (Calcd)(%)	61.65 (61.41)	4.26 (4.12)	6.29 (6.93)	20.01 (19.59)

13. Reaction of tri-cyclohexyl tin chloride with Na-Salt of  
4'-(2-methyl-4-hydroxy benzeneazo) nitrobenzene (L<sup>10</sup>H)

A mixture of 1 gm of Na-Salt and 1.45 gm of tri cyclohexyl tin chloride in 75 ml of dry methanol was refluxed for 12 hours and was filtered. The alcohol was removed completely from the filtrate and the residue was treated with cold, dry benzene. The benzene extract was concentrated to a very small volume and pet ether was then added and kept overnight at room temperature, when needle shaped red coloured crystals separated out, which on several recrystallisation from benzene-pet ether mixture yielded the bright red coloured crystals of organotin derivatives having m.p. 130°C, yield 50%.

Analytical data

$C_{31}H_{43}O_3N_3Sn$	<u>C</u>	<u>H</u>	<u>N</u>	<u>Sn</u>
Found (Calcd)(%)	60.02 (59.64)	6.81 (6.89)	5.99 (6.73)	19.97 (19.03)

14. Reaction of tri-butyl tin chloride with Na-Salt of 4'-  
(2-methyl-4-hydroxy-benzeneazo) nitrobenzene (L<sup>10</sup>H)

A mixture of 1 gm of Na-Salt and 1.165 gm of tributyl tin chloride in 75 ml of dry benzene was refluxed for 40 hours and was filtered. The benzene was removed completely from the filtrate and the residue was treated with cold, dry benzene and filtered. The pet ether was added to the concentrated filtrate in slight excess

and allowed to cool for few hours when a solid separated out which on several recrystallisation from benzene-pet ether mixture yielded the bright orange coloured organotin derivative having m.p.  $147^{\circ}\text{C}$ , yield 40%.

Analytical data

$\text{C}_{25}\text{H}_{37}\text{O}_3\text{N}_3\text{Sn}$	<u>C</u>	<u>H</u>	<u>N</u>	<u>Sn</u>
Found (Calcd) (%)	54.01 (54.97)	6.97 (6.78)	7.49 (7.69)	20.99 (21.75)



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## CHAPTER - IV

### ELECTRONIC SPECTRA, INFRARED SPECTRA OF ARYLAZOPHENOLS AND THEIR ORGANOTIN DERIVATIVES.

#### IV.A ELECTRONIC SPECTRA

##### 1. INTRODUCTION

##### 1.1 RESULTS AND DISCUSSION

#### IV.B INFRARED SPECTRA

##### 2. GENERAL FEATURES

##### 2.1 RESULTS AND DISCUSSIONS

##### REFERENCES

#### IV A. Electronic Spectra

##### 1. Introduction

The electronic spectra of azobenzene and related compounds have been studied extensively by several workers<sup>1,2,3-9,21-24</sup> and have been interpreted in terms of molecular orbital description<sup>1,2,10</sup>. 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 the  $\pi-\pi^*$  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. This is easily explained in terms of molecular orbital treatment of the azobenzene system. The upper MO for the first  $n-\pi^*$  and  $\pi-\pi^*$  transitions is the perturbed orbital originating from the anti-bonding orbital of the azo group and its energy is almost independent of the nature of the aryl groups. The orbital energy level diagram for trans- and Cis- azo groups is shown in fig. '1'. The lower orbital of the first  $\pi-\pi^*$  transition is the orbital arising from the perturbation of the higher bonding  $\pi$ -orbital 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.

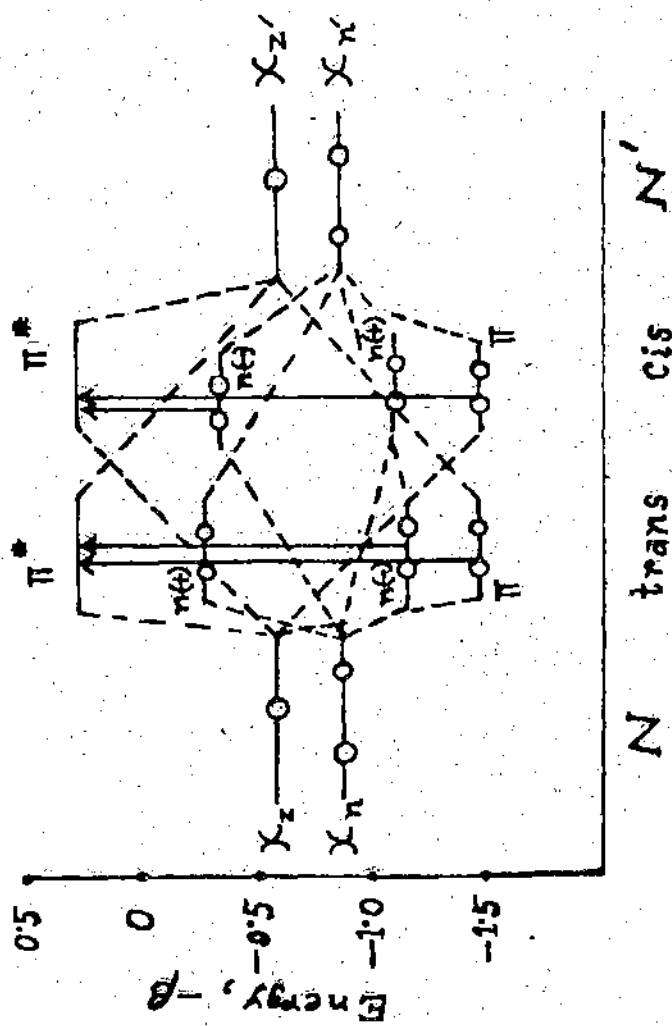
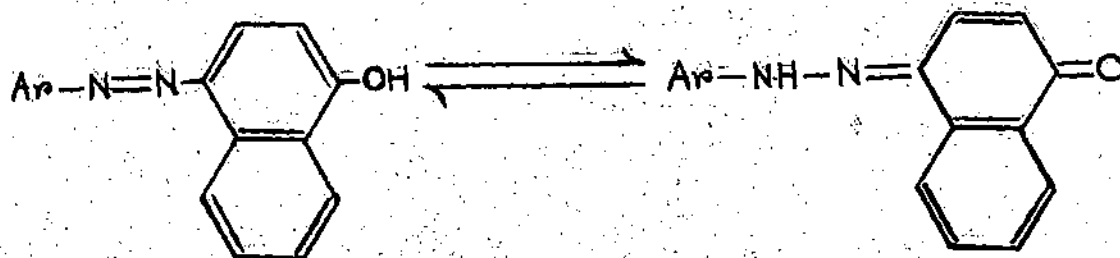


Figure - 1 Orbital energy levels of the *trans*- and *cis*-azo groups. Vertical arrows indicate allowed transitions.

Substituents like  $\text{-NH}_2$ ,  $\text{-NMe}_2$ ,  $\text{-OH}$ ,  $\text{-COOH}$  etc, which are capable of producing large bathochromic shifts of the  $\pi\text{-}\pi^*$  transitions by extending the conjugation, may often shift the first  $\pi\text{-}\pi^*$  band in the azo compound to such an extent that the characteristic  $n\text{-}\pi^*$  absorption is masked by the strong absorption.

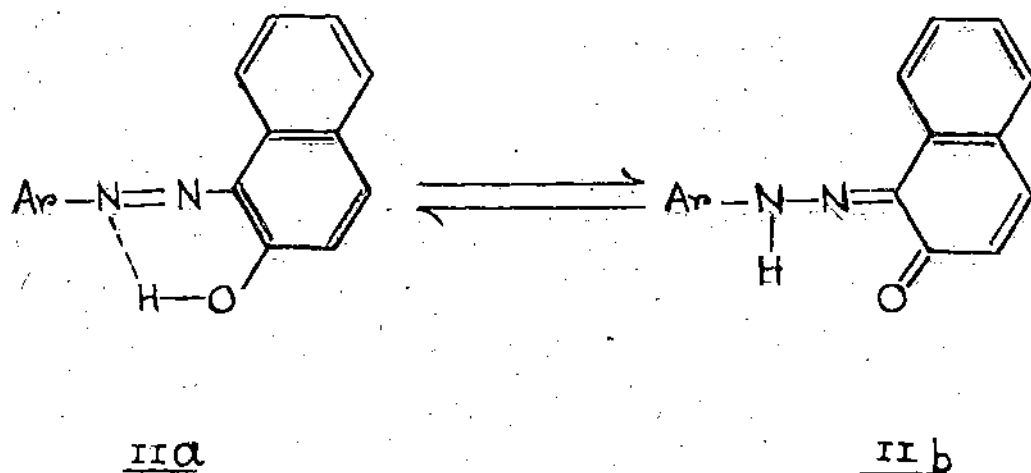
In the absence of specific solvent-solute interactions the electronic absorption spectra of the azo-compounds do not show any strong solvent dependence apart from a small red shift of both the  $\pi\text{-}\pi^*$  and  $n\text{-}\pi^*$  bands<sup>1,12</sup>. However, the presence of  $\text{-OH}$  group in the aryl part of the azo compounds often leads to a strongly solvent dependent absorption spectrum due to the possibility of (a) hydrogen bond formation by the phenolic  $\text{-OH}$  group 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<sup>6,8,9,13</sup>.

In phenyl azonaphthols, the presence of an isobestic point in the visible absorption curves measured in a variety of solvents has been given as an evidence for the presence of equilibrium (I) in phenyl azonaphthols<sup>6,14,15</sup>. Both the azo and hydrazone forms may be stabilised in suitable donor solvents by external hydrogen bonds formed by the -OH and -NH group respectively. However, with a given solvent the phenolic hydrogen generally forms stronger bonds than the -NH group and the concentration of the azo form increases in the order: hexane < ethyl alcohol < benzene < chloroform < 50% ethyl alcohol < acetic acid, in contrast to observation aryl azo- $\beta$ -naphthol series. This effect is considerably enhanced by ortho substituents which sterically inhibit the formation of the external hydrogen bonds in the hydrazone tautomer and thus, unexpectedly low concentration of the phenyl hydrazone form is present in the ortho substituted 1-aryl azo-4-naphthols<sup>8</sup>. On the other hand, both the tautomers in 1-arylaazo-2-naphthols (IIa, IIb) are unable to form external hydrogen bonds and the concentration of the more polar ketonic structure increases in the order of solvents:



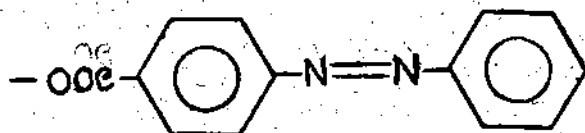
hexane < benzene < ethyl alcohol < chloroform < acetic acid < water, approximately in the line with increasing dielectric constants<sup>9</sup>.

Though a large number of metal complexes, particularly those of chromium, nickel, cobalt and copper, of hydroxy and o-carboxyl substituted azo compounds have been prepared because of their importance in the dye industry, comparatively little attention has been paid to the study of the electronic spectra of the metal derivatives<sup>17-19,25</sup>. No detailed general account of the effect of co-ordination on the electronic spectra of the azo compounds is so far available. In the early work by Ernsberger and Brode<sup>25</sup>, a comparison of the absorption spectra of a series of phenyl-azo-p-cresol,  $\beta$ -naphthol and  $\beta$ -Naphthylamine derivatives with those of the copper, nickel and cobalt compounds has been made. The metal derivatives were found to exhibit a new band in the visible region together with the absorption bands corresponding to those found in the parent azo dye. The new bands in the metal complexes occur at the same position for a given metal, regardless of the dye with which it is combined and may, therefore, be ascribed to an electronic transition within the metal atom only.

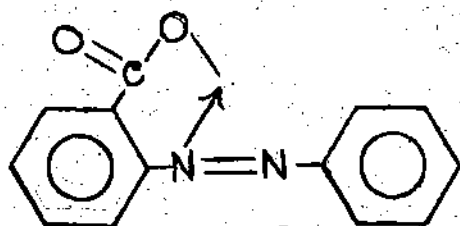
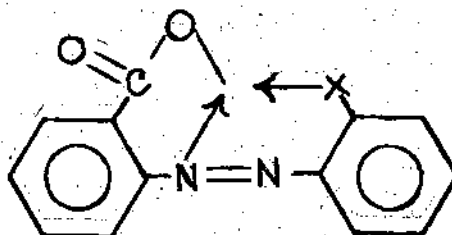
Absorption spectra of organotin derivatives of (aryl azo) benzoic acids have been reported by Majee and Banerjee<sup>26</sup> where it is shown that organotin (aryl azo) benzoates may be classified into three categories viz. (i) derivatives of O-(arylaazo) benzoic acids where the coupling components has no donor groups (e.g.  $-NR_2$ ,  $-OH$  and  $-OMe$  etc.) at the ortho position, (ii) derivatives of O-(arylaazo)



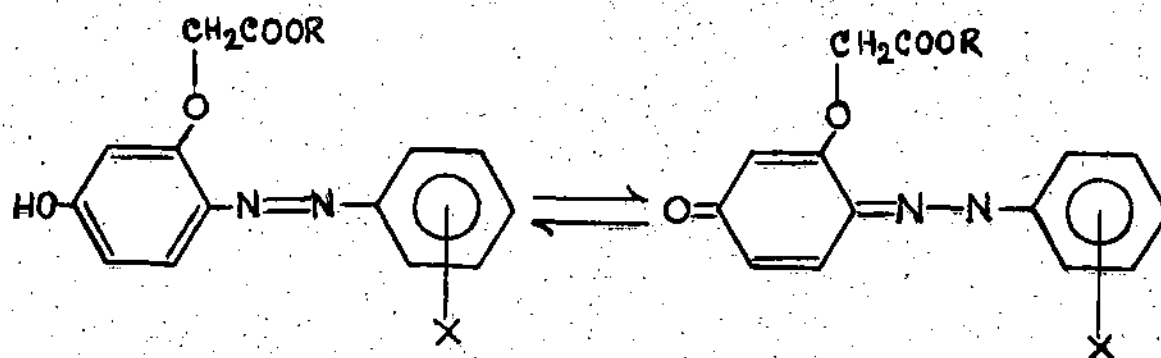
benzoic acids where the coupling components have a donor group at the ortho position and (iii) derivatives of the p-(aryazo) benzoic acids. This classification actually corresponds to ligating ability of the compounds. Thus the first group of compounds represent the derivatives of the ligands which are potentially bidentate, the second group represent potentially terdentate ligands while the p-carboxy ligands are only monodentate (III-V).



Monodentate (III)

Bidentate  
(IV)(X = -NR<sub>2</sub>, -OH, -OMe)  
Terdentate (V)

Another interesting possibility is the azo-hydrazone tautomeric equilibrium of the following type.

VIVII

All the three types, viz., mono dentate, bidentate and terdentate, are theoretically possible in the present series of ligands which are structurally analogous to the carboxylates except for the replacement of the  $-\text{COOH}$  group by  $-\text{OH}$  group. Unfortunately, triorganotin derivatives could not be obtained except in the case of p-hydroxy derivatives<sup>64</sup> although polymeric organotin products are obtained in other cases. The large amount of electronic absorption data already available in the case and organotin compounds of other types of aryl azo benzene derivatives<sup>26,67,68,70-72</sup>, however, provide a reasonable basis for the interpretation of the absorption data on the present series of compounds.

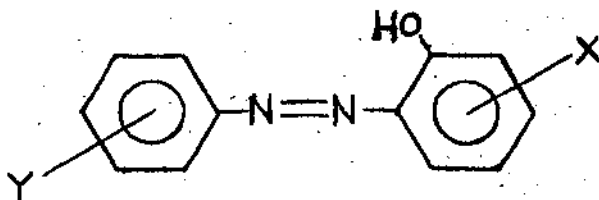
The electronic absorption spectra of almost all the compounds are characterised by the presence of three absorption bands in the

UV-Visible region. The lowest wave length peak in the 250-280 nm region undoubtedly originates from the perturbed local excitation in the aryl groups, while the absorption above  $\sim 330$  nm is associated with the  $\pi-\pi^*$  transition involving the azo group. The low intensity  $\pi-\pi^*$  band which occurs in  $\sim 440-460$  nm is generally hidden under the tail of the high intensity  $\pi-\pi^*$  transition involving the azo group. Thus, the most characteristic feature of the electronic absorption spectra of the substituted aryl azo phenols is the presence of a strong absorption in the  $\sim 300-400$  nm region.

### 1.1. Results and Discussion

The long wave length absorption maxima of the ligands are given in Table 1.

A general feature of the absorption spectra of almost all the compounds having -OH group in the O-position of the type VIII is the presence of two absorption maxima in the 330-480 nm region indicating the presence of tautomeric equilibrium in solution. Such equilibrium has already been established in the case of carboxylate derivatives<sup>26</sup>.



VIII

In the absence of any tautomeric or solvent-solute equilibria or intramolecular H-bonding, the absorption spectrum of compounds of the type IX and X are expected to be very similar except for a small shift that may arise due to the small difference in the inductive and mesomeric effect of the -OH group in the two systems.

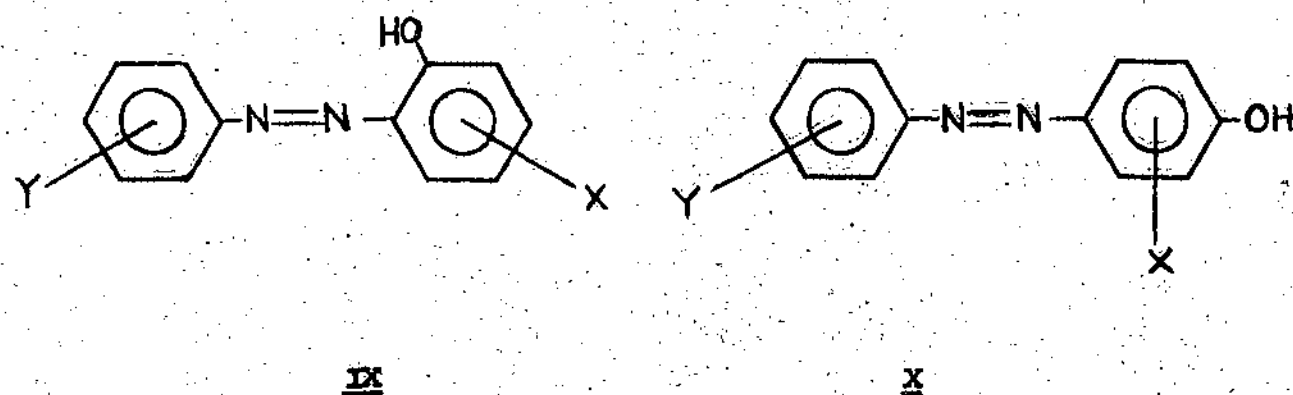


Table - 1

Long wave length Absorption Maxima (in nm) of the aryl azo phenols used in the present study

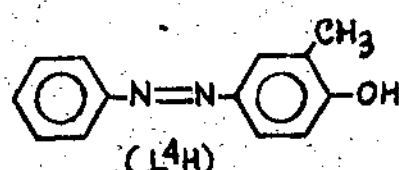
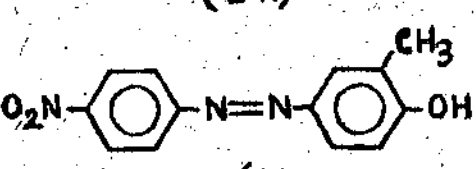
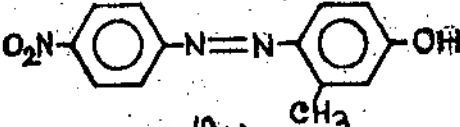
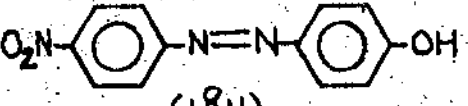
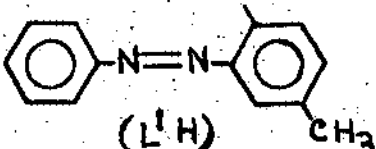
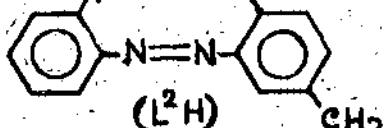
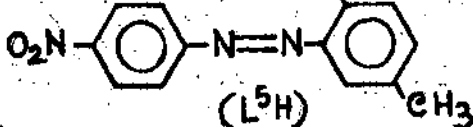
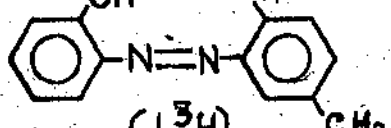
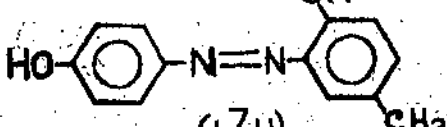
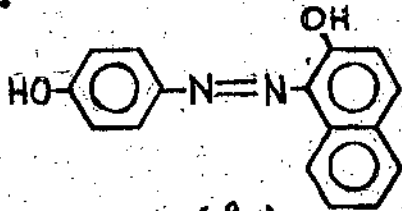
Ligand	SOLVENT	
	Methanol	Benzene
1.  (L <sup>4</sup> H)	350	350
2.  (L <sup>6</sup> H)	385	375

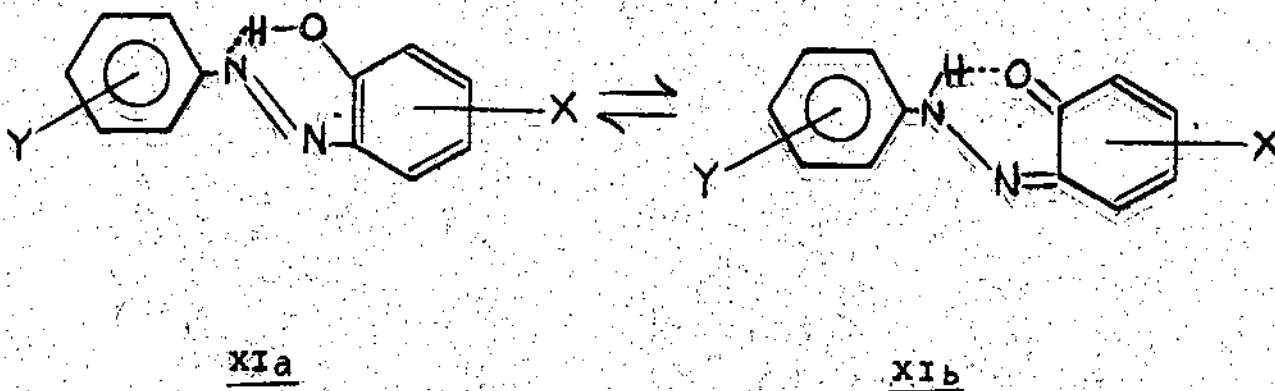
Table - 1 (Contd..)

Ligand	Methanol	Benzene
3.  ( $L^{10}H$ )	370	375
4.  ( $L^8H$ )	375	370
5.  ( $L^1H$ )	340	340
6.  ( $L^2H$ )	320,400	330,405
7.  ( $L^5H$ )	335,410	340,425
8.  ( $L^3H$ )	415,435	412,430
9.  ( $L^7H$ )	350,440	355,440
10.  ( $L^9H$ )	380,480	380,470

An examination of the data given in Table - 1 shows the presence of only one strong transition in the  $\sim 340-400$  nm region due to  $\pi-\pi^*$  transition in compounds of types X while those of type IX show two absorption maxima, one in the  $\sim 320-400$  nm region as in the case of the type X compounds and the other in the region  $\sim 400-480$  nm.

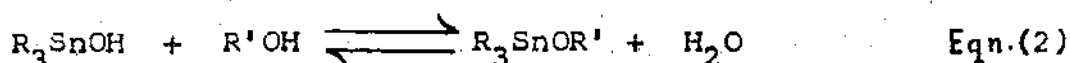
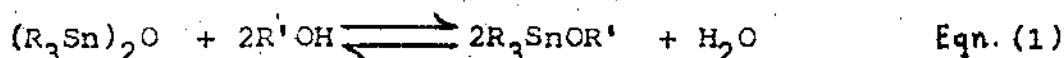
The additional band at much longer wave length in compounds of the type IX should be attributed to the presence of the hydrazone form in equilibrium with the azo form<sup>1,6-9,26,61</sup>. This is consistent with the known behaviour of the hydrazone form which always absorb at longer wave length compared to the corresponding azo form<sup>27</sup>.

Both the azo (XIa) and the hydrazone (XIb) forms are stabilised through intramolecular hydrogen bond as is the case with 1-aryldiazo-2-naphthols<sup>9</sup>.



The presence of azo-hydrazone tautomerism in the ligands of type IX and the presence of intramolecular hydrogen bond explains the low reactivity of these ligands towards the organotin oxides.

The reaction between the organotin oxides and hydroxides with phenols/alcohols may be looked upon as an acid-base reaction.



In fact the reaction of bis(triethyltin)oxide with phenols was first carried out to demonstrate the basicity of an organotin oxide<sup>16</sup>. The reaction is, therefore, strongly dependent on the acidity of the phenol. As evidenced by the electronic absorption spectra, the ligands with -OH group at the 2-position are stabilised through intra molecular hydrogen bonding resulting in lowering the acidity of hydroxylic proton.

On the other hand, the electronic spectra of the 4-hydroxy compounds (type X) do not show any evidence of azo-hydrazone tautomerism. Type X ligands are therefore expected to react with the organotin oxides according to eqn. (1) unless the arylazo group reduces the acidity of the phenolic proton considerably. The reactivity of the phenolic proton in the arylazo phenols towards base was therefore probed by studying the electronic spectra in presence of varying concentration of alkali. The absorption maxima of some of the ligands in ethanol and ethanol containing  $\sim 10^{-2} M$  NaOH are given in table-2.

Table - 2

Absorption bands of ligands in ethanol and  
 $\sim 10^{-2}$  M NaOH in ethanol.

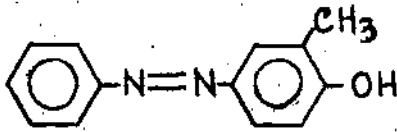
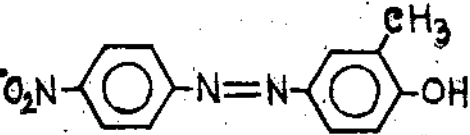
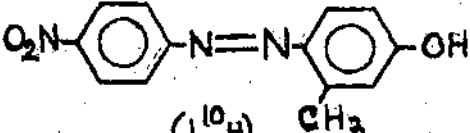
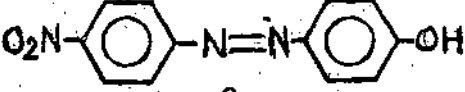
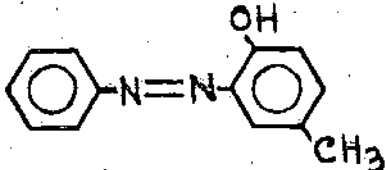
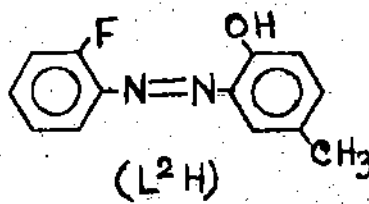
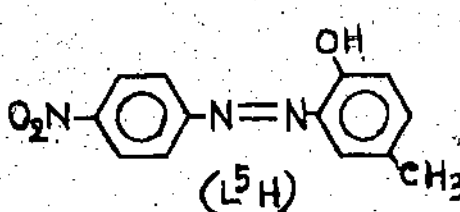
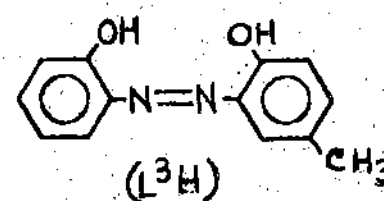
Ligand	Ethanol $\lambda_{\max}(\text{nm})$	$\sim 10^{-2}$ M NaOH in ethanol
1.  (L <sup>4</sup> H)	350	350
2.  (L <sup>6</sup> H)	385	530
3.  (L <sup>10</sup> H)	375	375, 530
4.  (L <sup>8</sup> H)	380	505
5.  (L <sup>1</sup> H)	345	345



Table - 2 (Contd.)

6.	 (L <sup>2</sup> H)	325,400	325,490
7.	 (L <sup>5</sup> H)	335,415	355,545
8.	 (L <sup>3</sup> H)	425	425

A few representative spectra shown in Figs. 2 to 7 demonstrate the effect of  $\text{OH}^-$  on the electronic spectra of the ligands. It can be seen that alkali has very little effect on the spectra for a number of ligands, while in other cases, notably the nitro substituted ligands, a new absorption at  $\sim 490-545 \text{ nm}$  is found. The intensity of the new band increases with alkali concentration with consequent decrease in the original absorption maxima in the  $\sim 330-380 \text{ nm}$  region. Clearly, the new <sup>band at</sup>  $\sim 490-500 \text{ nm}$  is due to the anion of the ligand ( $\text{L}^-$ ). The large bathochromic shift in the anion,

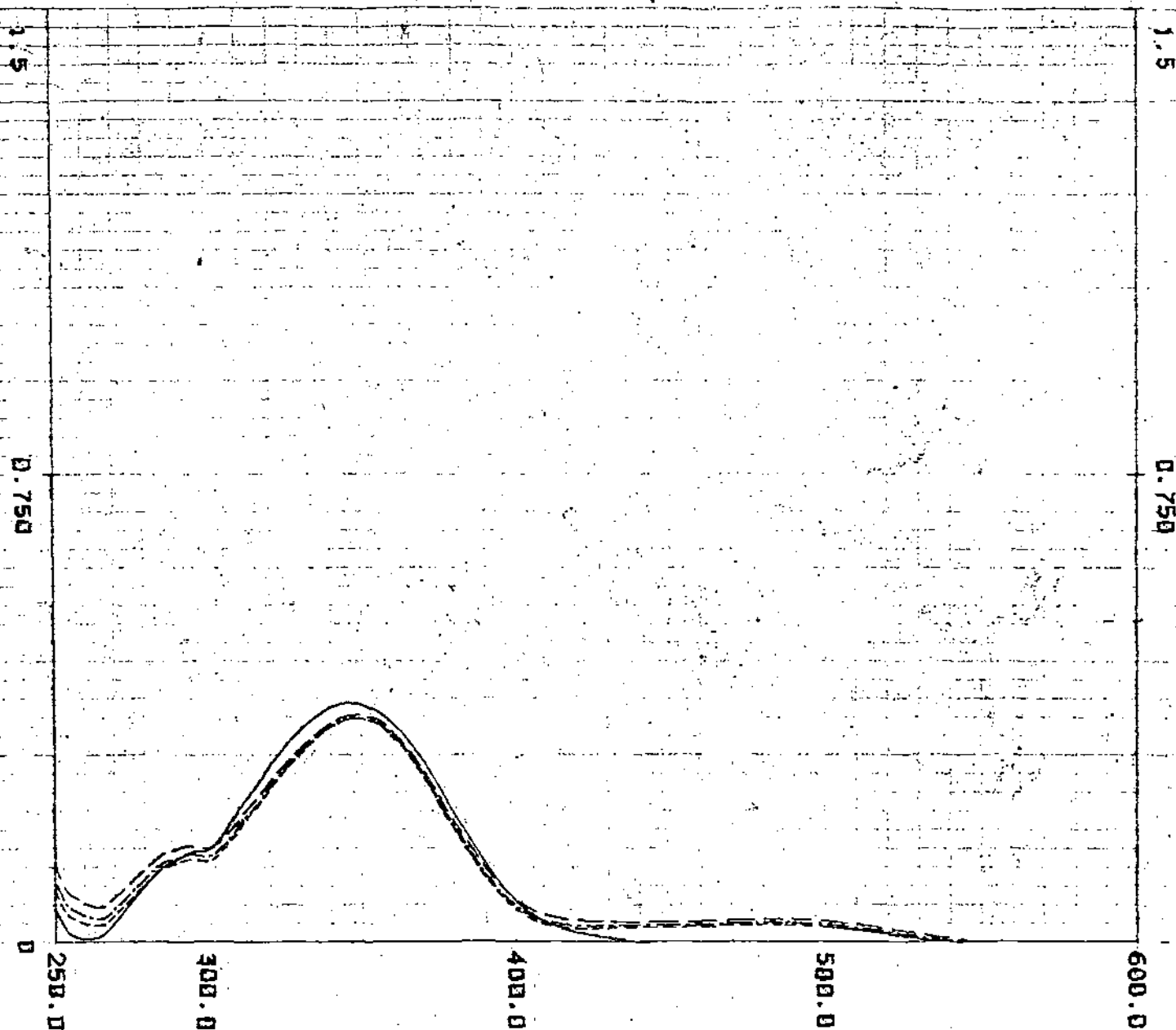


Figure - 2 Electronic absorption spectra of  
 (a)  $L^1H$  in Ethanol —————  
 (b)  $L^1H$  in Ethanol containing concentration of NaOH-----

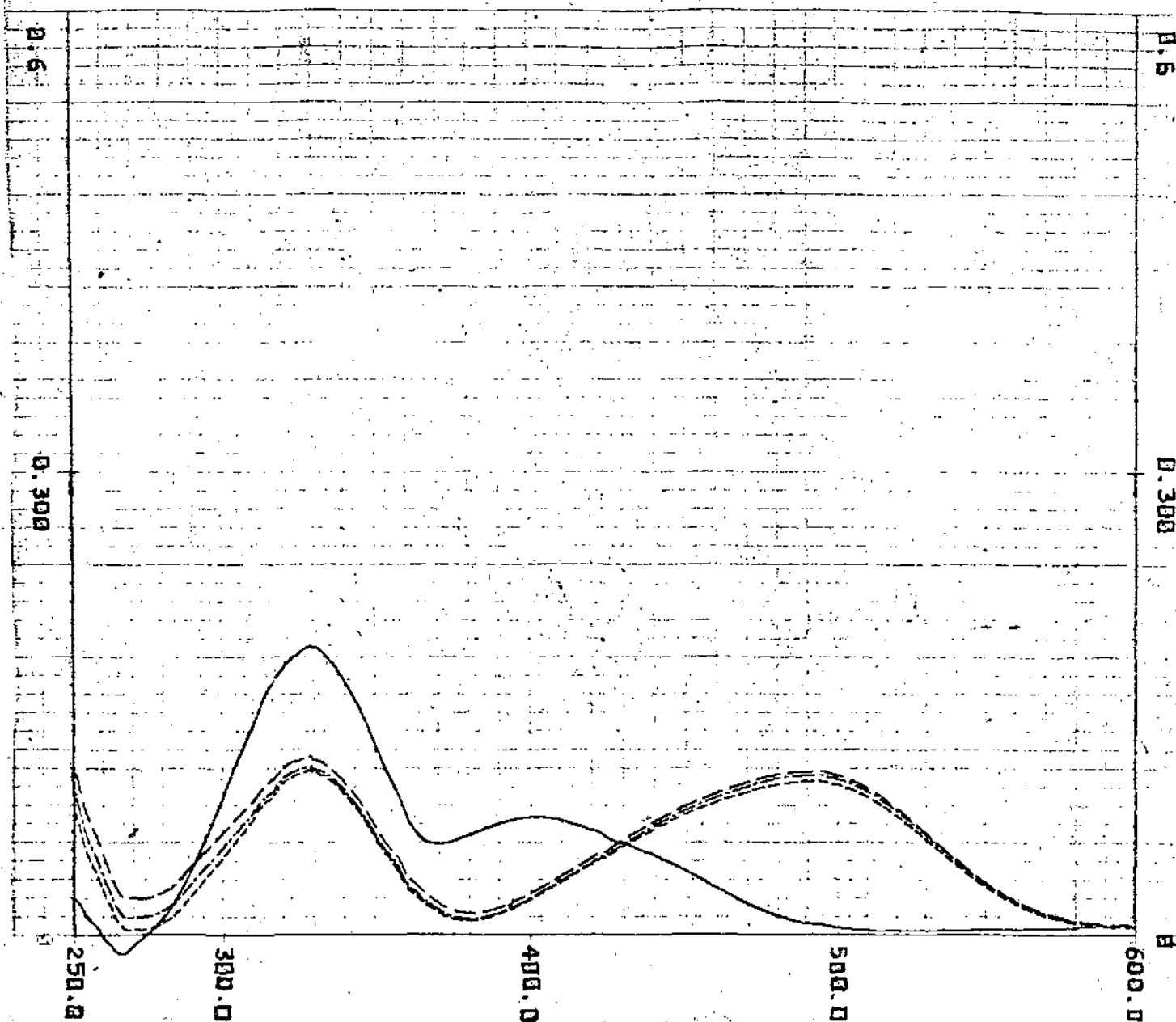


Figure - 3

Electronic absorption spectra of

(a)  $L^2H$  in Ethanol ———

(b)  $L^2H$  in Ethanol containing varying concentration of NaOH ----

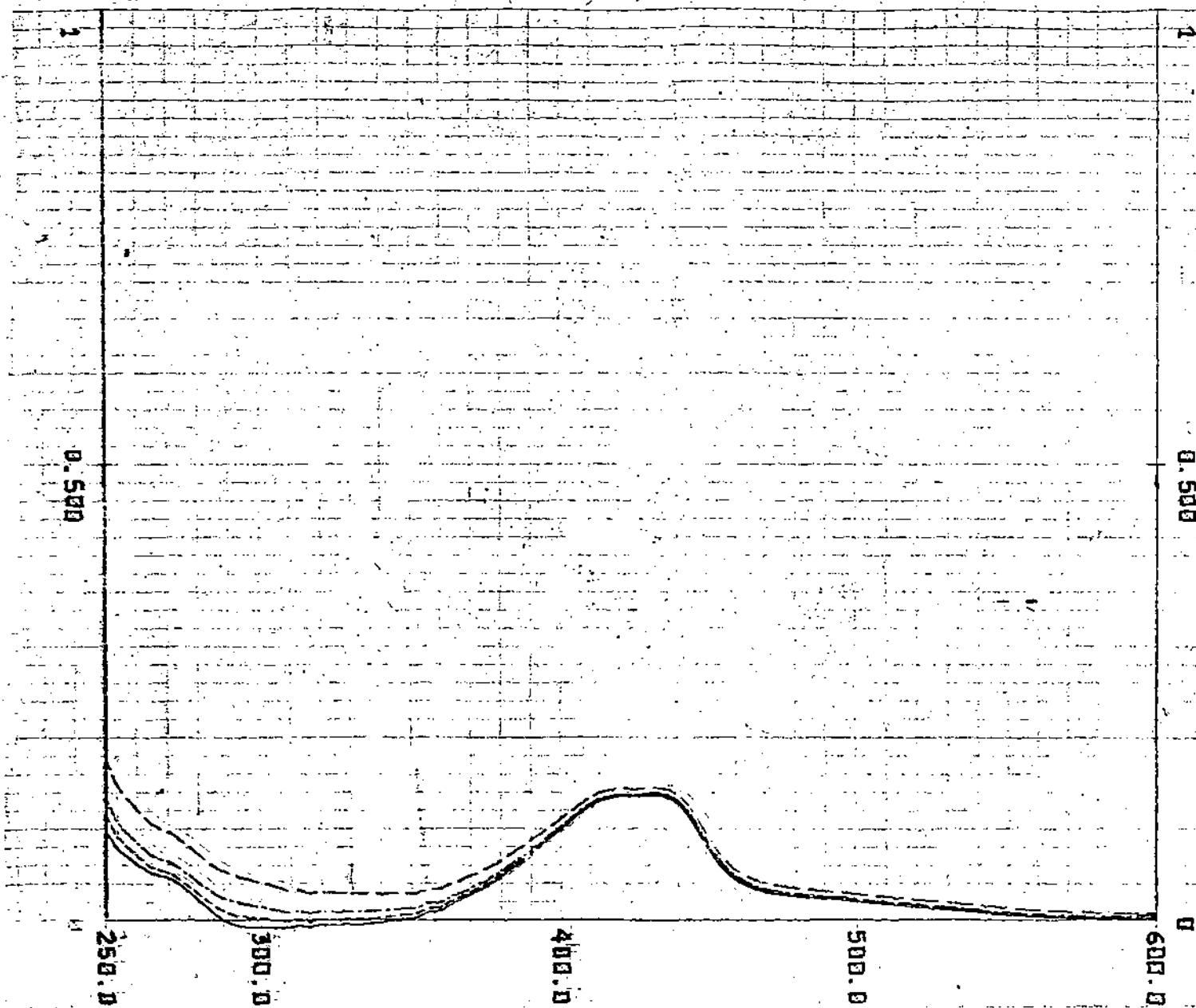
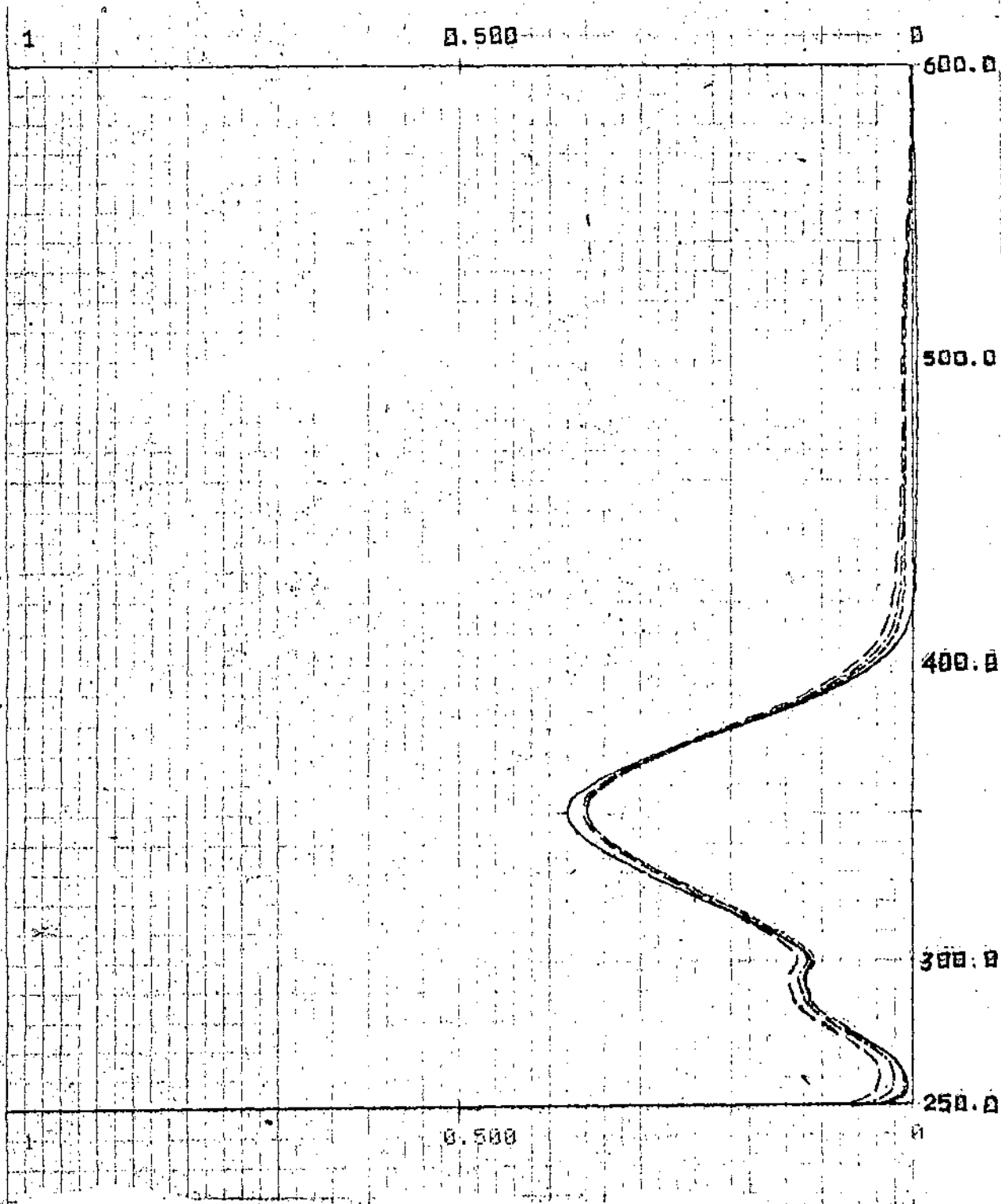


Figure - 4

Electronic absorption spectra of

(a)  $L^3H$  in Ethanol———

(b)  $L^3H$  in Ethanol containing varying concentration of NaOH----

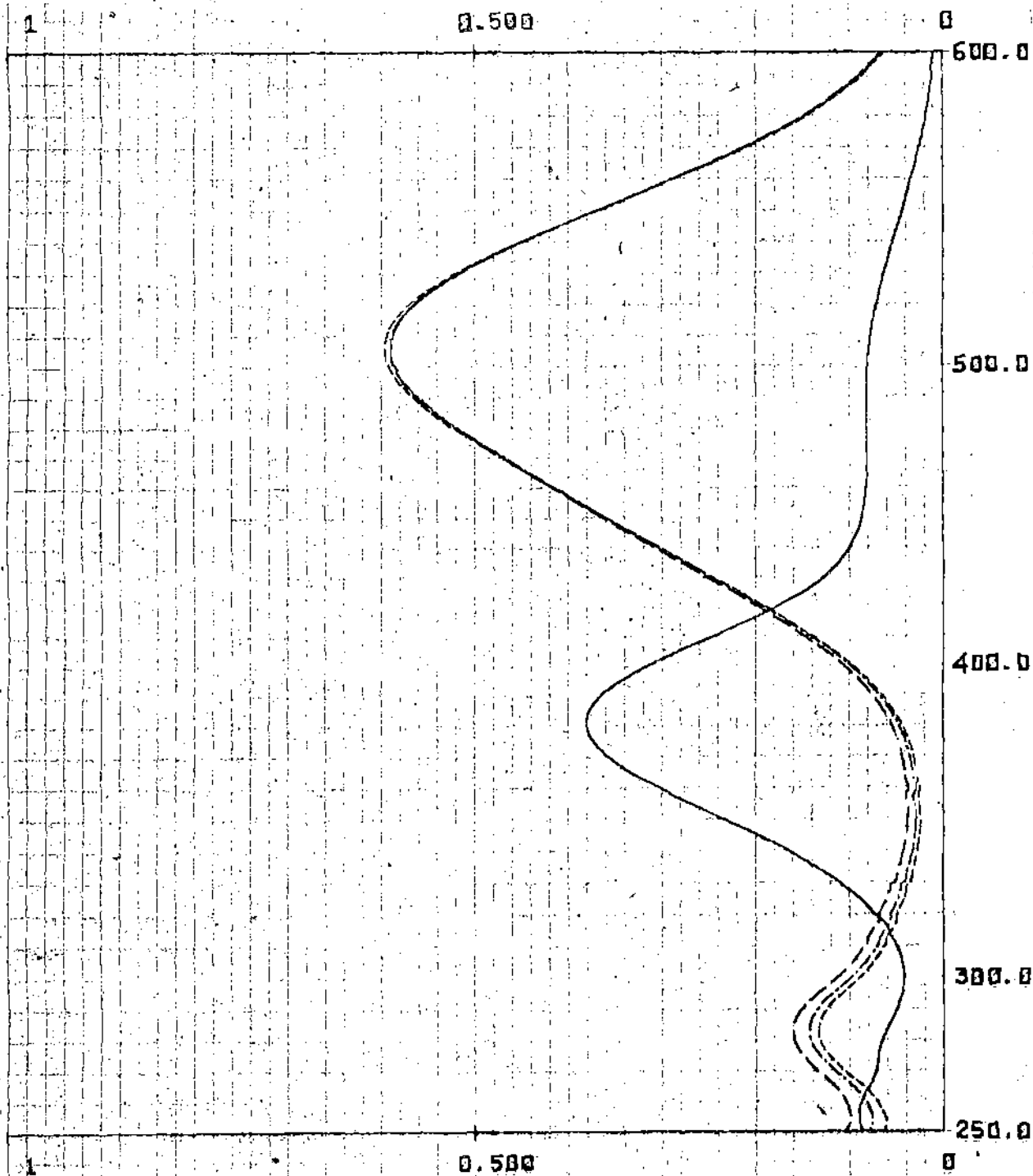


Electronic absorption spectra of

(a)  $4H$  in Ethanol

(b)  $4H$  in Ethanol containing varying concentration of NaOH

Figure - 5



Electronic absorption spectra of  
 (a)  $L^8H$  in Ethanol \_\_\_\_\_  
 (b)  $L^8H$  in Ethanol containing varying concentration of  $NaOH$  \_\_\_\_\_

Figure - 6

Electronic absorption spectra of  $L^8H$  in Ethanol containing varying concentration of  $NaOH$

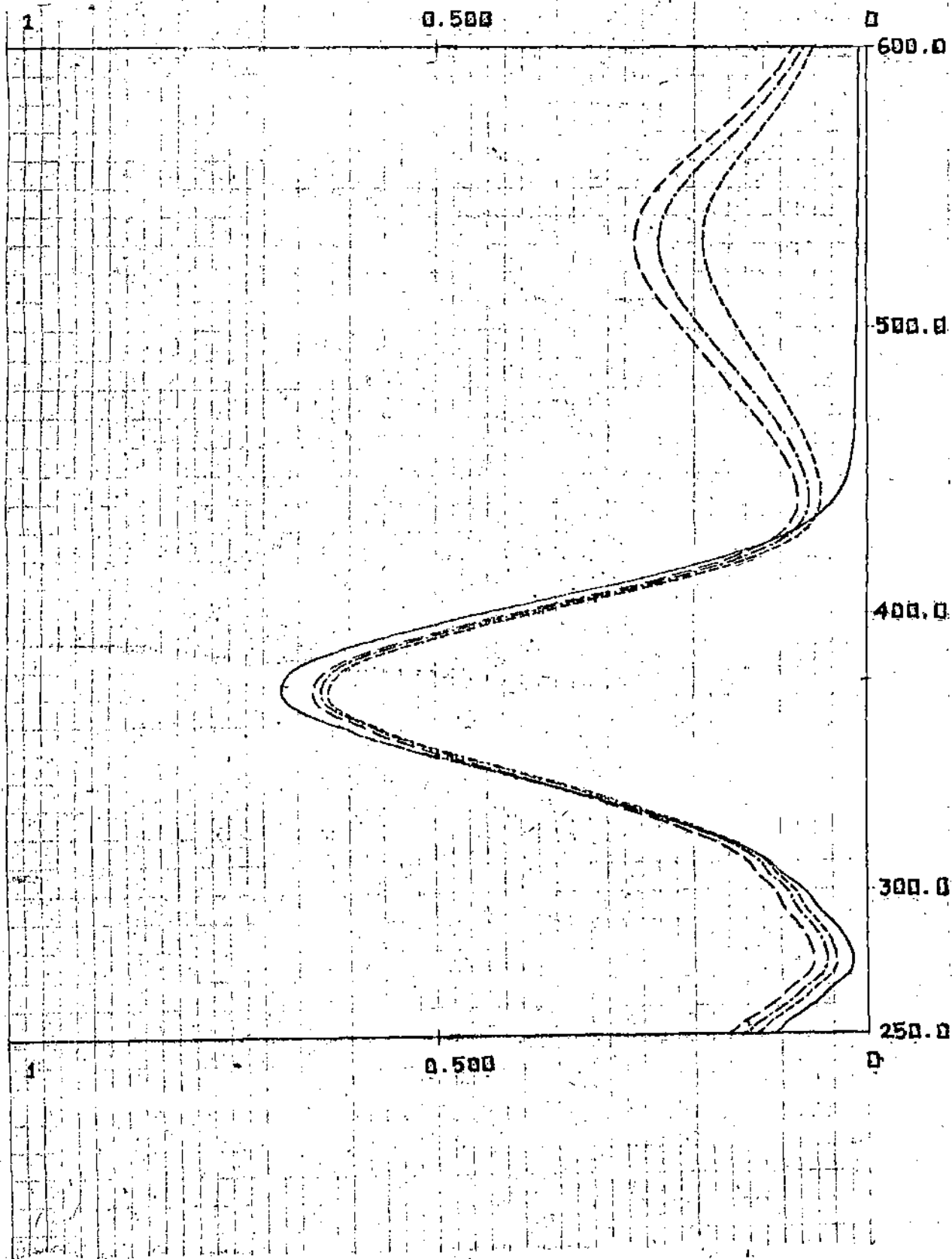
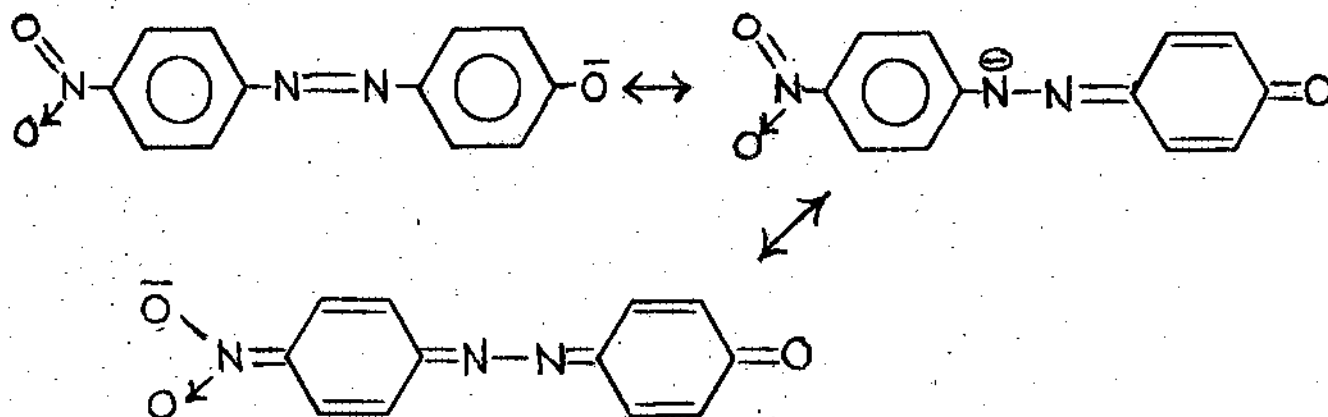


Figure - 7 Electronic absorption spectra of  
 (a)  $L^{10}H$  in Ethanol  
 (b)  $L^{10}H$  in Ethanol containing varying concentration of NaOH

particularly in the case of nitro substituted aryl azo phenols, results from increased electron delocalization (XII).



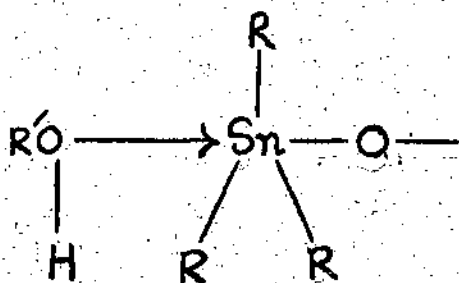
### XII

Except for the nitro substituted ligands, the addition of alkali has no noticeable effect on the absorption spectra of the ligands until very high  $\text{OH}^-$  concentration is used. Thus,  $\text{L}^3\text{H}$  and  $\text{L}^4\text{H}$  remain almost unaffected even when large excess of  $\text{OH}^-$  concentration ( $> 500$  times) is used.

While the extremely low acidity of the hydroxylic proton in the present group of ligands inhibits the normal reaction given by eqn. (1), it does not preclude an alternative path of reaction under more severe conditions, e.g., prolonged azeotropic distillation. Because of the well known Lewis acidity of the tin atom in organotin oxides and halides, nucleophilic attack at the tin atom under suitable condition is possible. The low acidity of the hydroxylic



proton in the aryl azo phenol is indicative of lower electron withdrawal from the oxygen atom through conjugation with the aromatic rings. Consequently, the oxygen atom is expected to be electron rich compared to other type of phenols. Thus, a situation, ideal for a nucleophilic attack by donor group at the tin atom is realised (XIII).

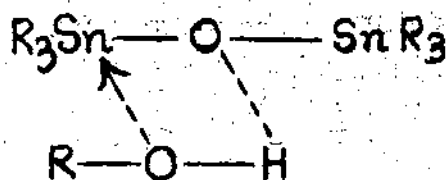


### XIII

Studies on the reaction between  $(\text{R}_3\text{Sn})_2\text{O}$  and nitroso naphthols and related compounds, e.g.,  $\alpha$ -nitroso- $\beta$ -naphthol,  $\beta$ -nitroso- $\alpha$ -naphthol, diacetyl monooxime,  $\alpha$ -benzil oxime etc.<sup>9,10</sup> have shown that these group of ligands also fail to react according to eqn. (1). Instead, a variety of polymeric products formed by extensive cleavage of the R-Sn bonds are obtained.

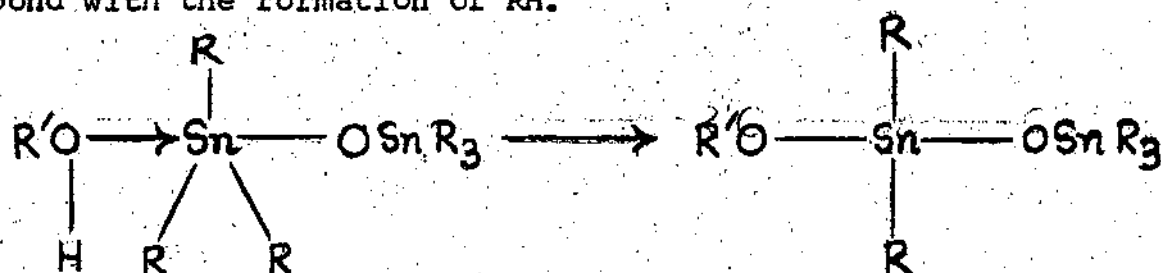
Undoubtedly, the formation of the  $\text{R}_3\text{SnL}$  type compounds by the reaction of  $(\text{R}_3\text{Sn})_2\text{O}$  with  $\text{R}'\text{OH}$  proceeds via a frontal attack (XIV) as <sup>it</sup> depends on the basicity of the organotin component and

the acidity of the ligand proton.



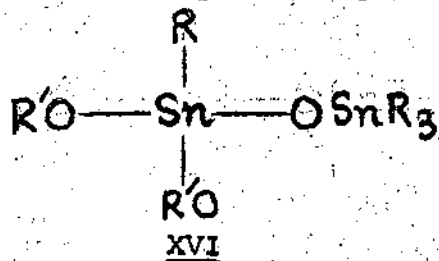
XIV

The comparison of XIII and XIV immediately reveals that in case of XIII the reaction may proceed via the cleavage of the Sn-R bond with the formation of RH.



XV

Due to the presence of two Sn-O bonds which are highly polar ( $\delta^+ \text{Sn} - \delta^- \text{O}$ ), the Lewis acidity of the tin atom in XV is increased considerably. The intermediate XV will therefore react readily through nucleophilic attack by the ligand leading to XVI



The increase in the number of polar Sn-O bonds, further increases the Lewis acidity. The tin atom in XVI therefore, tends to stabilize through increasing its coordination number by solvation. The bulk of the ligands prevent further nucleophilic attack or complexation at the tin atom. Hydration of the tin atom by moisture invariably present in the solvent under normal working condition is expected to be quite facile because of small size of the molecules. Because of reaction conditions (prolonged refluxing), displacement of some of the highly polar Sn-O bonds, by -OH groups becomes highly probable. This leads ultimately to the formation of  $RLSn(OH)_2$  type of products. Intermolecular coordination through the -OH groups increases the coordination number at the tin atom which inhibits further nucleophilic attack.

Evidence for the formation of benzene as a reaction product has been given by Dutta<sup>38</sup> in the slow decomposition of  $(Ph_3Sn)_2O$  to polymeric diphenyl stannoxanes,  $(Ph_2SnO)_n$  on stirring with  $CdI_2$  in diethyl ether. This reaction is believed to proceed through nucleophilic<sup>attack</sup> at the tin atom in the intermediate complex,  $(Ph_3Sn)_2O \cdot CdI_2$ .<sup>38,39</sup>

A very important conclusion that follows from the present study and the earlier studies on the reaction of  $(R_3Sn)_2O$  with a variety of ligands containing OH group is that the driving force for a frontal attack by the -OH group resulting in the formation of triorganotin derivatives of the ligand is determined by the ability of the hydroxylic proton to interact with the oxygen atom of the Sn-O-Sn bonds. As a result, whenever a transition complex of the

type XIV is unfavourable, reaction may proceed by nucleophilic attack at the tin atom (XIII) leading to polymeric products.

The absorption maxima in the organotin derivatives obtained in the present study are given in table-3.

Table - 3

Long wave length Absorption Maxima (in nm) of the organotin derivatives of the aryl azo phenols used in the present study.

Organotin derivatives	S O L V E N T	
	Methanol	Benzene
$\text{PhL}^1\text{Sn}(\text{OH})_2$	335	345
$\text{PhL}^2\text{Sn}(\text{OH})_2$	435	425
$\text{PhL}^3\text{Sn}(\text{OH})_2$	415, 435	412, 430
$\text{PhL}^5\text{Sn}(\text{OH})_2$	315, 395	315, 380
$\text{PhL}^7\text{Sn}(\text{OH})_2$	355, 455	360, 450
$\text{BuL}^7\text{Sn}(\text{OH})_2$	355, 440	360, 445
$\text{Ph}_3\text{SnL}^8$	373	370
$\text{Cy}_3\text{SnL}^8$	368	373
$\text{Bu}_3\text{SnL}^8$	385	375
$\text{PhL}^9\text{Sn}(\text{OH})_2$	375, 470	382, 470
$\text{BuL}^9\text{Sn}(\text{OH})_2$	370, 470	390, 475
$\text{Ph}_3\text{SnL}^{10}$	385	380
$\text{Cy}_3\text{SnL}^{10}$	390	380
$\text{Bu}_3\text{SnL}^{10}$	395	385

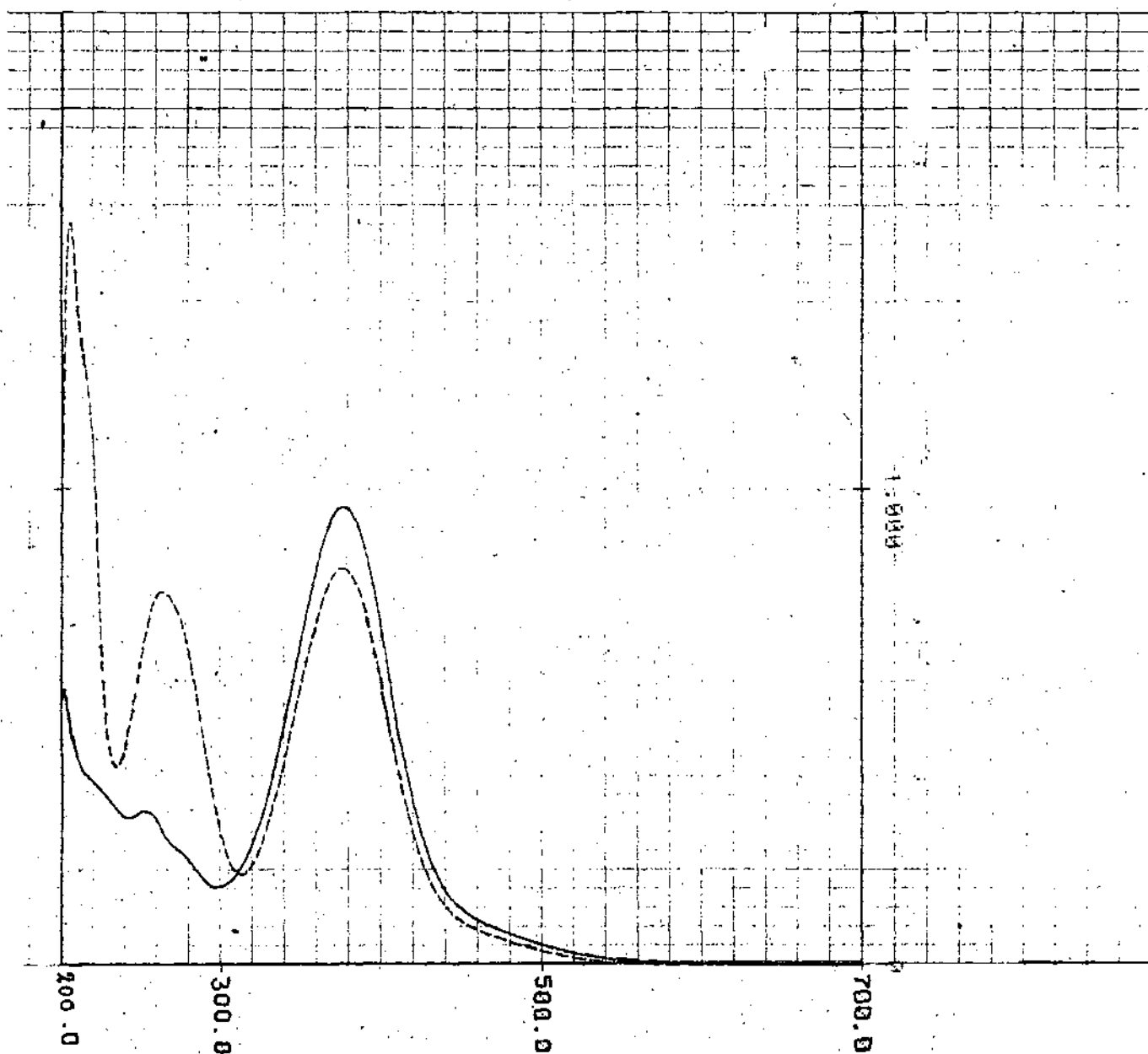


Figure - 8

Electronic absorption spectra of

(a)  $L^B$  in Methanol : —————

(b)  $Ph_3CnL^B$  in Methanol : - - - - -

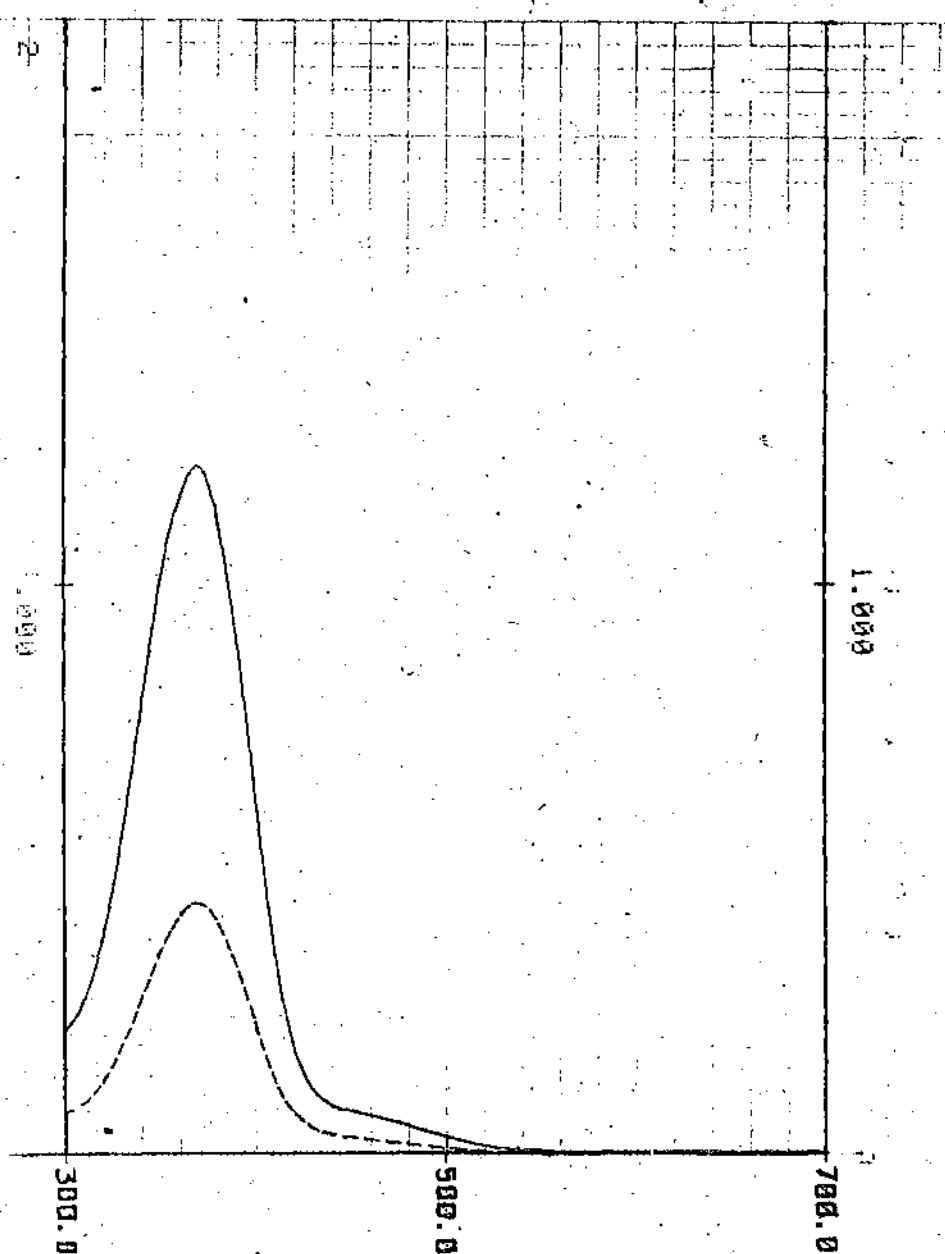


Figure - 9

Electronic absorption spectra of

(a)  $L^S$  in Benzene: —

(b)  $Ph_3SnL^S$  in Benzene: - - -

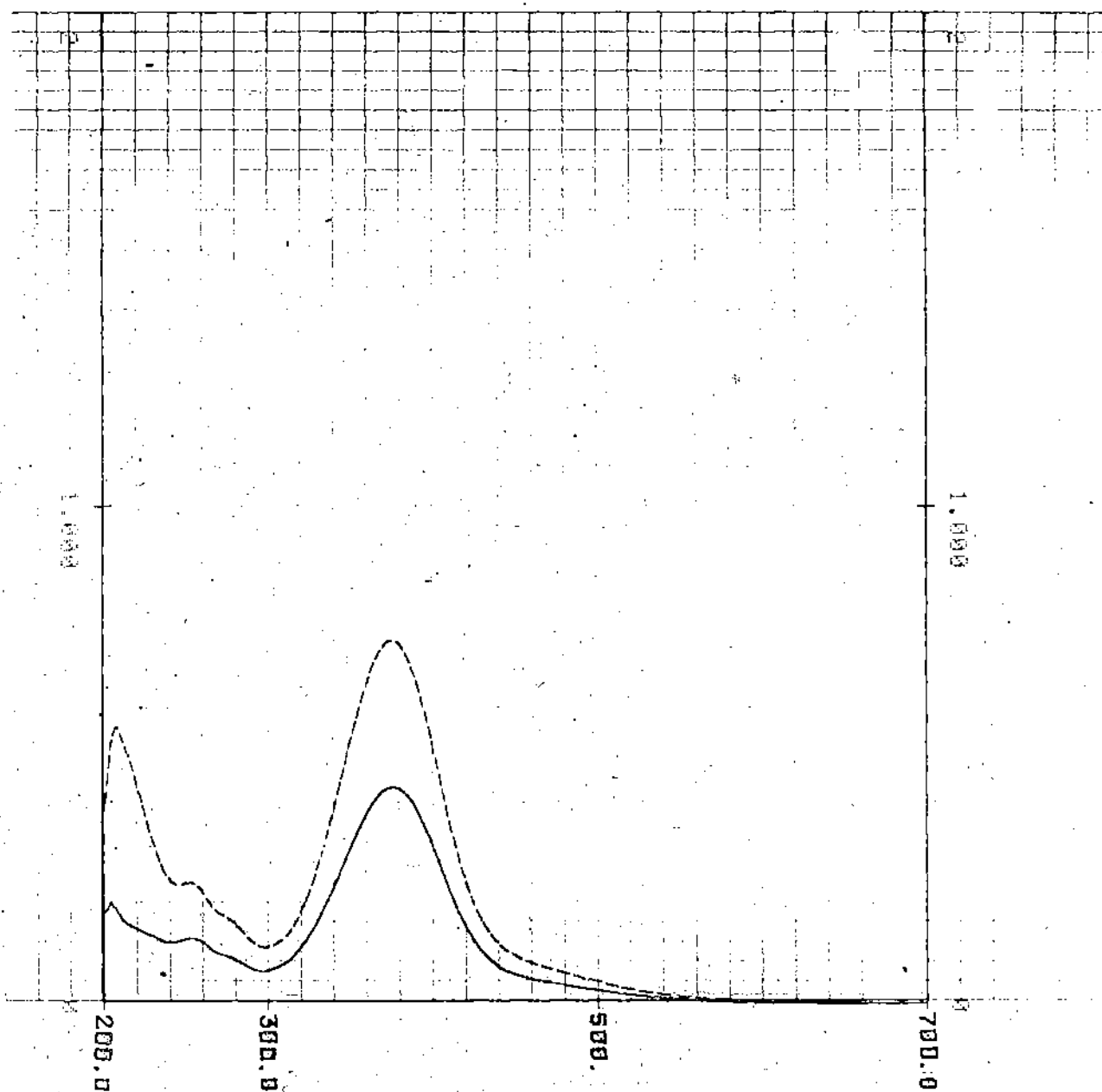


Figure - 10 Electronic absorption spectra of  
 (a)  $L^{III}$  in Methanol: ———  
 (b)  $Cy_3BNL^{III}$  in Methanol: - - -

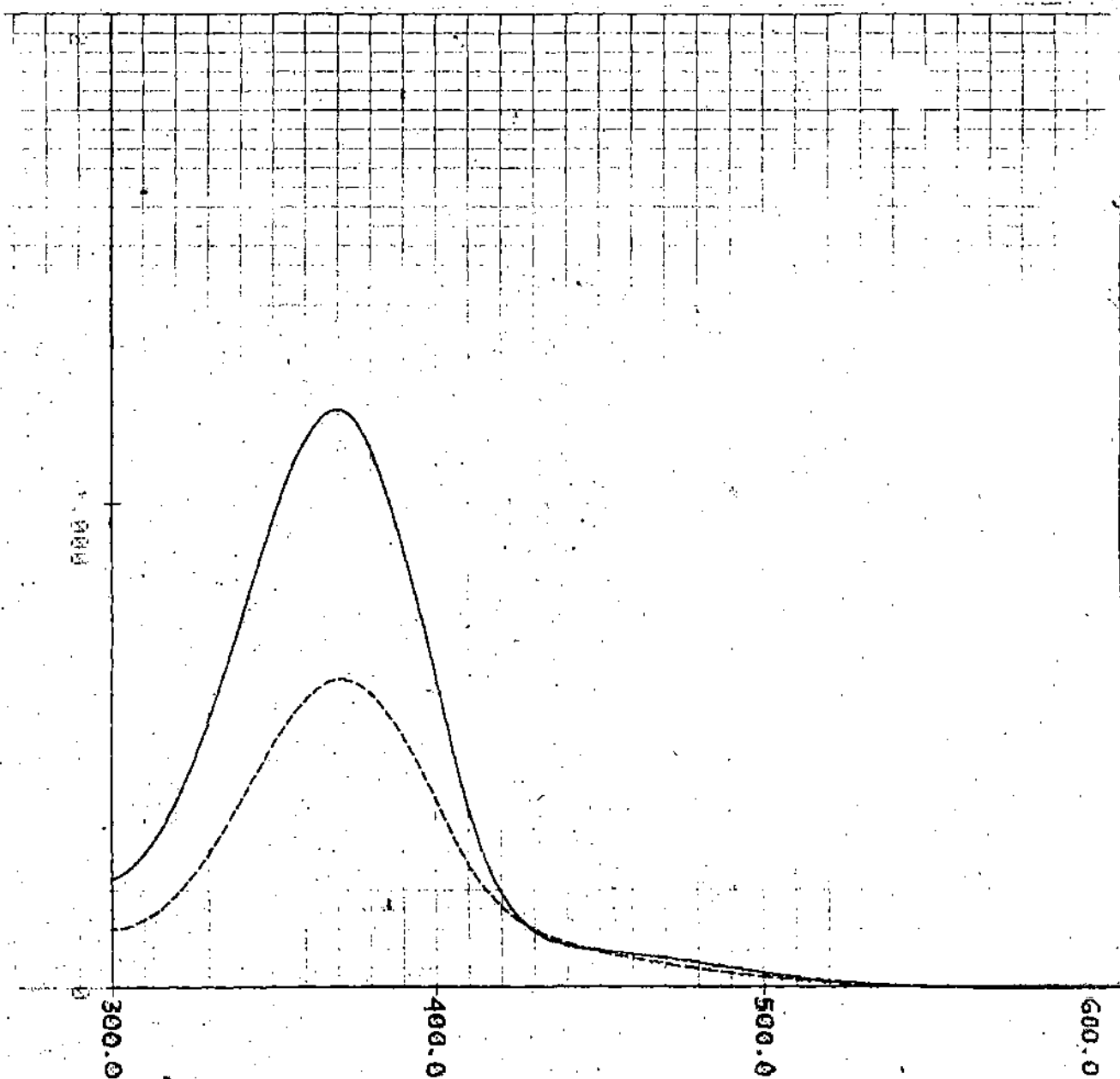


Figure - 11 Electronic absorption spectra of  
 (a)  $L^{\text{III}}$  in Benzene : —————  
 (b)  $C_7H_5NL^{\text{III}}$  in Benzene : - - - - -



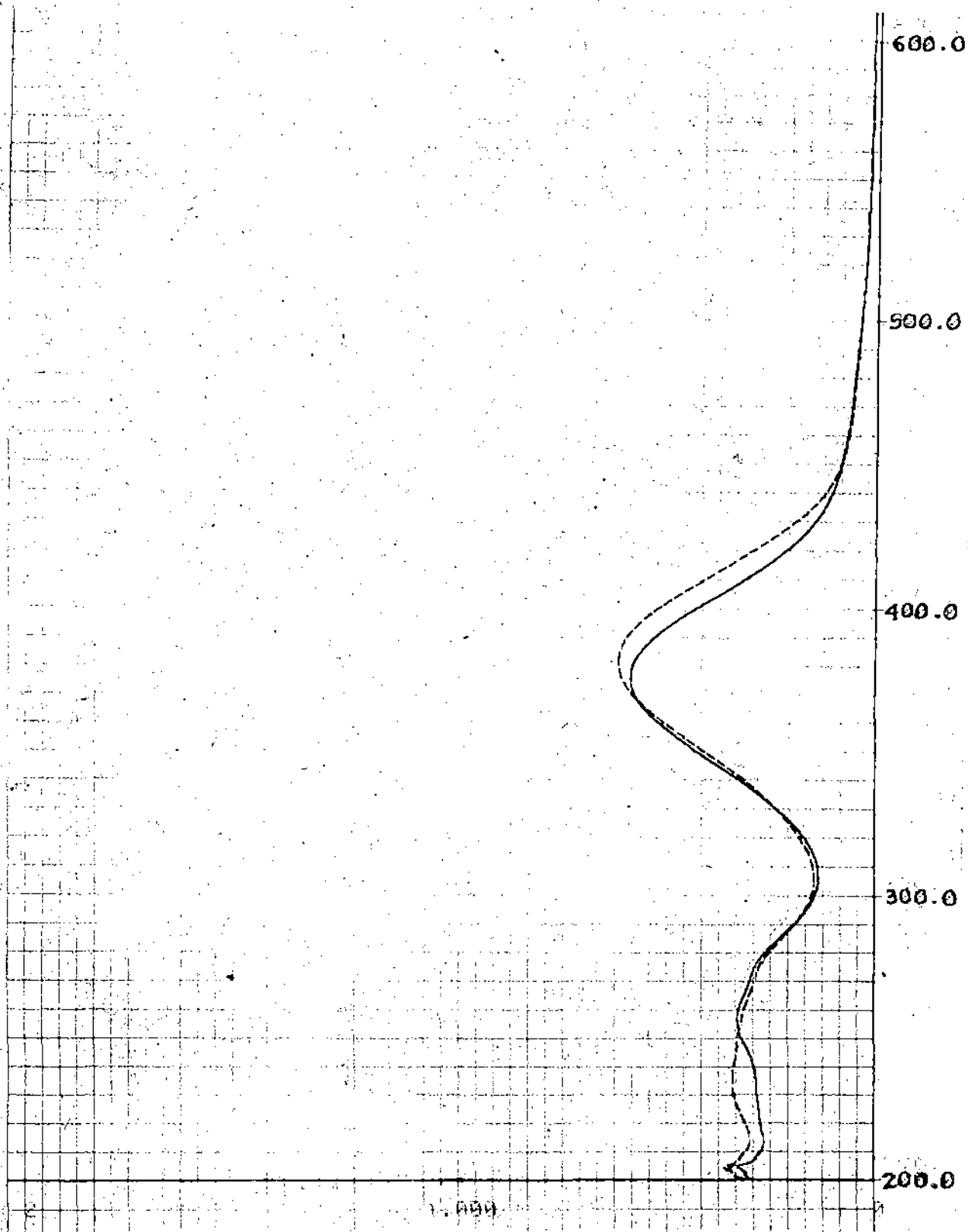


Figure - 12 Electronic absorption spectra of

(a) LiH in Methanol ;

(b) Bu<sub>3</sub>SnLi in Methanol ;

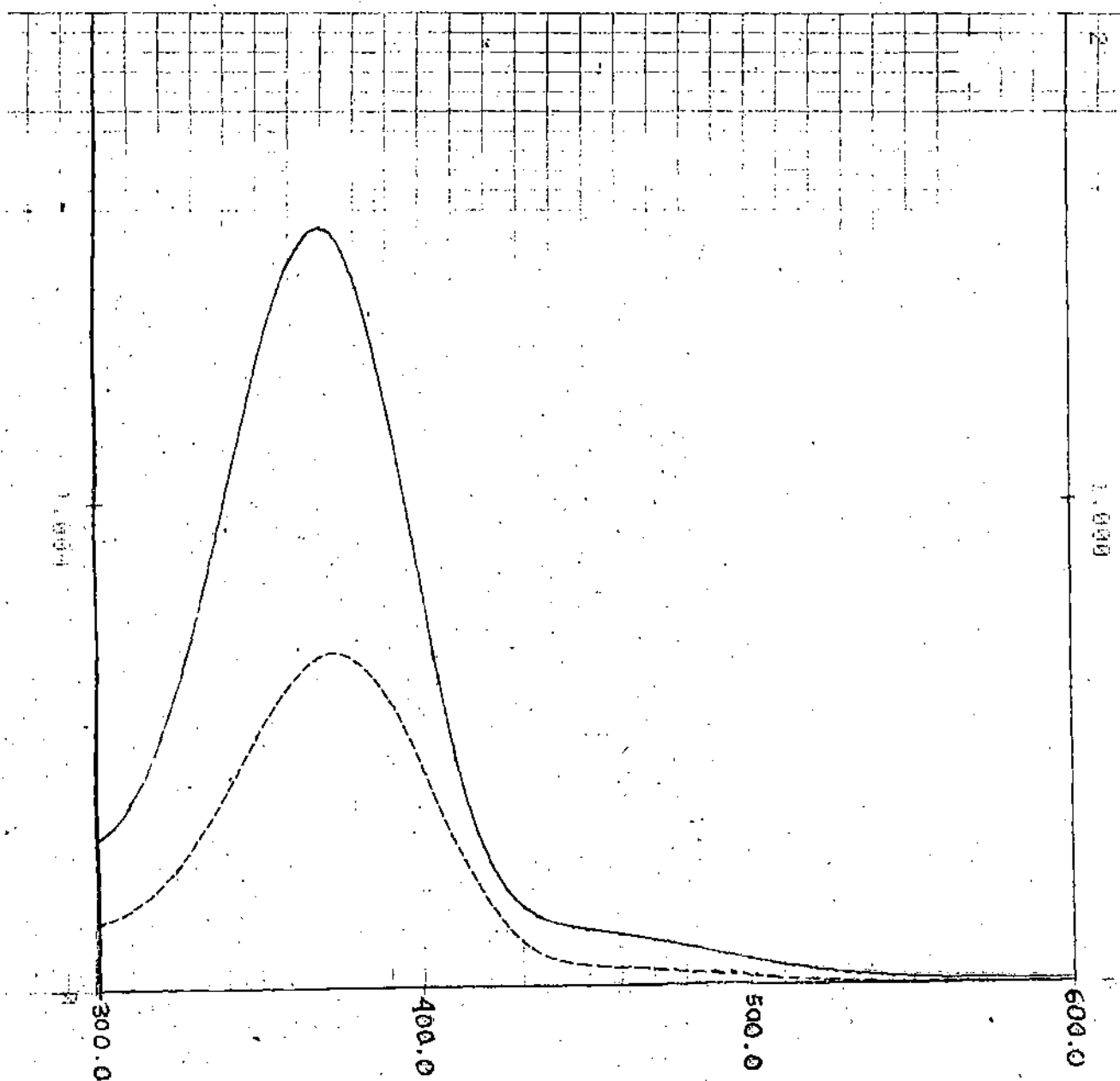


Figure - 13 • Electronic absorption spectra of  
 (a)  $L.H.$  in Benzene • —————  
 (b)  $Bu_3SnL^8$  in Benzene • - - - - -

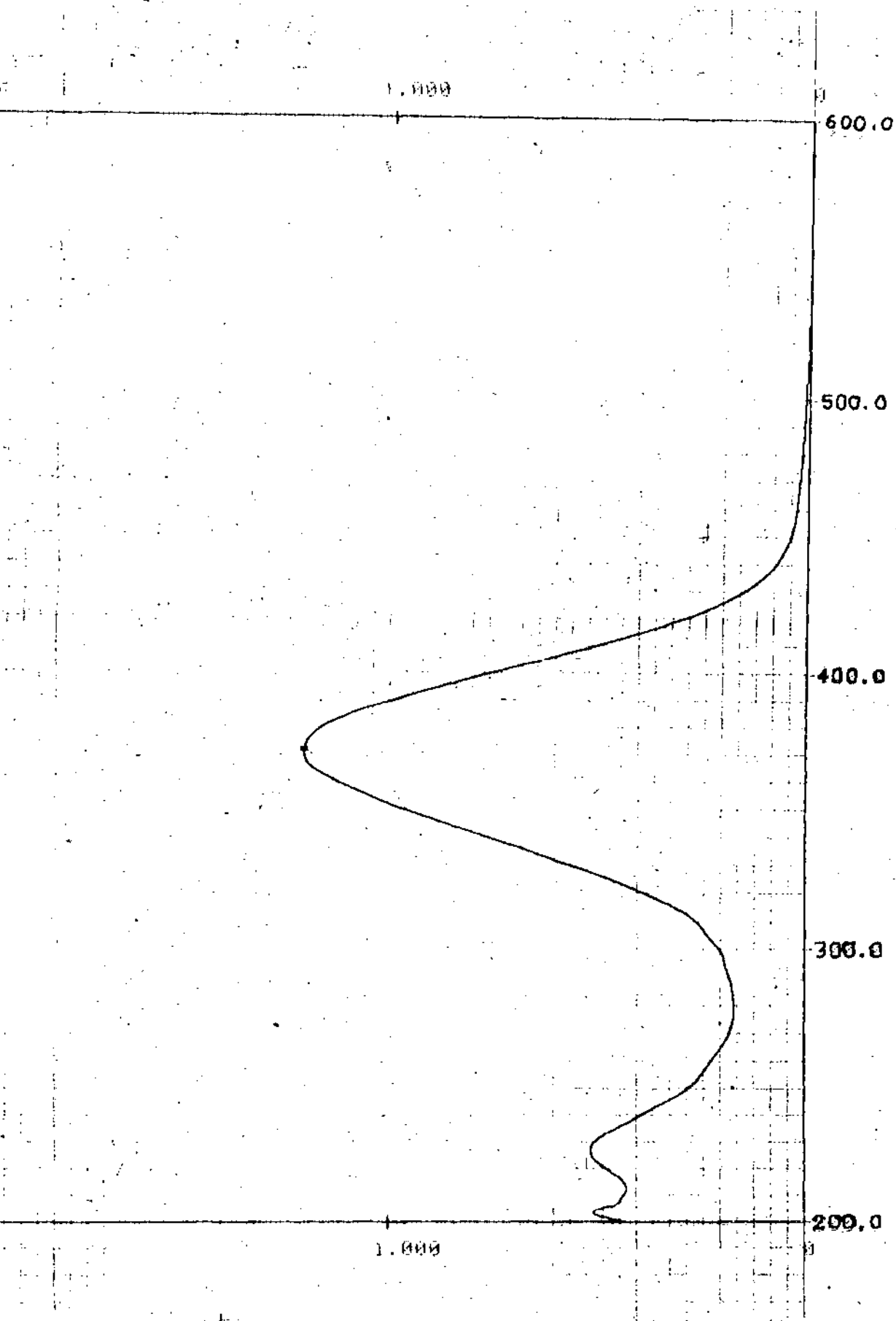
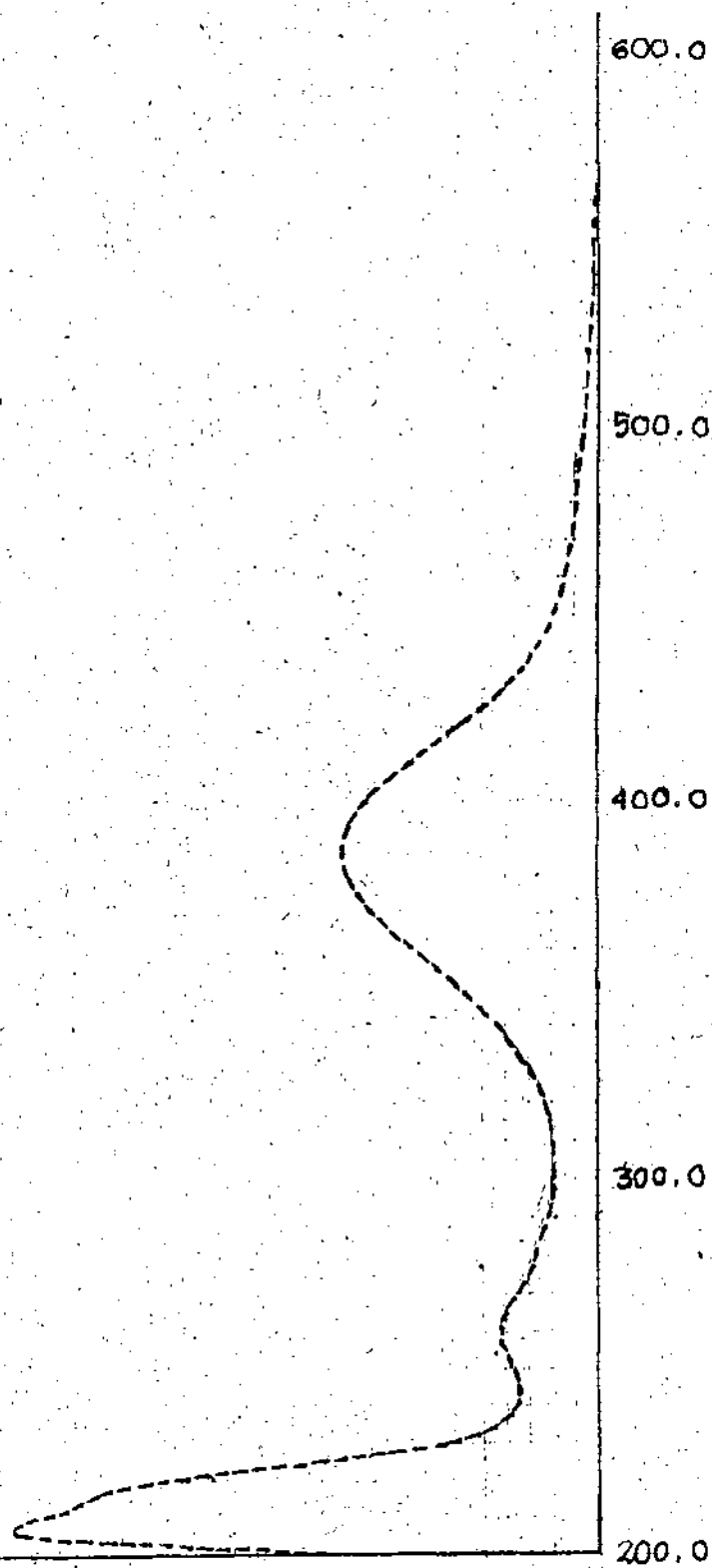


Figure - 14 Electronic absorption spectra of <sup>10</sup>L-H in Methanol :

Figure - 15 Electronic absorption spectra of  
 $\text{Ph}_3\text{Sn}^{10}$  in Methanol :



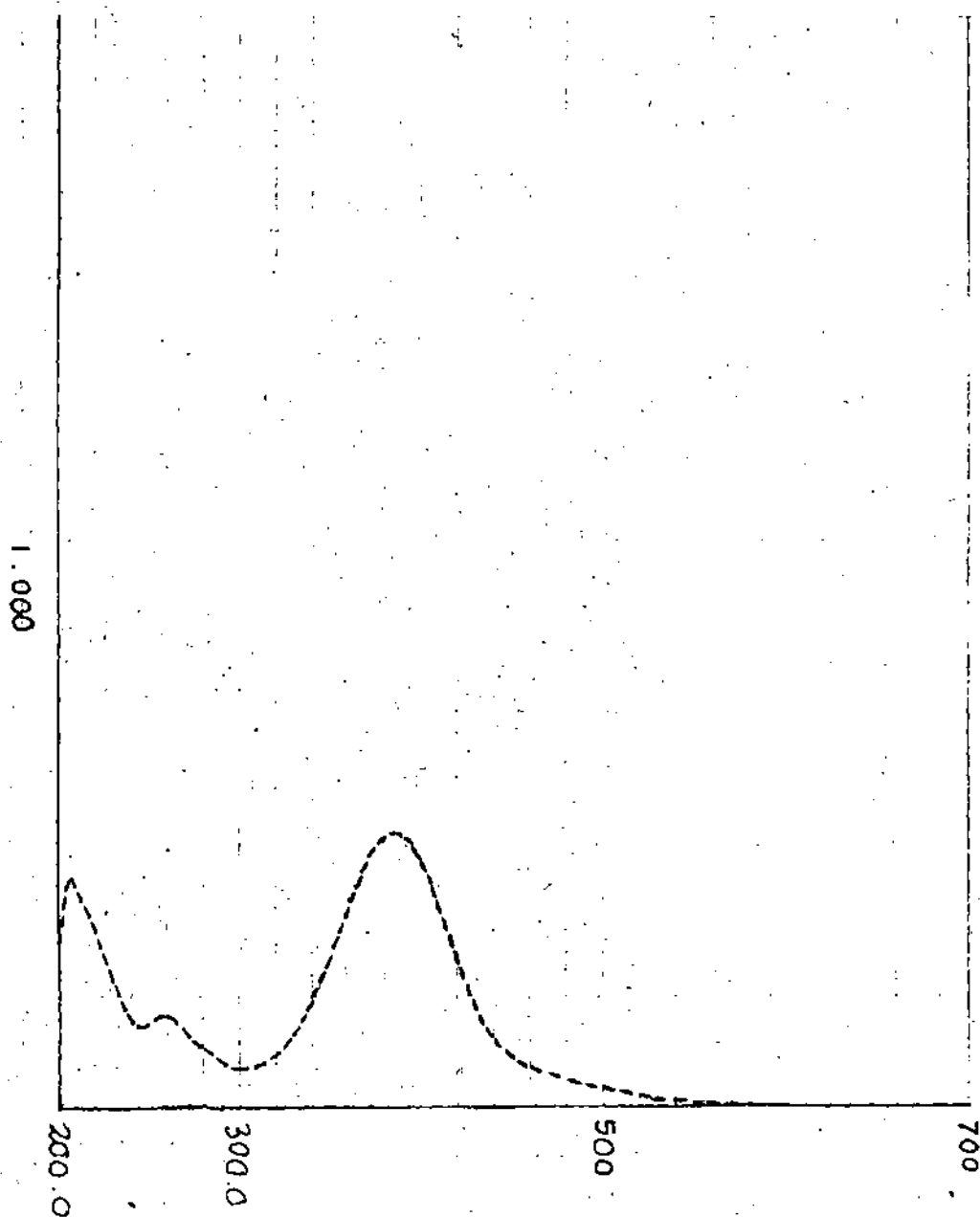


Figure - 16      Electronic absorption spectra of  
 $\text{Cy}_3\text{SnL}^{10}$  in Methanol:-----

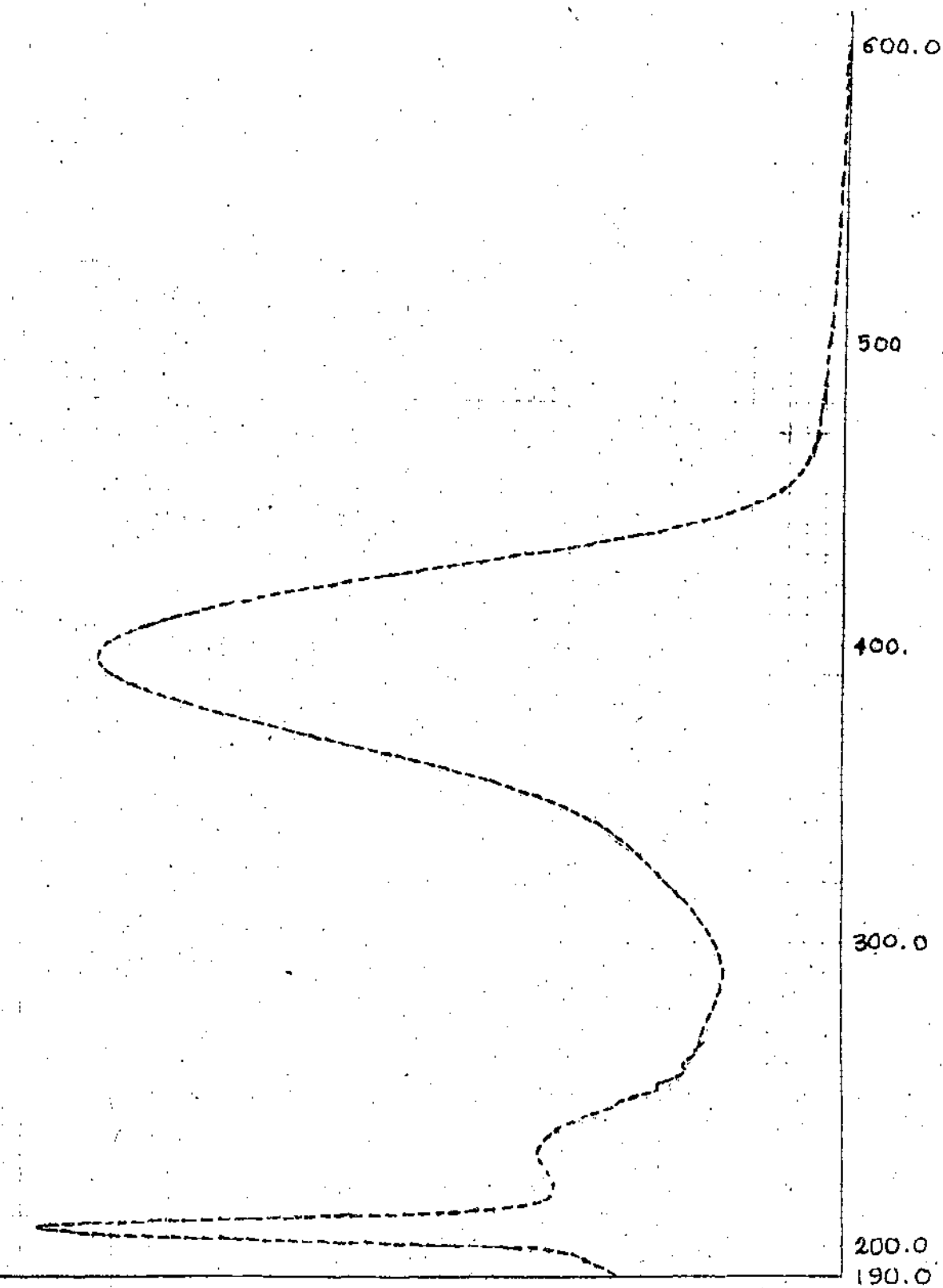


Figure - 17 Electronic absorption spectra of

$\text{Bu}_3\text{SnLi}^{10}$  in Methanol : -----

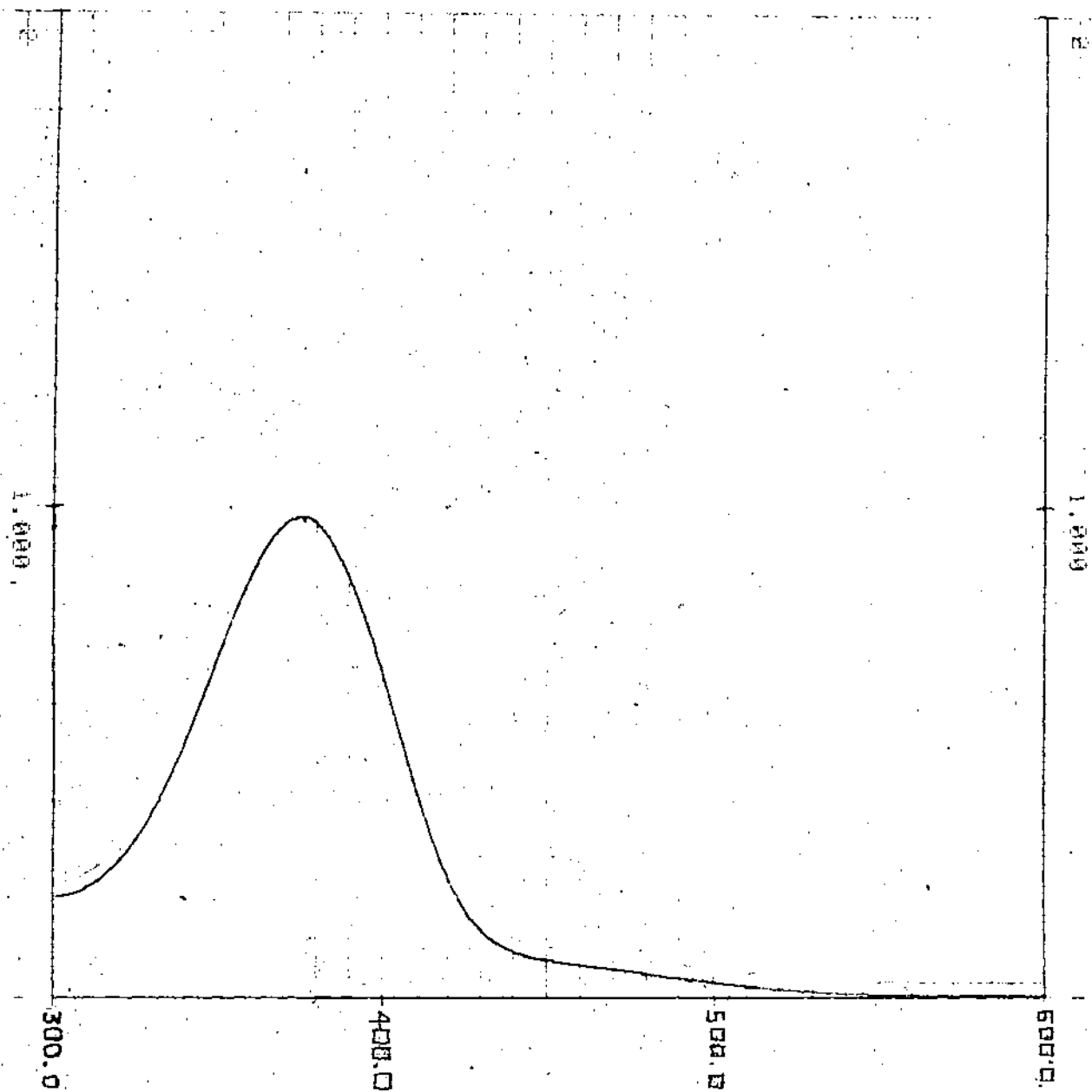


Figure - 18 Electronic absorption spectra of  $L^{10}$  in Benzene

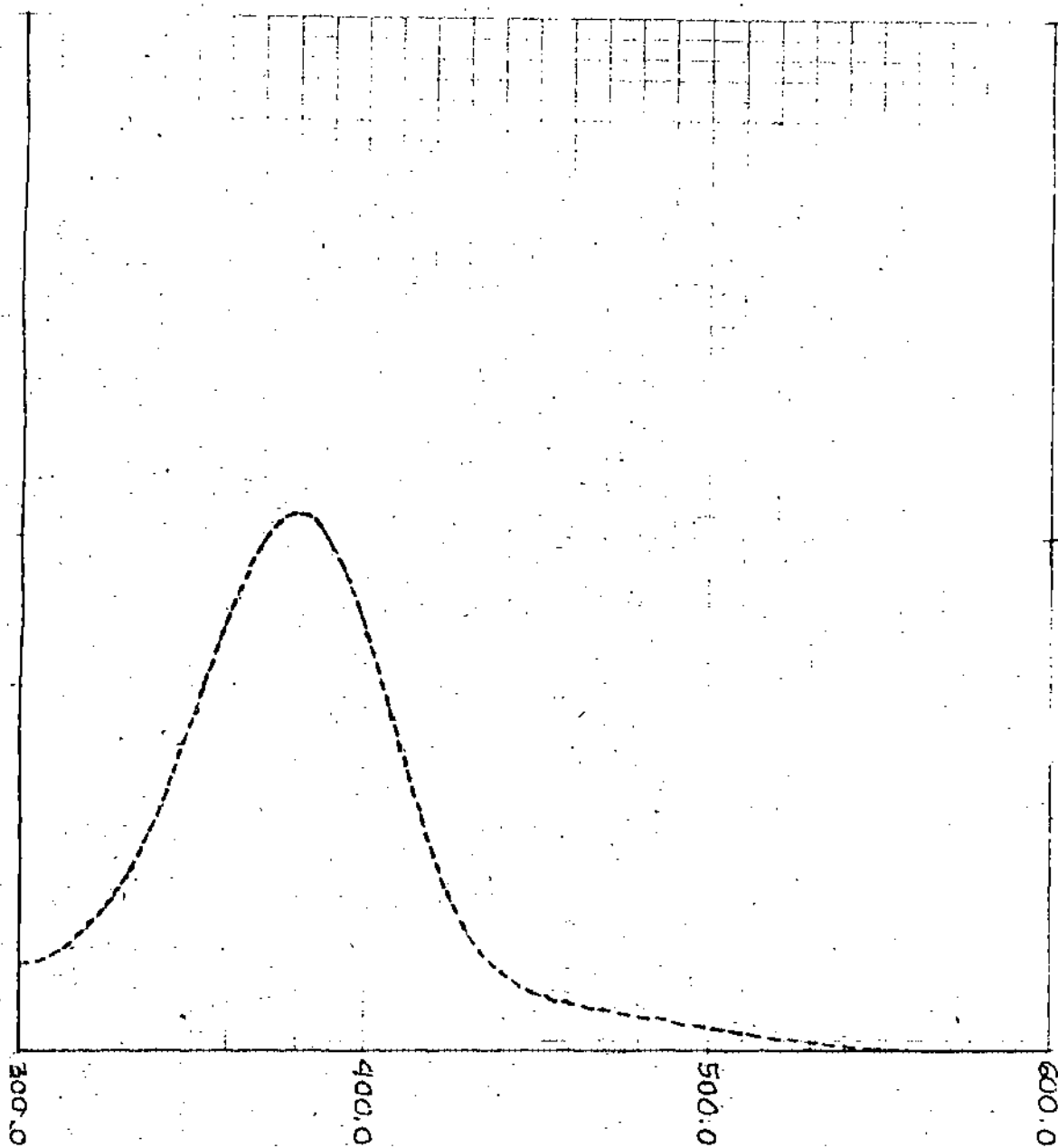


Figure - 19 Electronic absorption spectra of  $\text{Ph}_3\text{SnL}^{10}$  in Benzene : -----



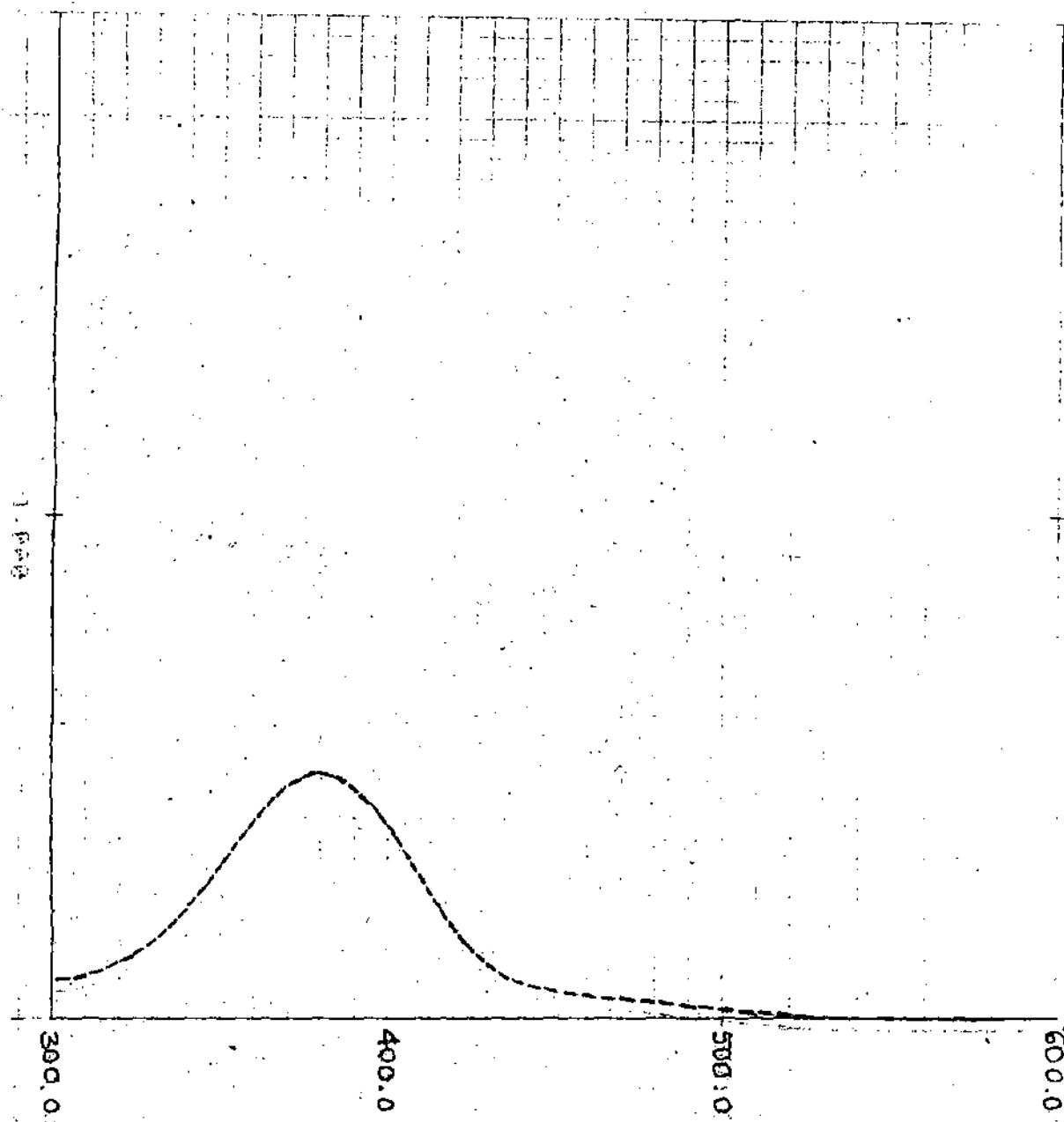


Figure - 20 Electronic absorption spectra of  $\text{Cy}_3\text{SnL}^{10}$  in Benzene :-----

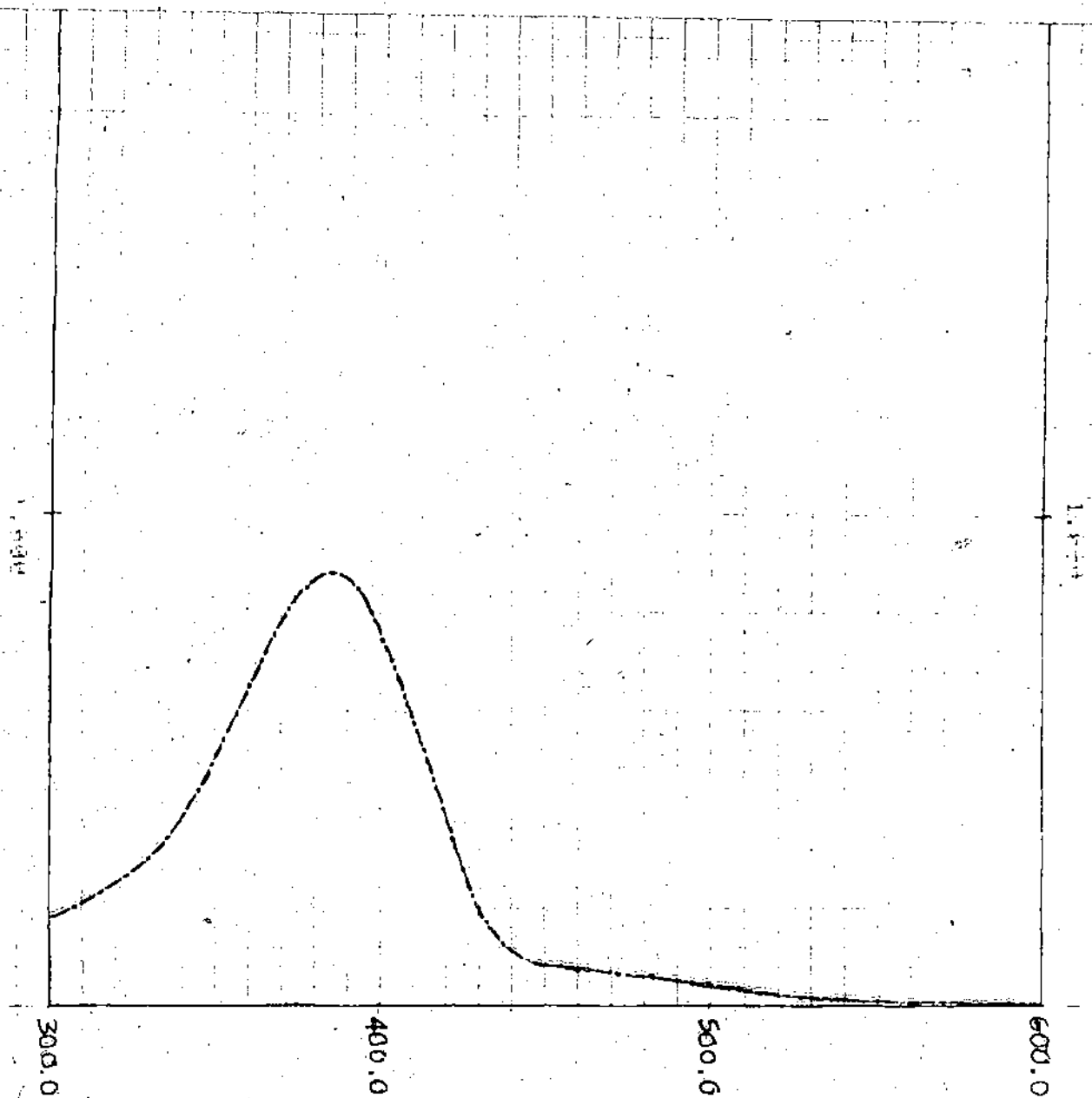


Figure - 21

Electronic absorption spectra of  
 $\text{Bu}_3\text{SnLi}^{10}$  in Benzene

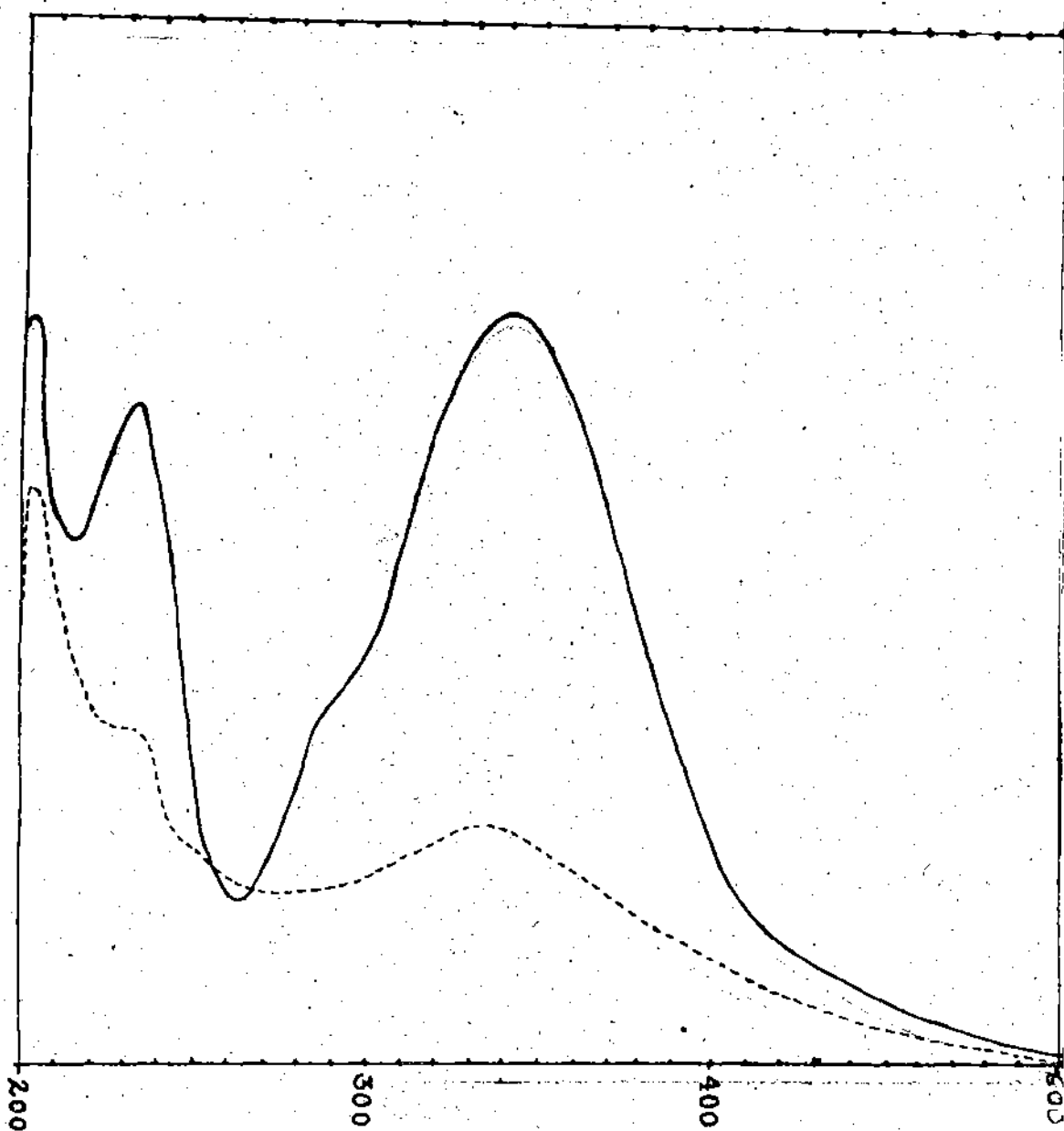


Figure - 22 Electronic absorption spectra of

(a)  $L^I H$  in Methanol: —

(b)  $PhL^I Sn(OH)_2$  in Methanol: - - -

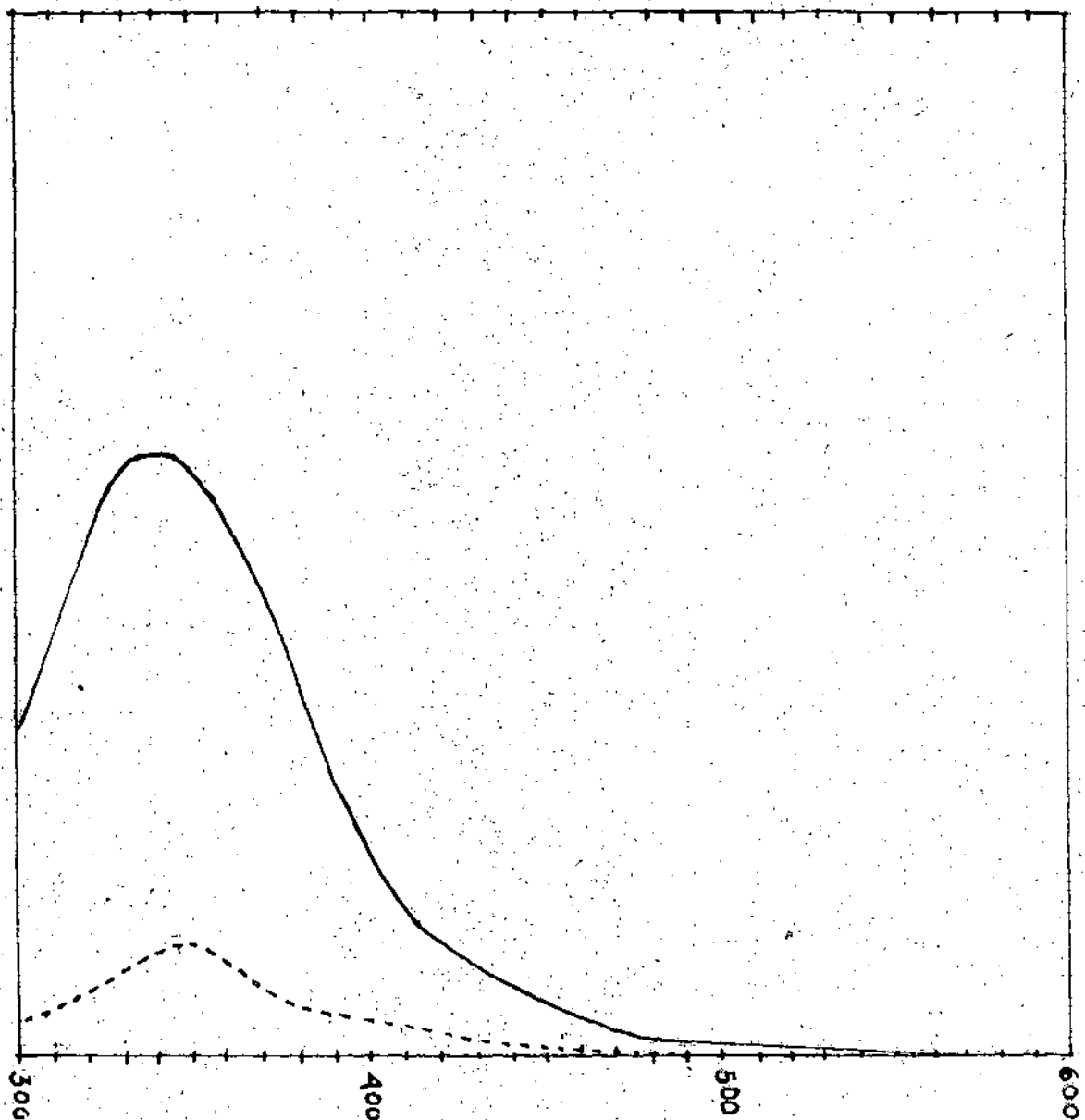


Figure - 23 Electronic absorption spectra of

(a)  $L^1H$  in Benzene : —————

(b)  $PhL^1Sn(CH_3)_3$  in Benzene : - - - - -

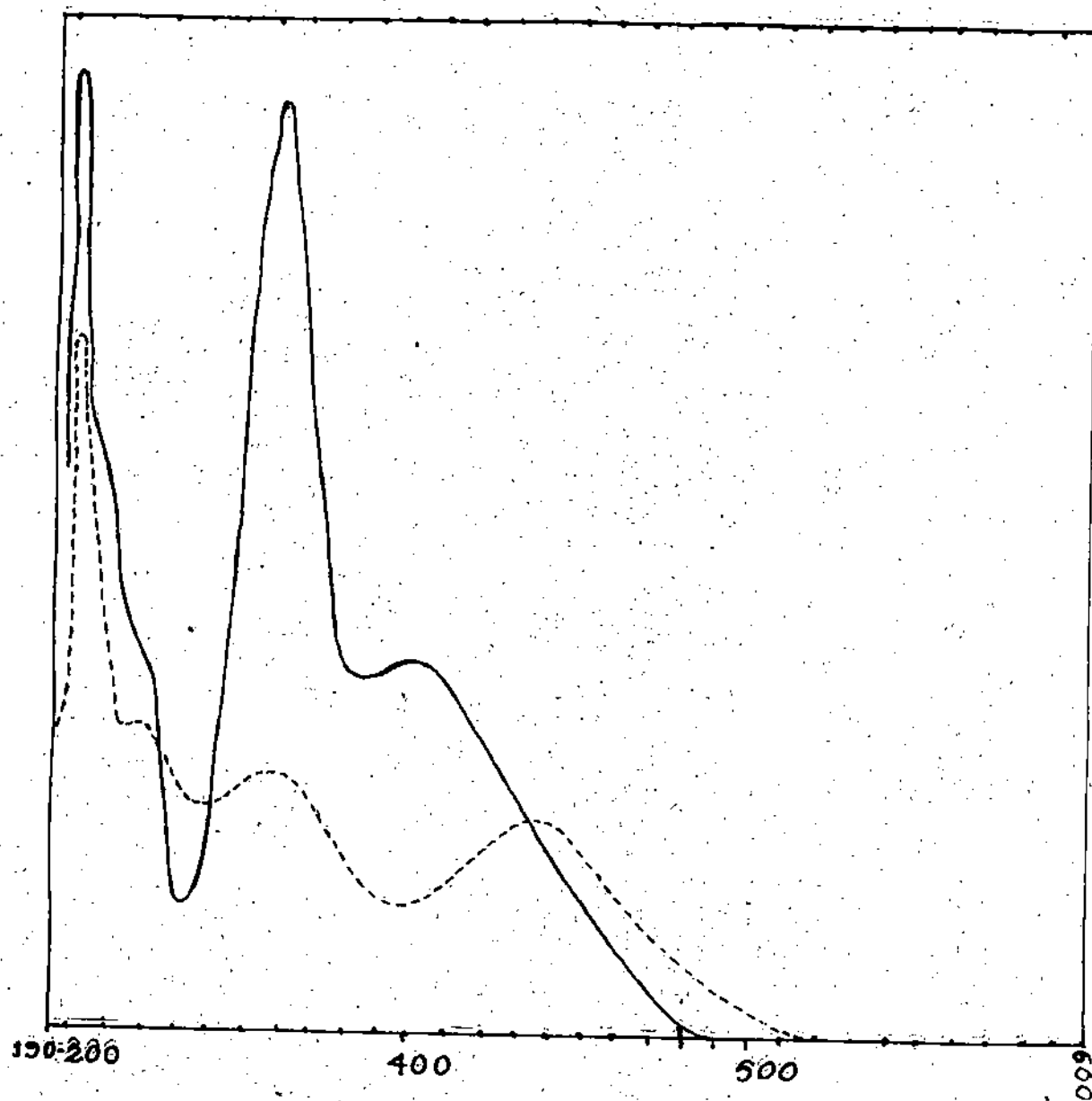


Figure - 24 Electronic absorption spectra of

(a)  $L_2H$  in Methanol : —————

(b)  $PhL_2Sn(CH_3)_2$  in Methanol : - - - - -

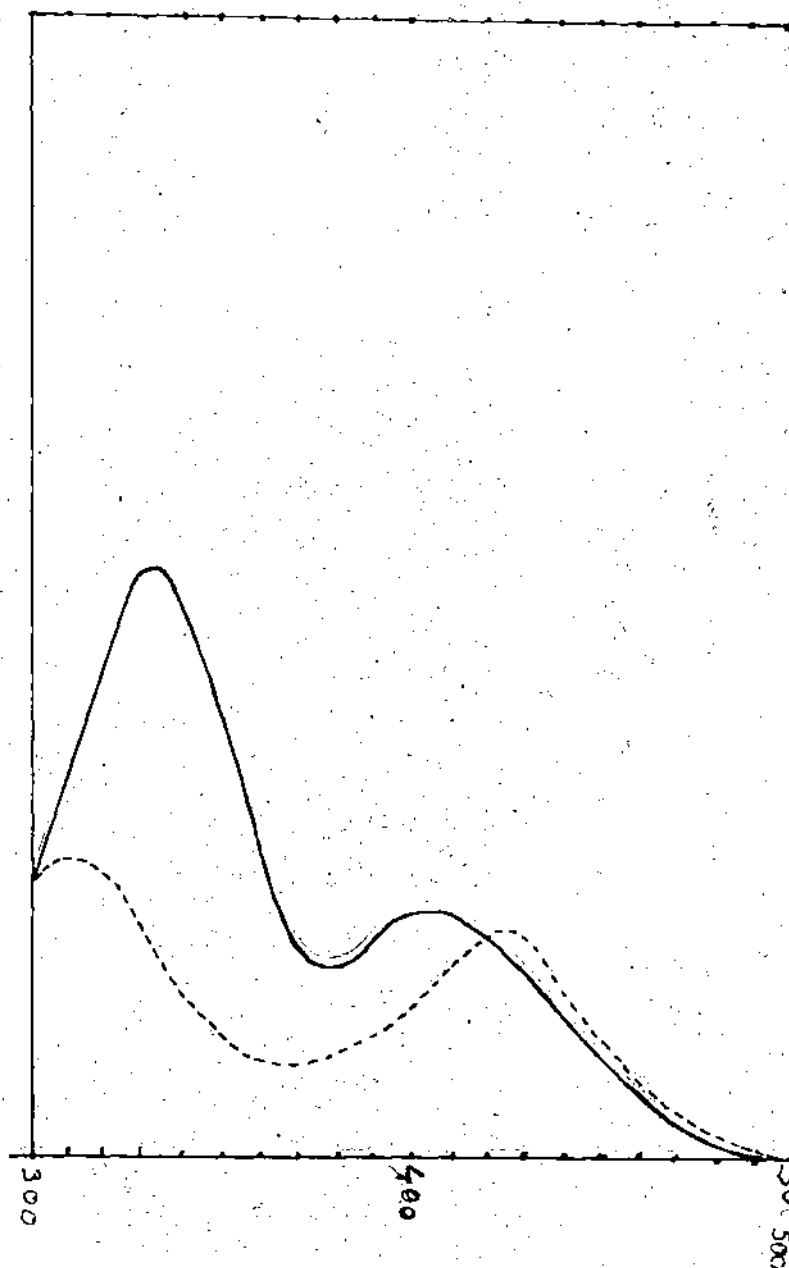


Figure - 25

Electronic absorption spectra of

(a)  $L^2H$  in Benzene : —————

(b)  $PhL^2Sn(OH)_2$  in Benzene : - - - - -

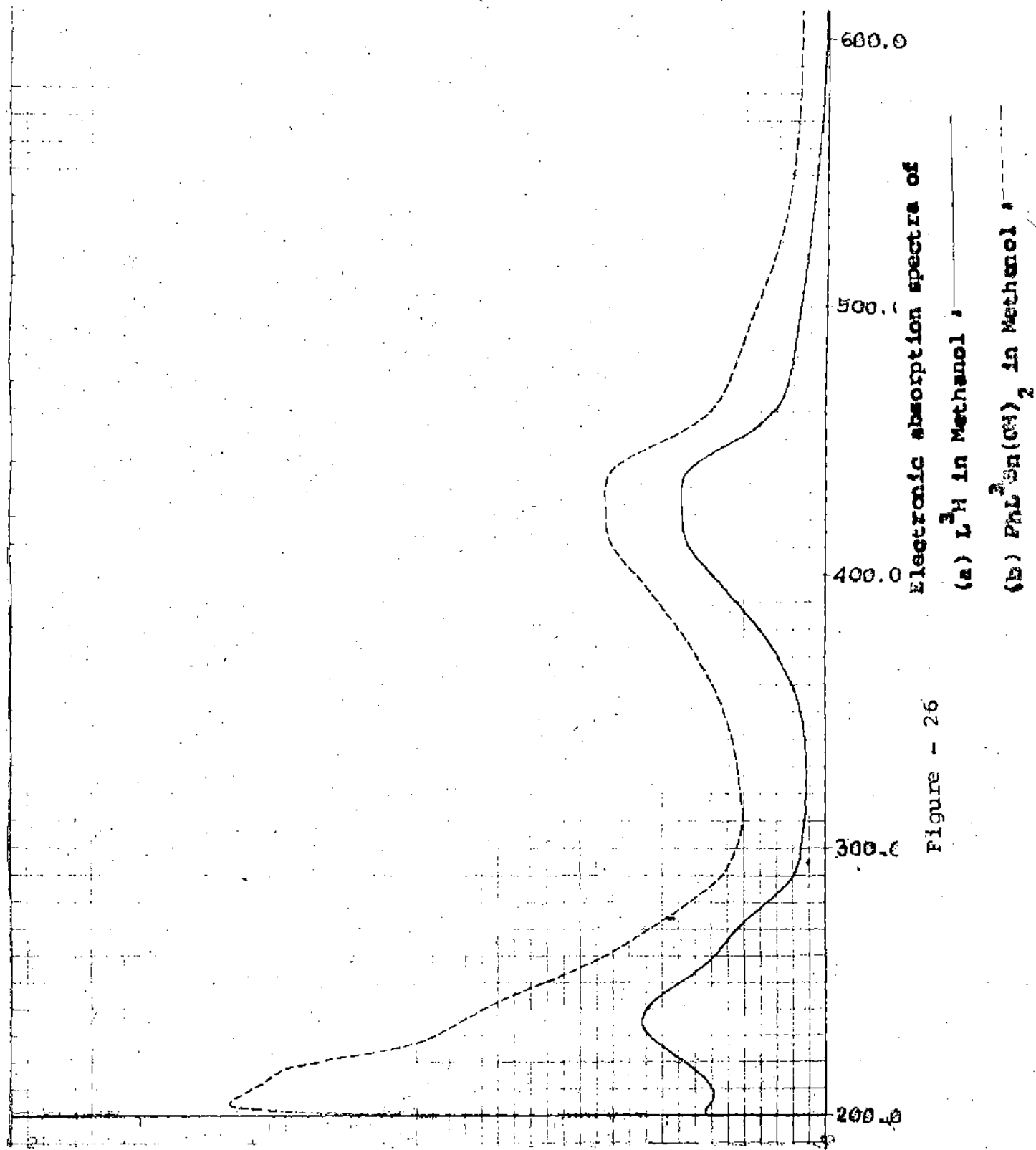
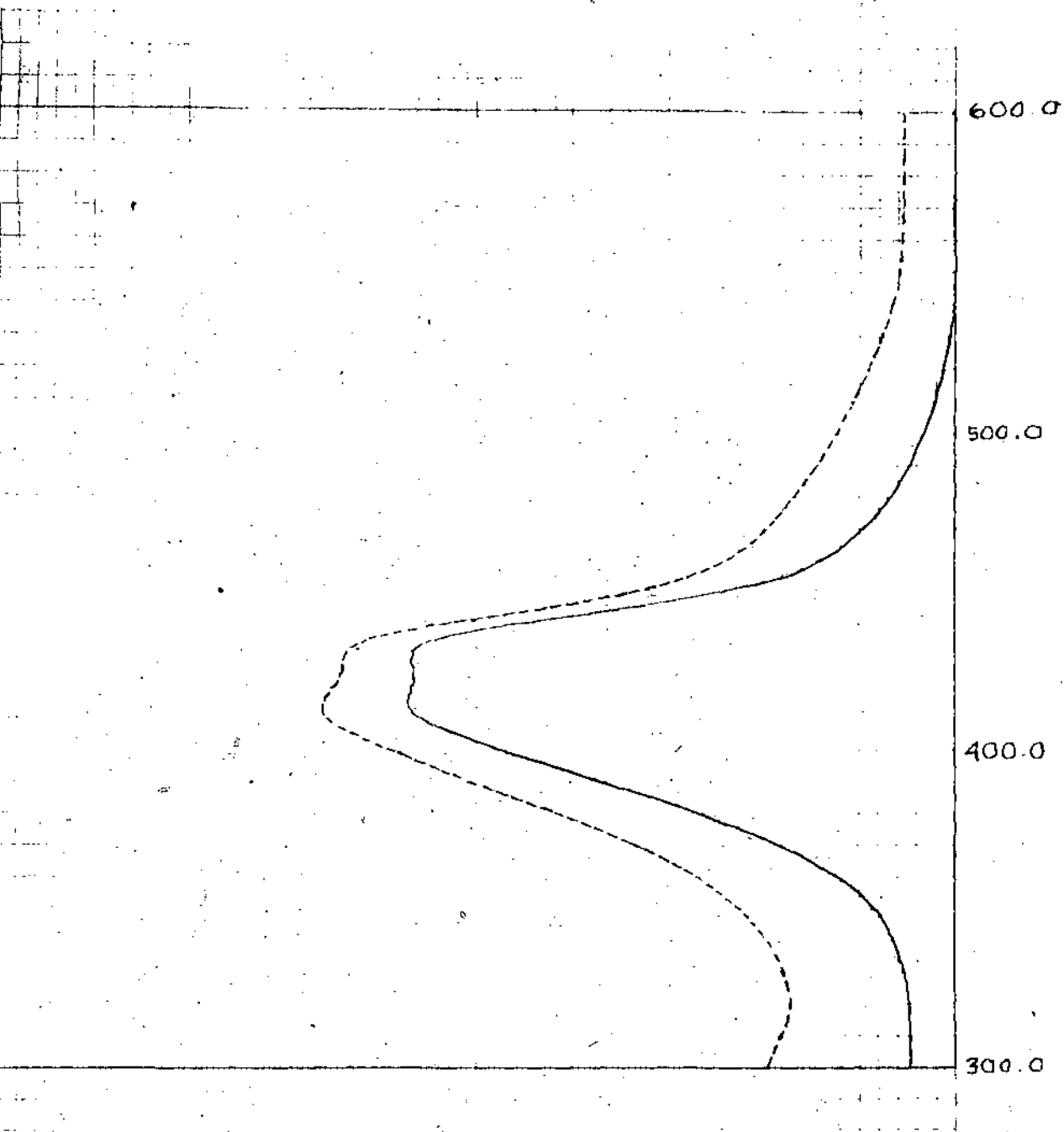


Figure - 26



Electronic absorption spectra of

Figure - 27

(a)  $L^3H$  in Benzene : —

(b)  $PhL^3Sn(OH)_2$  in Benzene : - - -



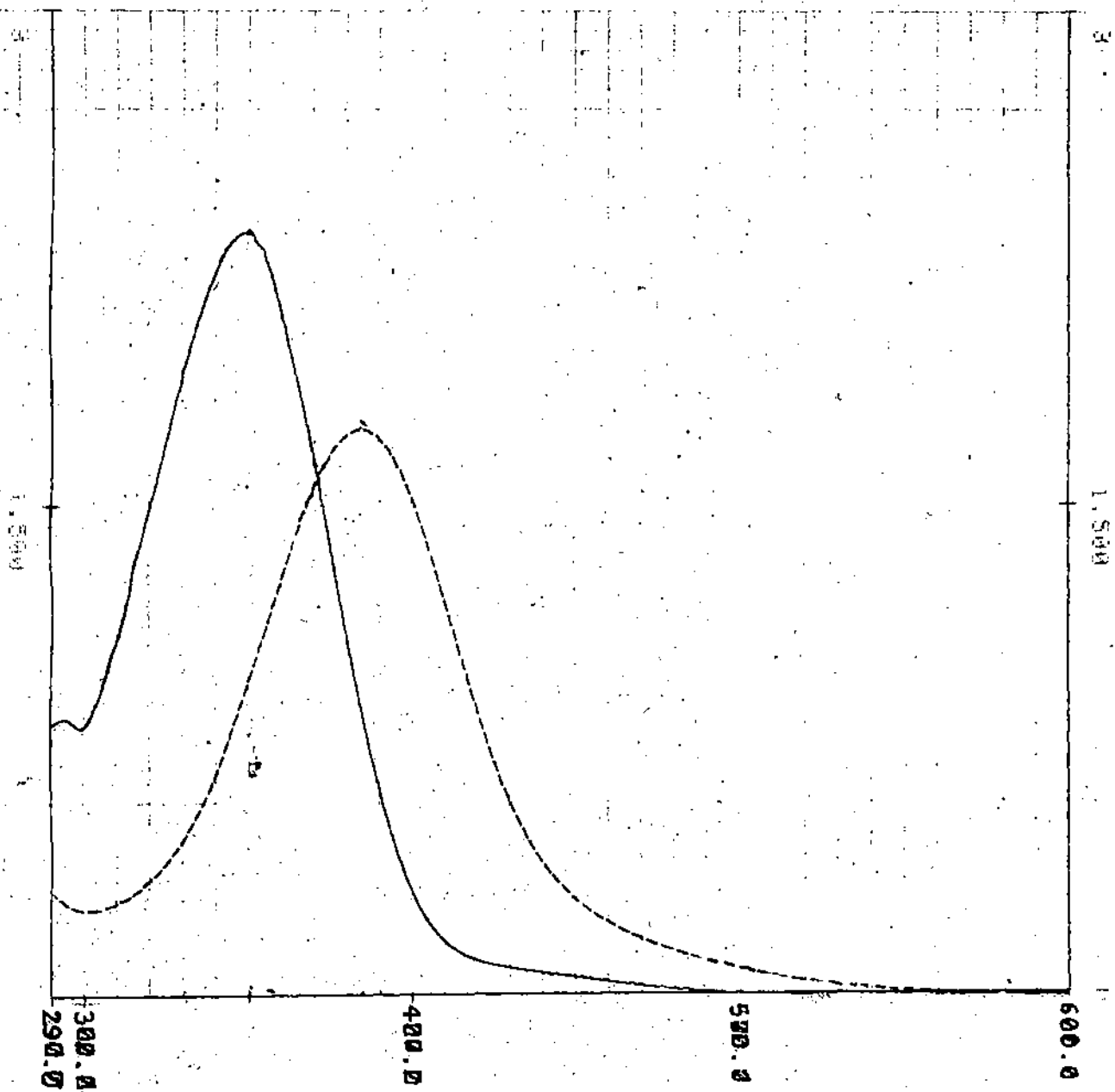


Figure - 28

Electronic absorption spectra of

(a) L<sup>4</sup>H in Methanol : —————

(b) L<sup>6</sup>H in Methanol : - - - - -

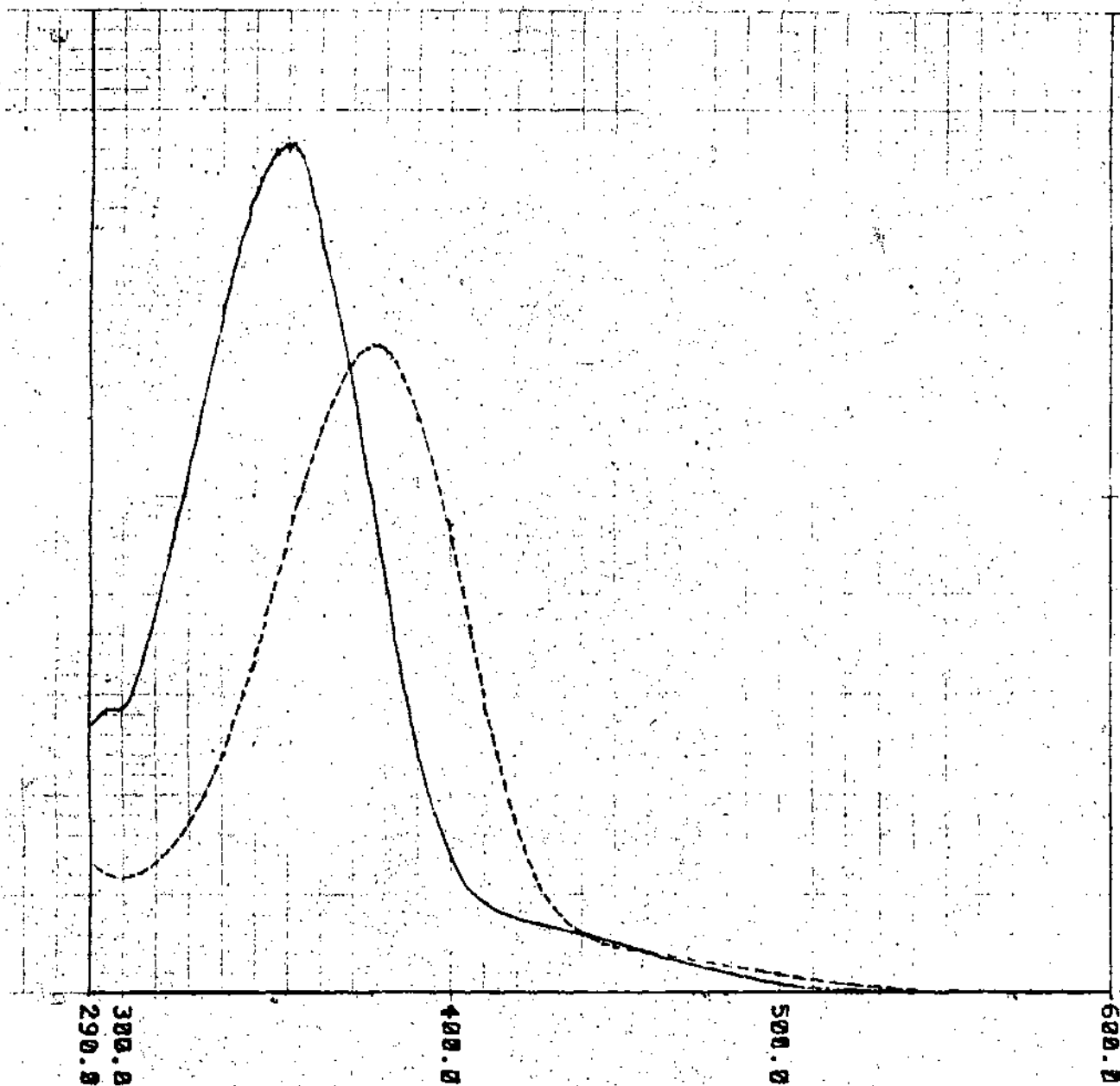
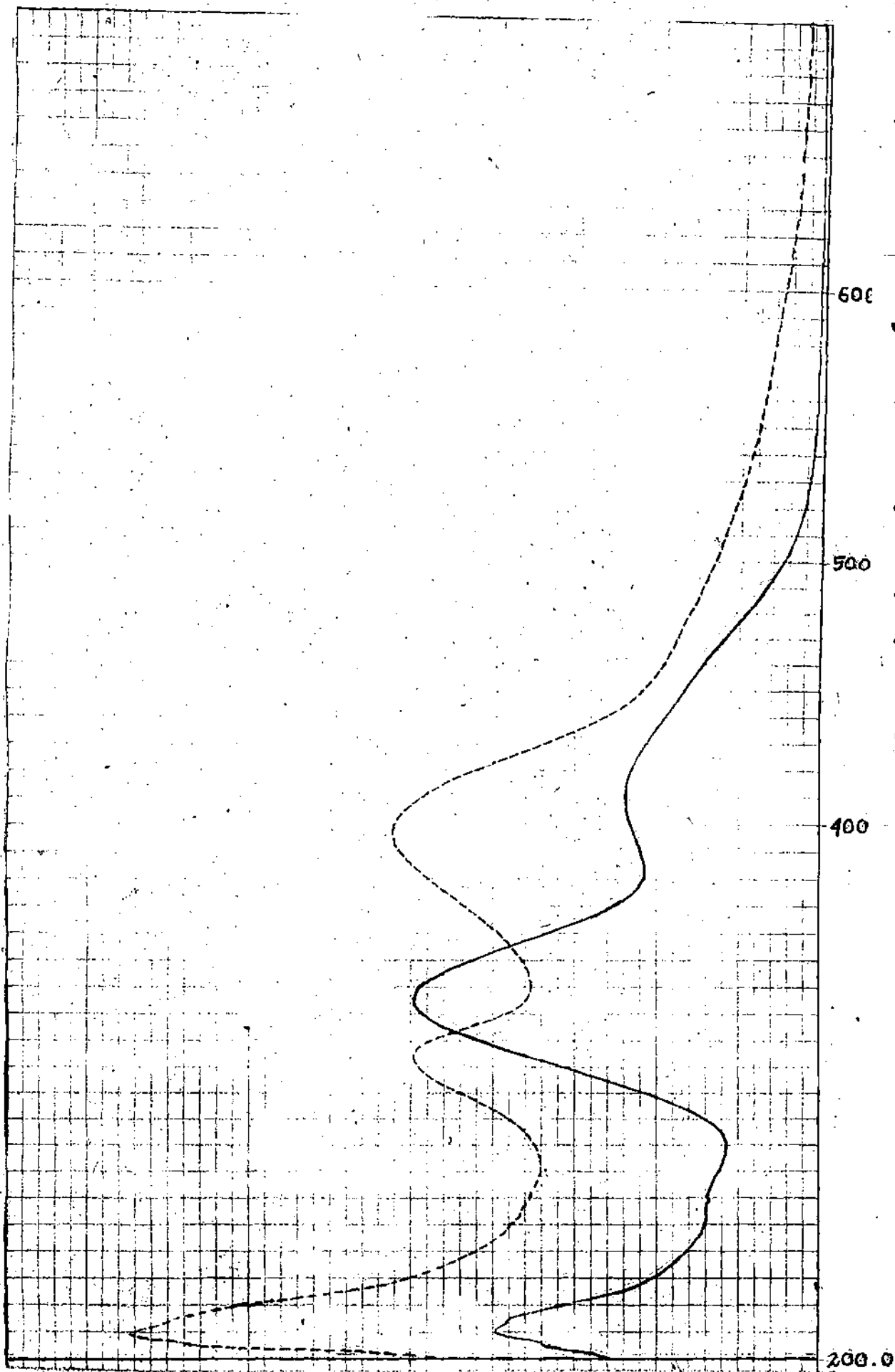


Figure - 29

Electronic absorption spectra of

(a)  $L^4H$  in benzene : \_\_\_\_\_

(b)  $L^4H$  in benzene : \_\_\_\_\_



Electronic absorption spectra of

Figure - 30

(a)  $L^3H$  in Methanol : —

(b)  $PhL^3Sn(OH)_2$  in Methanol : - - -

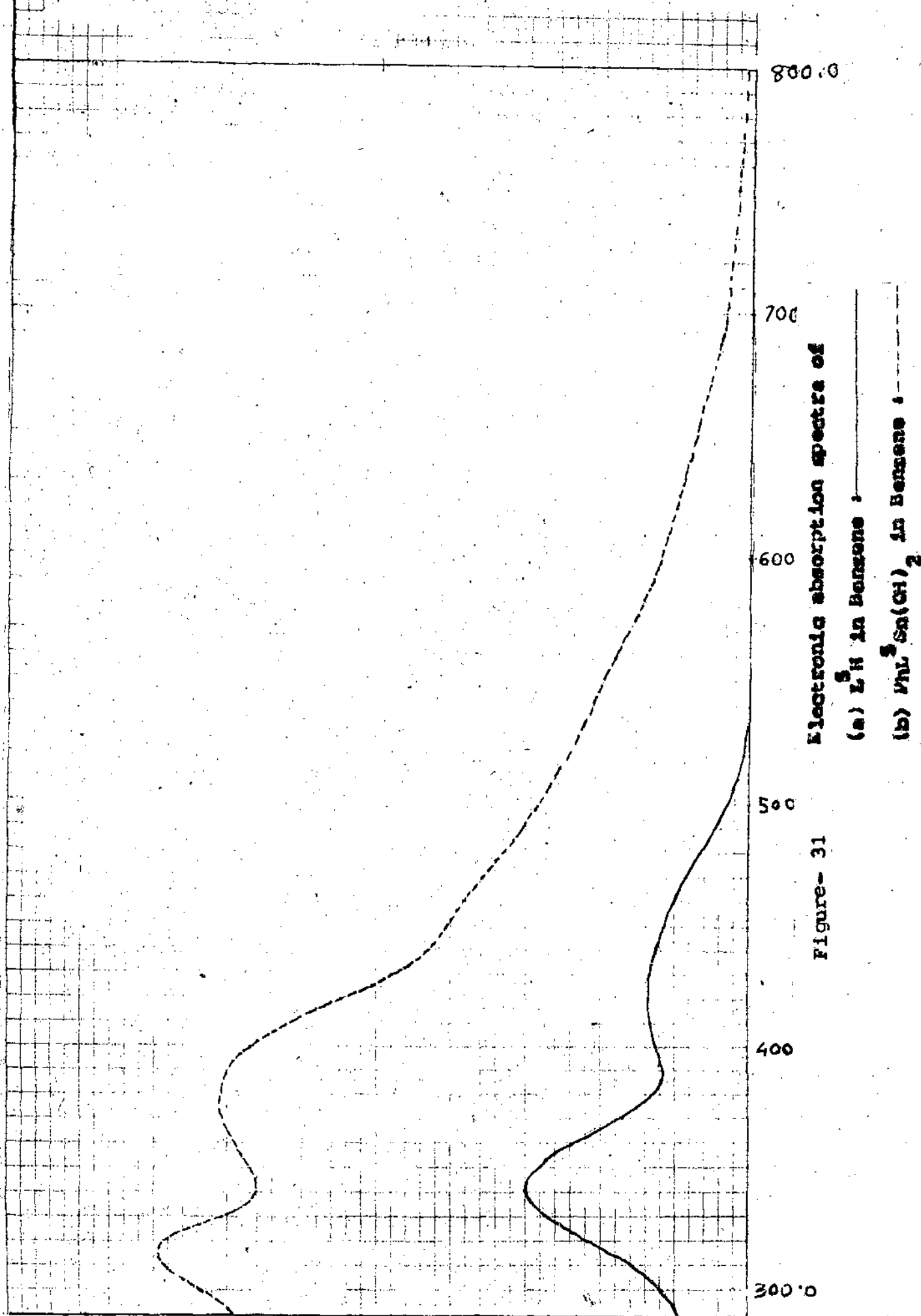


Figure- 31

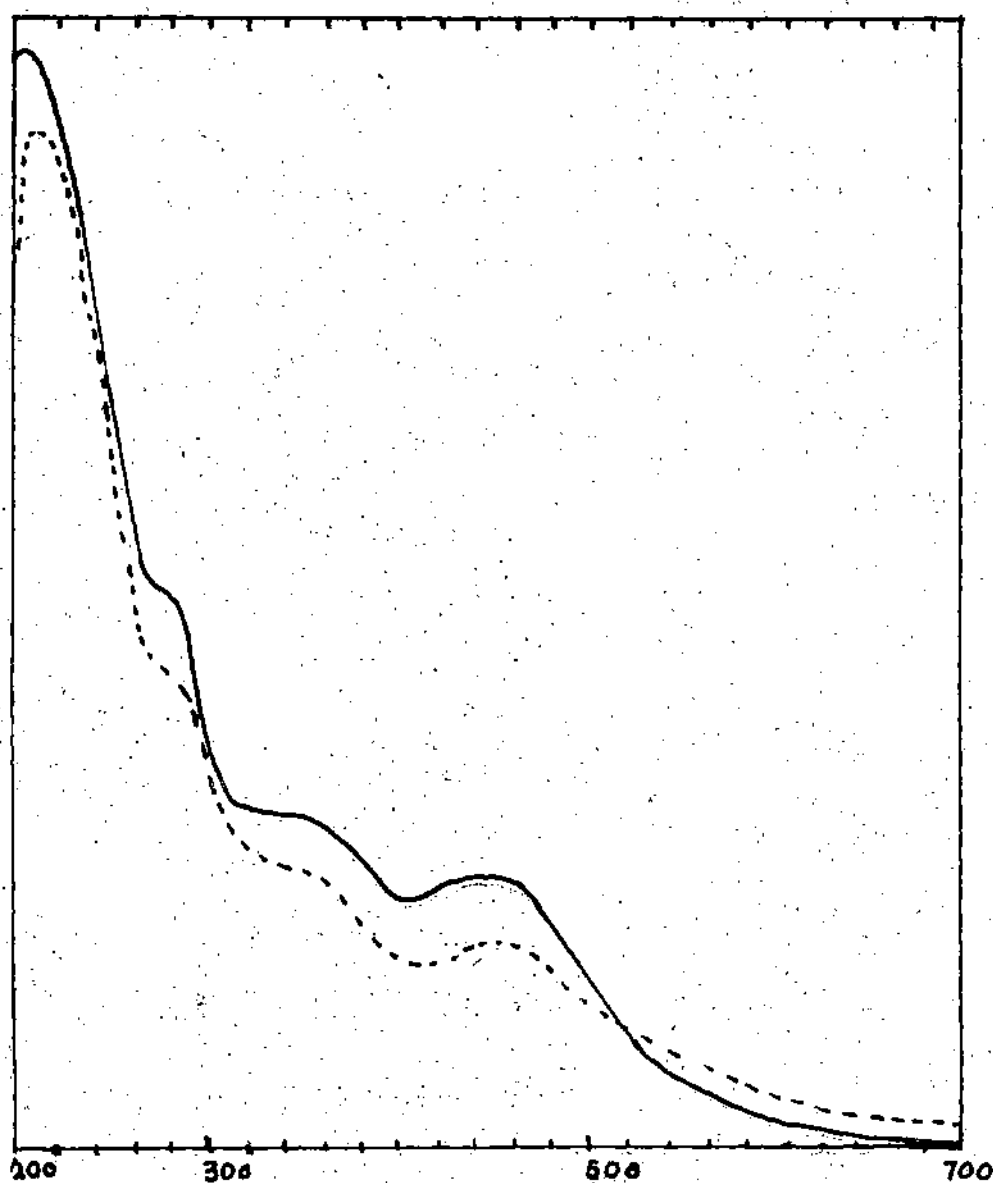


Figure - 32

Electronic absorption spectra of

(a)  $L^7H$  in Methanol : —————

(b)  $PhL^7Sn(CH_3)_2$  in Methanol : - - - - -

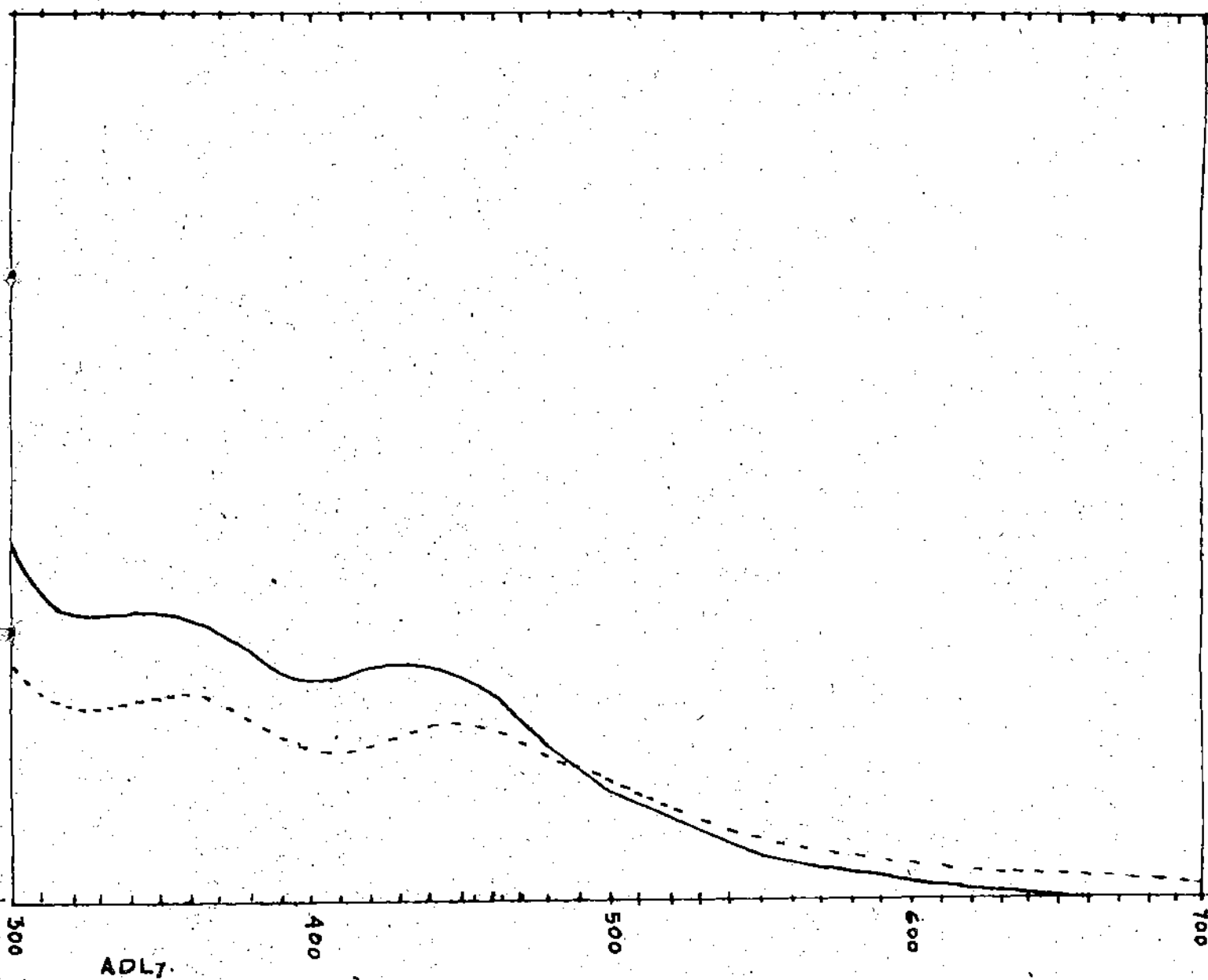


Figure - 33

Electronic absorption spectra of

(a)  $L^7H$  in Benzene : \_\_\_\_\_

(b)  $PhL^7H$  in Benzene : \_\_\_\_\_

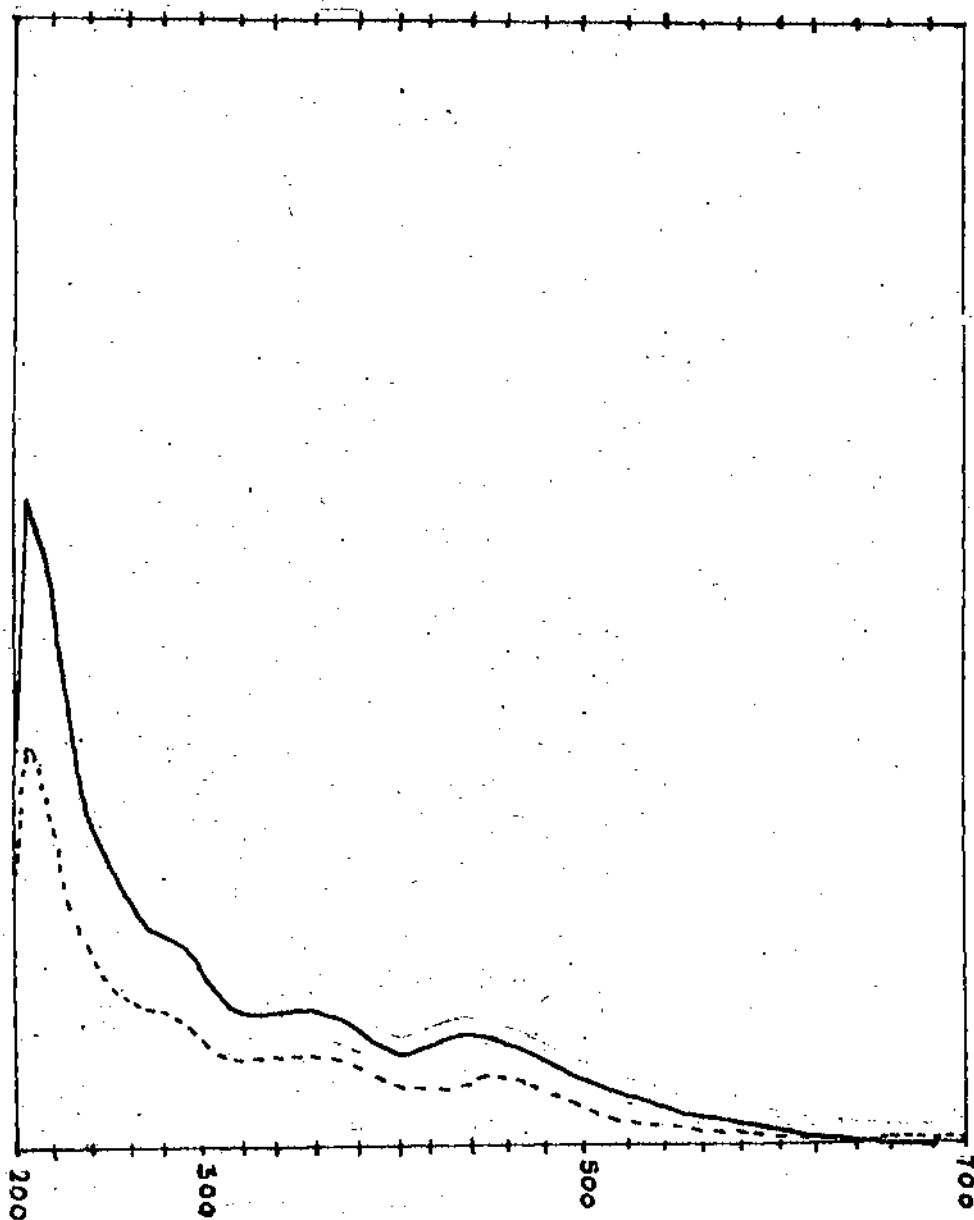


Figure - 34

Electronic absorption spectra of

(a)  $L^7H$  in Methanol : —————

(b)  $BuLi^7Sn(OH)_2$  in Methanol : - - - - -

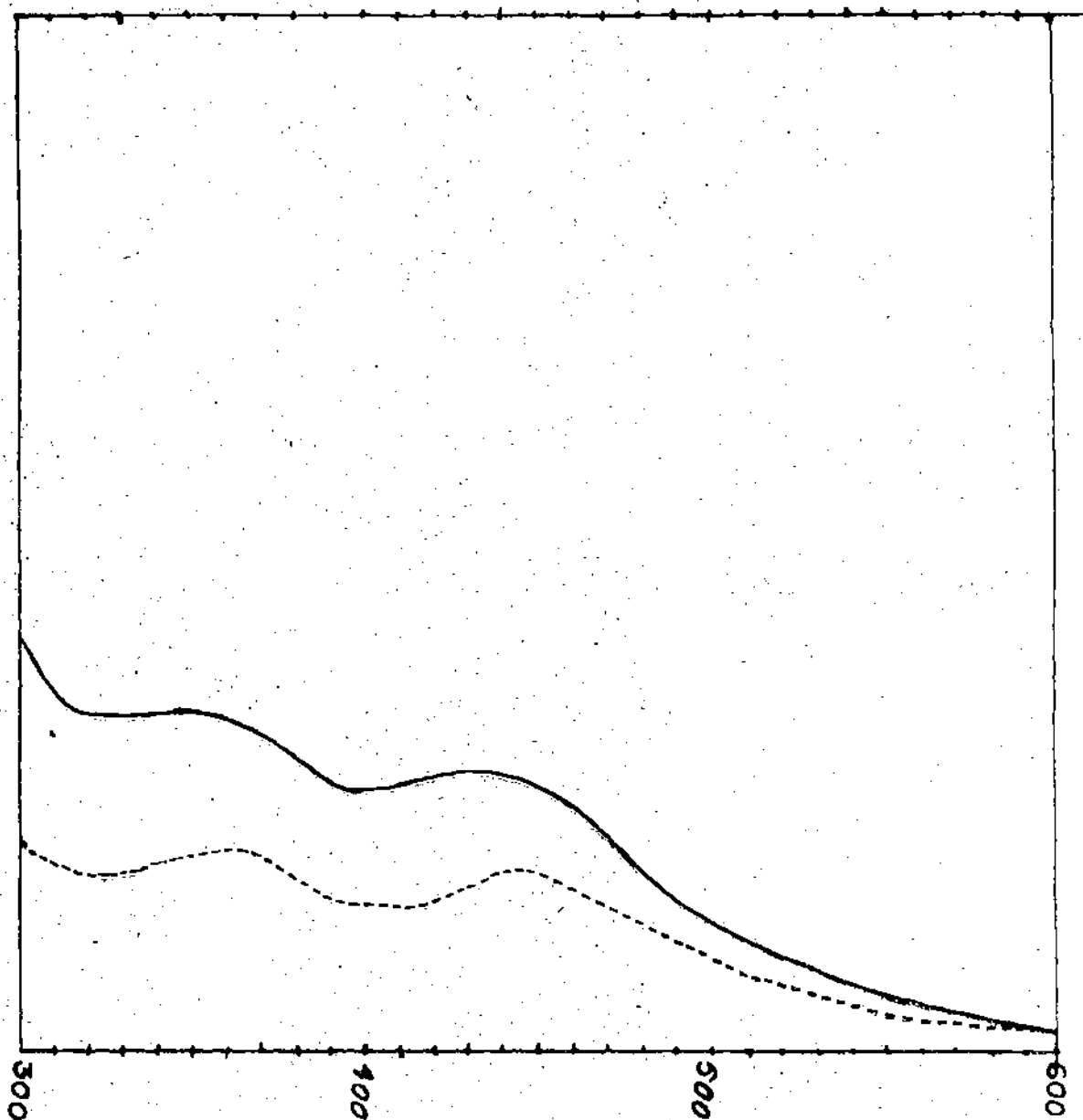


Figure - 35

Electronic absorption spectra of

(a)  $\text{L'H}$  in Benzene : \_\_\_\_\_

(b)  $\text{BuLi}^7\text{Sn}(\text{CH}_3)_2$  in Benzene : \_\_\_\_\_



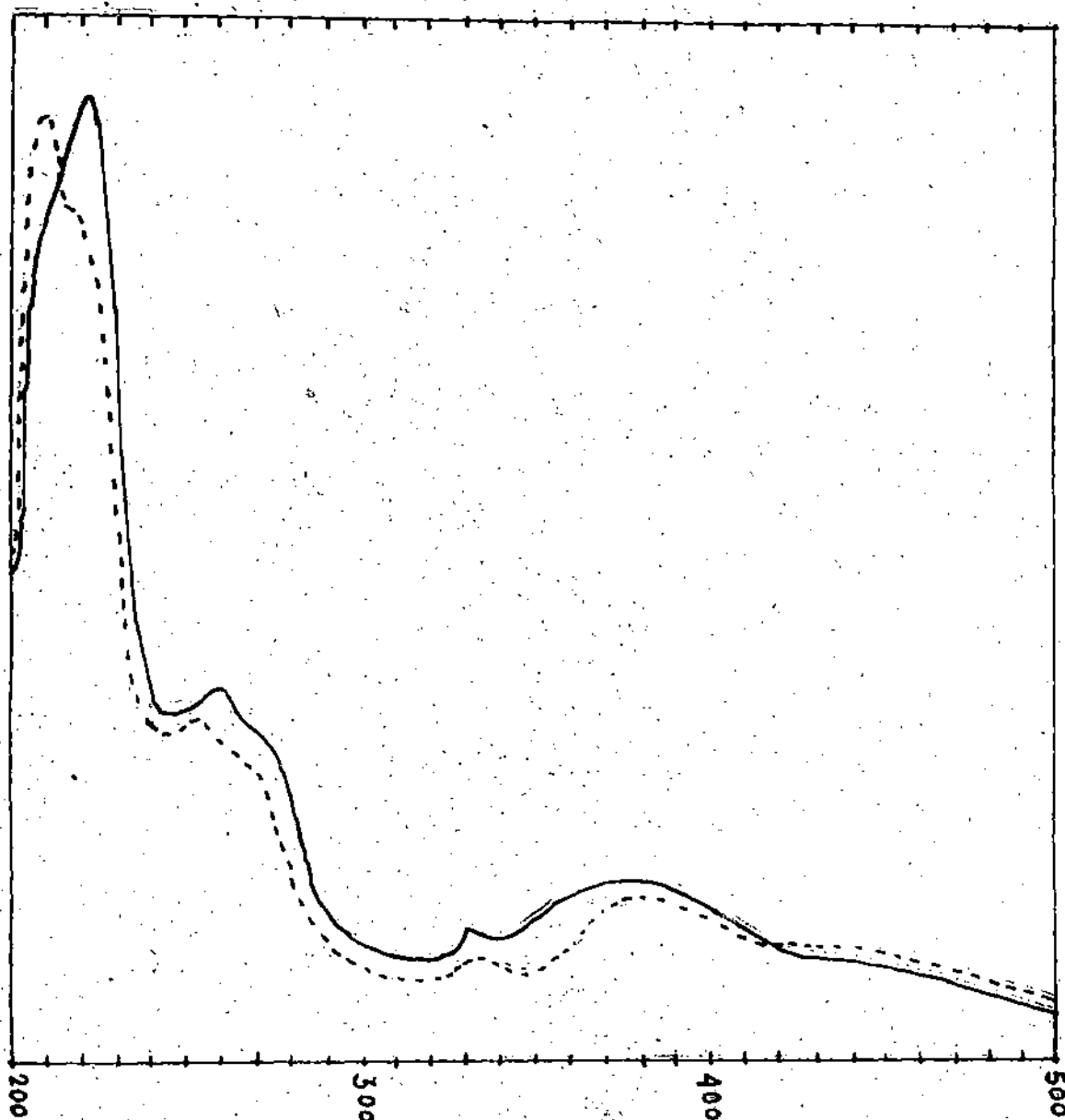


Figure - 36

Electronic absorption spectra of

(a)  $L^D$  in Methanol : ———

(b)  $PhL^D Sn(OH)_2$  in Methanol : - - -

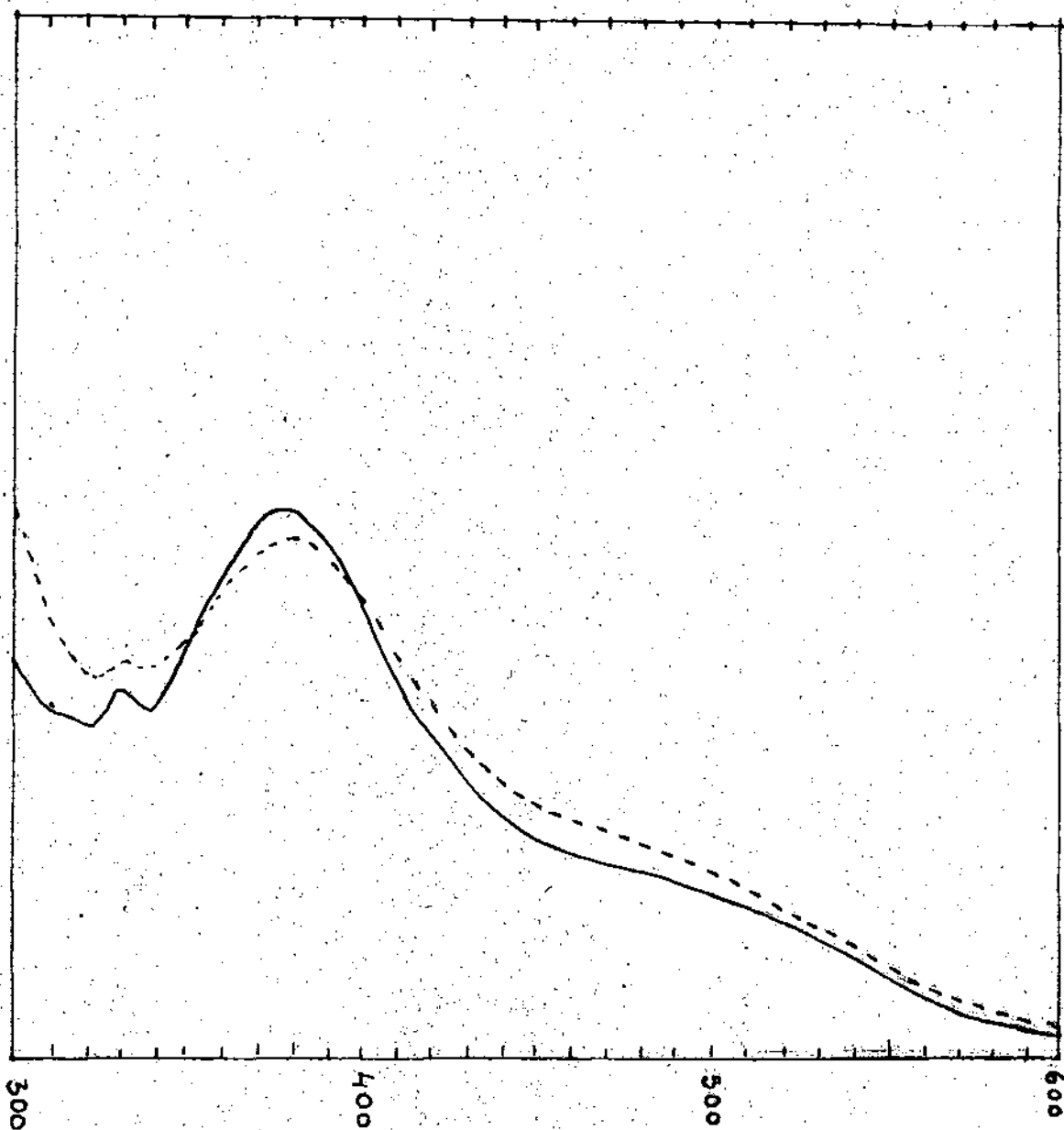


Figure - 37

Electronic absorption spectra of

(a)  $L^9M$  in Benzene : —————

(b)  $PhL^9Sn(OH)_2$  in Benzene : - - - - -

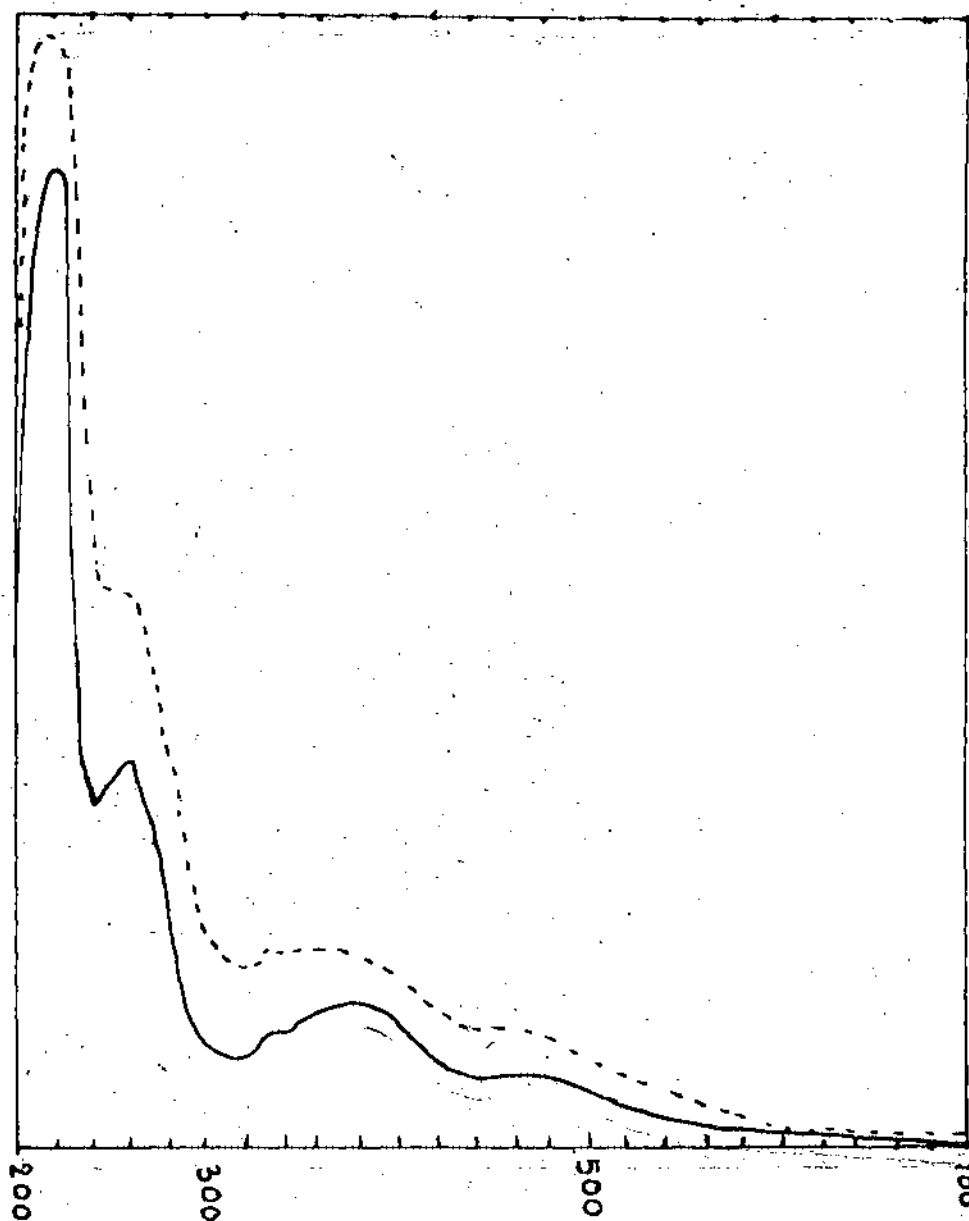


Figure - 38

Electronic absorption spectra of

(a)  $L^8H$  in Methanol: —

(b)  $Bul^9Sn(OH)_2$  in Methanol: - - -

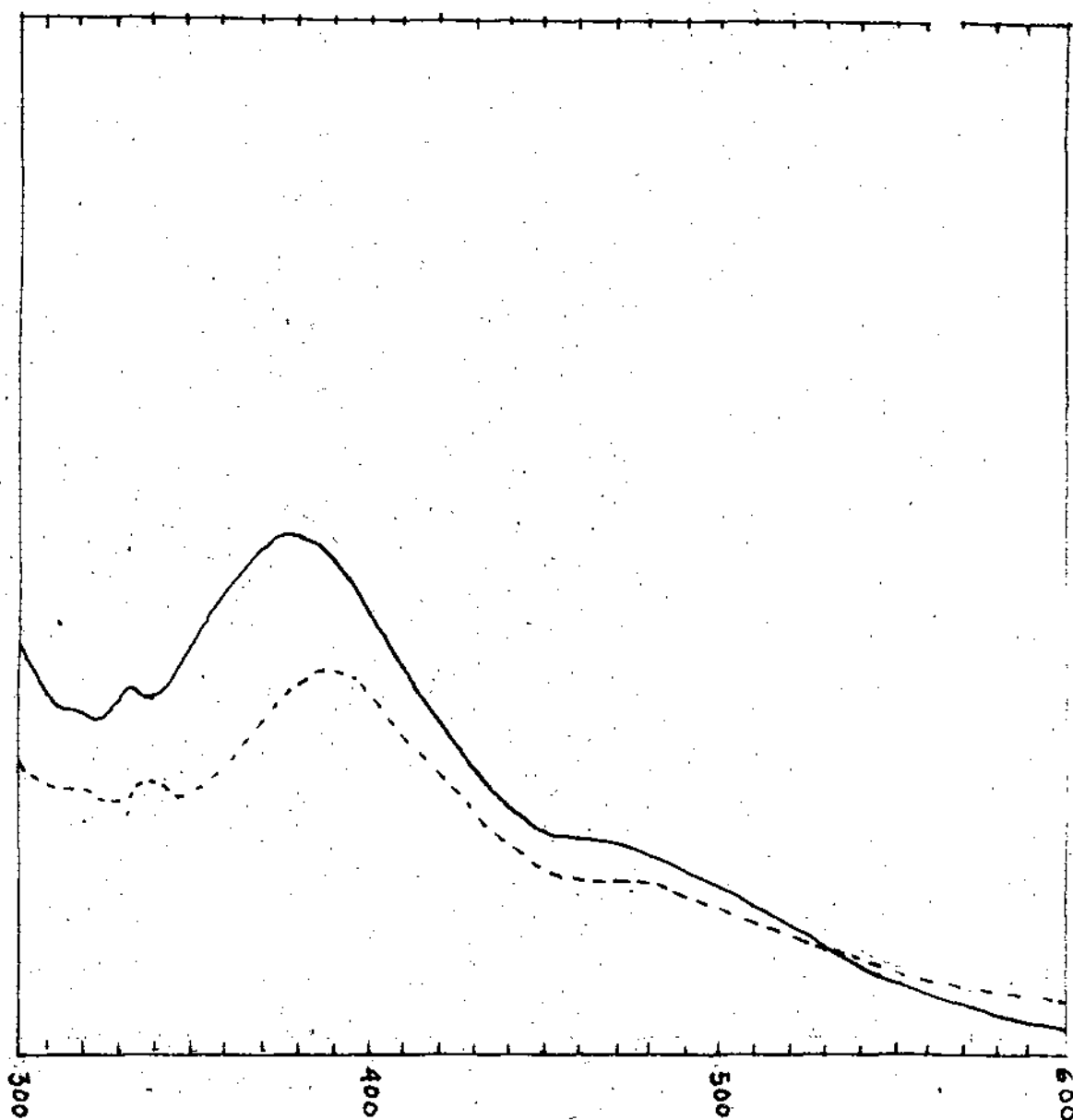


Figure - 39

Electronic absorption spectra of

(a)  $L^2H$  in Benzene : —————

(b)  $BuLi^2Sn(OH)_2$  in Benzene : - - - - -

The absorption spectra of the organotin derivatives are very similar to <sup>that</sup> of the corresponding ligand. While small bathochromic shifts are observed in the case of the derivatives of the ligands  $L^2H$  and  $L^5H$ , no significant shift of the absorption maxima is observed in other cases. This rules out the possibility of any coordination between the azo-N atom and the Sn atom.

#### IVB. Infrared Spectra

##### 2. General features

The IR spectra of the organotin arylazo phenoxy compounds are very complex. Though complete assignment of the absorption bands in these compounds is not possible, important structural information may be obtained from a qualitative assignment of bands due to Sn-O, Sn-OH, Sn-C and -N = N- stretching modes. Not all these modes could be identified with certainty because of the presence of strong absorptions due to the aryl groups in regions where these modes are expected. Before discussing the IR spectra of the different types of organotin-aryl-azo-phenoxy compounds, it would be therefore useful to discuss the main features of the IR spectra.

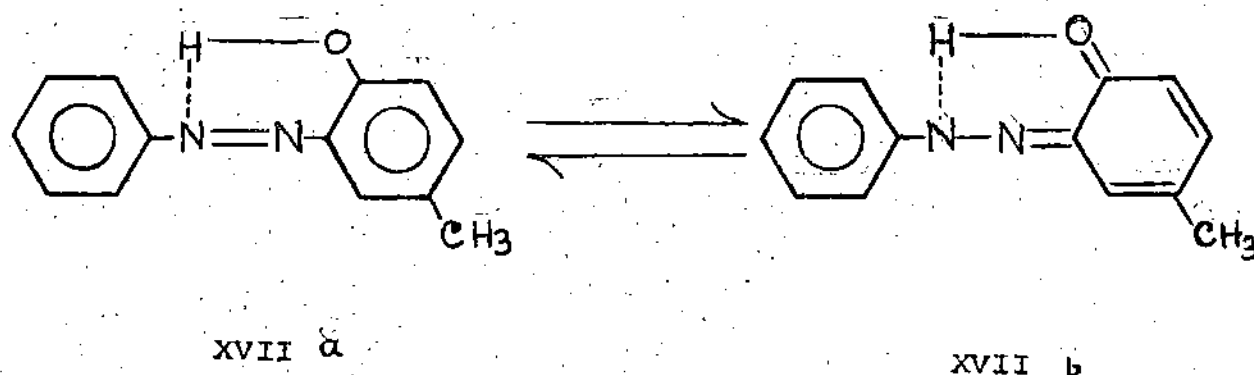
The main functional groups in the series of ligands include the -OH and -NO<sub>2</sub> group attached to the aromatic rings in addition to the -N = N- group. In the organotin derivatives, absorptions due to Sn-O and Sn-C stretch are also expected to be observed. Based on these considerations, the main features in the IR spectra of the aryl azo phenols and their organotin derivatives may be summarised as follows:

1) 3200-3600  $\text{cm}^{-1}$  Region

Absorption in this region is expected in the free ligands and the polymeric organotin derivatives formulated as  $\text{RLSn}(\text{OH})_2$ . The data in table-4 shows that almost all the compounds usually show a broad to very broad absorption in this region. The o-hydroxy compounds in general, have extremely broad absorption in these region as expected due to intramolecular H-bonding leading to azo-hydrazone tautomeric equilibrium<sup>28,33,35,40-43,60</sup>. This is in keeping with the two long wave length absorption bands in their electronic spectra (Table 3). In some cases the bands are so broad (e.g.,  $\text{L}^5\text{H}$ ,  $\text{L}^7\text{H}$ ,  $\text{L}^9\text{H}$ ) that it is not possible to locate the absorption maxima with certainty. In such cases, the range is shown in the table 4. On the other hand, in the p-nitro-azo-phenols of the type  $\text{L}^6\text{H}$ ,  $\text{L}^8\text{H}$  and  $\text{L}^{10}\text{H}$  where the -OH group is in p-position thereby eliminating the possibility of intramolecular hydrogen bonding as well as intermolecular hydrogen bonding (due to electron withdrawal by the highly electronegative  $-\text{NO}_2$  group from the -OH group), relatively sharp absorption around  $\sim 3500 \text{ cm}^{-1}$  is observed. However, in  $\text{L}^4\text{H}$ , where the p-nitro group is absent, the  $\nu(\text{OH})$  occurs at a considerably lower wave length of  $3200 \text{ cm}^{-1}$  indicating the presence of intermolecular H-bonds in such cases.

Compounds with two -OH groups, e.g.,  $\text{L}^3\text{H}$ ,  $\text{L}^7\text{H}$  and  $\text{L}^9\text{H}$ , either exhibit two absorptions (as in case of  $\text{L}^3\text{H}$ ) or a very broad absorption band ( $\text{L}^7\text{H}$ ,  $\text{L}^9\text{H}$  etc).

An interesting feature is observed in  $L^1H$  which shows a very strong and broad absorption at  $3450\text{ cm}^{-1}$  in addition to another medium intensity band  $3200\text{ cm}^{-1}$ . This may be due to the presence of both the azo and hydrazone forms in equilibrium even in the solid phase:



The N-H stretch of the hydrazone form is expected to absorb in the region of  $3200\text{ cm}^{-1}$ .

b)  $1300\text{--}1500\text{ cm}^{-1}$  region.

The  $\text{-N}=\text{N-}$  stretch and the symmetric and asymmetric  $\text{NO}_2$  stretches are expected to occur in this region. Although a number of workers have attempted to identify and correlate the  $\text{-N}=\text{N-}$  stretch in azo compounds, Miller<sup>32</sup> has emphasised the absence of any diagnostically useful band in this region. Since aromatic groups have strong absorption in the same region, it is often difficult to locate the  $\text{-N}=\text{N-}$  stretch absorption, particularly, in view of the low intensity of absorption due to  $\text{-N}=\text{N-}$  stretch. In the present work, it has not been possible to identify the  $\text{-N}=\text{N-}$  stretch in

the IR spectra with any degree of certainty. As such, the  $-N = N-$  stretch has not been included in the table.

In the nitro compounds the absorptions due to symmetric and asymmetric NO stretches occur in this region<sup>28,29-33,38,39,44</sup>.

The symmetric NO stretch is found in the present series of ligands as a strong absorption between  $1320-1340\text{ cm}^{-1}$ . On the other hand, the asymmetric stretch, expected to occur in  $1500-1530\text{ cm}^{-1}$  region<sup>28,33,40-44</sup>.

The symmetric NO stretch is found in the present series of ligands as a strong absorption between  $1320-1340\text{ cm}^{-1}$ . On the other hand, the asymmetric stretch, expected to occur in  $1500-1530\text{ cm}^{-1}$  region<sup>28,33,40-44</sup> being close to the characteristic aromatic ring vibration around  $1500\text{ cm}^{-1}$  can be seen as a separate band only in few compounds (e.g.,  $L^6H$ ,  $L^{10}H$  and the corresponding organotin compounds) while in the other cases the band occurs as hump or shoulder at  $\sim 1500\text{ cm}^{-1}$  overlapped by the aromatic absorption at the same region.

#### c) $1100-1300\text{ cm}^{-1}$ region

This region is of interest in the present series of compounds because the C-O stretch of the phenol is expected to give rise to a strong absorption in this region. Since this band represent C-O stretch which interact with the OH deformation to some extent, one would expect a shift in the absorption in the organotin derivatives. The data in table-4 show that this absorption occurs in  $1200-1280\text{ cm}^{-1}$ .

#### d) $450-700\text{ cm}^{-1}$ region.



Both  $\nu(\text{Sn-O})$  and  $\nu(\text{Sn-C})$  are expected in this region <sup>28,29,33,39-42,60</sup>.  $\nu(\text{Sn-C})$  is probably very weak in these compounds since comparison with the ligand spectra showed no new bands attributable to  $\nu(\text{Sn-C})$ . On the other hand, new absorption bands are found in the  $\nu 550-650 \text{ cm}^{-1}$  region. The position, intensity as well as the shape of the bands are very similar to those found for Sn-O stretch in organotin compounds containing Sn-O <sup>28,29-34,36,37,43,45-66,69</sup>.

## 2.1. Results and Discussion

A glance at the table - 4 and the IR spectra shows that the triorganotin derivatives of the type  $\text{R}_3\text{SnL}$  formed by the ligands  $\text{L}^8\text{H}$  and  $\text{L}^{10}\text{H}$  are characterised by a small shift of the  $\nu(\text{C-O})$  towards lower frequency, the occurrence of a new band around  $570-600 \text{ cm}^{-1}$  attributable to  $\nu(\text{Sn-O})$  and the absence of the  $\nu(\text{OH})$  absorption of the parent ligand. These observations confirm the formulation of the compounds as  $\text{R}_3\text{SnL}$ . The frequencies due to the  $-\text{NO}_2$  group are almost unaffected in the organotin derivatives, a slight lowering of  $\nu_{\text{as}}(\text{NO}_2)$  occurs in some cases. However, because of the overlapping with the aromatic ring absorption in this region, the peak positions could not be ascertained in all cases. A small lowering of the  $\text{NO}_2$  stretch is, however, expected since the large polarity of the Sn-O bond ( $\text{Sn}^{\delta+} - \text{O}^{\delta-}$ ) will tend to increase the contribution of the resonating form of the type as follows:

Table - 4

Characteristic IR absorptions (in  $\text{cm}^{-1}$ ) in the ligands and their organotin derivatives

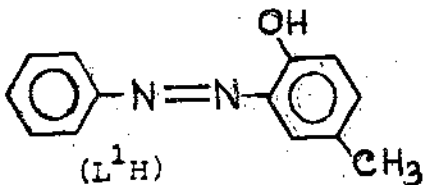
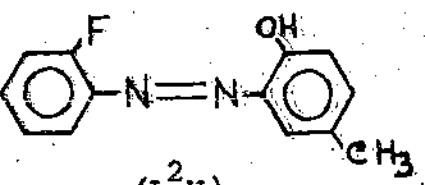
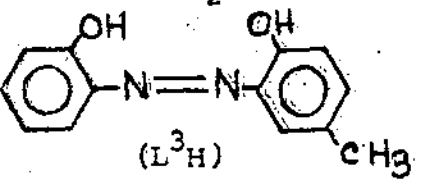
Compounds	$\nu(\text{O-H})$	$\nu_{\text{as}}(\text{NO}_2)$	$\nu_{\text{s}}(\text{NO}_2)$	$\nu(\text{C-O})$	$\nu(\text{Sn-O})$
1.  (L <sup>1</sup> H)	3450(br) 3200(m)	-	-	1250	-
2. $\text{PhL}^1\text{Sn}(\text{OH})_2$	3430(br)	-	-	1250	560(s)
3.  (L <sup>2</sup> H)	3440(br)	-	-	1280	-
4. $\text{PhL}^2\text{Sn}(\text{OH})_2$	3420(br)	-	-	1260	550, 570(s, br)
5.  (L <sup>3</sup> H)	3400 } 3300 }	-	-	1225 } 1255 }	-

Table - 4 (Contd..)

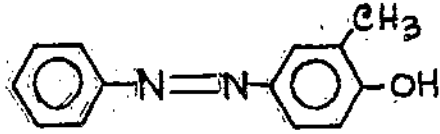
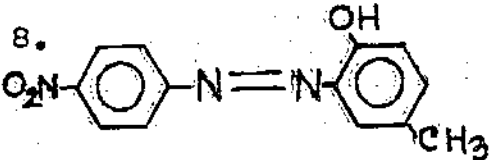
Compounds	$\nu(\text{O-H})$	$\nu_{\text{as}}(\text{NO}_2)$	$\nu_{\text{s}}(\text{NO}_2)$	$\nu(\text{C-O})$	$\nu(\text{Sn-O})$
6. $\text{PhL}^3\text{Sn}(\text{OH})_2$	3390 } 3300 }	-	-	1230 } 1260 }	565(s, br)
7.  ( $\text{L}^4\text{H}$ )	3200(m)	-	-	1250	-
8.  ( $\text{L}^5\text{H}$ )	$\sim 3300\text{-}3400(\text{v, br})$	1510	1330	1235	-
9. $\text{PhL}^5\text{Sn}(\text{OH})_2$	$\sim 3300\text{-}3450(\text{v, br})$	1500	1335	1230	-

Table - 4 (Contd..)

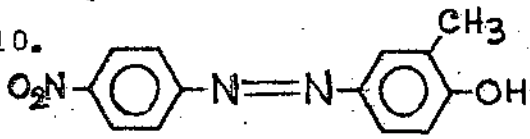
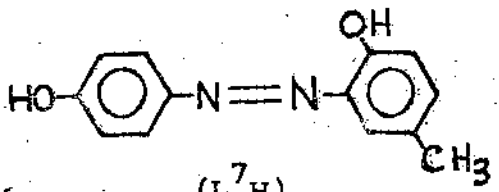
Compounds	$\nu(\text{O-H})$	$\nu_{\text{as}}(\text{NO}_2)$	$\nu_{\text{s}}(\text{NO}_2)$	$\nu(\text{C-O})$	$\nu(\text{Sn-O})$
10.  $(\text{L}^6\text{H})$	3500	1520	1340(s)	1270	-
11.  $(\text{L}^7\text{H})$	3320(s,br)	-	-	1270	-
12. $\text{PhL}^7\text{Sn}(\text{OH})_2$	$\sim 3200-$ $3400(\text{v},\text{br})$	-	-	1270	550
13. $\text{BuL}^7\text{Sn}(\text{OH})_2$	$\sim 3400(\text{v},\text{br})$	-	-	1270	-

Table - 4 (Contd..)

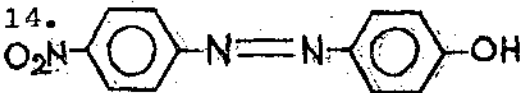
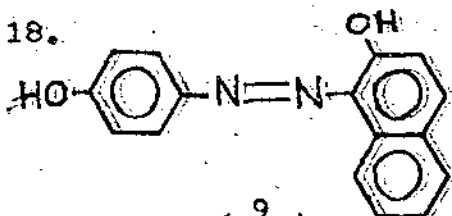
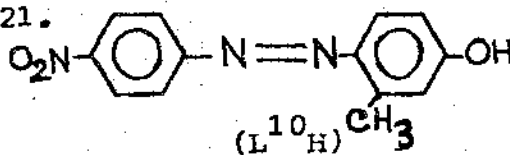
Compounds	$\nu(\text{O-H})$	$\nu_{\text{as}}(\text{NO}_2)$	$\nu_{\text{s}}(\text{NO}_2)$	$\nu(\text{C-O})$	$\nu(\text{Sn-O})$
14.  (L <sup>8</sup> H)	3420	1505	1330	1275	-
15. $\text{Ph}_3\text{SnL}^8$	-	1505	1330	1255	580
16. $\text{Bu}_3\text{SnL}^8$	-	$\sim 1500$	1330	1280	625
17. $\text{Cy}_3\text{SnL}^8$	-	1500	1330	1270	575
18.  (L <sup>9</sup> H)	$\sim 3150$ 3350(v,br)	-	-	1205	-
19. $\text{PhL}^9\text{Sn}(\text{OH})_2$	3350(v,br) $\sim 3300-3450(\text{v,br})$	-	-	1205	610(s,br)

Table - 4 (Contd..)

Compounds	$\nu(\text{O-H})$	$\nu_{\text{as}}(\text{NO}_2)$	$\nu_{\text{s}}(\text{NO}_2)$	$\nu(\text{C-O})$	$\nu(\text{Sn-O})$
20. $\text{BuL}^9\text{Sn}(\text{OH})_2$	$\sim 3200-$ 3350(v,br)	-	-	-	670   620   (s) 540
21. 	3480 (3340)	1520	1340	1250	-
22. $\text{Ph}_3\text{SnL}^{10}$	-	1515	1340	1240	580
23. $\text{Bu}_3\text{SnL}^{10}$	-	-	1320	1230	-
24. $\text{Cy}^3\text{SnL}^{10}$	-	1505	1330	1230	600

br = broad; m = medium; s = strong; v,br = very broad

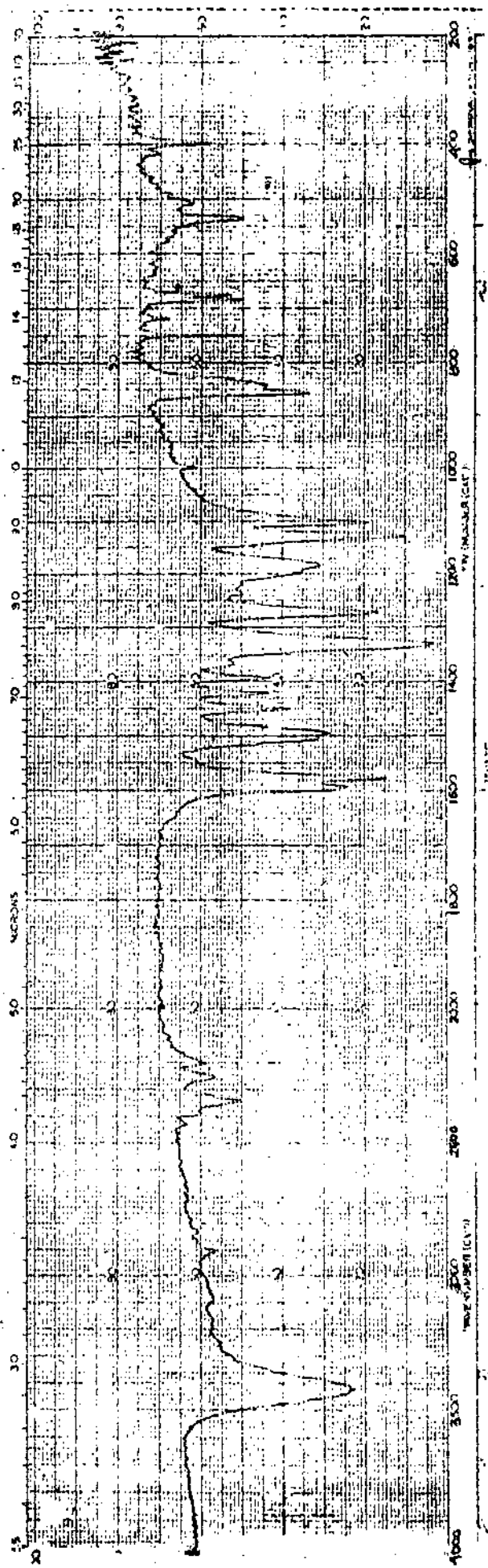


Figure - 40      Infrs red spectrum of L<sub>8</sub>H

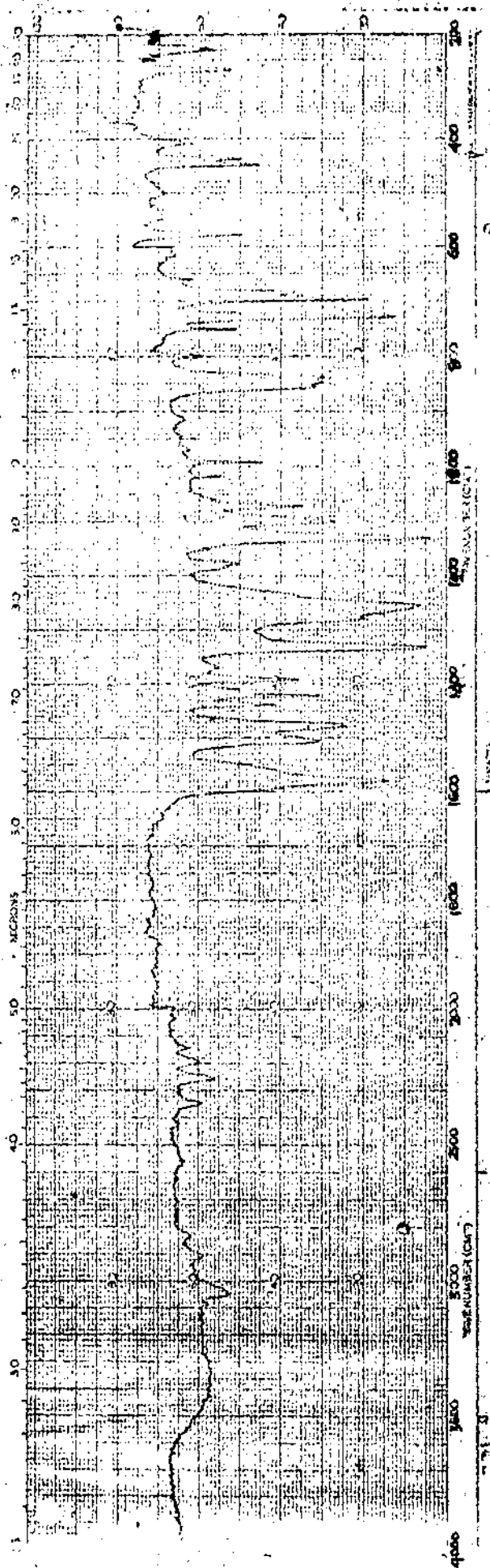


Figure - 41      Infra red spectrum of  $\text{Ph}_3\text{SnI}$



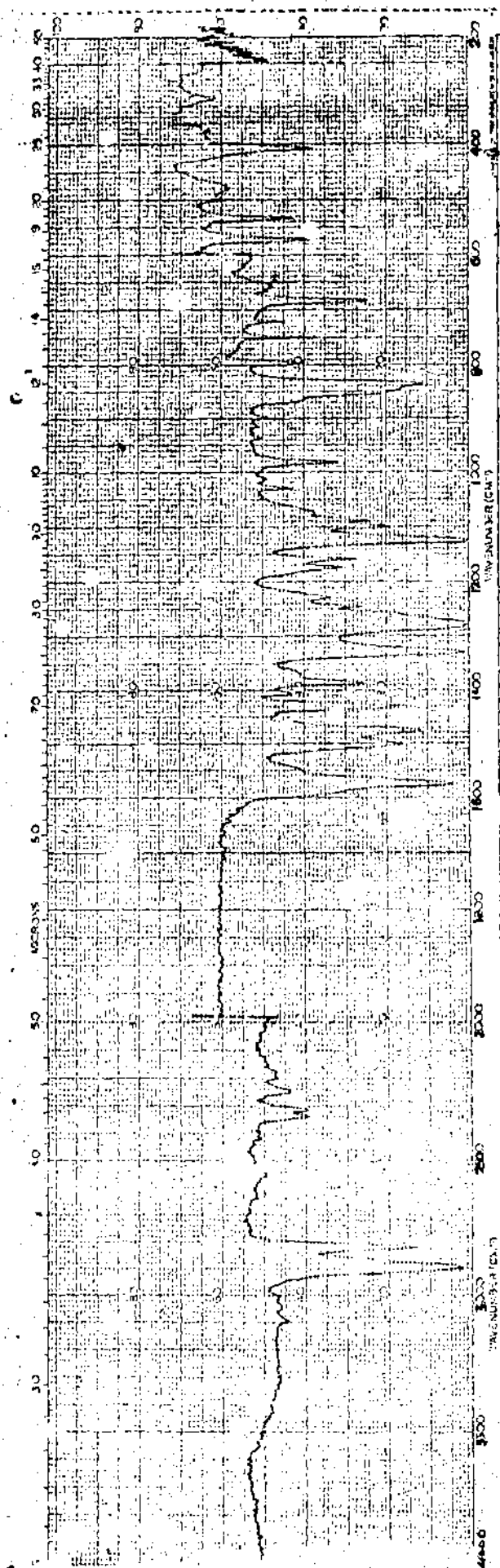


Figure - 42      Infrared spectrum of  $Cy_3SnL$

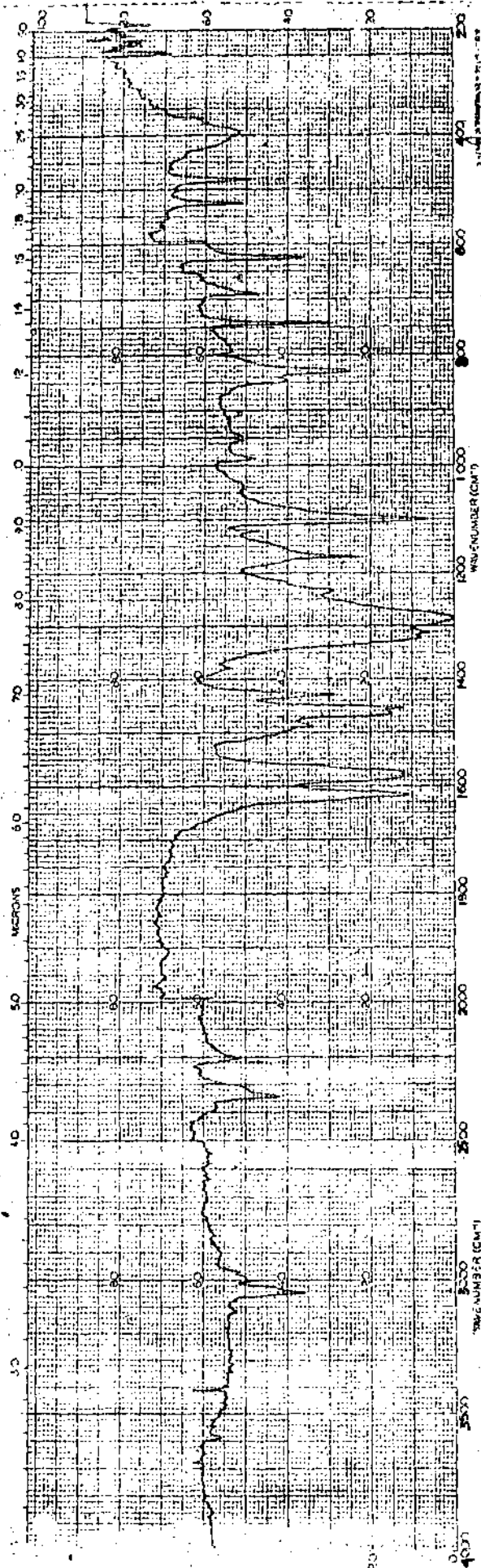


Figure - 43      Infrared spectrum of  $Ba_2SnL_8$

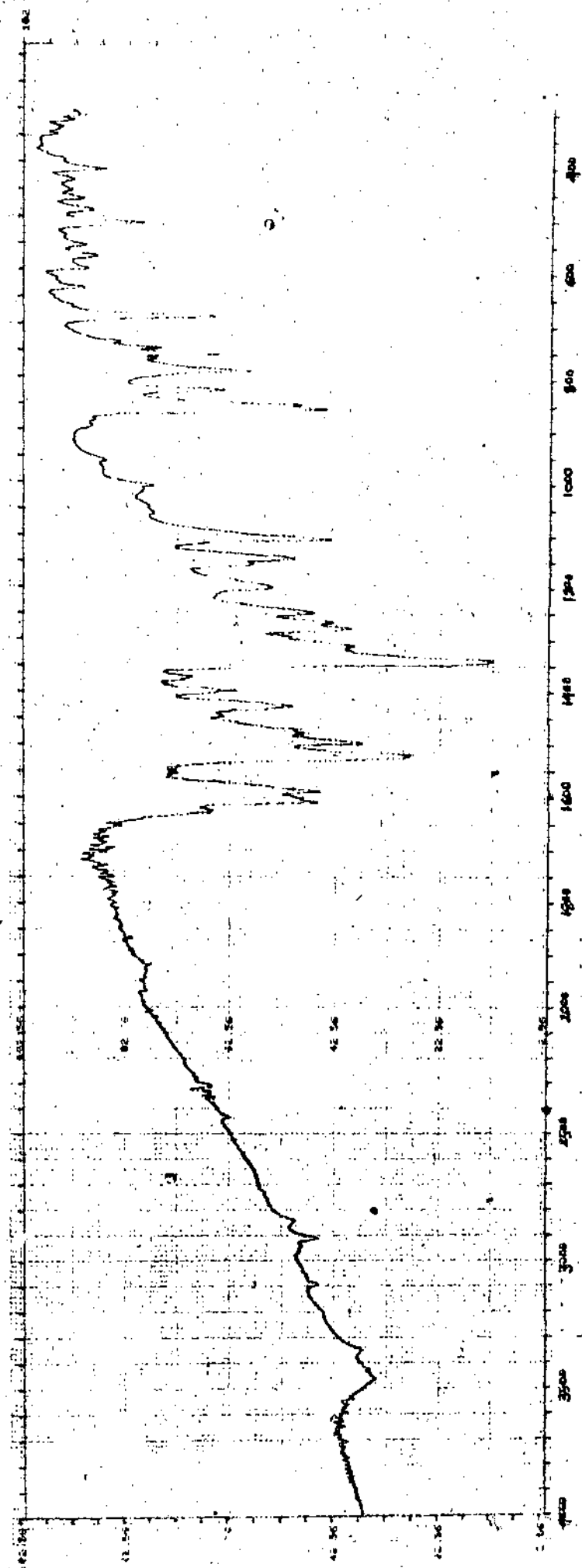


Figure - 44 Infrared spectrum of L<sup>10</sup>H

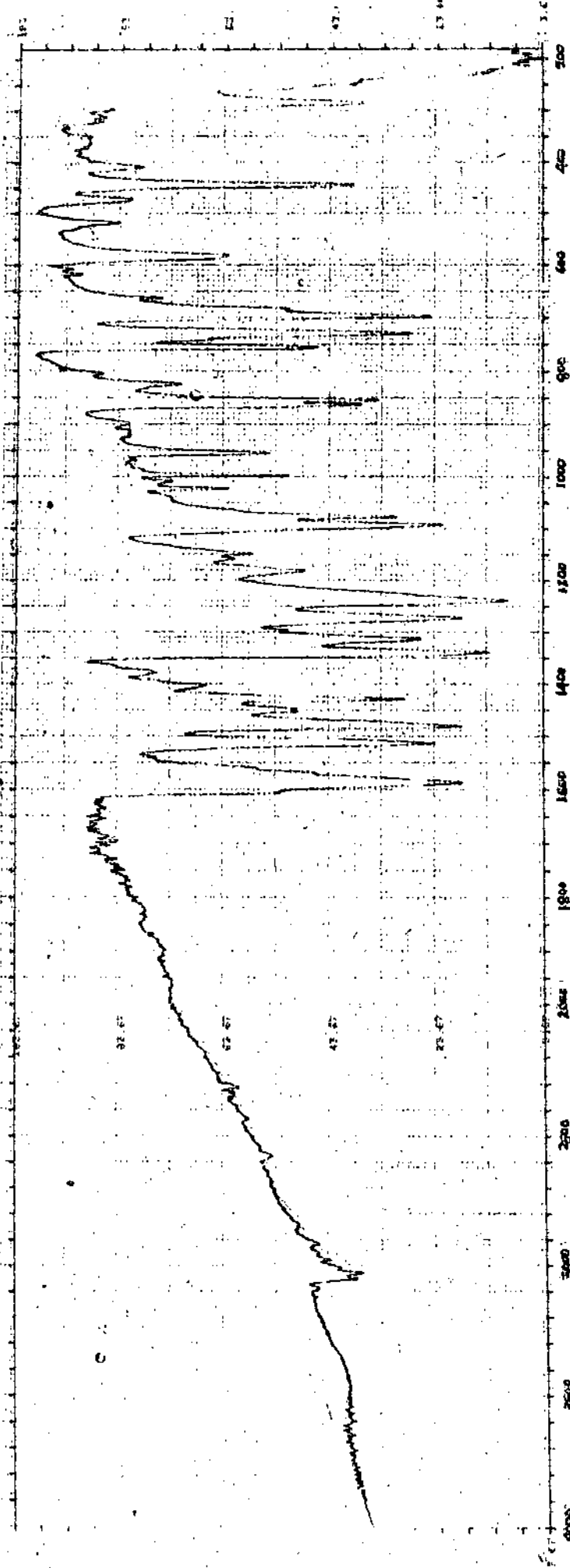


Figure - 45      Infra red spectrum of  $Mn_3SnL^{10}$

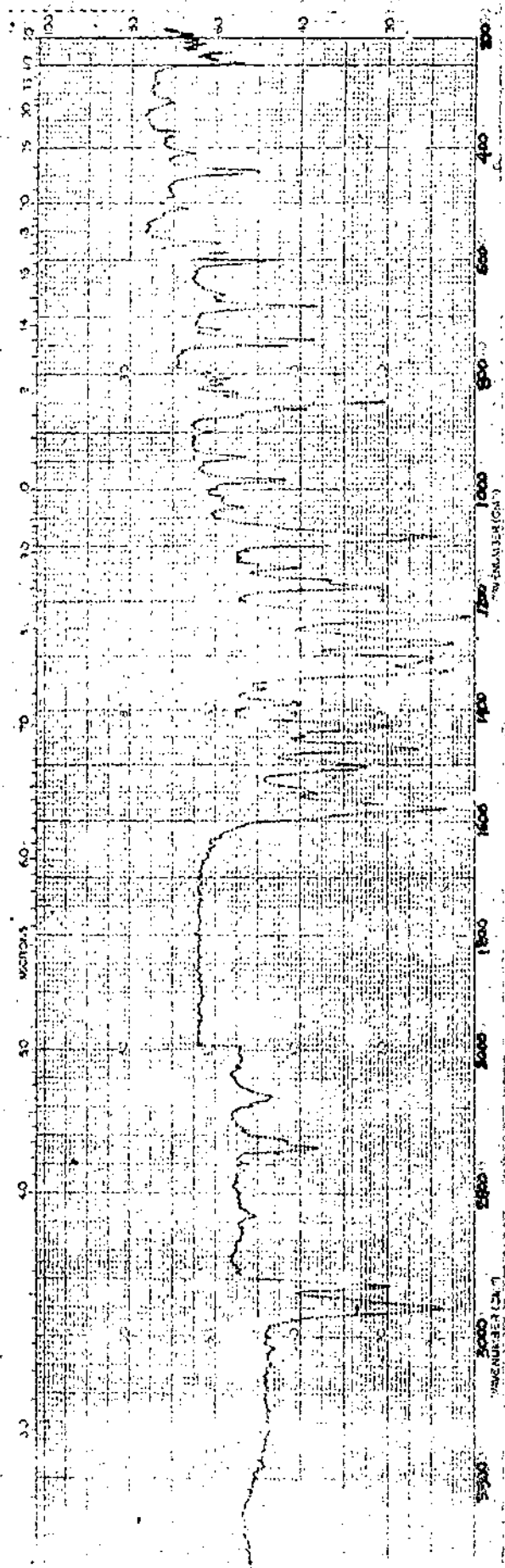


Figure - 46      Infrared spectrum of Cy<sub>3</sub> sul<sup>10</sup>

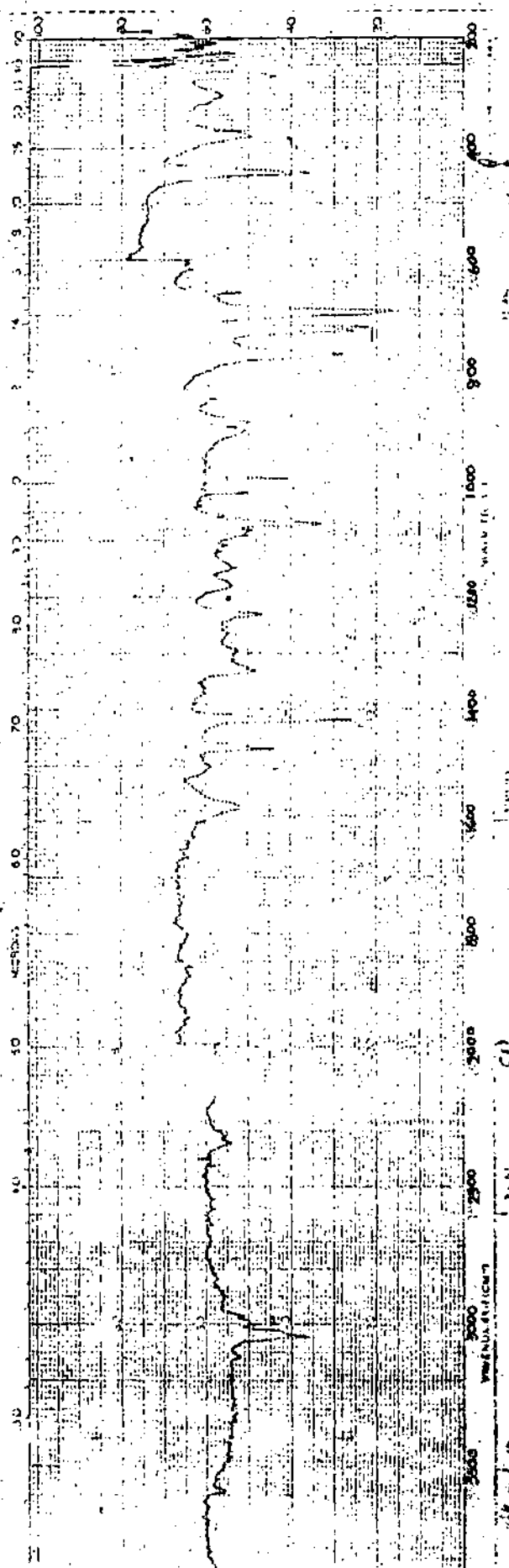


Figure - 47       $\text{Bu}_3\text{SnLi}$       Infra red spectrum of  $\text{Bu}_3\text{SnLi}$

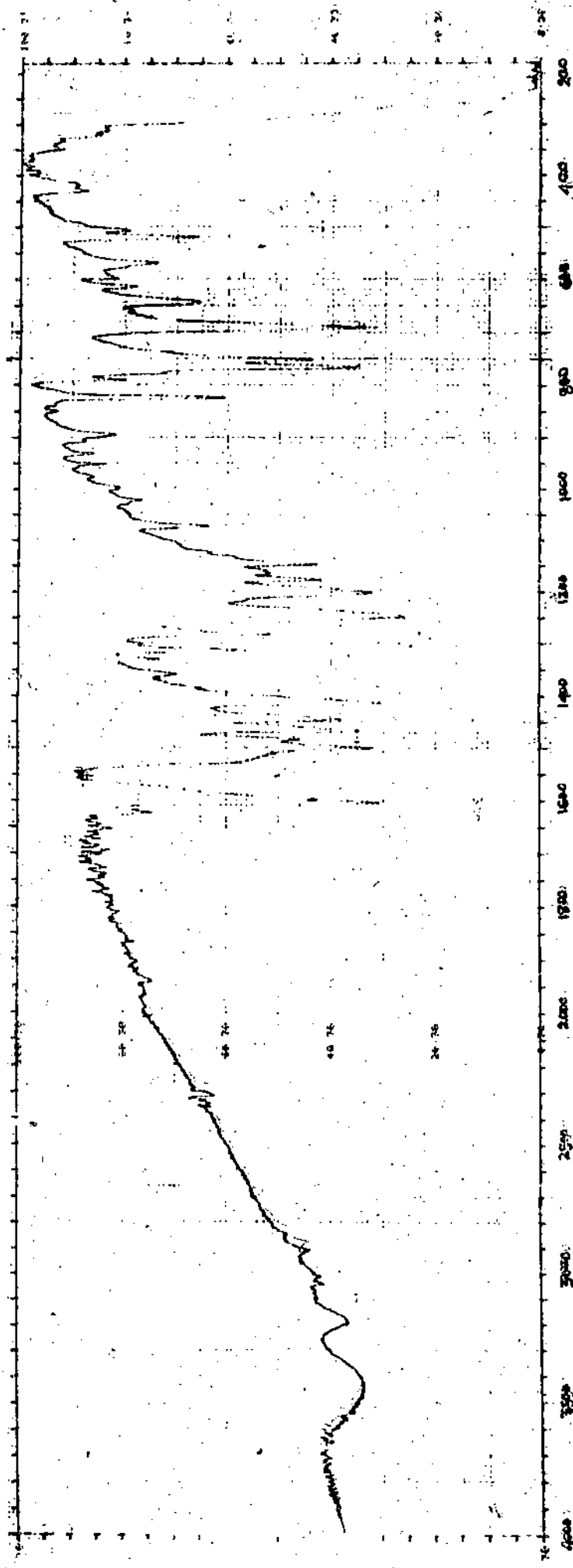


Figure - 48 Infrared spectrum of L<sup>1</sup>H

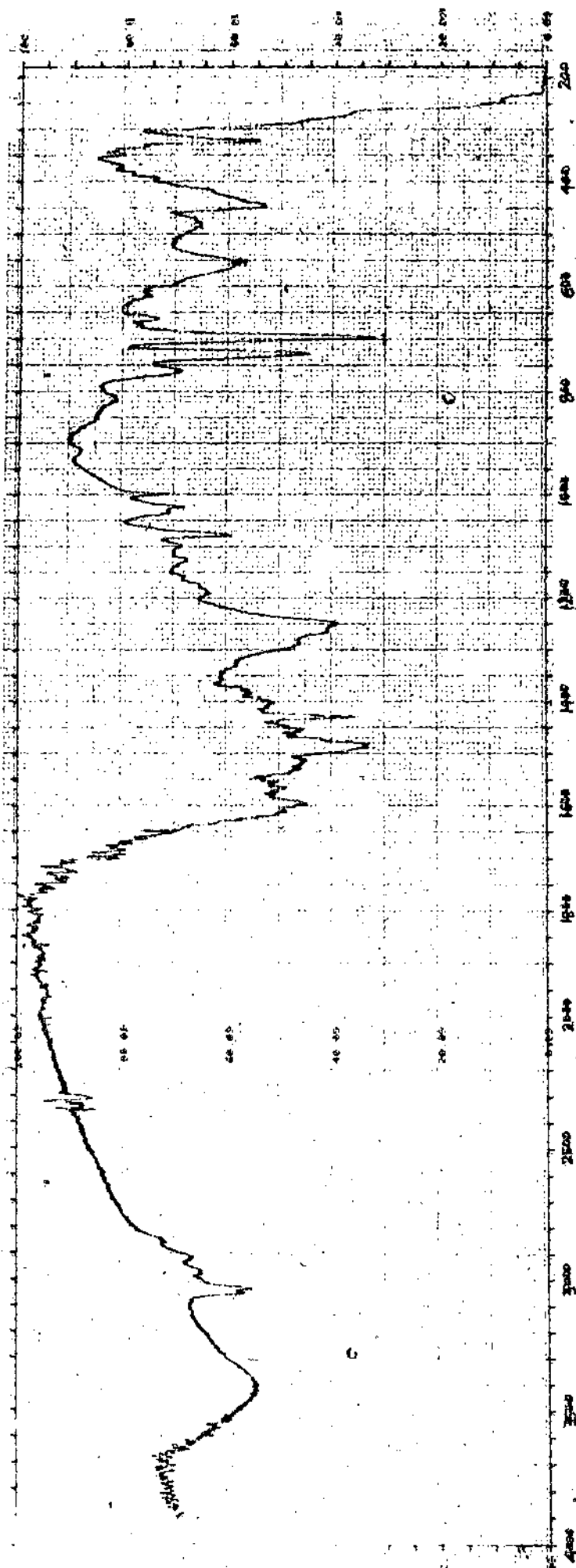


Figure - 49      Infrared spectrum of  $\text{PhLi}(\text{OH})_3$



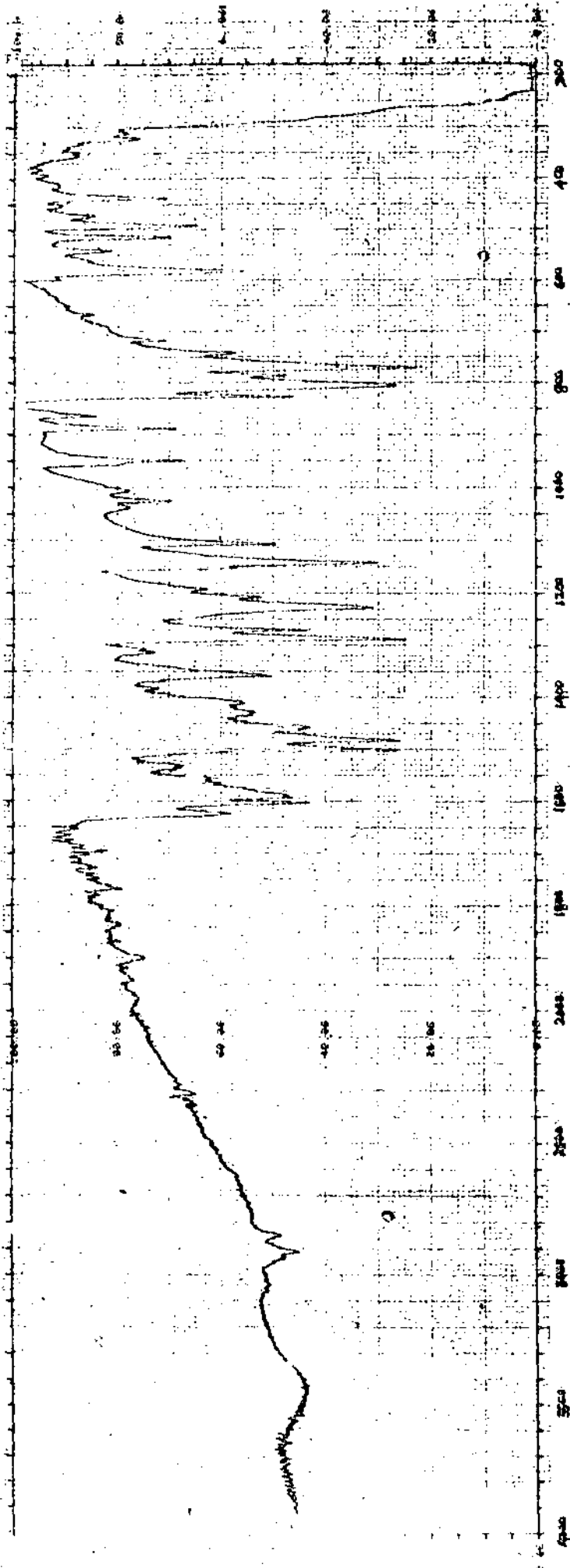


Figure - 50      Infrared spectrum of L<sub>2</sub>H

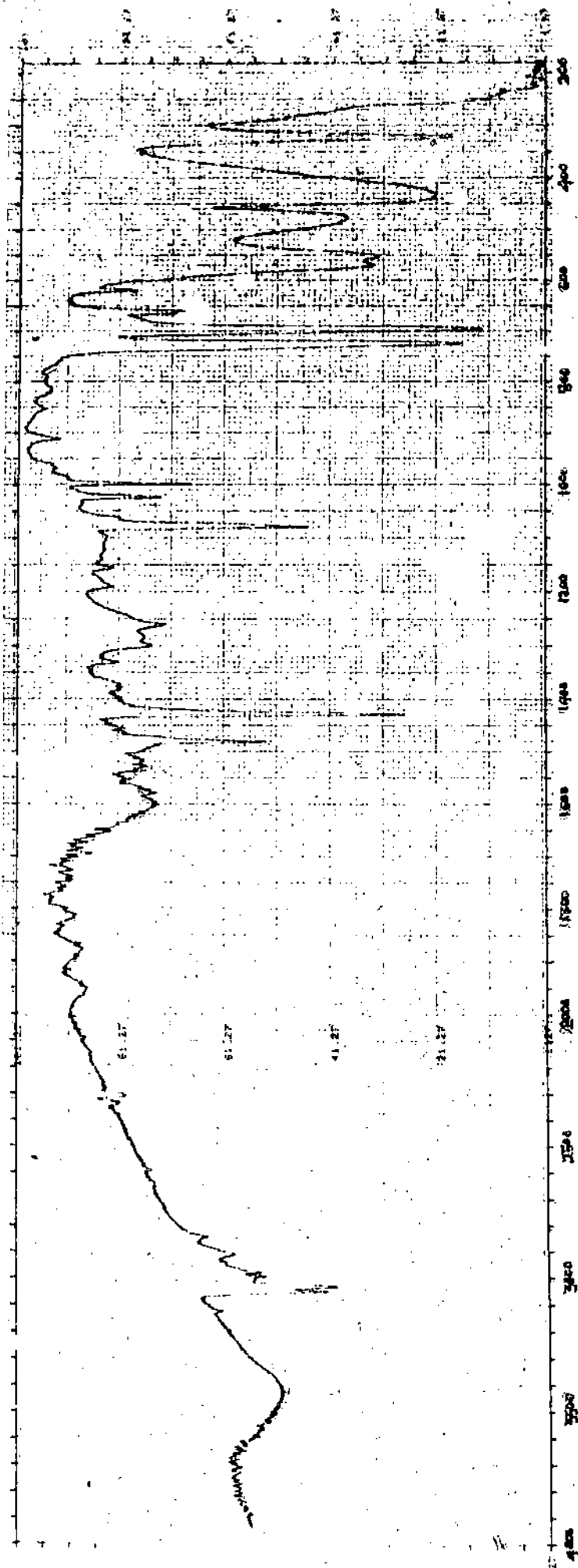


Figure - 51      Infra red spectrum of  $\text{Ph}_{1.2}\text{Sn}(\text{OH})_2$

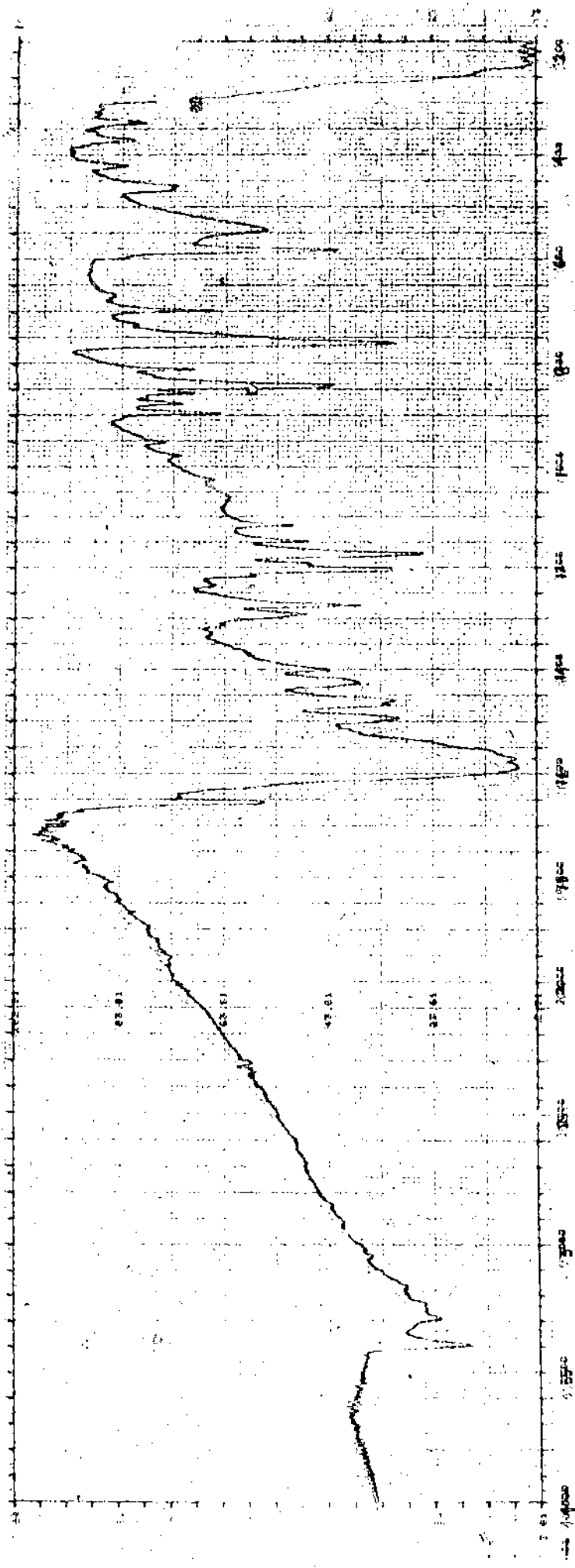


Figure - 52      Infra red spectrum of  $L^2H$

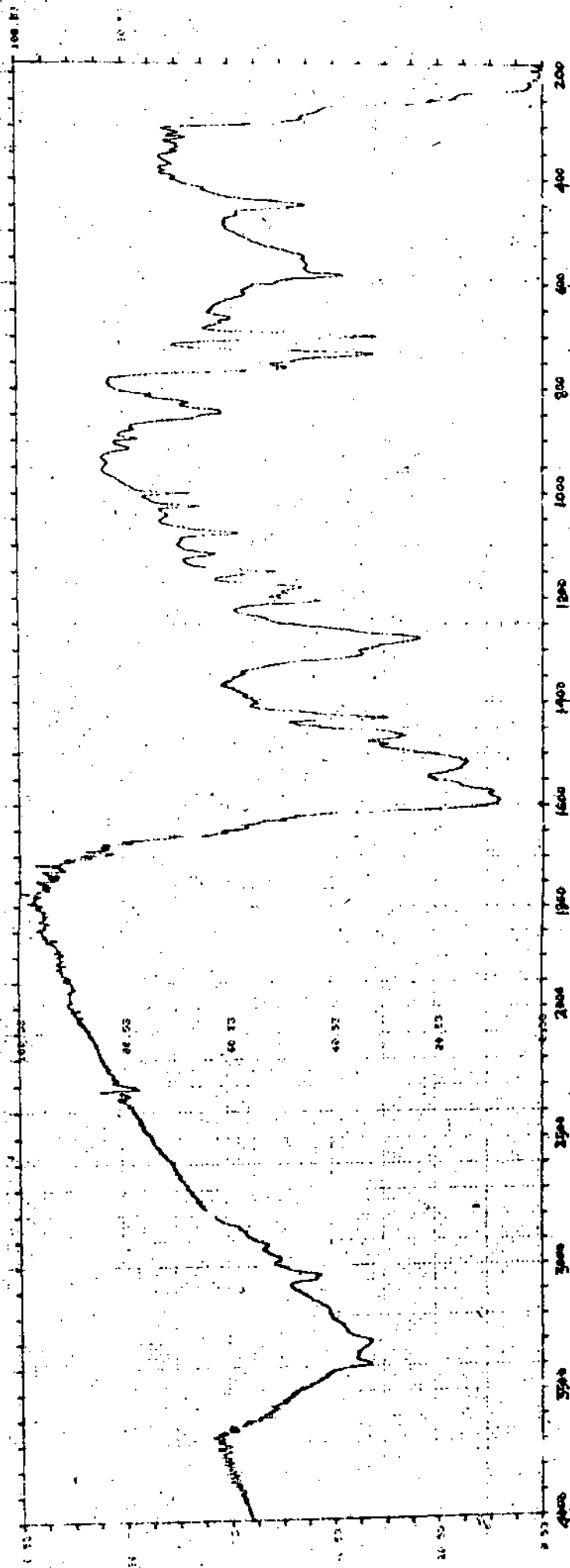


Figure - 53      Infra red spectrum of  $\text{PhL}_3\text{Sn}(\text{OH})_2$

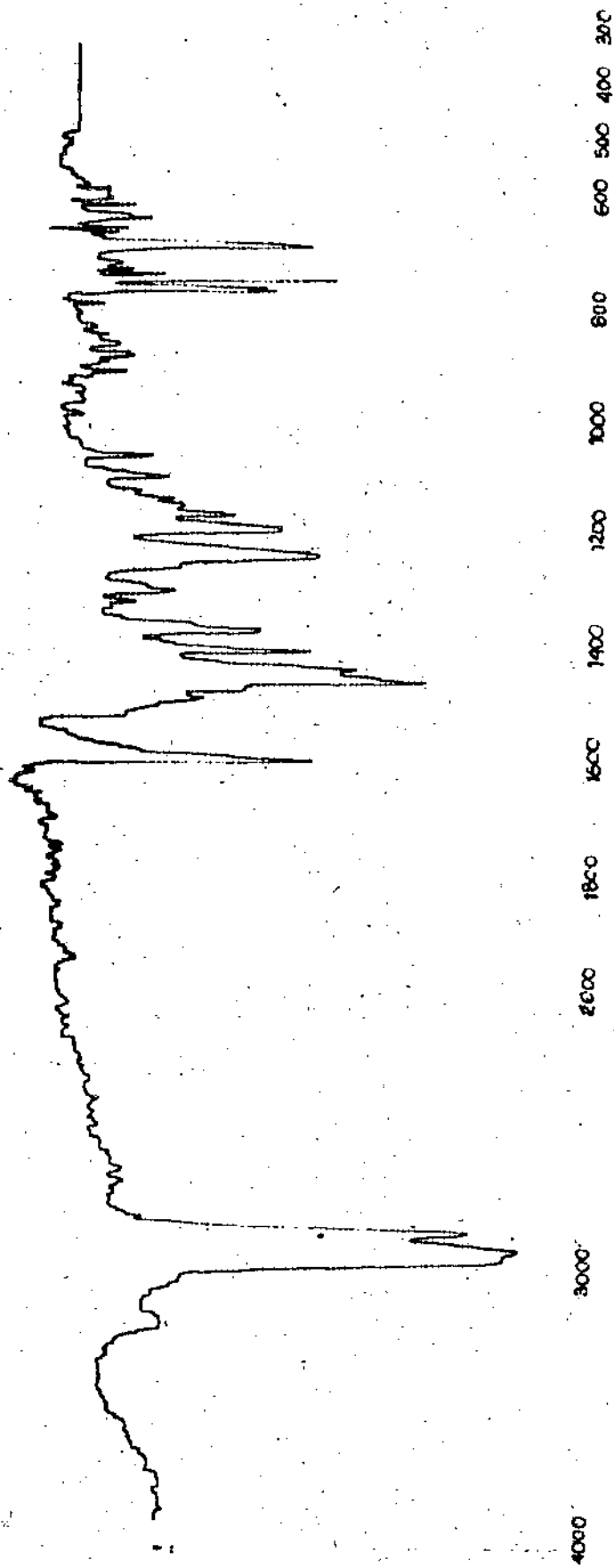


Figure -- 54      Infrared spectrum of L<sup>4</sup>H

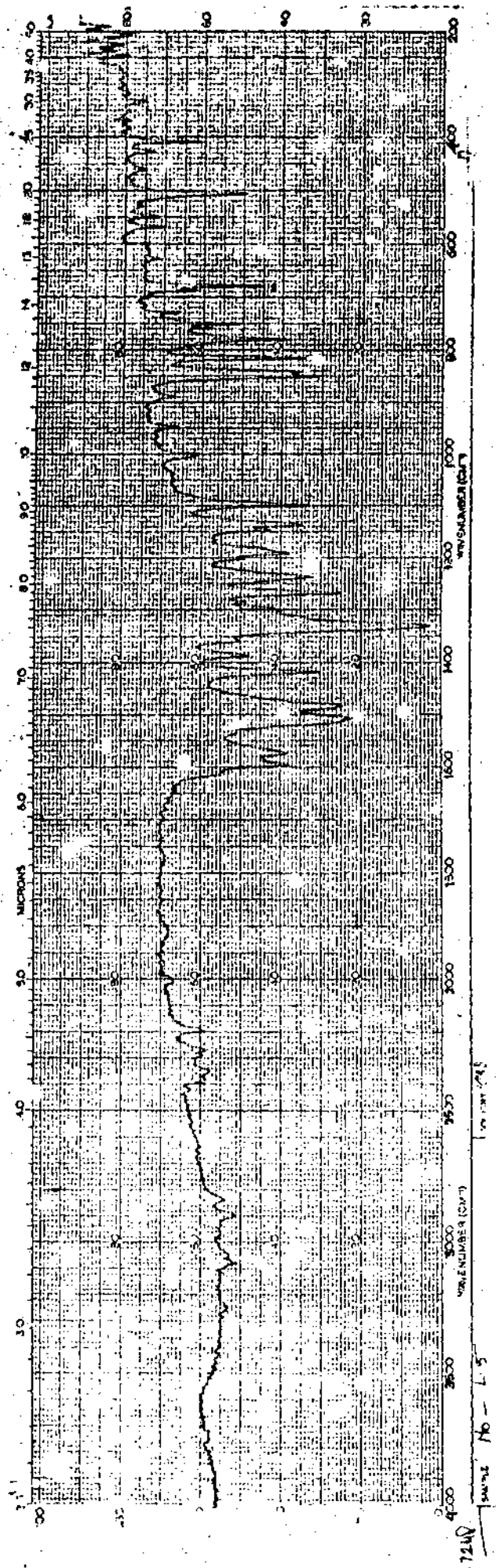


Figure - 55 Infrared spectrum of L5H

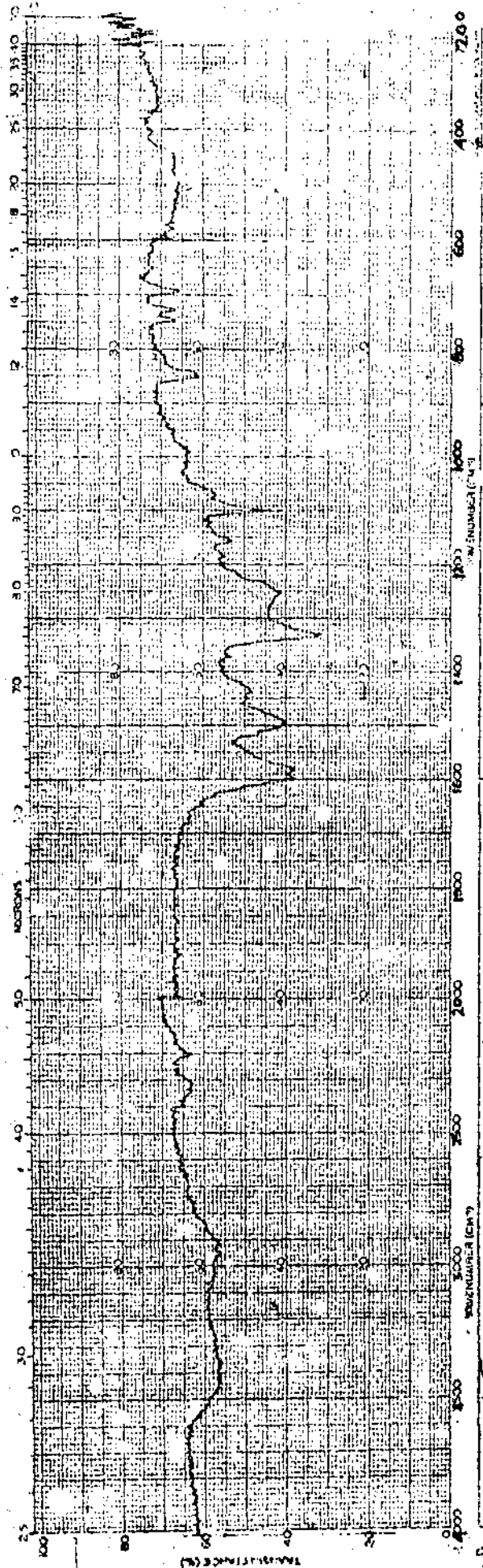
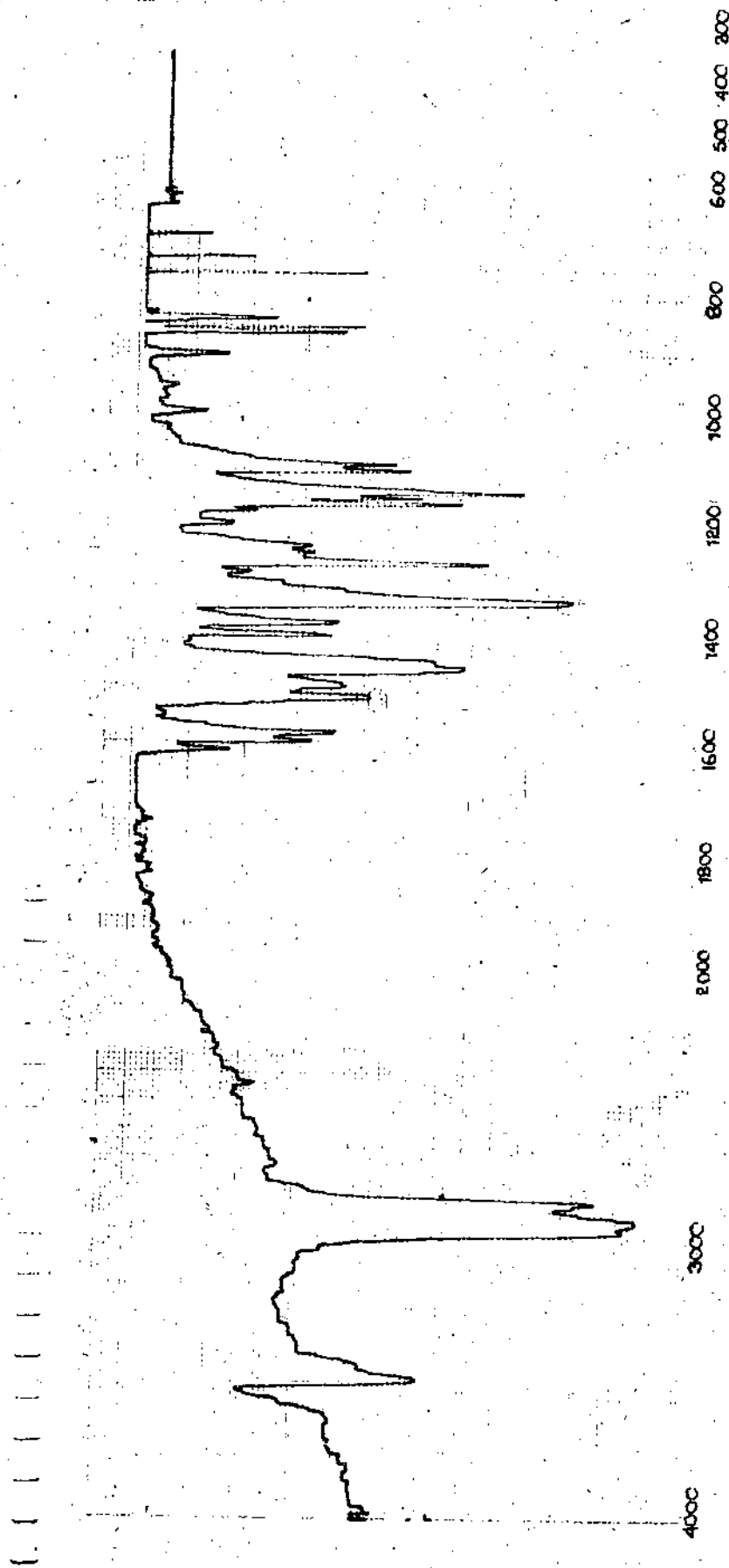


Figure - 56      Infra red spectrum of  $\text{PHL Sn}(\text{OH})_2$



infrared spectrum of LNH

Figure - 57



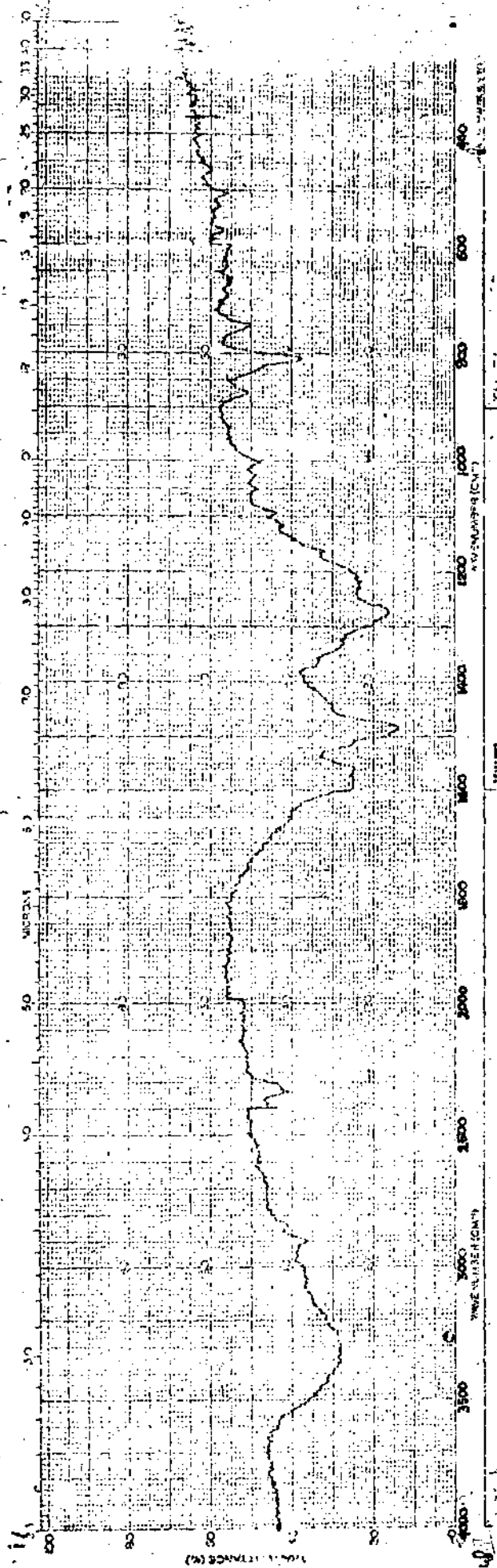


Figure - 58      Infra red spectrum of L<sup>7</sup>H

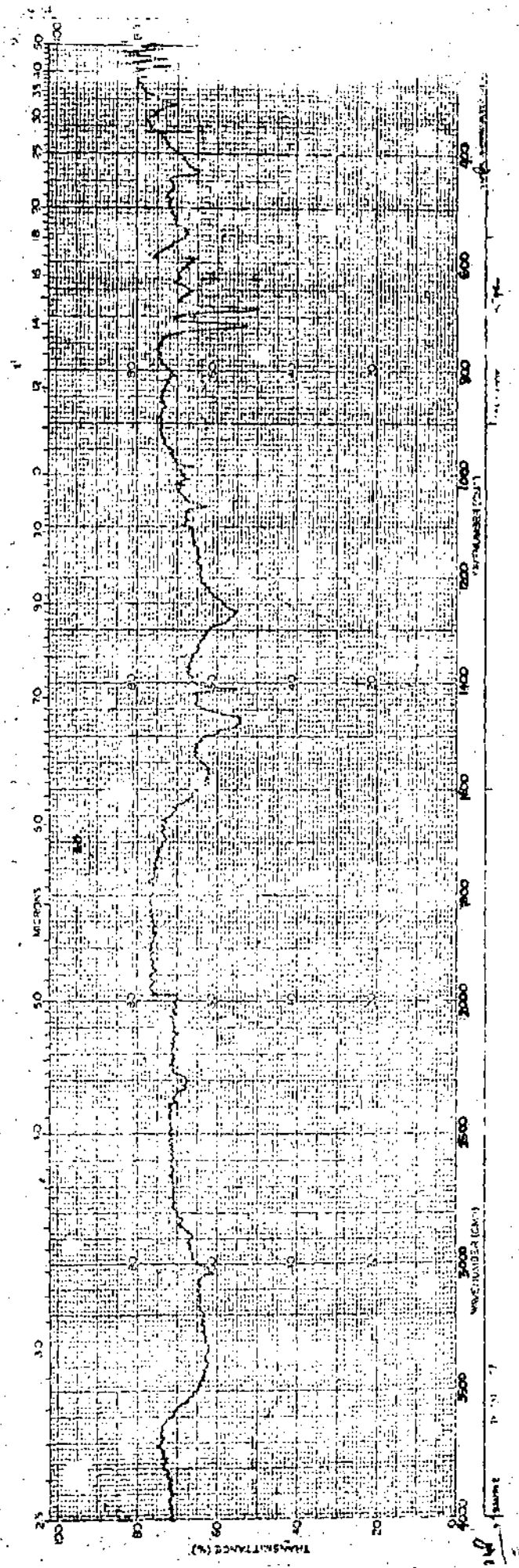


Figure - 19      Infra red spectrum of  $\text{Ph}^7\text{Se}(\text{OH})_2$

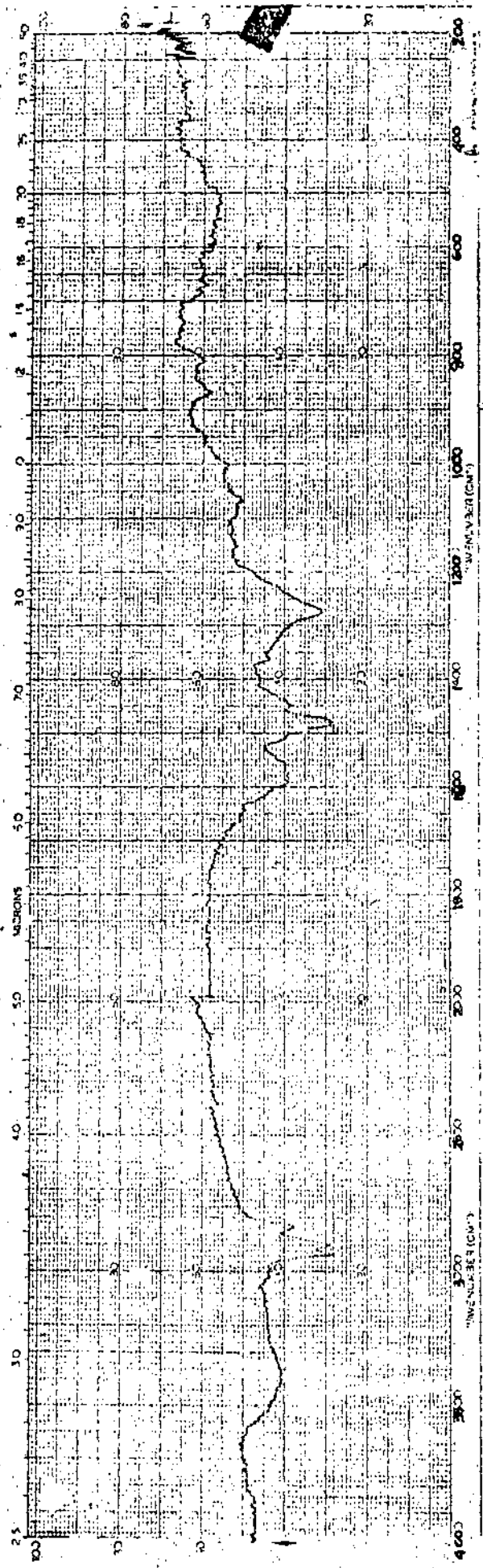


Figure - 60      Infra red spectrum of  $\text{BuLi}^7\text{Sn}(\text{CH}_3)_2$

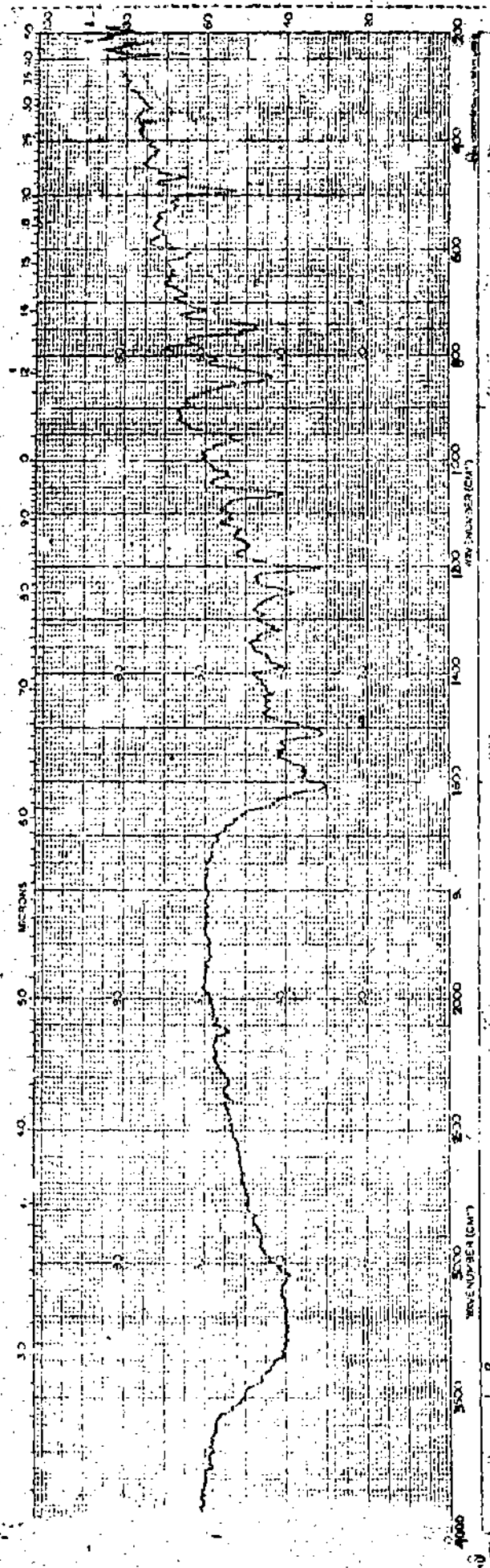


Figure - 61      Infra red spectrum of L H 9

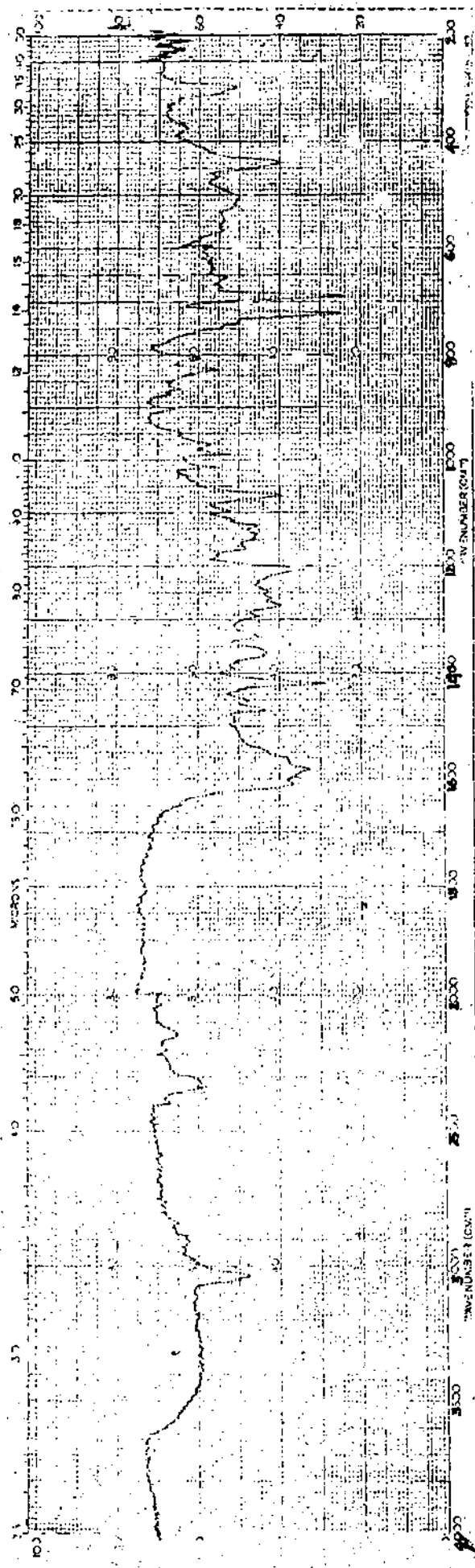


Figure - 62      Infra red spectrum of  $\text{PhLiSn(OH)}_2$

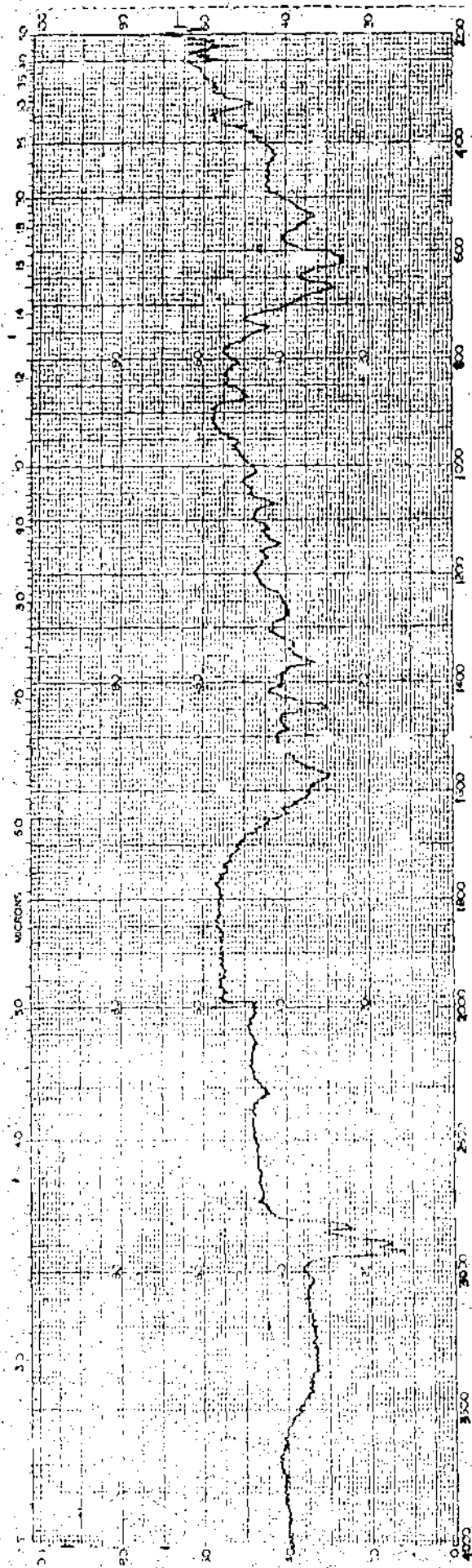
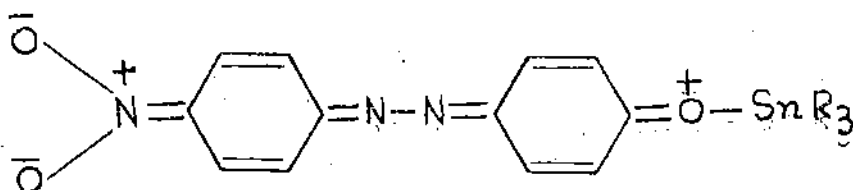


Figure - 63      Infra red spectrum of  $\text{BaU Sn(OH)}_2$



## XVIII

This resonating form is expected to increase the  $\nu(\text{C-O})$  in the organotin compounds due to increased double bond character of CO bond. However, the  $1200\text{--}1280\text{ cm}^{-1}$  band contains significant contribution from the OH deformation mode. As such replacement of H-atom of the OH group by bulky  $\text{-SnR}_3$  group is expected to lower this frequency. The actual position of the  $\nu(\text{C-O})$  band in the organotin compounds will be determined by these two opposing effects. That the contribution -OH deformation is quite significant in the  $1250\text{--}1280\text{ cm}^{-1}$  band is shown by the lowering of the frequency in almost all the triorganotin derivatives excepting  $\text{Bu}_3\text{SnL}^8$  and  $\text{Cy}_3\text{SnL}^8$ .

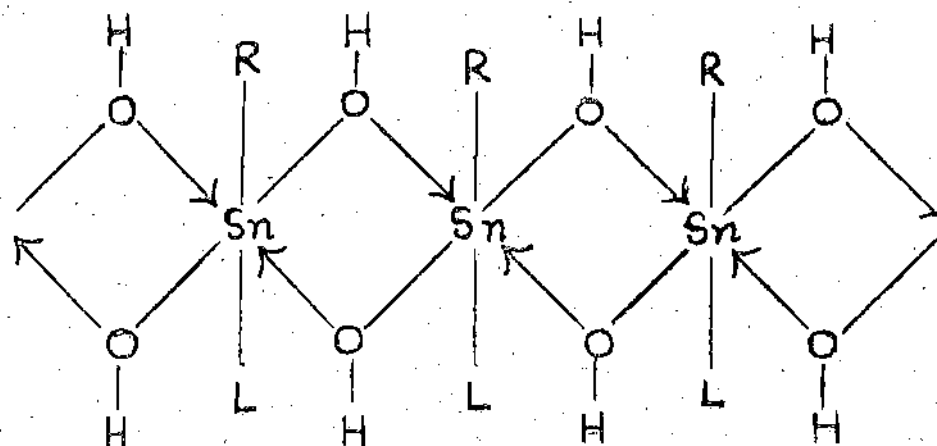
The two group of organotin derivatives, viz.  $\text{R}_3\text{SnL}$  type and  $\text{RLSn(OH)}_2$  type, show an interesting feature in the  $\nu(\text{C-O})$  absorption. As already discussed, the first group is characterised by a lowering of  $\nu(\text{C-O})$ . In the second group,  $\nu(\text{C-O})$  is generally unaffected. This group of compounds is further characterised by a very broad absorption around  $3200\text{--}3500\text{ cm}^{-1}$  showing the presence of bonded -OH groups. In

addition, new absorptions of medium to strong intensity absorptions are also observed. Unlike, in the  $R_3SnL$  compounds, these bands are somewhat broad indicating a polymeric structure involving Sn-O groups.

The characteristic features of the compounds formulated as  $RLSn(OH)_2$  on the basis of analytical data may now be summarised as follows:

- i) Extremely low solubility in common organic solvents
- ii) Infusibility upto  $300^\circ\text{C}$
- iii) Absence of intramolecular coordination involving the azo group and the tin atom as shown by the electronic absorption spectra
- iv) Very broad  $\nu(\text{O-H})$  absorption as at  $3200-3500\text{ cm}^{-1}$  in the IR spectra.
- v) Broad or multiple absorption in the  $\nu(\text{Sn-O})$  region ( $\sim 500-650\text{ cm}^{-1}$ ).

All the observations point to the presence of intermolecular coordination through the  $-\text{OH}$  group. The most probable structure for the  $RLSn(OH)_2$  type of compounds is therefore as follows:





Similar hydroxy bridged polymeric structures have been proposed for  $\text{PhSn}(\text{OH})_2\text{OCO}^{\text{H}^{39}}$ ,  $\text{Sn}_2\text{Ox}_2(\text{OH})_6^{\text{H}^{39}}$   $\nearrow$  Ox = 8-hydroxy quinolate 7etc.

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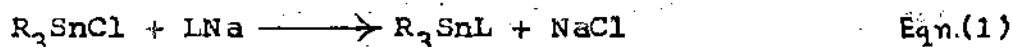
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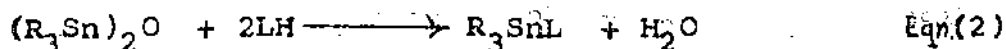
The thesis consists of four chapters. The first chapter attempts to present an overview of the organotin chemistry with particularly emphasis on the bonding and structure in organotin compounds.

The second chapter gives a brief account of the organotin alkoxides, phenoxides and related compounds.

The third chapter deals with the (i) preparation of the arylazophenols used as ligands in the present study, (ii) the reactions of the ligands with the triorganotin oxides,  $(R_3Sn)_2O$ , and (iii) preparation of the triorganotin derivatives,  $R_3SnL$  ( $LH =$  aryl azo phenol), using the reaction:



The results presented in this chapter shows that the aryl azo phenols do not undergo the normal reaction (eqn. 2) with  $(R_3Sn)_2O$ .



Azeotropic distillation or use of dessicants has no effect.

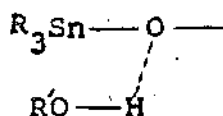
On the other hand, prolonged refluxing of mixtures of stannoxanes with the arylazo phenols produced infusible (m.p)  $300^\circ C$ ) and sparingly soluble organotin derivatives with empirical formula of  $RLSn(OH)_2$ . The yields are quite low and the period of refluxing varied considerably (from  $\sim 12$  hours to  $\sim 72$  hours). In

some cases, no reaction took place.

The aryl azo phenols with a nitro substituents, e.g. 4'-(4-hydroxy benzene azo) nitrobenzene, because of their higher acidity, form the Na/K salt easily which could be reacted with  $R_3SnCl$  to yield the triorganotin derivatives,  $R_3SnL$ . These compounds are crystalline in nature with well defined melting points and are soluble in common organic solvents. The compounds are stable in air.

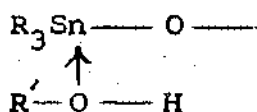
The last chapter deals with electronic and IR spectral studies on the ligands and the organotin derivatives.

The electronic spectral studies show that the acidity of the -OH group in the ligands are very low except in the nitro substituted compounds and, therefore, the stannoxanes fail to react via the transition complex I.



I

The Lewis acidity of the organotin compound takes a dominant role under this situation and reaction can proceed through nucleophilic attack at the tin atom (II).

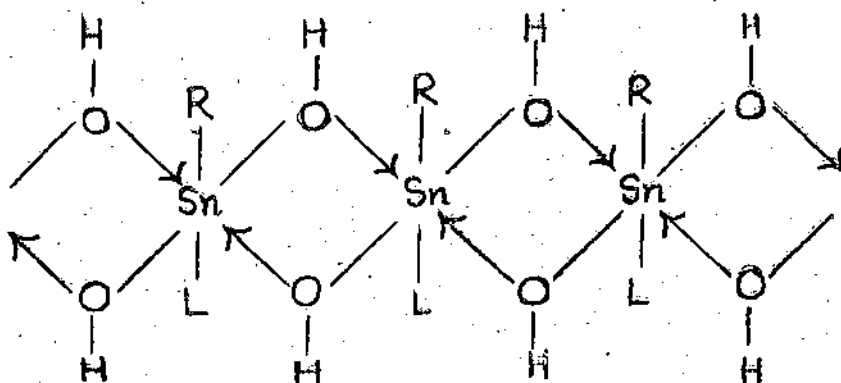


## II

As a result, instead of the expected reaction (eqn. 2), polymeric products formed through the cleavage of R-Sn bonds are obtained.

The IR studies show the presence of  $\nu(\text{Sn-O})$  absorption in the  $\text{R}_3\text{SnL}$  derivatives around  $\sim 570 \text{ cm}^{-1}$ ,  $\nu(\text{C-O})$  of the ligand is slightly lowered in the organotin compounds in some cases.

The IR spectra of the products  $\text{R}_2\text{Sn}(\text{OH})_2$ , are characterised by broad band in the  $\sim 500\text{--}600 \text{ cm}^{-1}$  region due to  $\nu(\text{Sn-O})$  and very broad absorption around  $\sim 3400\text{--}3500 \text{ cm}^{-1}$  indicating involvement of the -OH groups in inter molecular coordination. On the basis of available information  $\text{R}_2\text{Sn}(\text{OH})_2$  compounds are represented as follows:



## III

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