ARYLOXYACETIC ACIDS : POTENTIAL LIGANDS FOR MONOMERIC ORGANOTIN CARBOXYLATES

ON THE PREPARATION, STRUCTURE AND BIOLOGICAL PROPERTIES OF ORGANOTIN (IV) ARYLOXYACETATES.

Thesis

Submitted for the Degree of Doctor of Philosophy (Science) of the University of North Bengal

by

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Dedicated

to the memory of

M.N. KUMAR

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Investigations embodied in this thesis entitled "Aryloxy-acetic acids : Potential ligands for monomeric organotin carboxylates", were initiated in May, 1983 in the department of Chemistry, North Bengal University under the encouraging supervision of Dr. T.K.Chattopadhyay, Reader of this department. A brief record of the objective and nature of this work has been presented in the "PREFACE".

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P R E F A C E

The great interest evinced among organotin chemists for the study of organotin carboxylates may be attributed to two major factors. Firstly, the great variety of structural possibilities encountered among compounds of this class, which are predominantly polymeric with bridging bidentate carboxyl groups besides some stray cases of monomeric molecules having unidentate or bidentate chelating carboxyl groups, stimulates attempts to synthesise monomeric tri- and di-organotin carboxylates in solid phase. Secondly, the biocidal properties of the organotin carboxylates and the consequent application to the pest control, ecology problems, veterinary medicine, human medicine and merine antifouling agents etc. are the reasons for an unusual increase in production of these types of compounds in recent years. Both these factors are also interconnected to some extent because it has been suggested recently that the structure of the organotin carboxylates is significantly connected with their practical application.

In an attempt to prepare organotin carboxylates which would have monomeric structure both in solid and solution phases, we selected the phenoxyacetic acid and it's substituted derivatives as the ligands. We hoped that the Lewis basicity of the phenoxy

oxygen atom would be sufficient for formation of intramolecular co-ordinate bond with the organotin residue leading to monomeric species in preference to the normally observed polymeric ones.

Although this particular objective and our aspiration could not be realised in full, yet in this course of our detailed and systematic work, we have been able to synthesise tri- and di-organotin aryloxyacetates having very interesting structural features as well as very significant biocidal characteristics.

The work presented in this thesis is dividedinto four chapters.

In Chapter - I, a brief review of organotin carboxylates with reference to their methods of preparation, physical and chemical properties, biological characteristics and structures (including major instrumental methods for determining the structures) have been discussed.

In Chapter - II, a short review of the phenoxyalkanoic acids and their metal complexes have been presented.

In Chapter - III, we have described preparation of a large number of tri- and di-organotin (IV) aryloxyacetates. The structures of the compounds in solid state and in solution have been deduced from IR, NMR (^{13}C, ^{17}O and ^{119}Sn), ^{119m}Sn Mössbauer and UV spectral data. In solid state, the triorganotin (IV) compounds form polymeric chains with bidentate bridging carboxyl groups. In non-coordinating solvents, these compounds are present as pseudo-tetrahedral molecules, whereas in a co-ordinating solvent they form complexes with

one solvent molecule, the central tin atom exhibiting the trans-trigonally bipyramidal coordination. The diorganotin (IV) compounds form, both in solid state and in non-coordinating solvents, monomeric molecules containing bidentate asymmetrically chelated carboxyl groups. In coordinating solvent, they form complexes with octahedral coordination around the tin atom.

In Chapter - IV, a few studies for evaluating the biological properties of the organotin derivatives have been presented. It has been found that organostannylation increases the biocidal properties of the parent carboxylic acids significantly. It also appears that the biocidal activities of the organotin component and the carboxylic acid substrate are mutually complemented resulting in the much enhanced activity of the organotin aryloxyacetates.

C O N T E N T S

CHAPTER - I

Organotin Carboxylates : A Brief Review

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Organotin Carboxylates : A brief review

I. A. Introduction:

Organotin carboxylates comprise one of the most important class of compounds in the even expanding field of organotin chemistry. Apart from the theoretical and structural interests, organotin carboxylates are finding tremendous importance in industry and agriculture. Many of these groups of compounds have already found important uses and new applications are likely to emerge in the near future.

The compounds containing -OCOR groups bonded to tin which may be either monomeric or polymeric are of the three general types, viz. $R_3SnOCOR'$, $R_2Sn(OCOR')_2$ and $RSn(OCOR')_3$ where R and R' may be same or different groups. Tin tetra-carboxylates, $Sn(OCOR)_4$, are not organotin compounds in the strict sense of the term, but are nevertheless included in the discussion of organotin carboxylates for the sake of comparison and convenience. Many discussions with varying degrees of details are available on these compounds[1-4] and as such only the more important aspects will be presented here.

I. B. Preparation

A number of methods are employed for the synthesis of organotin carboxylates, one of the most important being the reaction between organotin oxides (or hydroxides) and carboxylic acids or their anhydrides[5-13].

$$R_3SnOSnR_3 + 2R'COOH \longrightarrow 2R_3SnOCOR' + H_2O$$

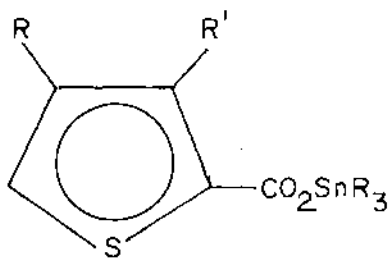
$$R_3SnOSnR_3 + (R'CO)_2O \longrightarrow 2R_3SnOCOR'$$

$$R_2SnO + 2R'COOH \longrightarrow R_2Sn(OCOR')_2 + H_2O$$

The water produced in these reactions is removed usually by azeotropic distillation or alternatively by refluxing at higher temperature[14] for example :

$$Bu_3SnOSnBu_3 + 2 \text{ (HO-C}_6\text{H}_4\text{-COOH)} \xrightarrow{100\text{-}110^{\circ}C} 2 \text{ (HO-C}_6\text{H}_4\text{-COOSnBu}_3\text{)} + H_2O$$

A number of organotin thiophene carboxylates[15] of the type I and II have been prepared from the thiophene carboxylic acids and R_3SnOH or $(R_3Sn)_2O$



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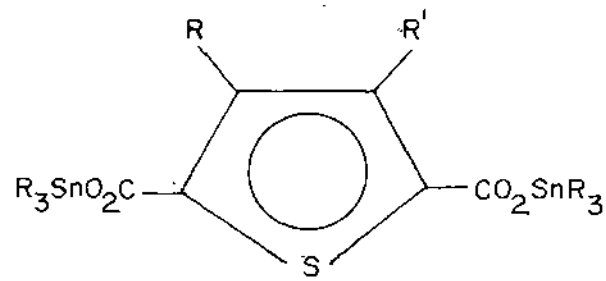


(II)

R = Ph, H; R' = Bu, Me, Cyclo-C_6H_{11}, etc.

The triphenyltin carboxylates, Ph_3SnO_2CR (R = Ph, p-$MeOC_6F_4$, p-$EtOC_6F_4$), p-$(Ph_3SnO_2C)_2C_6F_4 \cdot H_2O$ and o-$(Ph_3SnO_2C)_2C_6F_4H_2O$ have been prepared by the reaction of Ph_3SnOH with the appropriate polyfluoro carboxylic acids in MeOH[16].

Organotin carboxylates have also been prepared by the reaction of the corresponding organotin halides with the alkali metal or silver salts of carboxylic acids either by stirring at RT or by refluxing the reactants in a suitable solvent[12,17-19].

$$R_nSnX_{4-n} + (4-n)MOCOR' \longrightarrow R_nSn(OCOR')_{4-n} + (4-n)MX$$

(M = Na, Ag, K or Tl; X = halogen)

Another method for the preparation of organotin esters involves the cleavage of one or more organic groups of tetraorganotin compounds by carboxylic acids[20,21].

$$R_4Sn + nR'CO_2H \longrightarrow R_{4-n}Sn(OCOR')_n + nRH$$

In this acidolysis reaction, the cleavage of organic groups depends on the acid strength, nature of the groups R and R' and also on the temperature[22-24]. Vinyl groups are cleaved more readily than saturated alkyl radicals, but less readily than phenyl[25] and successive groups are lost with increasing difficulty. Tetralkyltin is more reactive than tetravinyltin[21].

A novel method of preparation of tri-alkyltin carboxylates by electrochemical method using the cleavage of organic groups from R_4Sn (R = Me, Et, Pr, Bu) and Hg(I) carboxylates have been described by Tagliavini et al[26]. At room temperature tetramethyltin produces trimethyltin acetate when treated with Hg(I) acetate in MeOH.

$$2Me_4Sn + Hg_2(OCOMe)_2 \longrightarrow 2Me_3SnOCOMe + 2Hg + C_6H_6$$

Organotin hydrides react with carboxylic acids to form the corresponding organotin esters[27-28] with the evolution of hydrogen.

$$R_3SnH + R'COOH \longrightarrow R_3SnOCOR' + H_2$$

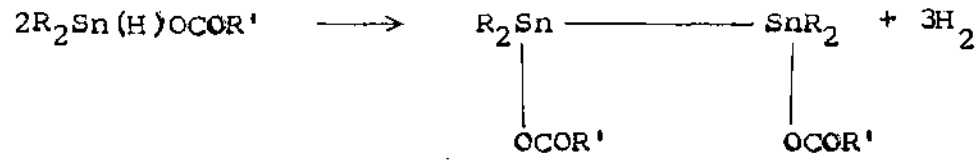
$$R_2SnH_2 + 2R'COOH \longrightarrow R_2Sn(OCOR')_2 + 2H_2$$

The initially formed dicarboxylate equilibrates with unreacted dihydride as follows[29].

$$R_2Sn(OCOR')_2 + R_2SnH_2 \rightleftharpoons 2R_2Sn(H)OCOR'$$

(III)

With di-n-butyltin dihydride, the intermediate hydride carboxylate (III, R = n-Bu) decomposes to give distannane dicarboxylates (IV, R = n-Bu) when the acid is deficient.



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Using similar methods distannane 1,2-di carboxylates have also been prepared[27,30,31]. The nature of the products sometimes depends on the carboxylic acid. Action of benzoyl peroxide on di n-butyltin dihydride produces 1,2-dibenzoate[32].

Halocarboxylate derivatives of organotin compounds are most conveniently synthesised by heating equimolecular mixture of the diorganotin dicarboxylates and the diorganotin dihalides in an inert solvent[33,34].

$$Bu_2SnBr_2 + Bu_2Sn(OAc)_2 \longrightarrow 2\ Bu_2Sn(Br)OAc$$

These compounds may also be prepared by the reaction as follows[35,36].

$$Bu_2SnCl_2 + KOCOR' \longrightarrow Bu_2Sn(Cl)OCOR' + KCl$$

At 100°C trimethyltin chloride reacts with carboxylic acids to give diorganochlorotin carboxylates[37] which may also be prepared by the exchange reaction between dimethyltin dichlorides and triorganotin carboxylates in CCl_4 or C_6H_6 at room temperature[33].

$$Me_3SnCl + RCOOH \longrightarrow Me_2Sn(OCOR)Cl + MeH$$

$$R_2SnCl_2 + R'_3SnOCOR'' \longrightarrow R_2Sn(OCOR'')Cl + R'_3SnCl$$

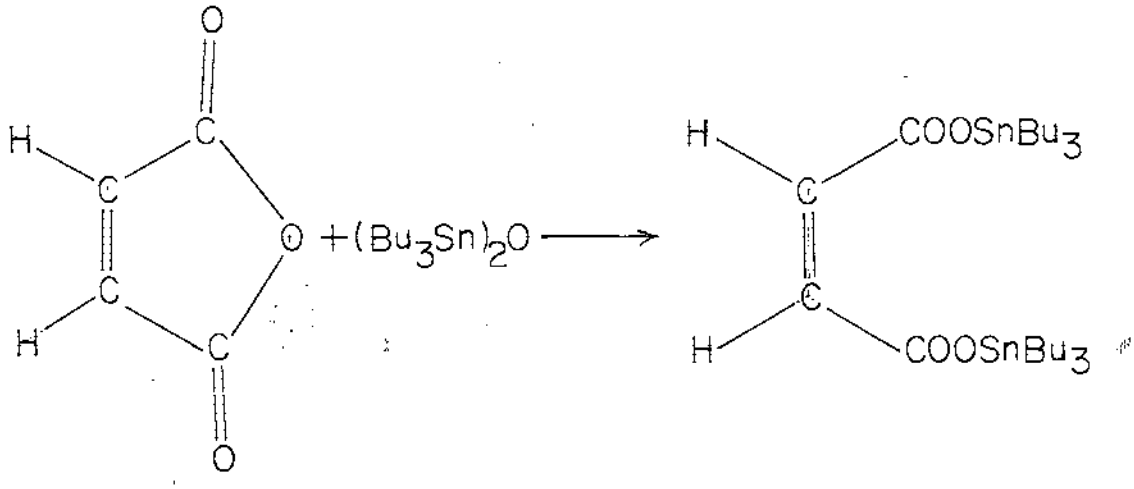
A number of dialkylhalotin acetates have been synthesised according to the reactions[38].

$$(R_2ClSn)_2O + 2CH_3COOH \longrightarrow 2R_2ClSnOCOCH_3 + H_2O$$

$$(R_2ClSn)_2O + (CH_3CO)_2O \longrightarrow 2R_2ClSnOCOCH_3$$

$$R_2SnO + Cl\text{-}\underset{\underset{O}{\|}}{C}\text{-}R \longrightarrow R_2Sn\underset{\underset{Cl}{|}}{O}COR$$

Anhydride of an unsaturated acid (e.g., maleic anhydride) when reacted with hexabutyl distannoxane produces disubstituted organotin esters[39].



Organotin carboxylates may also be prepared from the carboxylic esters by the following reactions[40,41].

$$(R_3Sn)_2O + R'COOEt \longrightarrow R_3SnOCOR' + R_3SnOEt$$

$$R_3SnOH + R'COOEt \longrightarrow R_3SnOCOR' + EtOH$$

Tricarboxylate derivatives of the type $RSn(OCOR')_3$ are usually prepared from the corresponding organotin trichloride by the action of silver salts of carboxylic acids[42].

$$RSnCl_3 + 3R'COOM \longrightarrow RSn(OCOR')_3 + 3MCl$$

I.C. Physical Properties of Organotin Carboxylates

In organotin carboxylates the Sn - O bond is essentially covalent but undergoes polar reactions depending on the solvents and the attacking groups. This is why the carboxylates with small organic groups are more soluble in alcohol, ether etc. than in water[4]. The solubility of triorganotin carboxylates is low in common organic solvents because of their polymeric associated structures. Many of the carboxylates have low melting points indicating these to be covalent compounds.

The polymeric stannoic acids are colourless and infusible. A few of them are soluble in chloroform and carbon tetrachloride and are reasonably stable towards hydrolysis.

The melting points (or boiling points) of some common organotin esters are listed in Table - 1[1,2,4,42-45].

Table - 1

Compounds	B.P. (^{o}C/mm Hg)	M.P. (^{o}C)
I. $R_3SnOCOR'$		
$Me_3SnOCOMe$		196.5 - 197.5
$Ph_3SnOCOH$		202 - 203
$Ph_3SnOCOPh$		84 - 85.5
$Bu_3SnOCOH$	120 - 125/0.7	
$Bu_3SnOCOMe$		85
$Bu_3SnOCOPh$	166 - 168/1	
$(Cy\text{-}Hex)_3SnOCOMe$		62-63
$Pr_3SnOCOCF_3$	88-90/1	
II. $R_2Sn(OCOR')_2$		
$Bu_2Sn(OCOMe)_2$	144.5-145.5/10	
$Ph_2Sn(OCOMe)_2$		116-117
$Bu_2Sn(OCOCH = CHMe)_2$		34
$Bu_2Sn(OCOC_{11}H^{n}_{23})_2$		22-24
III. $R_2SnX(OCOR')$		
$Et_2SnCl(OCOMe)$		94
$Bu_2SnBr(OCOMe)$		67-68.5
IV. $RSn(OCOR')_3$		
$BuSn(OCOCH_3)_3$	117-119/1	
$EtSn(OCOPh)_3$	171-173/1	

I.D. Chemical properties of organotin carboxylates

Generally triorganotin carboxylates are hydrolytically stable, whereas the diorganotin derivatives undergo partial hydrolysis to produce $R_2Sn(OCOR')OSnR_2(OCOR')$ and $R_2Sn(OCOR')OSnR_2OH$[2,46].

The monoorganotin tricarboxylates are easily hydrolysed in EtOH (or benzene) solution to give polymeric monoorganotin oxycarboxylates[13,42]

$$nRSn(OCOR')_3 + nH_2O \xrightarrow{EtOH} \{RSn(O)OCOR'\}_n + 2nR'COOH$$

The most widely studied reactions of organotin carboxylates are decarboxylation and disproportionation. The thermal decarboxylation of triorganotin carboxylates[47] has been used for the preparation of trialkyltin hydrides[48].

$$R_3SnOCOH \xrightarrow{100\text{-}170^{\circ}C} R_3SnH + CO_2$$

$$[R = n\text{-Pr, n-Bu}]$$

Trialkyltin carboxylates of unsaturated acids give trialkylalkynyltins on decarboxylation[49,50].

$$Bu_3SnOCOC{\equiv}CPh \xrightarrow{60^{\circ}C} Bu_3SnC{\equiv}CPh + CO_2$$

$$R_3SnOCOC{\equiv}CCOOSnR_3 \xrightarrow{160^{\circ}C} R_3SnC{\equiv}CSnR_3 + 2CO_2$$

[R = Et, n-Pr, or n-Bu]

An interesting triphenylcyanomethyltin (yield 50%) is formed when triphenyltin cyanoacetate is heated under vacuum[51].

$$Ph_3SnOCOCH_2CN \xrightarrow{140\text{-}150^oC} Ph_3SnCH_2CN + CO_2$$

In the aliphatic series this type of conversion is less pronounced, the triorganocyanomethyltins are produced in low yield.

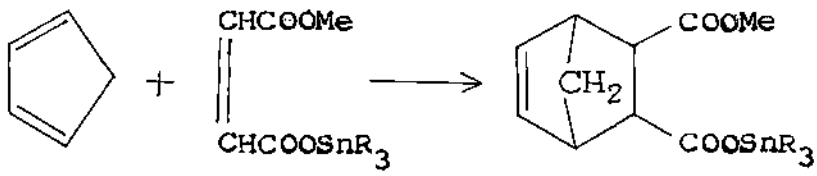
Thermal decomposition of $Ph_3SnOCOR$ (where R = C_6F_5, p-$MeOC_6F_4$ or p-$EtOC_6F_4$) in boiling pyridine give the corresponding polyfluorophenyltriphenyltins[16]. This also undergoes disproportionation reaction resulting in the formation of Ph_4Sn and $Ph_2Sn(OCOR)_2$. Para-$(Ph_3SnOCO)_2C_6F_4$ is readily decarboxylated to produce p-$(Ph_3Sn)_2C_6F_4$.

Seyferth et al[52] have used successfully the reaction of triorganotin carboxylates of halogen substituted carboxylic acids with cyclooctene as a carbene transfer reaction, although the reaction mechanism is not yet established.

$$R_3SnOCOCX_3 + \bigcirc\!\!=\!\!\bigcirc \longrightarrow \bigcirc\!\!-\!\!\bigcirc\!\!<\!\!\begin{matrix}CX_2\\ \end{matrix} + R_3SnX + CO_2$$

$$[\ R = Me, Ph;\ X = Cl, Br\ ]$$

Diels-Alder type reactions have been carried out with organotin carboxylates and dienes[35,39].



(R = Bu^n or Ph)

With thiols the following equilibrium is established and the reaction can be driven from left to right by removing the organic acid from the mixture[53].

$$R_3SnOCOR' + R''SH \rightleftharpoons R_3SnSR'' + R'COOH$$

Action of alkoxy derivatives of metals and metalloids on organotin carboxylates produce metallostannoxanes[54,55] as shown below:

$$Ph_3SnOAc + Ph_2Si(OEt)_2 \longrightarrow Ph_2Si(OSnPh_3)_2 + 2\ EtOAc$$

$$Bu_3SnOAc + Ti(OBu)_4 \longrightarrow Bu_3SnOTi(OBu)_3 \xrightarrow{(HOCH_2CH_2)_3N} Bu_3SnOTi(OCH_2CH_2)_3N$$

Organotin carboxylates readily undergo redistribution with other organotin compounds to form mixed organotin carboxylates[2,56,57].

$$Bu_3SnOCOC_5H_4N\text{-}2 + RSnCl_3 \xrightarrow{MeOH} RSn(OCOC_5H_4N\text{-}2)Cl_2 + Bu_3SnCl$$

〔 R = n-Bu, Ph 〕

$$R_2Sn(OCOR')_2 + R_2SnX_2 \longrightarrow 2R_2Sn(OCOR')X$$

〔 X = hal., OR, H, etc. 〕

In some cases carboxylate groups may be exchanged with other carboxylate groups as shown below[17,58] ;

$$AcOBu_2SnOSnBu_2OAc + 2\ Bu^tCOOH \longrightarrow (Bu^tCOO)Bu_2SnOSnBu_2(OCOBu^t) + 2AcOH$$

Oligomeric acetate is usually formed when a dialkyltin diacetate and a dialkyltin dialkoxide are heated at 180°C in water for 2 hrs[59,60]. Oligomeric α-ω -diacetoxy stannoxanes are also obtained by the reaction[61].

$$Bu_2Sn(OAc)_2 + H_2O \xrightarrow{CH_2N_2} AcO(Bu_2SnO)_nSnBu_2OAc + MeOAc$$

(n = 1, 3, 7, 15)

Generally the organotin esters are weaker Lewis acids than organotin halides, so complex formation by esters is less extensive than by the halides. This weaker acidity appears to be essentially an inductive effect and may be related to the lower electron-withdrawing power of the OCOR' group compared to chlorine atom[62]. The presence of electron-withdrawing organic groups attached to the tin and/or carboxylate moiety will favour complex formation, e.g., $Ph_3SnOCOCCl_3 \cdot MeOH$[63], $Me_3SnOCOC_5H_4N\text{-}2 \cdot H_2O$[64], and $(CH_2 = CH_2)_2Sn(OCOCF_3)_2 \cdot bipy$[65]. Thermodynamic data (ΔH^o, K) have been reported for the formation in benzene solution of 1/1 adducts of $Ph_2Sn(OCOMe)_2$, $Bu_2Sn(OCOMe)_2$ and $Bu_2Sn(OCOEt)_2$ with N-donor ligands like pyridine, 4-methylpyridine, N,N,N',N'- tetramethyl-1,2-diamino ethane and 1,10-phenanthroline[62].

I.E. Biological properties of Organotin Carboxylates

In contrast to inorganic tin compounds which are non-toxic, many organotin compounds are toxic to various organisms and have a variety of fungicidal, insecticidal and bacteriostatic activities. These compounds are, therefore, being used to a significant extent biocidal agents in agriculture and industry.

The toxicological and biological properties as manifested in the organotin carboxylates are summarised in Table -2[96,97,99].

Table - 2

Property	Compounds
1. Mammalian toxicity	$R_3SnOOC.CH_3$ (R = Me, Et, Pr, i-Pr, Bu, C_6H_{13}, C_8H_{17}, Ph)
2. Anthelmintic	Dibutyltindilaurate $Bu_2Sn(OOC(CH_2)_{10}CH_3)_2$
3. Fungicidal	
a) Agricultural	$Ph_3SnOOC.CH_3$, $BuSn(OOC.CH_3)_3$
b) Horticultural	$Bu_3SnOCO(Naphth)$
4. Phytotoxicity	$Ph_3SnOOC.CH_3$, $Ph_3SnOOC.C_6H_5$
5. Bacteriostatic	$Bu_3SnOOC.CH_3$, $Ph_3SnOOC.CH_3$, $Bu_3SnOOC.(CH_2)_4.COOSnBu_3$, $Bu_3SnOOC.C_6H_5$
6. Insecticidal	$Bu_3SnOOC.(CH_2)_6CH_3$, $Me_3SnOOC.CH_2Cl$, $Et_3SnOOC.C(Me) = CH_2$, $Pr_3SnOOC.C(Me) = CH_2$, $R_3SnOOC.CH_3$ (R = Me, Et, Bu, Ph)

I.F. Structures of organotin carboxylates

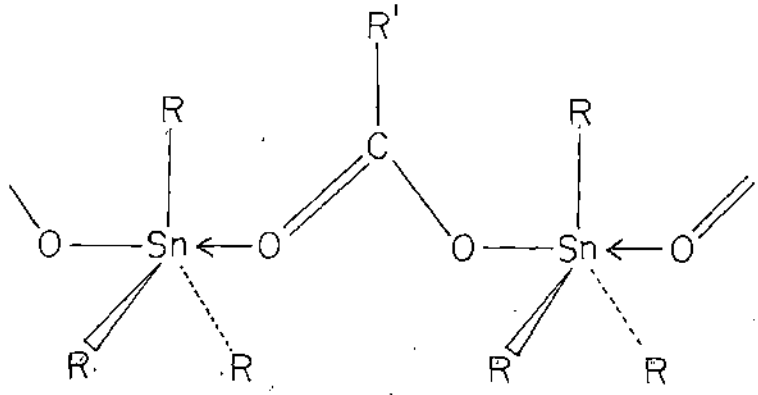
As early as 1961, it was pointed out by Beattie and Gilson[66] that intermolecular bridging through carboxyl oxygen atoms was an alternative to the previously postulated ionic bonding in organotin carboxylates by Freeman[67] and Okawara[68]. Since then, various physical methods like IR, ^{119m}Sn Mössbauer and ^{119}Sn NMR spectroscopy have been utilised to deduce structures of this class of compounds. The subject has been discussed and reviewed by several authors[1-3]. We present below the important physical methods on the basis of which structures of organotin carboxylates are deduced.

I. Infrared Spectroscopy:

(i) Carbonyl group absorptions:

A comparison of the IR spectra $Me_3SnOOCCH_3$ with that of $Me_3SiOOCCH_3$ points to the essential different of structures between these two class of compounds. The trimethyl silyl derivative possesses normal ester structure as evidenced by the appearance of asymmetric stretching frequency of the carboxyl group (ν_{as}OCO) at 1725 cm^{-1}[18,69]. The trimethyl stannyl acetate, on the other hand, shows ν_{as}(OCO) at 1576 cm^{-1}, the absorption frequency being similar to ν_{as}(OCO) of 1578 cm^{-1} in $NaOOCCH_3$. Presence of a symmetrical carboxyl group of the ionised $RCOO^-$ type $\angle^-$ ν_{as}(OCO) 1550-1610 cm^{-1}

and ν_s(OCO) 1300-1400 cm^{-1} _/ is, therefore, indicated[70]. All carboxylates of the type $R_3SnOOCR'$ and $R_2Sn(OOCR')_2$ (R = alkyl/aryl group) show such symmetric and asymmetric carbonyl absorptions in solid state. On dissolving the compounds in non-polar, non-coordinating solvents, the asymmetric stretching frequencies are raised to the region 1650-1700 cm^{-1} while the symmetric frequencies are lowered to a relatively small extent indicating that in solution the molecules possess ester-like structures. Further, the difference between the asymmetric and symmetric stretching frequency $\Delta\nu$ (ν_{as}OCO - ν_sOCO) is generally found to be less than 200 cm^{-1} in solid state and greater than 250 cm^{-1} in solution[69,71]. This has been interpreted in terms of bidentate and an almost symmetrical carboxyl group forming intermolecular bridges in solid state giving rise to polymeric carboxylates (VA) while in solution depolymerisation occurs resulting in ester-like monomeric species (VB)[30,72-74,85,86] having a mono dentate carboxyl group. Molecular weights of the carboxylates in benzene, CCl_4 also supports monomeric structures (VB) in solution with the exception of trimethyltin formate which exists as an equilibrium of associated and unassociated forms in $CHCl_3$[72]. On the other hand, when the group R bonded to the tin atom is too bulky or when there is branching at the carbon atom α- to the tin atom (e.g. triphenyltin 2-ethyl



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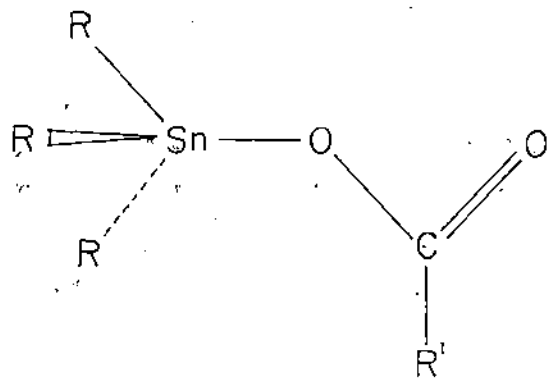


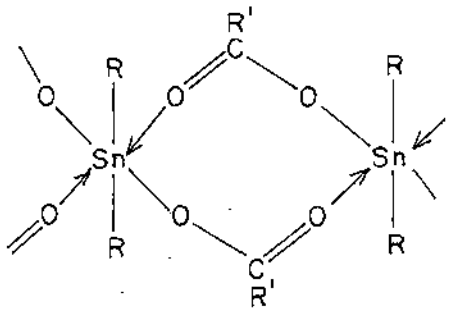
(VB)

hexoate) the compounds assume monomeric ester like structures in solid state as a result of steric hindrance exerted by the bulky organic groups[18,75-79]. Thus, tricyclohexyl, tri-isopropyl-, trineophyl- and tri-α-napthyl tin acetates absorb at 1645 cm^{-1} both in solid state and in solution confirming monomeric structures in both phases. Steric interaction between the alkyl or aryl groups bonded to tin and "tail" of the carboxylate group can also prevent polymerization. For Ph_3Sn derivatives, while $Ph_3SnOOCCHMe_2$ and $Ph_3SnOOCCH = CH_2$ are penta coordinate polymers,

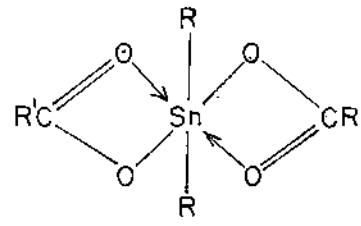
$Ph_3SnOOCCMe_3$, $Ph_3SnOOCCMe=CH_2$ and $Ph_3SnOOCCl_3$ are tetra coordinate monomers in the solid state[12]. Recently it has also been claimed that triphenyltin derivatives of substituted benzoic acids are always monomeric in solid state[85,86]. An analogous situation is also observed in the oxinate-carboxylates, e.g. $RSn(OX)_2OOCR'$ which also have monomeric structures in solid state[80]. Trimethyltin glycinate also has a polymeric chain structure in solid state ($\nu_{as}OCO$ and ν_sOCO are 1630 and 1398 cm^{-1} respectively), but bridging occurs via the NH_2 groups[81].

The structure of dialkyltin dicarboxylates was first suggested for dimethyltin diformate by Okawara[68] which included a linear Me_2Sn cation and a formate anion. Further studies have been carried out on dialkyltin diacetates[82,83] which suggest that in the neat liquid or solid state, those adopt a polymeric structure (VIA) with intermolecularly bridging carboxylate groups and an octahedral trans- R_2SnX_4 tin atom geometry. In solution, these compounds are monomeric as evidenced by raising of $\nu_{as}(OCO)$ frequencies. The molecules have been suggested to be octahedral with intra-molecularly chelated carboxyl groups (VIB)[2]. It is, however, equally likely that these compounds assume a non-chelated ester-like structures in solution (VIC). The dialkyl chlorotin carboxylates $R_2Sn(OCOR')Cl$ are also believed to possess inter-and intra-molecularly chelated structures in the solid state (VIIA) and solution (VIIB)

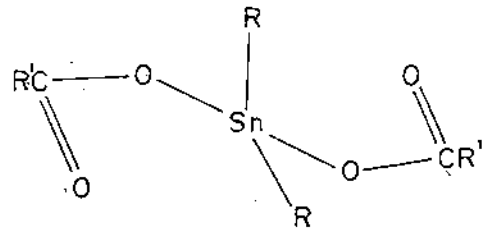
respectively with the tin atoms occupying a trigonal bipyramidal cis- R_2SnX_3 geometry[38].



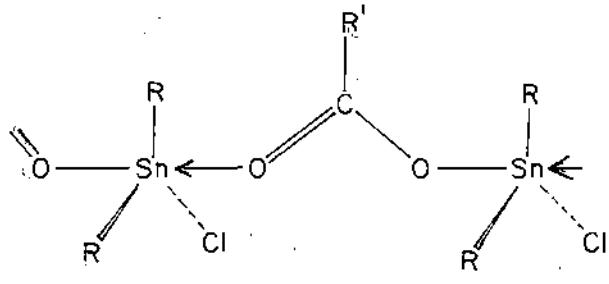
(VIA)



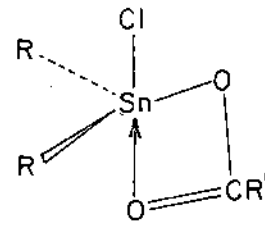
(VIB)



(VIC)



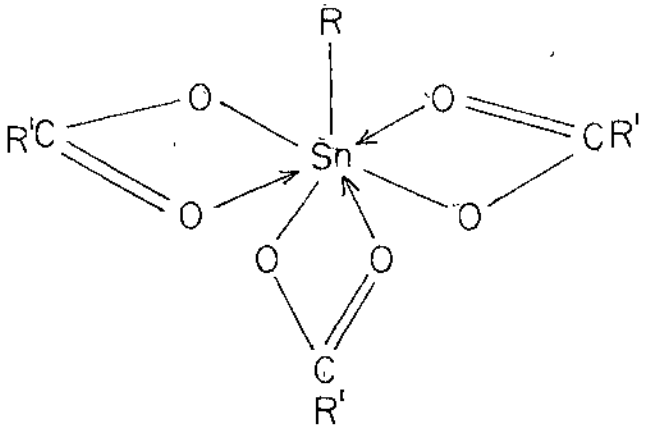
(VIIA)



(VIIB)

The structure of the bis (trimethyl stannyl) ester of a dicarboxylic acid (malonic acid) has recently been determined and shows that in $Me_3SnOOCCH_2COOSnMe_3$, each carbonyl group links planar Me_3Sn moieties intermolecularly to form a three-dimensional polymeric network[84].

The IR spectra of a number of monoorganotin tri-carboxylates in CCl_4 show coordinated carbonyl stretching bands, and, additionally, $BuSn(OOCMe)_3$ and $BuSn(OOCEt)_3$ were found to be monomeric in camphor solution[42]. This is indicative of a 7-coordinated tin atom geometry for these compounds (VIII).



(VIII)

Tin tetra carboxylates are also associated in solid state and undergo dissociation in solution to the monomeric species[2].

Infrared data on carboxyl group frequencies of some tri- and di-organotin carboxylates are summarised in Table - 3.

Table - 3

Carbonyl stretching frequencies in some organotin carboxylates (cm^{-1})

Compound	Solid state		Solution	
	$\nu_{as}(OCO)$	$\nu_{s}(OCO)$	$\nu_{as}(OCO)$	$\nu_{s}(OCO)$
1. $Me_3SnOOCH$	1575	1357	1585[a] 1648	1352
2. $Me_3SnOOC.CH_3$	1564	1346	1645	1314
3. $Me_3SnOOC.CH_2I$	1581	1383	1659	1320
4. $Me_3SnOOC.CH_2Cl$	1618	1382	1687	1339
5. $Me_3SnOOC.CCl_3$	1647	1348	1701	1295
6. $Me_3SnOOC.CF_3$	1652	1340	1720	1290
7. $Bu_3SnOOC.CH_3$	1572	1410	1647	1300
8. $Et_3SnOOC.CH_3$	1572	1412	1655	1302
9. $(C\text{-}Hex)_3SnOOC.CH_3$	1645	1408	1650	1304
10. $(i\text{-}Pr)_3SnOOC.CH_3$	1645	-	1645	-
11. $Me_3SnOOC.C_{11}H_{23}$	1567	1410	1642	1302
12. $Me_2Sn(OOC.CH_3)_2$	1560 1600	1438	1607	1433
13. $Et_2Sn(OOC.CH_3)_2$	1570 1600	1422	1607	1432
14. $Pr^n_2Sn(OOC.CH_3)_2$	1570 1605	1432	1609	1425
15. $Ph_3SnOOCH$	1559	1390	1644	1358

Contd..

Table - 3 (Contd..)

Compound	Solid state $\nu_{as}(OCO)$	Solid state $\nu_{s}(OCO)$	Solution $\nu_{as}(OCO)$	Solution $\nu_{s}(OCO)$
16. $Ph_3SnOOCCH_3$	1548	1420	1640	1370
17. $Ph_3SnOOC.C_2H_5$	1535	1412	1632	1381
18. $Ph_3SnOOC.CMe=CH_2$	1593	1346	1610	1360
19. $Ph_3SnOOCCH(Et)Bu$	1630	1336	1625	1340
20. $Ph_3SnOOC.CMe_3$	1622	1330	1624	1332
21. $Ph_3SnOOC.CCl_3$	1700	1305	1700	1292
22. $Ph_3SnOOC.C_6H_4NHCOCH_3$	1625	1338	1640	1352
23. $Ph_3SnOOC.C_6H_4OH$	1611	1345	1612	1347
24. $Ph_3SnOOC.C_6H_4Cl$	1640	1330	1650	1340
25. $Ph_3SnOOC.C_6H_4CH_3$	1620	1342	1626	1342

(a) both polymeric and monomeric forms are presented in equilibrium in $CHCl_3$

(ii) Tin-carbon stretching frequencies:

The di- and tri- alkyl tin compounds generally show two bands, $\nu_{as}(Sn-C)$ and $\nu_{s}(Sn-C)$ modes causing absorption essentially in the range 500-600 cm^{-1} and 470-530 cm^{-1} respectively[87]. The intensities of these bands vary considerably and, in some cases, only very weak absorption is observed. The position of the absorption bands depends also on the nature of the alkyl group. For example, in the compounds

$Bu^n_nSnX_{4-n}$ (X = halogen), ν_{as}(Sn-C) and ν_s(Sn-C) have been found to occur at 592-602 cm^{-1} and 503-522 cm^{-1} respectively[90]. In phenyltin derivatives, ν_{as} and ν_s(Sn-C) appear at 261-382 cm^{-1} and 225-249 cm^{-1} respectively[87].

However, the organotin carboxylates in solid state being polymeric with intermolecularly coordinated carboxyl groups, show only the ν_{as}(Sn-C) mode confirmingplanar R_3Sn or linear R_2Sn residues. In solution these compounds are depolymerised to tetrahedral stannyl esters and both asymmetric and symmetric Sn-C stretching vibrations are observed, as expected, for non planar R_3Sn and non-linear R_2Sn moieties. Thus, $Me_3SnOOCH$ in $CHCl_3$ shows both ν_{as} and ν_s(Sn-C) but as pyridine is added to the solution, the ν_s(Sn-C) band slowly disappears as the Me_3Sn group assumes a planar configuration in the penta-coordinated 1:1 pyridine complex[73].

ν(Sn-C) IR spectral data of some organotin carboxylates are shown in Table - 4[2,30,85,87,88].

Table - 4

Tin-Carbon stretching frequencies of some organotin carboxylates.

Compound	$\nu_{(Sn-C)}cm^{-1}$	
	Solid	Solution
1. $Me_3SnOOCH$	554	555,516
2. $Me_2SnOOCCH_3$	554	548,517
3. $Me_3SnOOCCH_2I$	551	
4. $Me_3SnOOCCH_2Br$	551	
5. $Me_3SnOOCCH_2Cl$	555	548,515
6. $Me_3SnOOC.C_2H_5$	552	595,516
7. $Me_3SnOOC.C_{11}H_{23}$	548	548,516
8. $Ph_3SnOOCC_6H_4CH_3$ [a]	228,267	
9. $Ph_3SnOOC.C_6H_2(CH_3)_3$ [a]	232,261	
10. $Ph_3SnOOC.C_6H_4OH$ [a]	228,267	
11. $Ph_3SnOOC.C_6H_4NO_2$ [a]	235,270	

a) these compounds have been shown to be tetra-coordinate monomers in solid state (ref. 85)

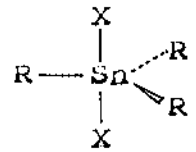
II. Mössbauer Spectroscopy:

Mössbauer spectroscopy offers an excellent tool for investigating structures of organotin compounds in terms of nature of bonding and coordination number of the tin atom. The two Mössbauer parameters of primary interest are the isomer shift, δ (mm/sec) and the quadrupole splitting ΔE_Q (mm/sec). The isomer shift values are

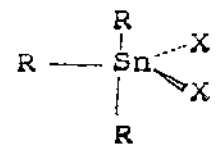
dependent upon the S-electron density at the ^{119}Sn nucleus, and, for all tin compounds, fall in the range ± 5 mm/sec, with a positive δ corresponding to an increase in nuclear S-electron density at the tin atom. Since the electron density at the tin nucleus is related to the S-electron density in the valance shell of the tin atom, δ should vary with the polarity of the tin-ligand bonds[89]. For example, for the series of anionic monobutylpentahalogeno stannate salts $M_2^+ [BuSnX_{5-n}Y_n]^{-2}$, an increase in electronegativity of the halogen attached to tin produces a steady reduction in the nuclear S-electron density, with a concomitant drop in δ. Similarly in a series of organotin derivatives which contain no inorganic radicals, e.g. R_4Sn, or in which the anionic group remains constant, such as R_3SnOH, the isomer shift increases with the electron donating power of the alkyl group. The strongly electron withdrawing nature of a phenyl group attached to tin is reflected in the isomer shift values of the phenyltin derivatives which are usually lower than their alkyltin counterparts. A change in coordination number or stereochemistry at the tin atom will also affect the isomer shift parameter. If the coordination number of the tin increases from four to five or six or seven, the increased use of the metal's 5d-orbitals for bonding results in a reduction in the 5s-electron density at the tin nucleus and a drop in δ, e.g., Ph_2SnI_2 : δ = 1.51 mm/sec, Ph_2SnI_2 bipy : δ = 1.41 mm/sec. For a given coordination

number, change of stereochemistry affects δ. Cis-complexes have significantly lower δ than the trans-complexes and this is probably due to a higher percentage S-character of the Sn-C bonds in the trans-isomer[89].

The δ values for most organotin (IV) compounds fall within the approximate range of -0.50 mm/sec to + 2.70 mm/sec.

If the tin atom has a perfectly spherical symmetry (Me_4Sn, for example), then only a single line is observed in the ^{119m}Sn Mössbauer spectra. However, any deviation of the ^{119}Sn nuclear charge from spherical symmetry results in a two-line quadrupole-splitting in the spectrum and ΔE_Q is the separation between the two peaks in mm/sec. The principal cause of any asymmetry in the ^{119}Sn nucleur charge is an imbalance in the tin atom's 5p valence electrons, which in turn is affected mainly by the spatial arrangements of the organic groups about the metal atom. For regular tetrahedral R_3SnX and R_2SnX_2 compounds ΔE_Q falls within the range 1.00-2.40 mm/sec. Five coordinate triorganotin compounds R_3SnX_2 may have various ΔE_Q values depending on the stereochemistry. For the trans- structure  , if both axial Sn-X bond lengths are equal, as in Me_3SnOH which consists of chains of planar Me_3Sn groups linked symmetrically by bridging X radicals, ΔE_Q is close to 3.00 mm/sec. However, an increasing difference

between the two axial Sn-X bond lengths causes a movement of ΔE_Q towards 4.00 mm/sec[89]. The cis-isomers of R_3SnX_2 give ΔE_Q values in the range 1.70-2.40 mm/sec while the trans-mer form



is expected to have values in the range 3.50-4.10 mm/sec[89]. Octahedral R_3SnX_3 compounds have ΔE_Q values from 0.00 mm/sec to ~ 3.50 mm/sec depending on cis- or trans-stereochemistry. Diorganotin compounds of the type of R_2SnX_4 have ΔE_Q values ~ 4.00 mm/sec and ~ 2.00 mm/sec for trans- and cis-isomers respectively[89]. The ΔE_Q values increase smoothly with increasing C-Sn-C angle for octahedral diorganotin complexes, for example, $Me_2Sn(OX)_2$ 2.02 mm/sec (C-Sn-C = 110.7°) and $Me_2Sn(acac)_2$ 4.02 mm/sec (C-Sn-C = 180°).

Herber et al[90] have argued that so long as the range of bond ionicities in a series of compounds is not too large, the ratio of quadrupole splitting to isomer shift ($\rho = \Delta E_Q/\delta$) can be used to distinguish between compounds in which the tin atom is penta-coordinate and those in which it is tetra- coordinate. They suggest that (with δ relative to SnO_2), a value of $\rho > 2.1$ is evidence of penta- coordination about the tin atom, whereas if $\rho < 1.8$, the tin atom is tetra- coordinate.

It is therefore obvious from the foregoing discussions that ^{119m}Sn Mössbauer spectroscopy provides a very effective tool for elucidating the structural varieties exhibited by organotin carboxylates. The two main types, e.g., the intermolecularly carboxyl

bridged polymeric molecules with penta- coordinate tin atom and the normal ester type tetra- coordinate species can be easily distinguished from the δ and ΔE_Q values as shown in Table - 5. The data in Table - 5 have been collected from references[2,12,18,87,88,92]. Effect of electronegative substituents attached to the carboxyl residue on the density of S-electrons at the tin nucleus and on the Sn-C bond ionicities have also been elucidated from the Mössbauer parameters[12,88,95].

Table - 5

^{119m}Sn Mössbauer parameters of some organotin carboxylates.

Compound	δ mm/sec	ΔE_Q mm/sec	Structure in solid state
1. $(Neophyl)_3SnOOCMe$	1.35	2.45	Monomer
2. $Bu_2Sn(OOCMe)_2$	1.40	3.45	Polymer
3. $Bu_2Sn(OCC.C_7H_{15})_2$	1.45	3.50	"
4. $Bu_2Sn(OOC.C_{17}H_{35})_2$	1.45	3.30	"
5. $Bu_2Sn(OOC.CH_2Cl)_2$	1.60	3.65	"
6. $Bu_2Sn(OOC.CCl_3)_2$	1.65	3.80	"
7. $Me_3SnOOC.CH_3$	1.35	3.68	"
8. $Me_3SnOOC.CCl_3$	1.44	4.15	"
9. $Me_3SnOOC.CF_3$	1.38	4.22	"

Contd..

Table - 5 (Contd..)

Compound	δ mm/sec	ΔE_Q mm/sec	Structure in solid state
10. $Bu_3SnOOC.CH_3$	1.46	3.64	Polymer
11. $Ph_3SnOOCH$	1.37	3.58	"
12. $Ph_3SnOOCMe$	1.27	3.40	"
13. $Ph_3SnOOCEt$	1.33	3.42	"
14. $Ph_3SnOOC.\underset{\underset{Me}{|}}{C} = CH_2$	1.21	2.26	Monomer
15. $Ph_3SnOOCH(Et)Bu$	1.21	2.26	"
16. $Ph_3SnOOCCMe_3$	1.21	2.40	"
17. $Ph_3SnOOC.CCl_3$	1.30	2.97	"

Besides the carboxylates mentioned in Table 5, there are also ^{119m}Sn Mössbauer investigations by Harrison et al[92] on the organotin complexes of arylazobenzoic acids prepared by Majee and co-workers[93,94].

III. X-ray Crystallography:

Single crystal X-ray crystallography has demonstrated chain polymeric involving bridging carboxylate groups and planar or near planar R_3Sn moieties (VA), structures for $Me_3SnOOC.Me$,

$Me_3SnOOC.CF_3$, $Me_3SnOOCH$, $(C_6H_5CH_2)_3SnOOC.Me$ and $(CH_2 = CH)_3SnOOCCCl_3$.[98] Trimethyltin glycinate $Me_3SnOOC.CH_2NH_2$ also has a polymeric chain structure but bridging occurs via the NH_2 groups[98]. Although tricyclohexyltin acetate was earlier shown to contain discreet monomeric molecules, recent more refined XRD analysis has revealed this compound and the tricyclohexyltin trifluoroacetate to be one-dimensional chain polymers involving, however, weakly Syn, anti-bridging carboxylato groups[92]. The first example of a truly monomeric carboxylate as demonstrated by X-ray crystallography is the compound triphenyltin ortho-(2-hydroxy-5-methyl-phenylazo) benzoate[92].

No X-ray studies are yet available on any diorganotin dicarboxylates or monoorganotin tri- carboxylates[98].

IV. ^{119}Sn NMR Spectroscopy:

Comparatively recently, ^{119}Sn NMR spectroscopy has emerged as yet another important physical method for characterisation of organotin carboxylates[86,87,88].

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CHAPTER– II

Phenoxyalkanoic Acids & Their Metal Complexes : A Short Review

CHAPTER - II

Phenoxyalkanoic acids and their metal complexes: A short review

IIA. Phenoxyalkanoic acids : Well-known Herbicides

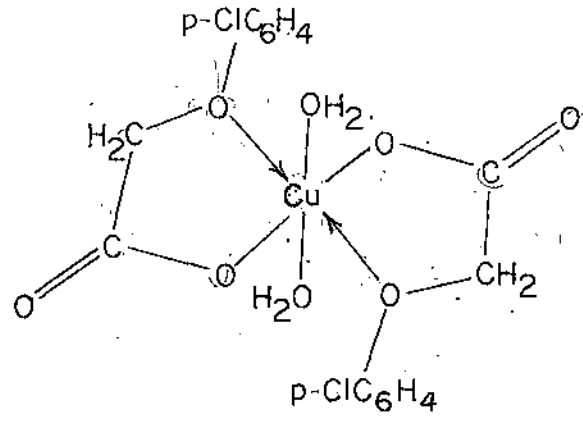
The phenoxyalkanoic acids constitute an important group of synthetic chemicals which have significant herbicidal activities depending on both the position and type of substituent in the benzene ring and on the side-chain configuration. These compounds belong to the large group of plant growth-regulating compounds designated as Auxins. Auxins may be defined as organic substances which at low concentrations (less than 10^{-3}M) promote growth along the longitudinal axis of shoots and inhibit elongation of roots. Natural auxins include indole-3-acetic acid (IAA) and related compounds, such as, 3-(indole-3-) propionic, 4-(indole-3)n-butyric, 3-(indole-3-) pyruvic acid and indole-3-acetaldehyde and indole-3-acetonitrile. Synthetic auxins, such as the herbicidal phenoxyalkanoic acids, show effects similar to those of the natural auxins in standard plant and plant tissue tests[1].

The acetic acid analogues of phenoxyalkanoic acids, such as 2, 4-dichlorophenoxyacetic acid (2,4-D), 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) and 4-chloro-2-methylphenoxyacetic acid (MCPA) are common commercial auxin herbicides and are used for the control of weeds in cereal crops, woody broad leaved plants, grass pastures and lawns, as defoliants as well as in many other situations[1]. Similar herbicidal activity is possessed by the analogous

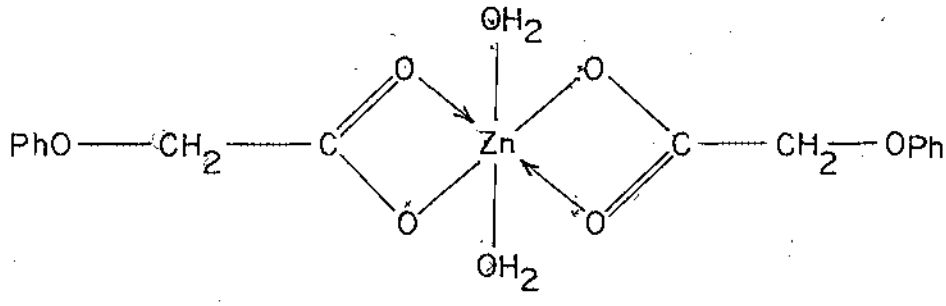
2-propionic acid homologues, e.g. 2-(2, 4-dichlorophenoxy) propionic acid, 2-(2,4,5-trichlorophenoxy)propionic acid and 2- [(4-chloro-o-tolyl)oxy] propionic acid. The 4-phenoxy-butyric acid herbicides are also widely used for similar purpose.

IIB. Metal and Organometallic Complexes:

Although metal chelate formation has been disproved as the mode by which the phenoxyalkanoic acid herbicides act[2], interaction of these carboxylic acids with common metal ions is of particular interest in relation to a basic understanding of their scavenging effect in aqueous media. C.H.L. Kennard et al have made a thorough study on the structure and bonding of complexes of phenoxyalkanoic acids with Cu(II) and Zn(II)[3-6]. It was found that the ligand behaves both as monodentate and bidentate depending on ring substitution and other factors. Thus, diaquabis (p-chloro phenoxyacetato) copper (II) is found from X-ray diffraction study to be a tetragonally distorted octahedral complex, the coordination sphere consisting of two water oxygens and two carbonyl oxygens from different bidentate phenoxyacetate ligands about the square plane while the axial positions are occupied by two ether oxygens (Fig. I). Cu (p-methoxy phenoxyacetato)$_2$(H_2O)$_2$ and Cu(p-nitrophenoxyacetato)$_2$(H_2O)$_2$ have similar bidentate chelate structures.



(I)



(II)

There are reports of preparation and physico-chemical study of rare earth element phenoxyacetates[7,8]. Analogous alkoxyacetates of trivalent lanthanoids have been synthesised and shown to involve coordination by both ether oxygen and carboxyl oxygen atoms[9].

Besides some organosilicon derivatives, no other organometallic complex of aryloxy acetic or the other aryloxy-alkanoic acids have yet been reported. The organosilicon derivatives prepared include[10-13] triorganosilyl esters $ROCH_2COOSiR'_3$

(R = C_6H_5; 4-ClC_6H_4; 2,4-$Cl_2C_6H_3$; 2-, 3- and 4-$CH_3C_6H_4$; 1-napthyl; 2,4,5-$Cl_3C_6H_2$ and R' = CH_3, C_2H_5, C_3H_7, C_6H_5, OCH_3, OC_2H_5). The compounds were prepared by (i) refluxing the aryloxyacetic acid with R'_3SiCl in toluene and (ii) refluxing $ROCH_2COOK$ with R'_3SiCl in DMF. Non-availability of the literatures prevents us from knowing details of the structure and bonding of these complexes.

A survey of the literature, however, shows that no attempt was made to study the effect of metal complexation on the herbicidal as well as other biological properties of the parent phenoxyalkanoic acids.

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CHAPTER–III

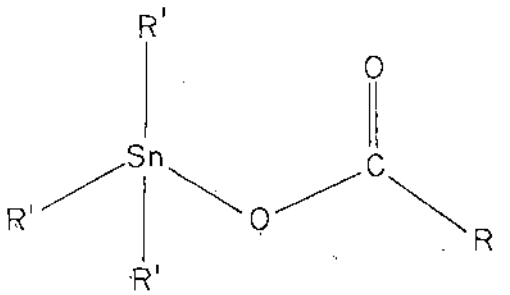
Preparation Of Organotin Aryloxyacetates & Spectroscopic Study Of Their Structures In Solution & Solid Phases

CHAPTER - III

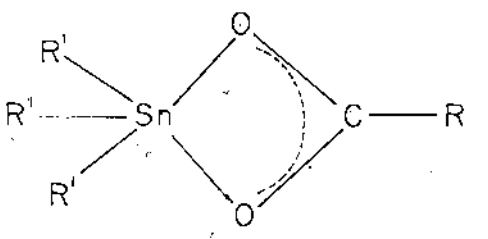
Preparation of Organotin aryloxyacetates and Spectroscopic Study of their structures in solution and solid phases.

IIIA. Introduction

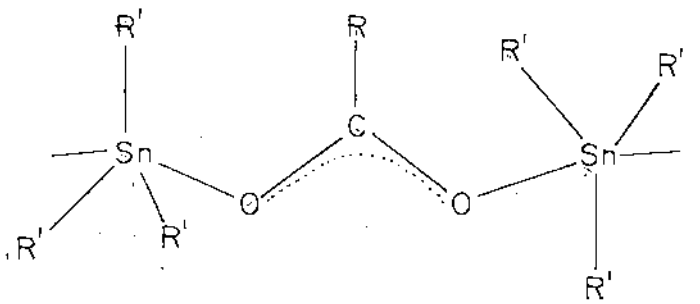
Triorganotin carboxylates are rich with structural possibilities, centered around the triad of structures I-III (R' = alkyl/aryl group; R=H, alkyl/aryl group). In addition to a tetrahedral geometry at tin arising from a monodentate carboxylate ligand (I), a bidentate ligand can either chelate (II) or bridge (III) tin atoms to result in variations on a trigonal



(I)



(II)



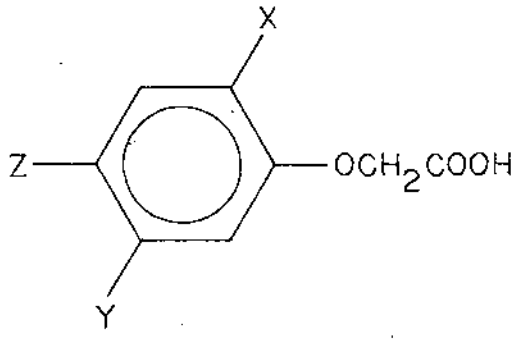
(III)

bipyramidal geometry at the metal atom. In the solid state, available examples are dominated by III[1,2] with only one crystallographically authenticated claim being made for structure I, namely, tricyclohexylstannyl 3-indolyl acetate[3]. Data for $Ph_3SnOOCC_6H_4X$ (X=2-NH_2, 4-NH_2, 2-NMe_2, 2-OH, 2-OMe or 4-SMe) have all been interpreted in terms of 5-coordinate structure II[4,5] although this has recently been questioned[6]. The only yet undisputed structure of type II has been demonstrated crystallographically for triphenyltin o-(2-hydroxy-5-methylphenylazo)benzoate[7]. In solution, the carboxylates normally have structure I[1,2] unless there are substituents on the ring in R with lone pairs of electrons or hydrogen bonding possibilities exist[6].

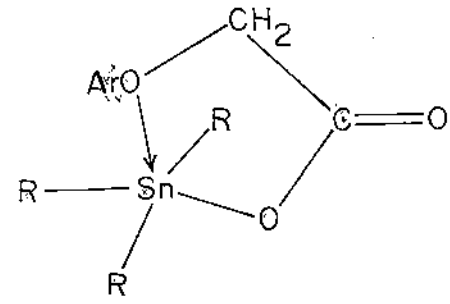
As compared to their triorganotin analogues, there are very few reports on the structures of the diorganotin carboxylates[1].

In the continued interest in this class of compounds, attempts to synthesise truely monomeric organotin carboxylates in solid phase are readily discernible. For example, triphenyltin derivatives of substituted benzoic acids have been shown from spectroscopic evidences to possess structure I in solid state[6,8-10]. Examples of monomeric carboxylates in which the carboxylate group is part of a chelated ring formed by intramolecular coordination of N$\longrightarrow$Sn has been provided by Majee et al[11-13] for tri- and di- organotin derivatives of arylazo benzoic acids, napthylazobenzoic acids, arylazoquinolinols and arylazophenoxyacetic acids.

Aryloxyacetic acids (IV) appear to be suitable ligands for realisation of intramolecularly coordinated monomeric organotin carboxylates of the type V in which the carboxylato group is part of a chelated ring.

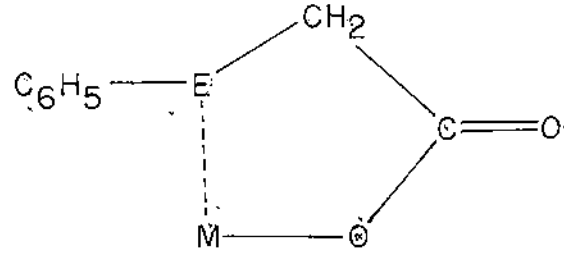


(IV)



(V)

In fact, a characteristical structural feature usually found in molecules and crystals of phenoxyacetates and phenylthioacetates of metals (transition metals in particular) is a five-membered chelate cycle (VI; M = metal atom, E = O or S).



(VI)

As seen, an important part in structure VI is played by the donor-acceptor intramolecular connection of the E atom and the central metal atom M^{14}.

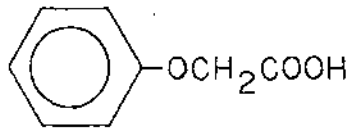
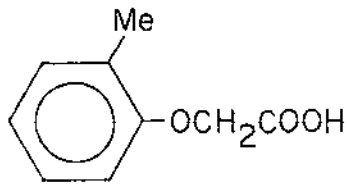
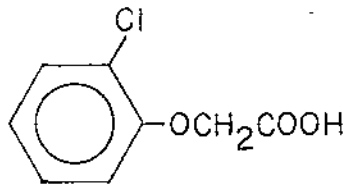
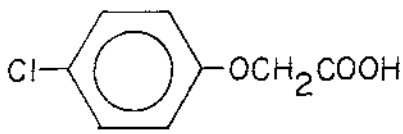
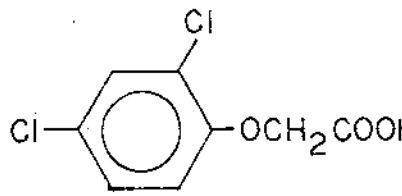
The present work was, therefore, undertaken with the following objectives:-

1. To synthesise tri- and di- organotin complexes of the aryloxyacetic acids (IV) and determine their structures in solid and solution phases.
2. To determine whether the basicity of the phenoxy oxygen atom is sufficient to form intramolecular coordinate bond with the organotin group leading to monomeric species in preference to the normally observed polymeric structures.
3. To determine whether substitution of the oxygen atom in IV by sulfur atom has any effect on the structures of the corresponding organotin phenylthioacetates.
4. To study the biocidal properties of the organotin carboxylates in which the biocidal activity of the R_nSn group and that of the carboxylic residue are expected to be mutually combined and complemented.

The aryloxyacetic acids (IV) and one phenylthioacetic acid used in the present work have been named and abbreviated as shown in Table 1. Also included in the Table is β-phenylpropionic acid. Reasons for its inclusion would be discussed in due course.

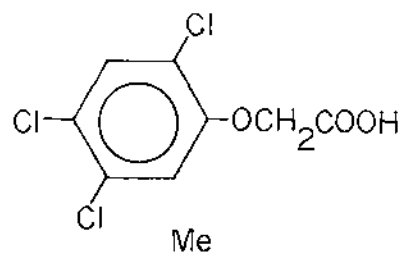
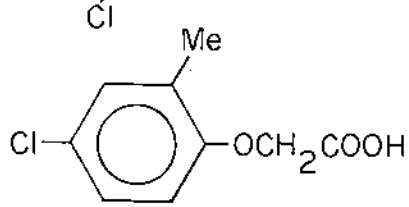
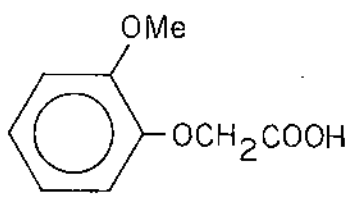
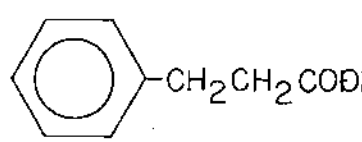
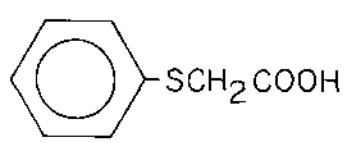
Talbe - 1

Ligands and their abbreviations

	Structure	Name	Abbreviation
1.		Phenoxyacetic acid	L_1H
2.		2-Methylphenoxyacetic acid	L_2H
3.		2-Chlorophenoxyacetic acid	L_3H
4.		4-Chlorophenoxyacetic acid	L_4H
5.		2,4-Dichlorophenoxyacetic acid	L_5H

Contd..

Table - 1 (Contd..)

Structure	Name	Abbreviation
6. 	2,4,5-Trichlorophenoxy-acetic acid	L_6H
7. 	4-chloro-2-Methyl phenoxyacetic acid	L_7H
8. 	2-Methoxyphenoxy acetic acid	L_8H
9. 	β-Phenylpropionic acid	L_9H
10. 	Phenylthioacetic acid	$L_{10}H$

All the aryloxyacetic acids were prepared by the reaction between the appropriate phenol and chloroacetic acid in NaOH solution. L_9H was prepared by reaction between sodium diethyl malonate and benzyl chloride followed by hydrolysis. $L_{10}H$ was purchased from M/S Fluka, Switzerland and was used as such.
Details are given in the experimental section.

IIIB. Methods of Preparation:

In order to prepare the organotin derivatives, the following methods were employed.

(i) Reaction of the carboxylic acids with the organotin oxide in dry benzene:

$$2\ ROCH_2COOH + (R'_3Sn)_2O \longrightarrow 2ROCH_2COOSnR'_3 + H_2O \quad \ldots (1)$$

$$2\ ROCH_2COOH + R'_2SnO \longrightarrow (ROCH_2COO)_2SnR'_2 + H_2O \quad \ldots (2)$$

(ii) Reactions of the carboxylic acids with the organotin halides in dry benzene:

$$ROCH_2COOH + R'_3SnCl \longrightarrow ROCH_2COOSnR'_3 + HCl \quad \ldots (3)$$

$$2ROCH_2COOH + R'_2SnCl_2 \longrightarrow (ROCH_2COO)_2SnR'_2 + 2HCl \quad \ldots (4)$$

(iii) Reactions of the Na/Ag - salts of the carboxylic acids with the organotin halides in dry methonol :

$$ROCH_2COOM + R'_3SnCl \longrightarrow ROCH_2COOSnR'_3 + MCl \quad \ldots (5)$$

$$2ROCH_2COOM + R'_2SnCl_2 \longrightarrow (ROCH_2COO)_2SnR'_2 + 2MCl \quad \ldots (6)$$

Addition of a few drops of diethylamine or pyridine was found to facilitate reactions (3) and (4).

The corresponding phenylthioacetates were also prepared by using similar reactions.

A summary of the reaction products together with the experimental conditions used in the present work are given in Table 2.

Table - 2

Summary of the reactions and products obtained

Sl. No.	Reactants (mole ratio)	Experimental conditions used	Product (m.p. °C, Yield %)
1.	L_1H + $(Bu_3Sn)_2O$ (2:1)	Refluxing for 6 hrs. in dry benzene; product recrystallized from pet. ether.	Bu_3SnL_1 (53-54°C, 78)
2.	L_1H + $(Pr_3Sn)_2O$ (2:1)	Stirring at RT for 10 hrs. in dry benzene; product recrystallized from pet. ether.	Pr_3SnL_1 (50-52°C, 60)

Contd..

Table - 2 (Contd..)

Sl. No.	Reactants (Mole ratio)	Experimental conditions used	Product (m.p. °C, Yield %)
3.	L_1H + $(Ph_3Sn)_2O$ (2:1)	Stirring at RT for 30 mins. in dry benzene; product purified by repeated precipitation from acetone-benzene mixture.	Ph_3SnL_1 (158°, 88)
3a.	L_1Na + Ph_3SnCl (2:1)	Stirring overnight at RT in spectral grade acetonitrile; product recrystallized from benzene-pet. ether mixture	Ph_3SnL_1 (158°, 72)
4.	L_1H + Me_2SnO (2:1)	Refluxing for 1 hr. in dry benzene; product recrystallized from benzene.	$Me_2Sn(L_1)_2$ (218°, 95)
4a.	L_1H + Me_2SnCl_2 (2:1)	Refluxing for 6 hrs. in dry benzene; product recrystallized from benzene	$Me_2Sn(L_1)_2$ (218°, 35)

Contd..

Table - 2 (Contd..)

Sl. No.	Reactants (mole ratio)	Experimental conditions used	Product (m.p. °C, Yield %)
5.	L_1H + Bu_2SnO (2:1)	Stirring at ~60°C for 3 hrs. in dry benzene; product recrystallized from benzene-pet. ether mixture.	$Bu_2Sn(L_1)_2$ (133-134.5°, 80)
6.	L_1H + Oct_2SnCl_2 (2:1)	Refluxing for 10 hrs. in dry benzene; product recrystallized from benzene-pet. ether mixture.	$Oct_2Sn(L_1)_2$ (114-116°, 40)
7.	L_2H + $(Bu_3Sn)_2O$ (2:1)	Refluxing for 6 hrs. in dry benzene; product recrystallized from pet. ether.	Bu_3SnL_2 (70.5-71.5°, 81)
8.	L_2H + Bu_2SnO (2:1)	Refluxing for 3 hrs. in dry benzene; product recrystallized from benzene-pet. ether mixture	$Bu_2Sn(L_2)_2$ (112-114°, 85)

Contd..

Table - 2 (Contd..)

Sl. No.	Reactants (mole ratio)	Experimental conditions used	Product (m.p. °C, Yield %)
9.	L_3H + $(Bu_3Sn)_2O$ (2:1)	Refluxing for 6 hrs. in dry benzene; product recrystallized from pet. ether	Bu_3SnL_3 (68.5-69.5°, 88)
10.	L_3Na + Ph_3SnCl (2:1)	Stirring overnight at RT in spectral grade acetonitrile; product purified by repeated precipitation from benzene-pet. ether mixture.	Ph_3SnL_3 (174°, 70)
10a.	L_3H + $(Ph_3Sn)_2O$ (2:1)	At first, stirring at RT for 10 mins. in dry benzene, then refluxing for 15 mins.; product purified by repeated precipitation from benzene.	Ph_3SnL_3 (174, 92)
11.	L_3H + Bu_2SnO (2:1)	Refluxing for 3 hrs. in dry benzene; product recrystallized from benzene-pet. ether mixture	$Bu_2Sn(L_3)_2$ (156°, 85)

Contd...

Table - 2 (Contd..)

Sl. No.	Reactants (mole ratio)	Experimental conditions used	Product (m.p. °C, Yield %)
12.	L_4H + $(Bu_3Sn)_2O$ (2:1)	Refluxing for 6 hrs. in dry benzene; product recrystallized from pet. ether.	Bu_3SnL_4 (74-76°, 70)
13.	L_4H + $(Ph_3Sn)_2O$ (2:1)	Stirring at RT followed by refluxing for 15 mins. in dry benzene; the product purified by precipitation from benzene-pet. ether mixture.	Ph_3SnL_4 (146, 90)
14.	L_4H + Bu_2SnO (2:1)	Refluxing for 3 hrs. in dry benzene; the product recrystallized from benzene-pet. ether mixture.	$Bu_2Sn(L_4)_2$ (125-126°, 82)
15.	L_4H + Oct_2SnCl_2 (2:1)	Refluxing for 36 hrs. in dry benzene; the product recrystallized from pet. ether.	$Oct_2Sn(L_4)_2$ (133°, 45)
15a.	L_4H + Oct_2SnO (2:1)	Stirring at RT for 1 hr. in dry benzene; the product recrystallized from pet. ether.	$Oct_2Sn(L_4)_2$ (133°, quantitative)

Contd..

Table - 2 (Contd..)

Sl. No.	Reactants (mole ratio)	Experimental conditions used	Product (m.p. °C, Yield %)
16.	L_5H + $(Bu_3Sn)_2O$ (2:1)	Refluxing for 6 hrs. in dry benzene; the product recrystallized from pet. ether.	Bu_3SnL_5 (82-84°, 86)
17.	L_5H + $(Ph_3Sn)_2O$ (2:1)	Stirring at RT for 30 mins.; the product purified by precipitation from ethanol soln.	Ph_3SnL_5 (175°, quantitative)
18.	L_5H + Bu_2SnO (2:1)	Refluxing for 2.5 hrs. in dry benzene; product recrystallized from benzene.	$Bu_2Sn(L_5)_2$ (167-170°, quantitative)
19.	L_6H + Bu_2SnO (2:1)	Refluxing for 2 hrs. in dry benzene; product recrystallized from benzene.	$Bu_2Sn(L_6)_2$ (160°, quantitative)
20.	L_7H + Bu_2SnO (2:1)	Refluxing for 4 hrs. in dry benzene; product recrystallized from benzene-pet. ether mixture.	$Bu_2Sn(L_7)_2$ (122°, quantitative)
21.	L_8H + $(Bu_3Sn)_2O$ (2:1)	Refluxing for 8 hrs. in dry benzene; product recrystallized from pet. ether.	Bu_3SnL_8 (68-70°, 72)

Contd..

Table - 2 (Contd..)

Sl. No.	Reactants (mole ratio)	Experimental conditions used	Product (m.p. °C, Yield %)
22.	L_8H + $(Ph_3Sn)_2O$ (2:1)	Refluxing for 15 mins. in dry benzene; product recrystallized from benzene.	Ph_3SnL_8 (145-148°, 88)
23.	L_8H + Bu_2SnO (2:1)	Refluxing for 3 hrs. in dry benzene; product recrystallized from benzene.	$Bu_2Sn(L_8)_2$ (120-122°, 79)
24.	L_9H + $(Bu_3Sn)_2O$ (2:1)	Refluxing for 4 hrs. in dry benzene; product recrystallized from pet. ether.	Bu_3SnL_9 (64-66°, 74)
25.	$L_{10}H$ + $(Bu_3Sn)_2O$ (2:1)	Refluxing for 8 hrs. in dry benzene; product recrystallized from pet. ether.	Bu_3SnL_{10} (63-67°, 90)
26.	$L_{10}H$ + Bu_2SnO (2:1)	Refluxing for 5 hrs. in dry benzene; product recrystallized from benzene-pet. ether mixture.	$Bu_2Sn(L_{10})_2$ (88-89°, 80)

An examination of Table - 2 would show that the reactions where organotin oxides are used (eqn. 1 and 2) are much faster and yields are also much higher. In some cases even stirring for a small period is sufficient for an almost quantitative reaction. On the other hand, reactions using eqn. 3-6 give low to moderate yields and require longer periods for complete reaction. All the reactions are neat without formmation of any side-product. The compounds are all colourless crystalline solids with well defined melting points and are very stable even in open air.

An interesting observation was made in reactions of $(Ph_3Sn)_2O$ with phenoxyacetic acid (L_1H) and 2,4-dichlorophenoxy-acetic acid (L_5H) in benzene. When the reaction mixture is either refluxed or kept at RT for a long time, another product having a higher m.p. ($>280^{o}C$) was obtained. This new product, however, had IR spectrum exactly similar to the product shown in Table -2. The analytical data of the two products were also same. The high melting compound was also appeared when the low melting normal product (depicted in Table - 2) was heated in benzene. But when this was heated in methanol, ethanol or acetone (instead of benzene), the product of higher melting point was never obtained. It seems that the two products may differ only in the degree of polymerisation.

IIIC. Analytical Data

Analytical data of the organotin derivatives are given in Table - 3. The data which agree well with theory clearly

indicate formation of well-defined organotin compounds.

Table - 3

Analytical data of the organotin aryloxyacetates and phenylthioacetates.

Sl. No.	Compounds	Found (Calc.) %			
		C	H	Sn	Others
1.	Bu_3SnL_1	54.59 (54.45)	7.59 (7.77)	26.79 (26.90)	
2.	Pr_3SnL_1	53.60 (51.17)	6.95 (7.42)	29.10 (29.77)	
3.	Ph_3SnL_1	61.55 (62.31)	4.94 4.39)	22.98 (23.71)	
4.	$Me_2Sn(L_1)_2$	47.15 (47.92)	4.39 (4.44)	26.12 (26.34)	
5.	$Bu_2Sn(L_1)_2$	54.09 (53.86)	6.14 (6.03)	21.98 (22.18)	
6.	$Oct_2Sn(L_1)_2$	59.85 (59.38)	7.39 (7.41)	17.95 (18.35)	
7.	Bu_3SnL_2	55.84 (55.41)	8.07 (7.97)	25.97 (26.07)	
8.	$Bu_2Sn(L_2)_2$	55.76 (55.44)	6.42 (6.44)	21.37 (21.07)	
9.	Bu_3SnL_3	50.75 (50.51)	7.03 (6.99)	24.53 (24.95)	7.57[a] (7.45)
10.	Ph_3SnL_3	58.41 (58.30)	3.90 (3.92)	22.65 (22.18)	6.82[a] (6.63)
11.	$Bu_2Sn(L_3)_2$	47.80 (47.72)	4.91 (5.00)	20.12 (19.65)	11.86[a] (11.74)
12.	Bu_3SnL4	50.42 (50.51)	7.08 (6.99)	24.65 (24.95)	7.75[a] (7.45)

Contd..

Table - 3 (Contd..)

Sl. No.	Compounds	Found (Calc.) %			
		C	H	Sn	Others
13.	Ph_3SnL_4	57.90 (58.30)	3.85 (3.92)	22.92 (22.18)	
14.	$Bu_2Sn(L_4)_2$	47.71 (47.72)	5.07 (5.00)	19.69 (19.65)	11.93[a] (11.74)
15.	$Oct_2Sn(L_4)_2$	53.69 (53.65)	6.61 (6.43)	16.10 (16.59)	
16.	Bu_3SnL_5	47.34 (47.09)	6.34 (6.28)	23.75 (23.29)	
17.	Ph_3SnL_5	54.92 (54.77)	3.63 (3.51)	20.93 (20.84)	12.68[a] 12.46)
18.	$Bu_2Sn(L_5)_2$	42.97 (42.83)	4.38 (4.19)	17.94 (17.64)	20.83[a] (21.07)
19.	$Bu_2Sn(L_6)_2$	38.18 (38.62)	3.50 (3.49)	16.28 (15.92)	
20.	$Bu_2Sn(L_7)_2$	49.90 (49.08)	5.30 (5.35)	19.15 (18.67)	
21.	Bu_3SnL_8	53.48 (53.54)	7.69 (7.65)	25.68 (25.22)	
22.	Ph_3SnL_8	60.98 (61.05)	4.48 (4.52)	22.79 (22.37)	
23.	$Bu_2Sn(L_8)_2$	52.32 (52.46)	6.23 (6.10)	20.08 (19.94)	
24.	Bu_3SnL_9	57.37 (57.44)	8.15 (8.21)	26.95 (27.06)	
25.	Bu_3SnL_{10}	52.80 (52.54)	7.36 (7.50)	26.10 (25.96)	6.87[b] (7.01)
26.	$Bu_2Sn(L_{10})_2$	50.69 (50.81)	6.12 (5.69)	21.15 (20.92)	11.03[b] (11.30)

a) Cl; b) S.

IIID. Molecular Weights

The molecular masses of some of the organotin compounds were determined by vapour pressure osmometry in benzene solution and, in some cases, by cryoscopy in benzene. The data, shown in Table - 4, clearly correspond to monomeric molecules in solution.

Table - 4

Molecular weights of the organotin carboxylates in non-polar solvents.

Sl. No.	Compound	Experimental molecular weight	Average Mol. Wt.	Mol. wt. calculated for monomer
1.	$Bu_2Sn(L_1)_2$	560, 548	554	535.7
2.	Bu_3SnL_2	390, 400	395	454.7
3.	$Bu_2Sn(L_3)_2$	590,598	594	603.7
4.	Bu_3SnL_4	468,479	473.5	475.2
5.	$Oct_2Sn(L_4)_2$	720,723	721.5	715.7
6.	Bu_3SnL_5	497,499	498	509.7
7.	$Bu_2Sn(L_5)_2$	656,672	659	672.7
8.	Ph_3SnL_8	530,522	526	530.7
9.	Ph_3SnL_9	460,480	470	466.7

IIIE. Infrared Spectra

Before discussing the infrared spectra of the compounds in detail, it would be useful to point out the different regions of interest to us.

i) 1550-1700 cm^{-1} : In this region $\nu_{as}(COO)$ is expected[1,2,15]. Because of the presence of strongly absorbing ring vibrational modes (of aromatic carboxylates) in this region which sometimes partly overlaps with $\nu_{as}(COO)$, the exact position of the peak is often somewhat uncertain.

ii) 1300-1450 cm^{-1}: $\nu_s(COO)$ is expected in this region[1,2,15]. Because of the presence of a number of aryl-oxygen stretching absorptions (for aromatic carboxylates) in this region, which are usually very strong, the identification of $\nu_s(COO)$ becomes uncertain in some cases.

iii) 1210-1310 cm^{-1} and 1010-1090 cm^{-1}: The absorptions associated with Aryl-O-CH_2COOH moiety are easily identifiable because of their intensities. Ar-O-CH_2 vibrations generally lead to two absorption bands at 1210-1310 cm^{-1} and 1010-1050 cm^{-1}[16]. The former may be looked upon as an aromatic C-O stretching frequency as in phenol while the low frequency band may be considered to be due to O-CH_2 vibrations (like primary alcohols). The latter band is expected to shift to somewhat higher frequency in the present case as a result of mixing with adjacent ν(C-C) stretch, the vibration being similar to the asymmetric ν(C-C-O) stretch in alcohols. Co-ordination by the oxygen atom of the carboxylic acid is expected

to affect these frequencies to some extent.

iv) 500-700 cm^{-1} : Deformation vibrations of the carboxyl group which are less distinct than valence vibrations mentioned above occur in these regions[16].

v) 450-600 cm^{-1} : Both ν_{as}(Sn-C) and ν_{s}(Sn-C) vibrations are expected in this region[1,2,17]. In Ph_3Sn-derivatives, however, ν(Sn-C) is found in the Far IR region[17].

vi) 250-300 cm^{-1} : ν(Sn-O) has often been located in this region[17]. In some cases, however, ν(Sn-O) was shown to occur in higher frequencies[11].

The IR spectra of the organotin carboxylates $(ArECH_2COO)_n SnR_{4-n}$ (where E=O or S) are quite complex. Bands due to ν(COO), ν(COC), ν(Sn-C) and ν(Sn-O) could not always be identified with certainity because of the presence of strong ligand vibrations in the regions where these modes occur. The spectral bands due to vibrations of the alkyl groups, phenyl ring, substituents on the phenyl ring, carboxylic group, methylene group, C-O-C, Sn-O and Sn-C bonds were assigned on the basis of comparison of the spectra of the compounds with those of the parent acids, their methyl esters, other tri- and di- organotin (IV) compounds and literature data[18-20].

The IR data are shown in Table - 5 and Table - 6.

Table - 5

Infrared frequencies of -COO- and $ArOCH_2$- groups of free acids and their organotin derivatives in solid phase and solution in CCl_4 (cm^{-1})

Sl. No.	Compounds	Solid phase				Solution phase			
		ν_{as}(COO)	ν_s(COO)	ν_{as}(C_{Aryl}-O)	ν_s(O-CH_2)	ν_{as}(COO)	ν_s(COO)	ν_{as}(C_{Aryl}-O)	ν_s(O-CH_2)
1.	L_1H	1740 1710	1240	1230-40[b]	1080	1730 1660	1220-40[b]	1210-40[b]	1090
2.	Bu_3SnL_1	1587	1421	1243 1220[a]	1085	1690 1665	1358 1340	1245 1218	1085
3.	Pr_3SnL_1	1585-90	1410	1255 1215	1080				
4.	Ph_3SnL_1	1580	1410	1260 1220	1075				
5.	$Me_2Sn(L_1)_2$	1645	1425	1240 1220	1075	1665	1435	1230 1220	1070
6.	$Bu_2Sn(L_1)_2$	1615	1416	1240[a] 1217	1083	1637	1407	1240 1218	1090
7.	$Oct_2Sn(L_1)_2$	1610-20	1415	1260 1220	1080				
8.	L_2H	1740 1705	1240	b	1080				
9.	Bu_3SnL_2	1577	1413	1243 1224	1085	1690 1666	1358 1340	1245 1225	1085

Contd..

Table -5 (Contd..)

Sl. No.	Compounds	Solid phase				Solution phase			
		$\nu_{as}(COO)$	$\nu_{s}(COO)$	$\nu_{as}(C_{Aryl}-O)$	$\nu_{s}(O-CH_2)$	$\nu_{as}(COO)$	$\nu_{s}(COO)$	$\nu_{as}(C_{Aryl}-O)$	$\nu_{s}(O-CH_2)$
10.	$Bu_2Sn(L_2)_2$	1553	1416	1245[a] 1228	1075	1640	1405	1247 1226	1080
11.	L_3H	1740 1710	1245	1240-60[b]	1090				
12.	Bu_3SnL_3	1583	1417	1235	1082	1690 1667	1355 1340	1245 1228	1080
13.	Ph_3SnL_3	1578	1415	1255 1235	1080	1665 1650[a]	1340	1260 1230	1075
14.	$Bu_2Sn(L_3)_2$	1610	1410	1230	1075				
15.	L_4H	1735 1705	1240	1240-50[b]	1080-90[b]	b	1220	1220-50[b]	1050
16.	Bu_3SnL_4	1585	1415	1245[a] 1225	1075	1690 1663	1358[a] 1342	1243 1225	1078
17.	Ph_3SnL_4	1580	1425	1260 1225	1075	1670 1650a	1340	1260 1230	1075
18.	$Bu_2Sn(L_4)_2$	1623	1420	1245 1220	1082	1645	1405	1247 1230	1082
19.	$Oct_2Sn(L_4)_2$	1610	1410	1255 1220	1090	1640	1410	1240 1220	1080-90[b]

Table - 5 (Contd..)

Sl. No.	Compounds	Solid phase				Solution phase			
		$\nu_{as}(COO)$	$\nu_{s}(COO)$	$\nu_{as}(C_{Aryl}-O)$	$\nu_{s}(O-CH_2)$	$\nu_{as}(COO)$	$\nu_{s}(COO)$	$\nu_{as}(C_{Aryl}-O)$	$\nu_{s}(O-CH_2)$
20.	Bu_3SnL_5	1585	1410	1255 1225	1075	1690 1660	1335	1245 1230	1080
21.	Ph_3SnL_5	1580	1420	1270 1240	1080				
22.	$Bu_2Sn(L_5)_2$	1608	1418	1235 1220[a]	1080	1643	1405	1232 1220[a]	1080
23.	$Bu_2Sn(L_6)_2$	1610	1410	1250 1230	1085				
24.	$Bu_2Sn(L_7)_2$	1610	1415	1260 1225	1080	1640	1400	1245 1225	1075
25.	Bu_3SnL_8	1620	1405	1255 1210	1075	1685 1650	1425	1250 1225	1075
26.	Ph_3SnL_8	1585	1420	1250 1220	1085	1660 1640[a]	1340	1240 1210	1070
27.	$Bu_2Sn(L_8)_2$	1615	1412	1255 1228	1073 1055	1640	1405	1255 1215	1070 1055

Contd..

Table - 5 (Contd..)

Sl. No.	Compounds	Solid phase				Solution phase			
		ν_{as}(COO)	ν_s(COO)	ν_{as}(C_{Aryl}-O)	ν_s(O-CH_2)	ν_{as}(COO)	ν_s(COO)	ν_{as}(C_{Aryl}-O)	ν_s(O-CH_2)
28.	L_9H	1690-1700	1220	-	-	1700-1710	1220	-	-
29.	Bu_3SnL_9	1580	1410	-	-	1650 1640	1340 1320	-	-
30.	Bu_3SnL_{10}	1575	1370	-	---	1665 1655	1340[a] 1327	-	-
31.	$Bu_2Sn(L_{10})_2$	1592	1370	-	-	1612	1360	-	-

a) shoulder; b) can not be assigned with certainity.

Table - 6

ν(Sn-C) and ν(Sn-O) of some tri- and di-organotinaryloxyacetates in solid phase.

Compound	ν_{as}(Sn-C) cm^{-1}	ν_{s}(Sn-C) cm^{-1}	ν(Sn-O) cm^{-1}
1. Ph_3SnL_1	280	250	270
2. Bu_3SnL_1	580	525	285
3. $Me_2Sn(L_1)_2$	580	530	280
4. $Bu_2Sn(L_1)_2$	595	500	270
5. Bu_3SnL_2	590	530	a
6. $Bu_2Sn(L_2)_2$	595	530	280
7. Ph_3SnL_3	285	255	a
8. $Bu_2Sn(L_3)_2$	613	540	280
9. Bu_3SnL_4	570	500	a
10. $Oct_2Sn(L_4)_2$	595	555	a
11. Bu_3SnL_5	560	535	268
12. $Bu_2Sn(L_5)_2$	610	530	275
13. $Bu_2Sn(L_6)_2$	595	535	285
14. $Bu_2Sn(L_7)_2$	600	525	290
15. Ph_3SnL_8	295	a	a
16. Bu_3SnL_8	620	520	285
17. $Bu_2Sn(L_8)_2$	600	500	a

a) can not be assigned unambiguously.

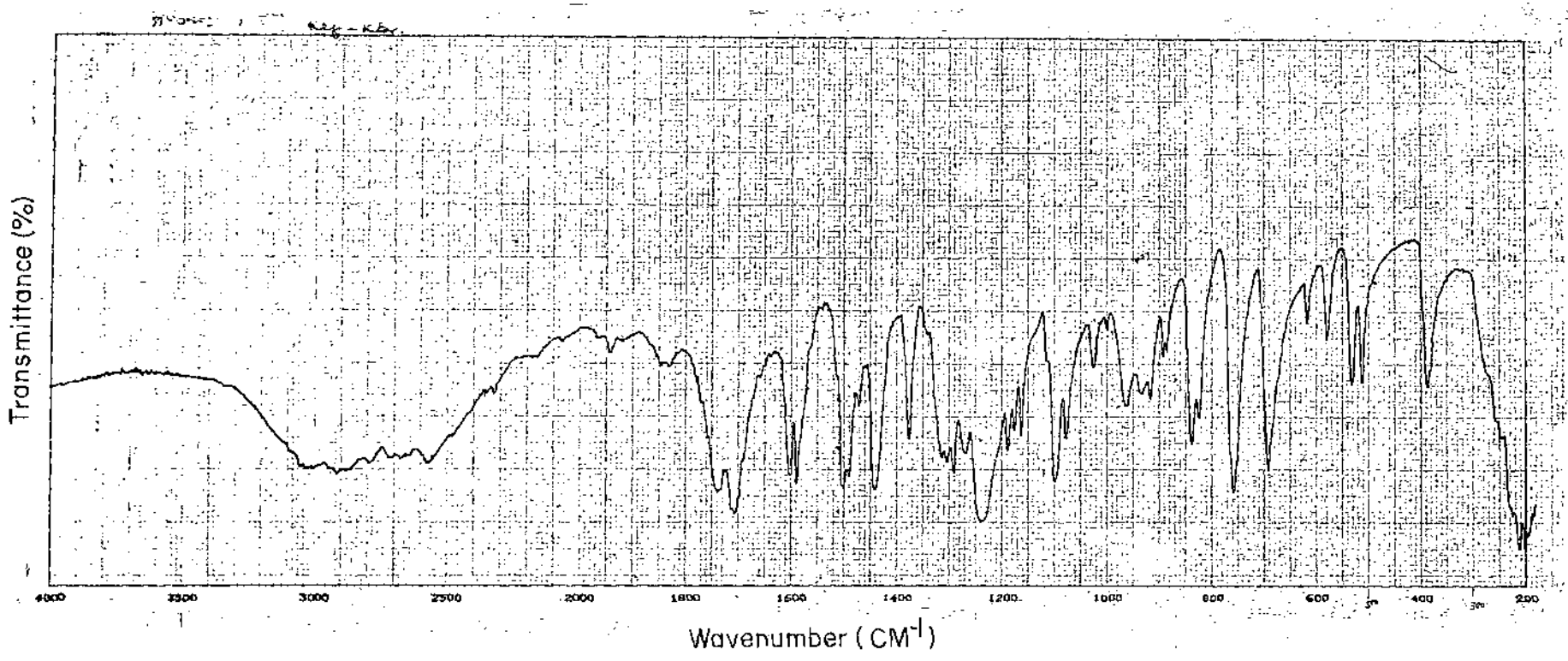


Fig.1. IR SPECTRUM OF L_1H IN KBr

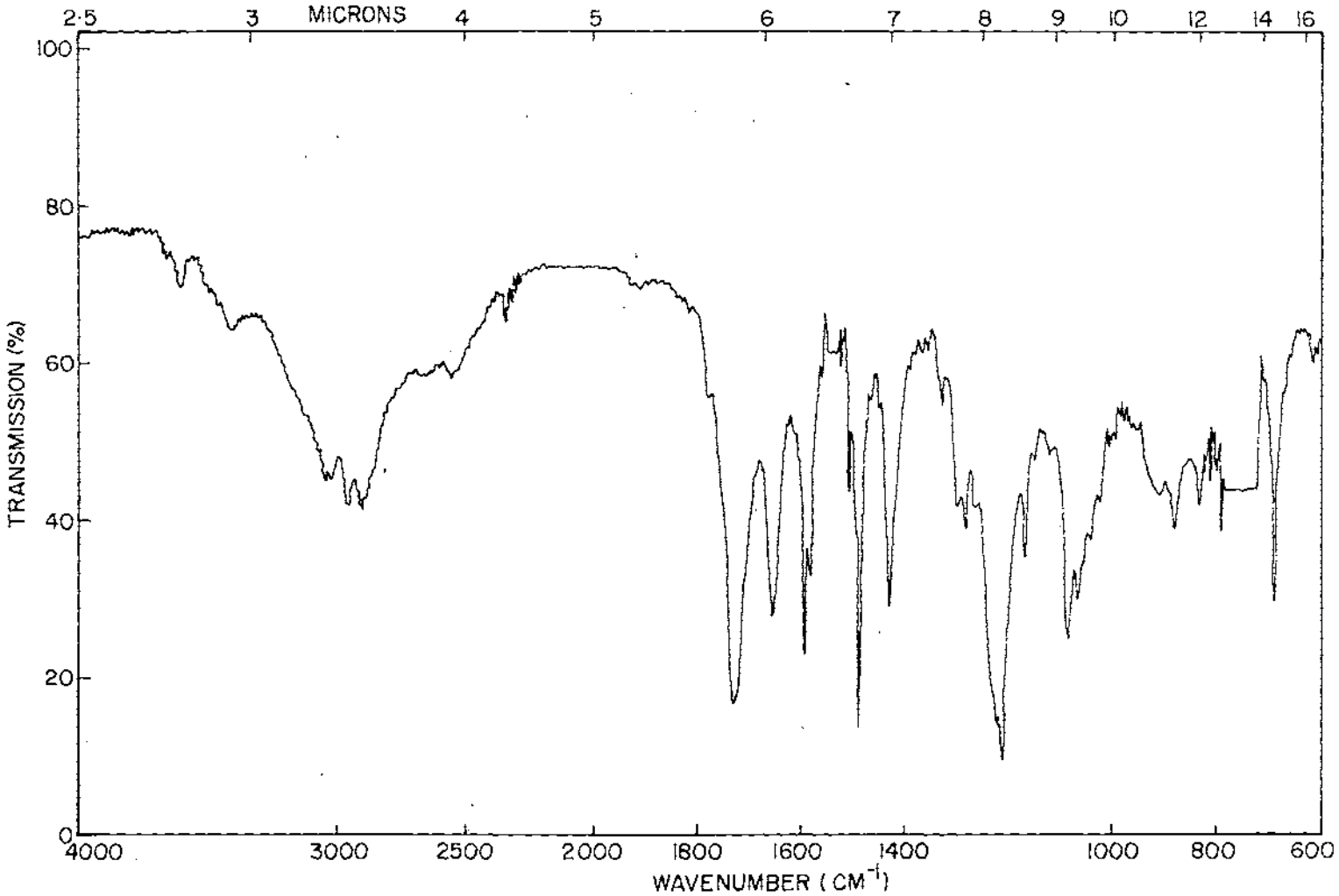


Fig.1a . IR SPECTRUM OF L_1H IN CCl_4

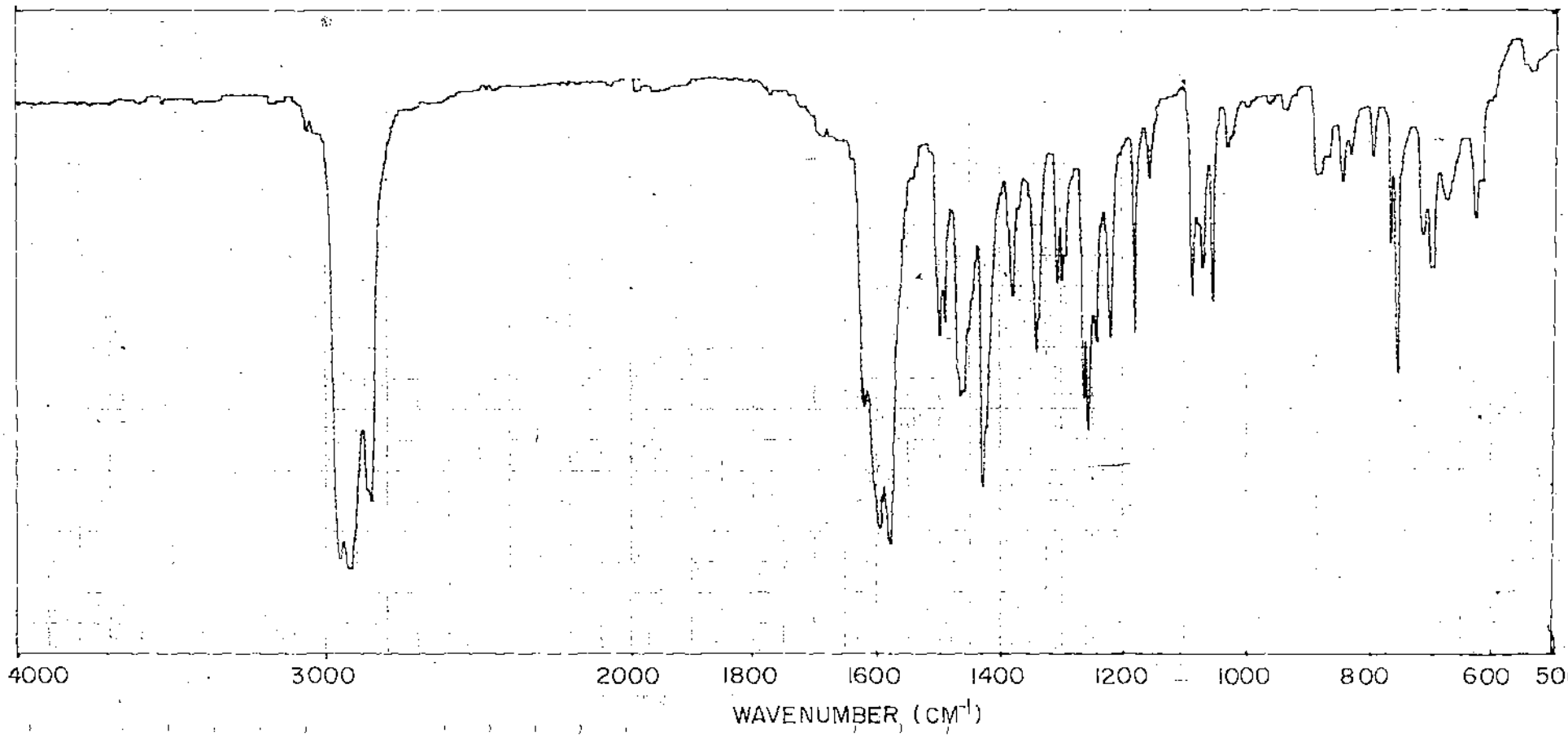
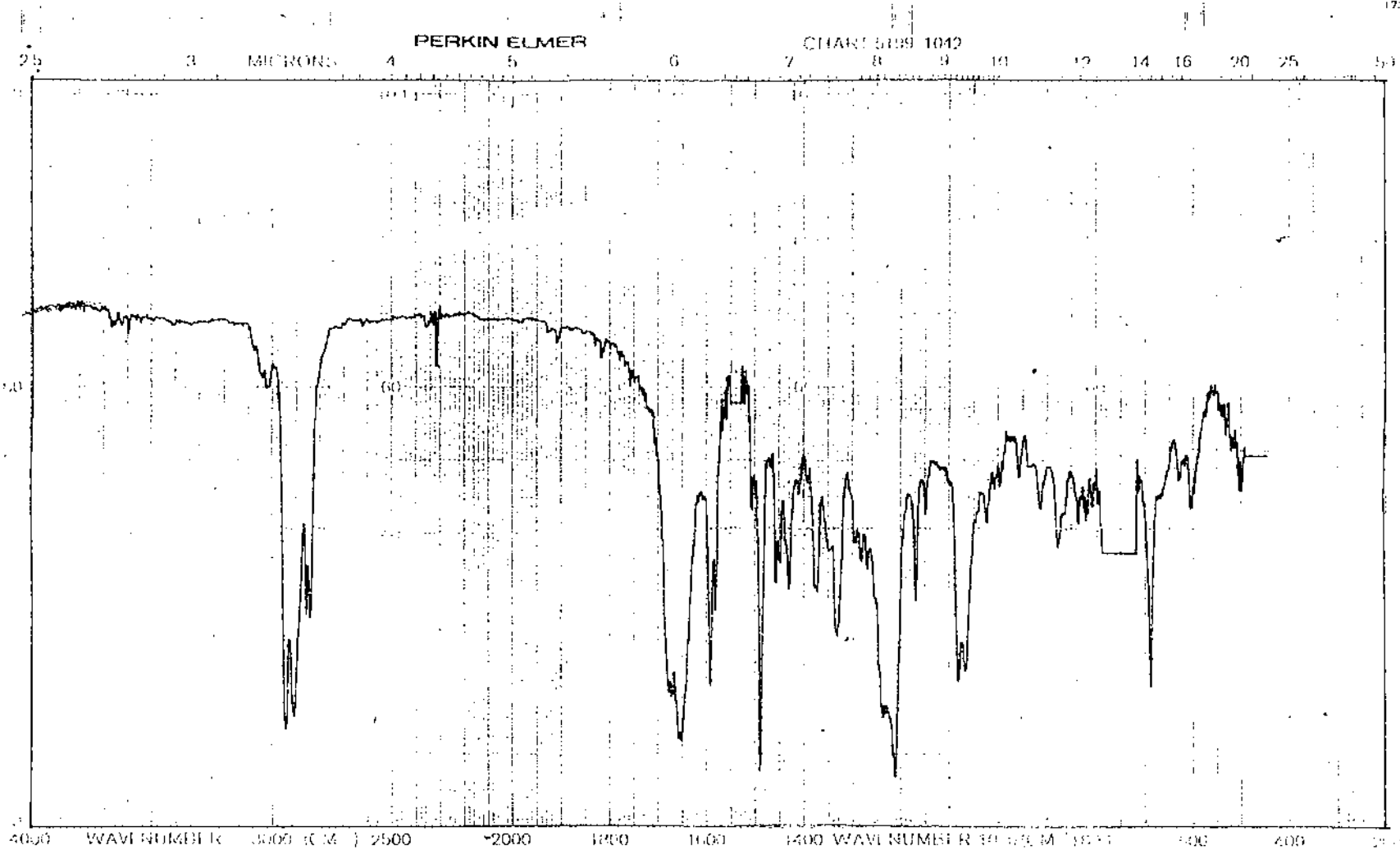


Fig.2. IR SPECTRUM OF Bu_3SnL_1 IN NUJOL



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SAMPLE 5 (–) ORIGIN D. K. Banerjee	REMARKS	SOLVENT CONCENTRATION	CELL PATH REFERENCE CCl_4	

Fig.2a. IR SPECTRUM OF Bu_3SnL_1 IN CCl_4

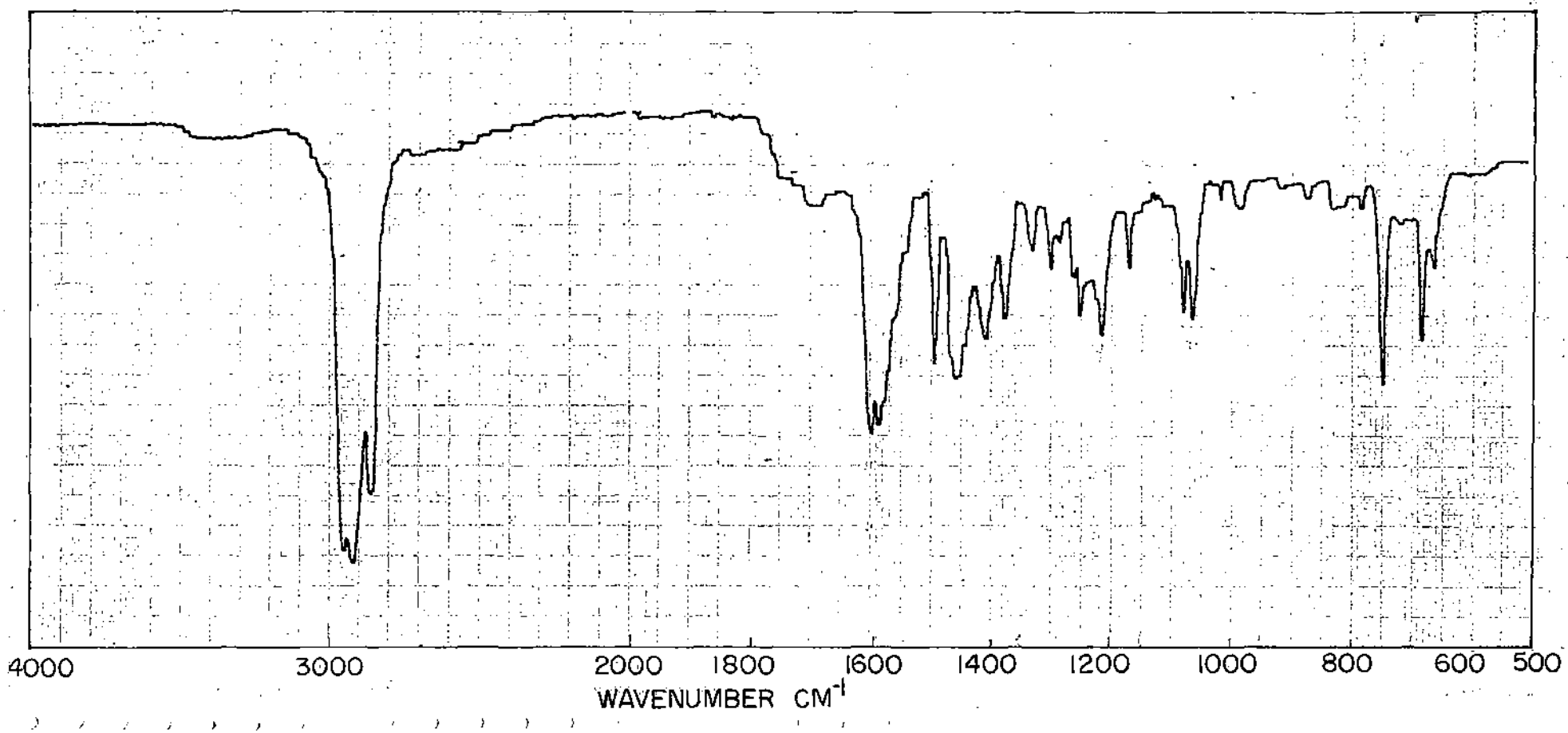


Fig. 3. IR SPECTRUM OF Pr_3SnL_1 IN NUJOL

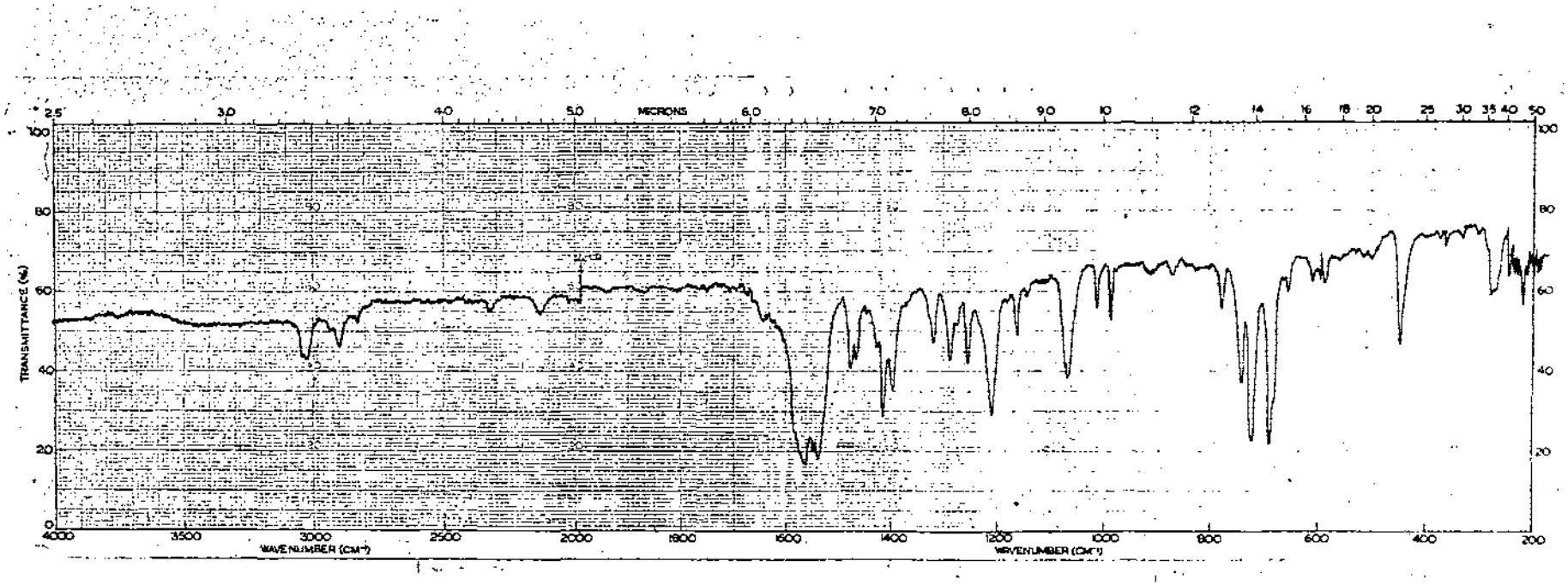


Fig.4. IR SPECTRUM OF Ph_3SnL_1 IN CsI

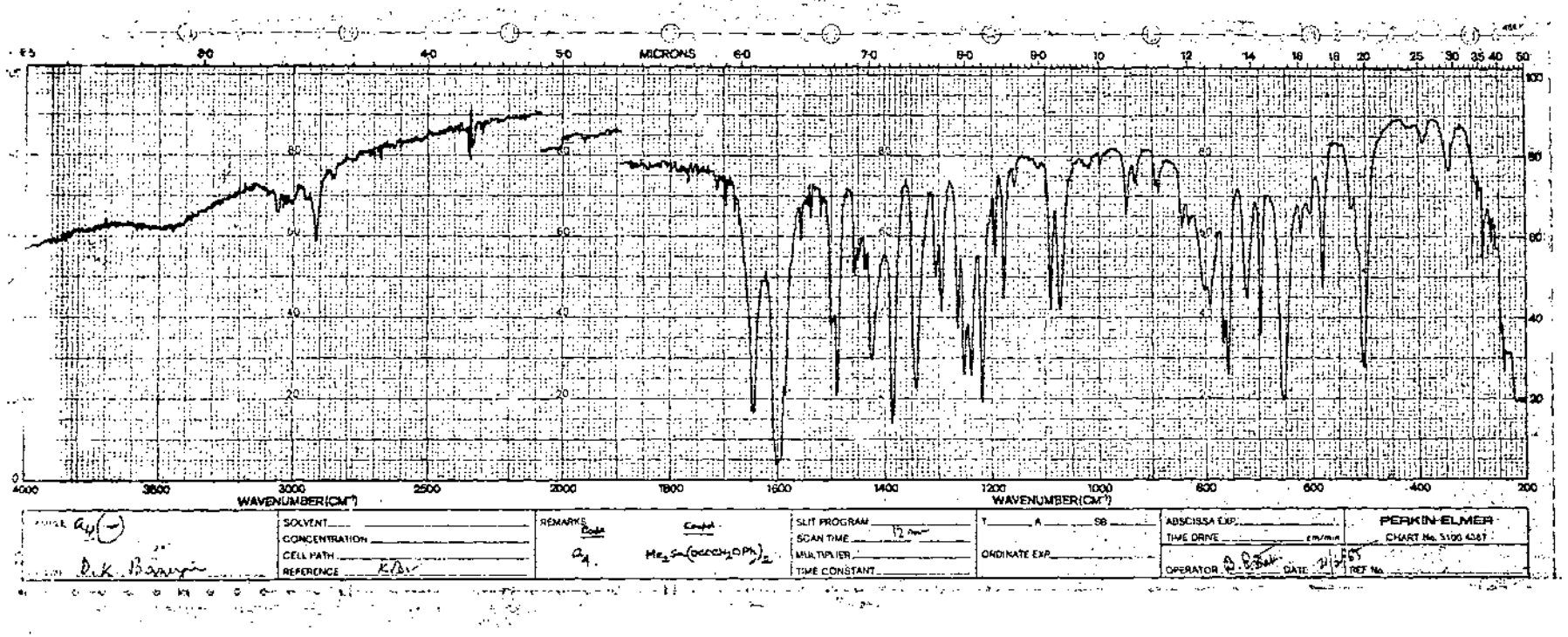


Fig.5. IR SPECTRUM OF $Me_2Sn(L_1)_2$ IN KBr

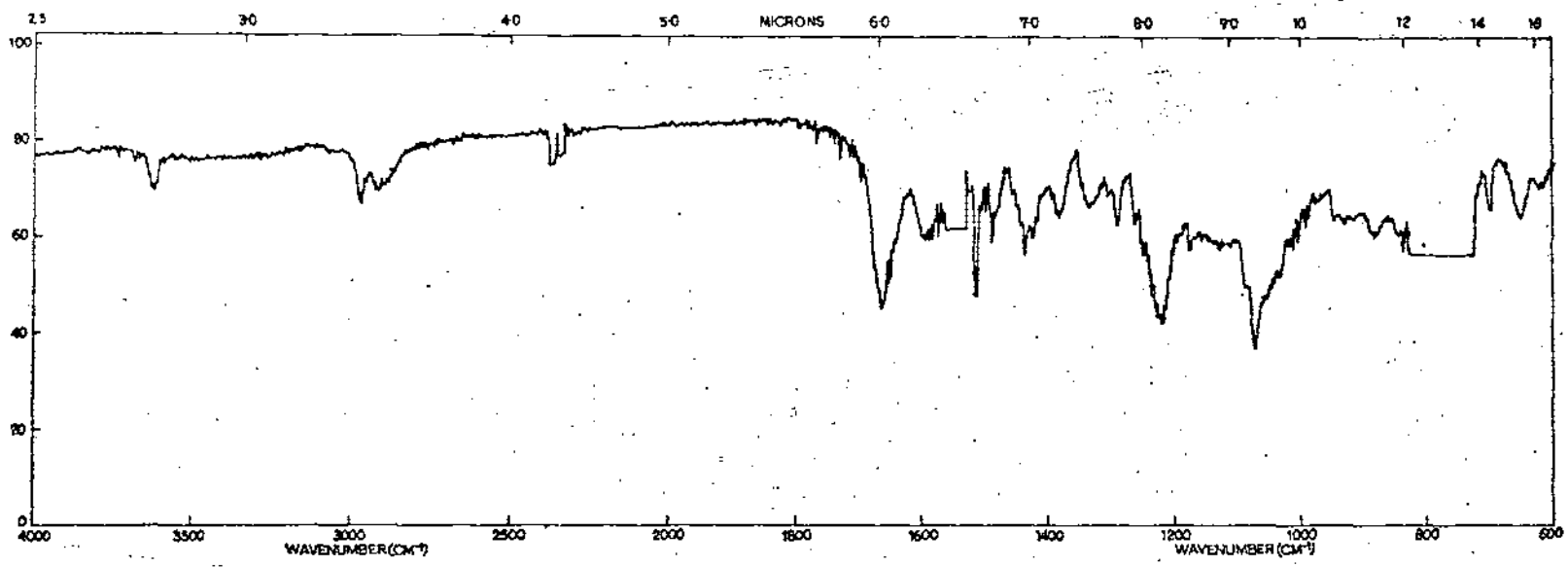


Fig.5a . IR SPECTRUM OF $Me_2Sn(L_1)_2$ IN CCl_4

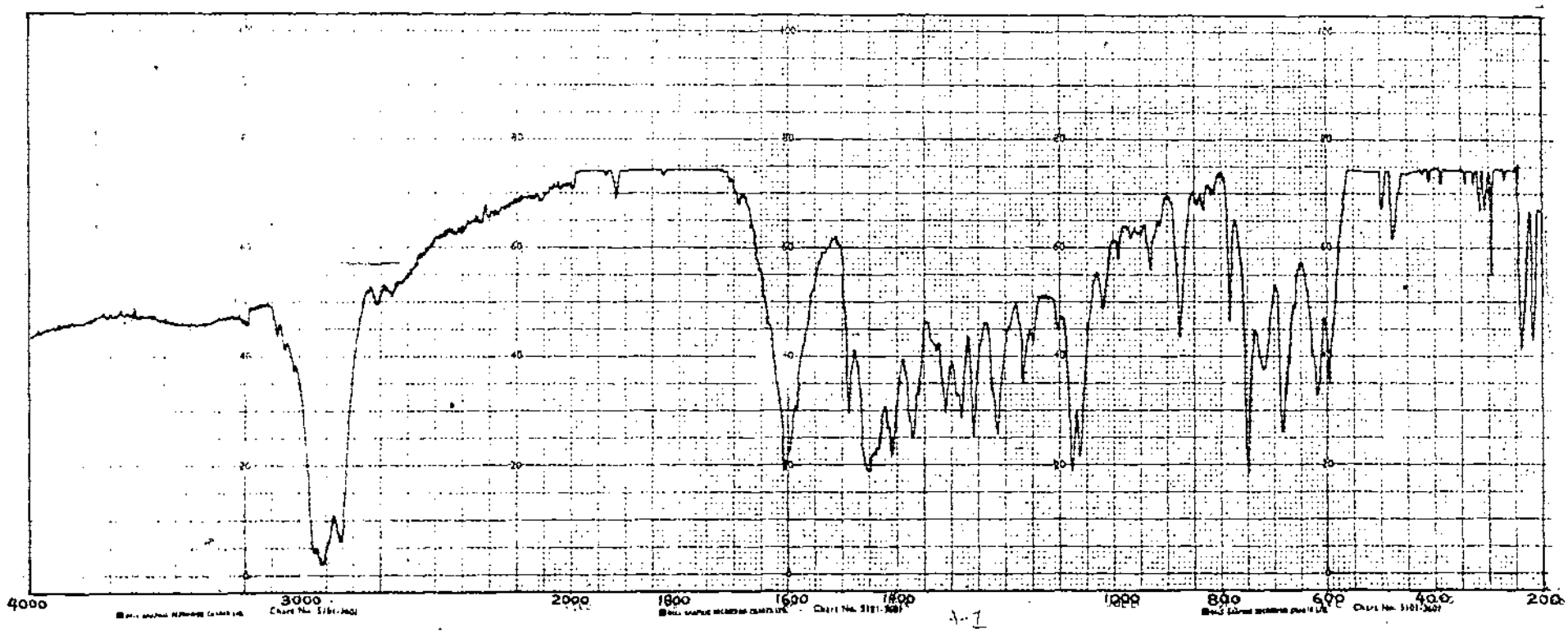


Fig.6. IR SPECTRUM OF $Bu_2Sn(L_1)_2$ IN NUJOL

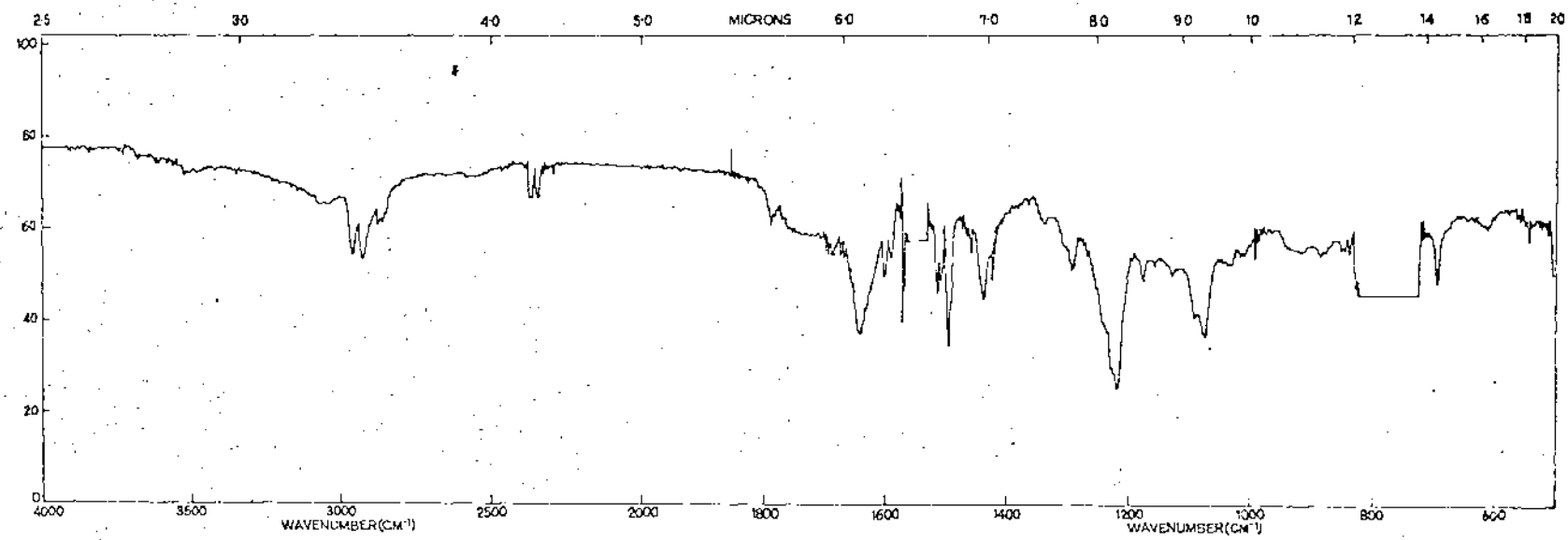


Fig.6a. IR SPECTRUM OF $Bu_2Sn(L_1)_2$ IN CCl_4

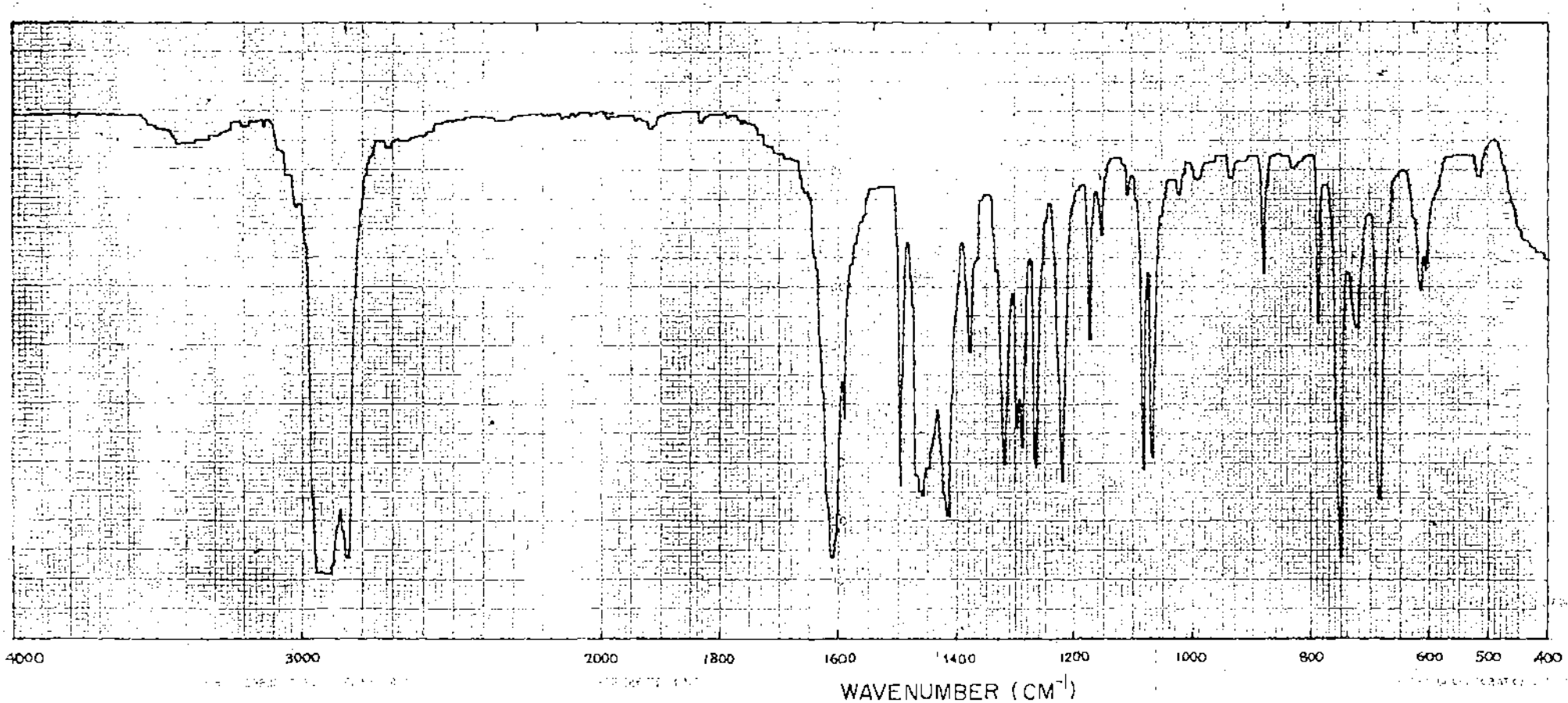


Fig. 7 : IR SPECTRUM OF $Oct_2Sn(L_1)_2$ IN NUJOL

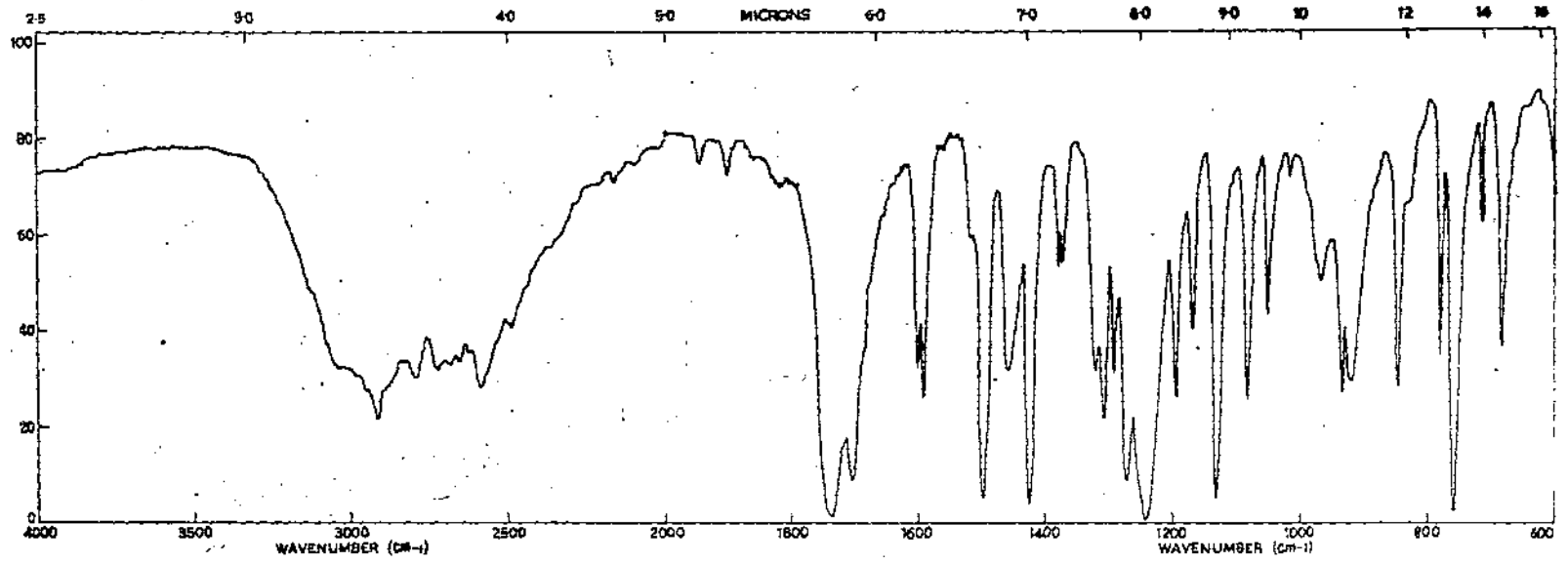


Fig.8 .IR SPECTRUM OF L_2H IN KBr

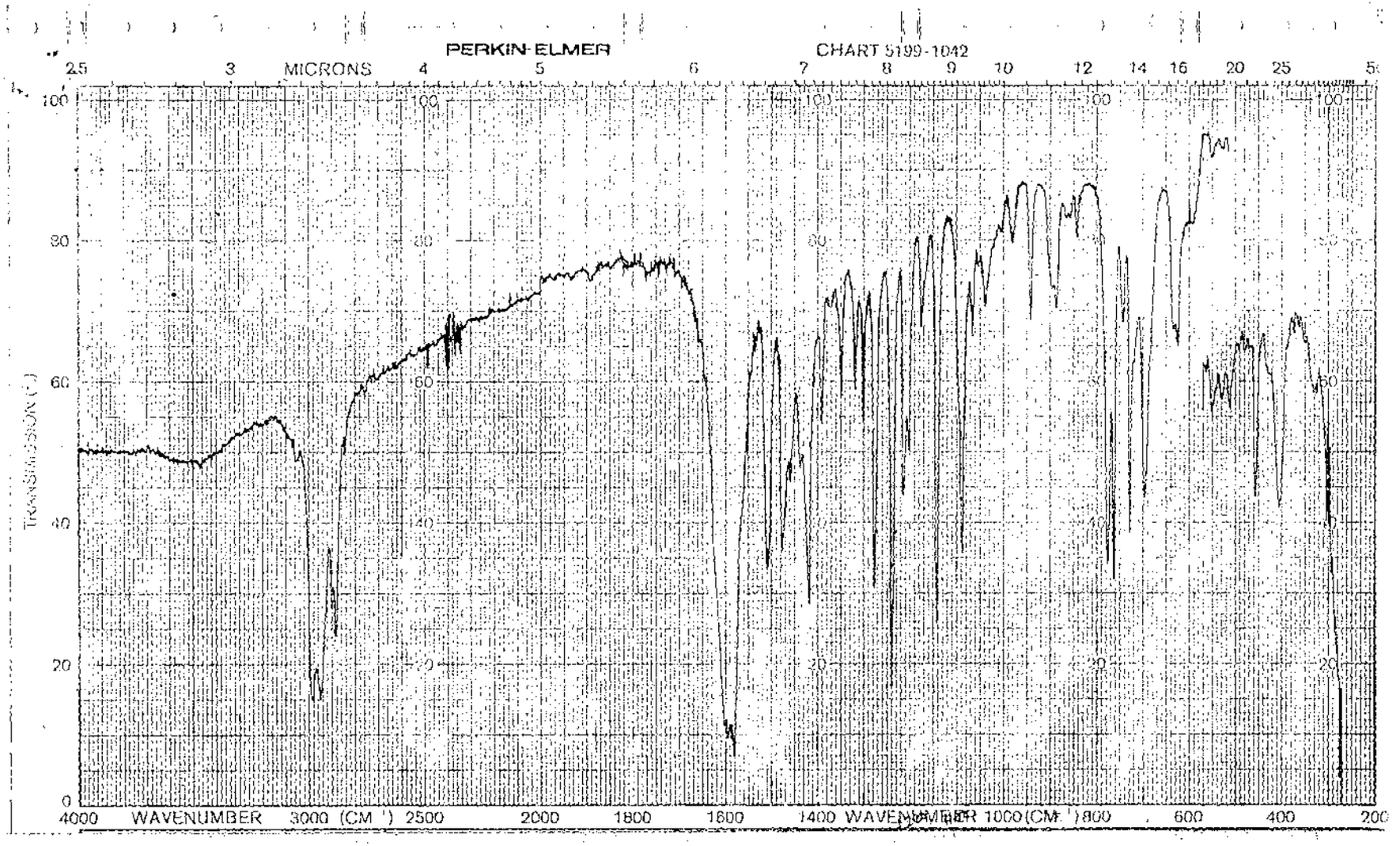


Fig.9 . IR SPECTRUM OF Bu_3SnL_2 IN KBr

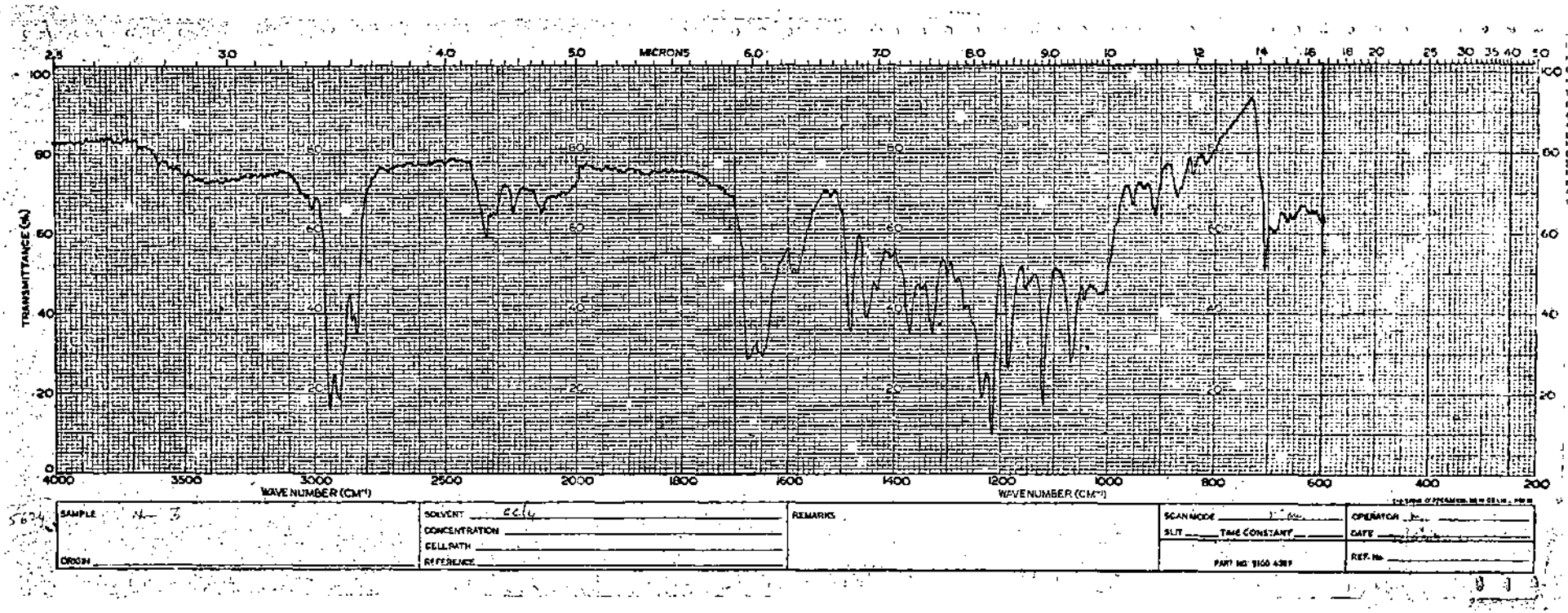


Fig.9a. IR SPECTRUM OF Bu_3SnL_2 IN CCl_4

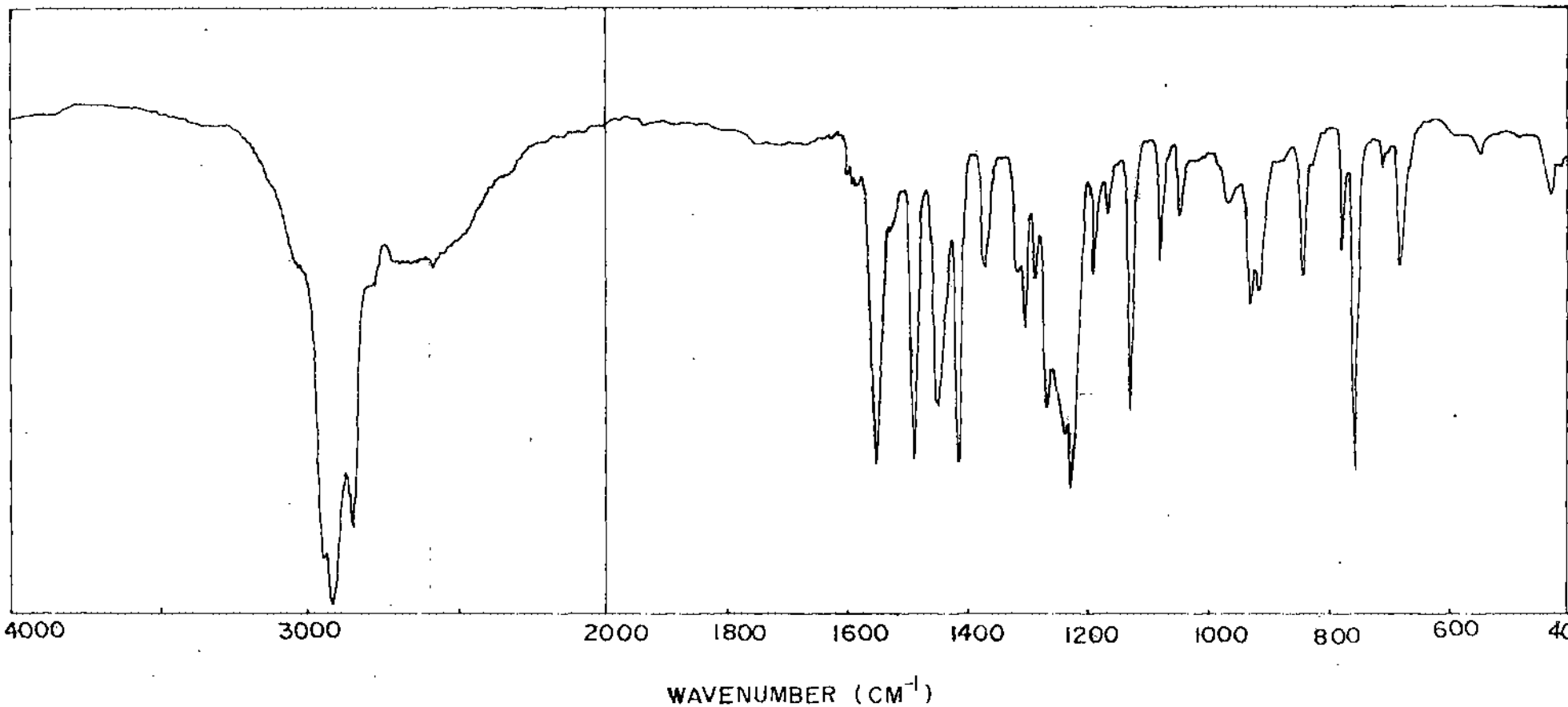


Fig.10. IR SPECTRUM OF $Bu_2Sn(L_2)_2$ IN NUJOL

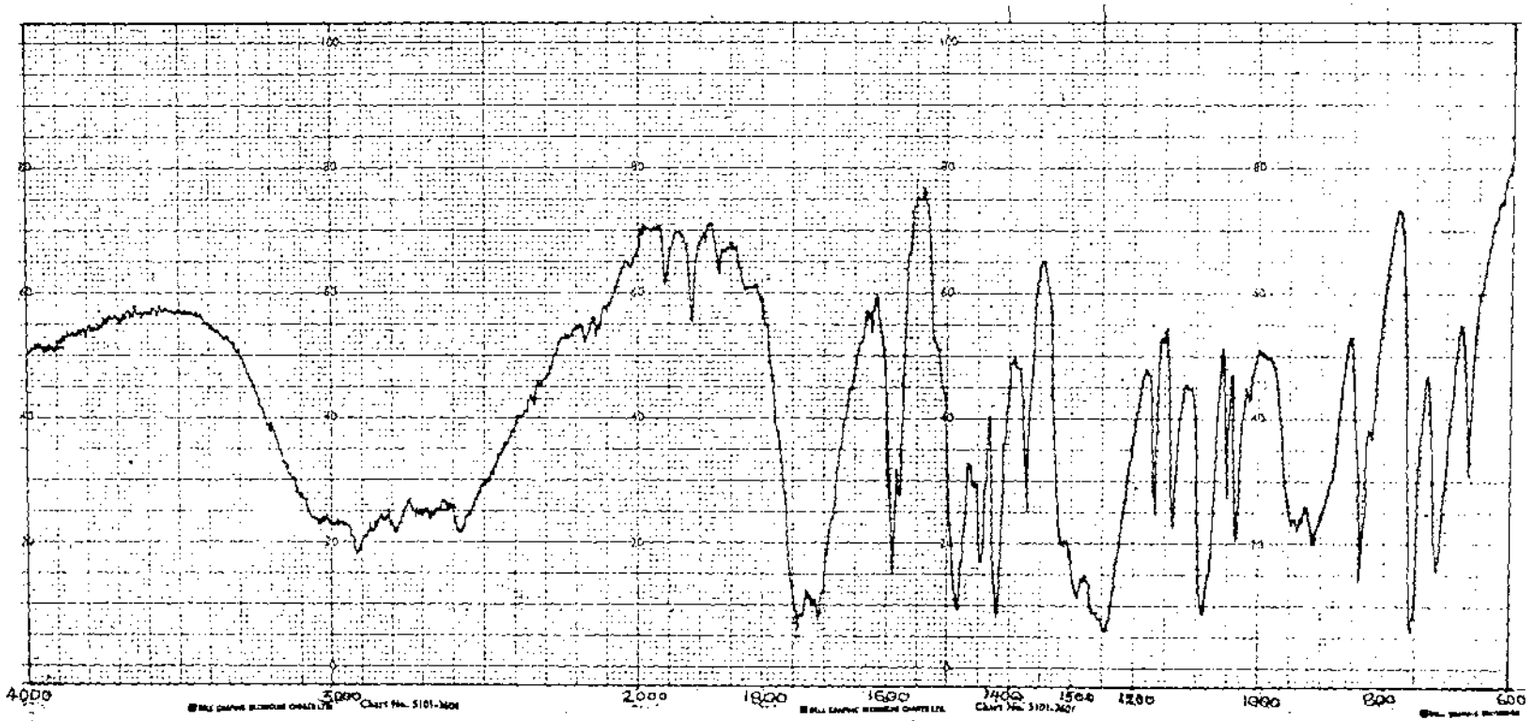
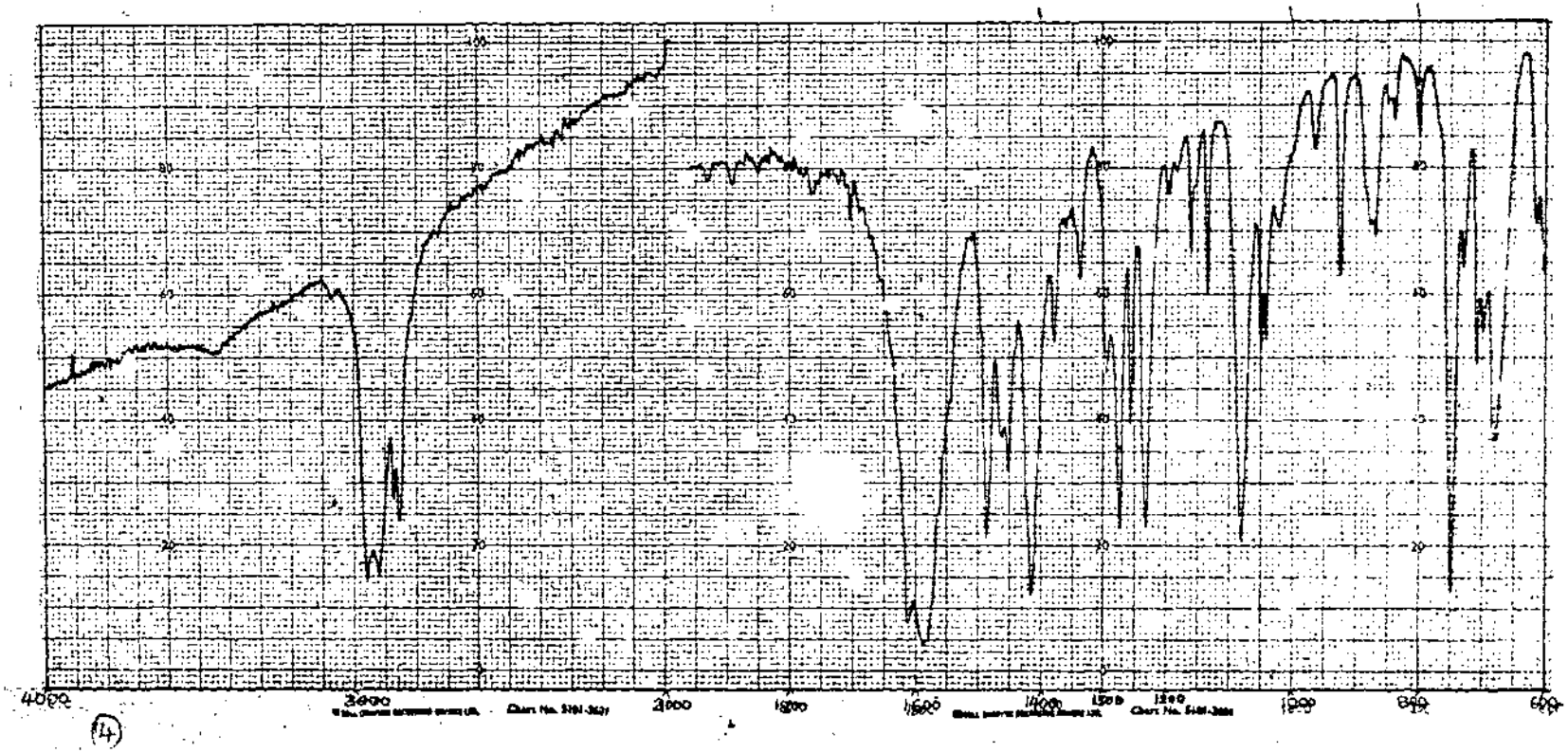


Fig.II. IR SPECTRUM OF L_3H IN KBr



(14)

Fig. 12. IR SPECTRUM OF Bu_3SnL_3 IN KBr

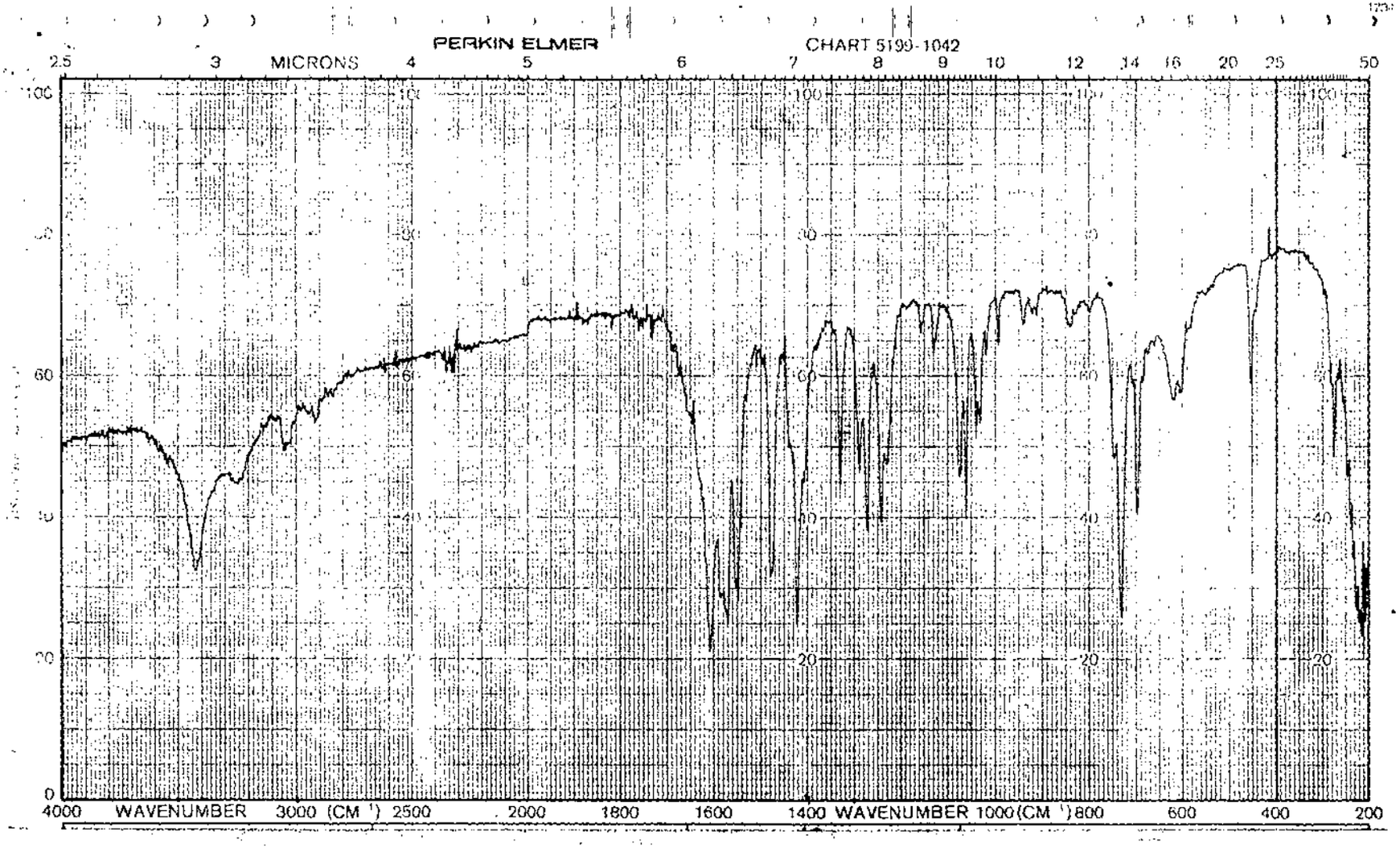


Fig. 13 .IR SPECTRUM OF Ph_3SnL_3 IN KBr

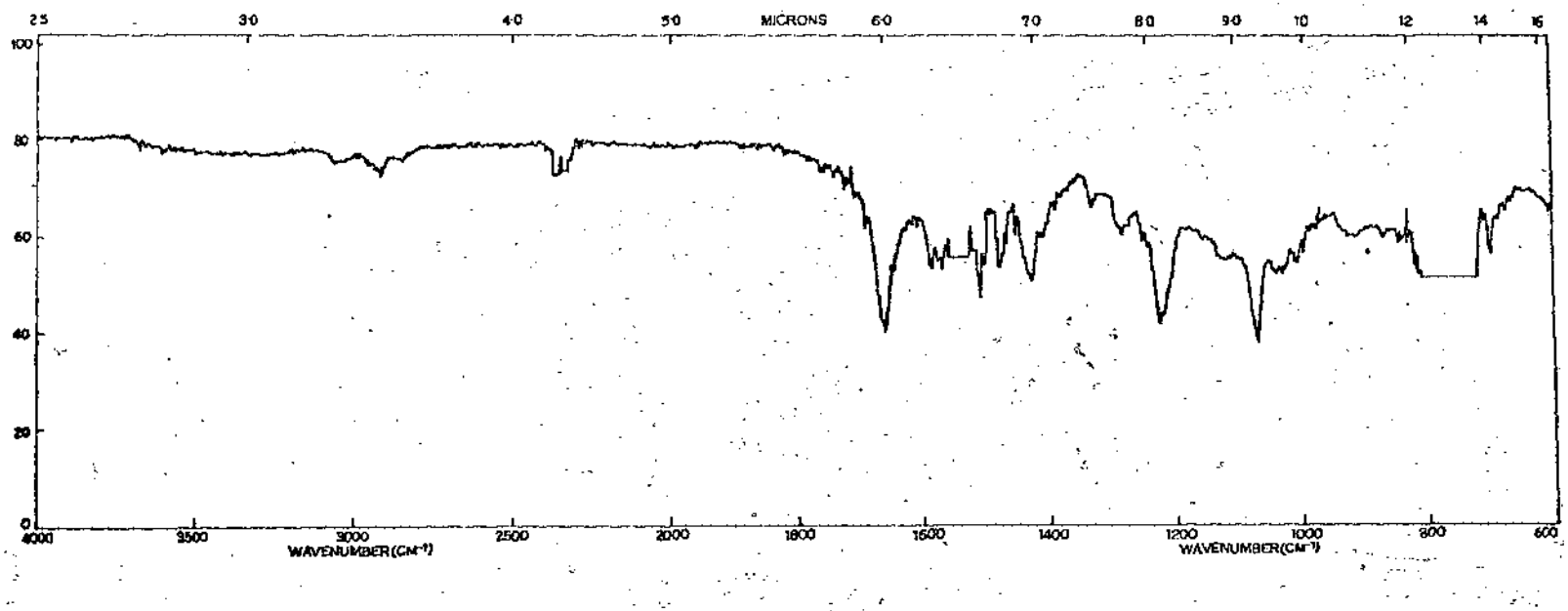


Fig.13a . IR SPECTRUM OF Ph_3SnL_3 IN CCl_4

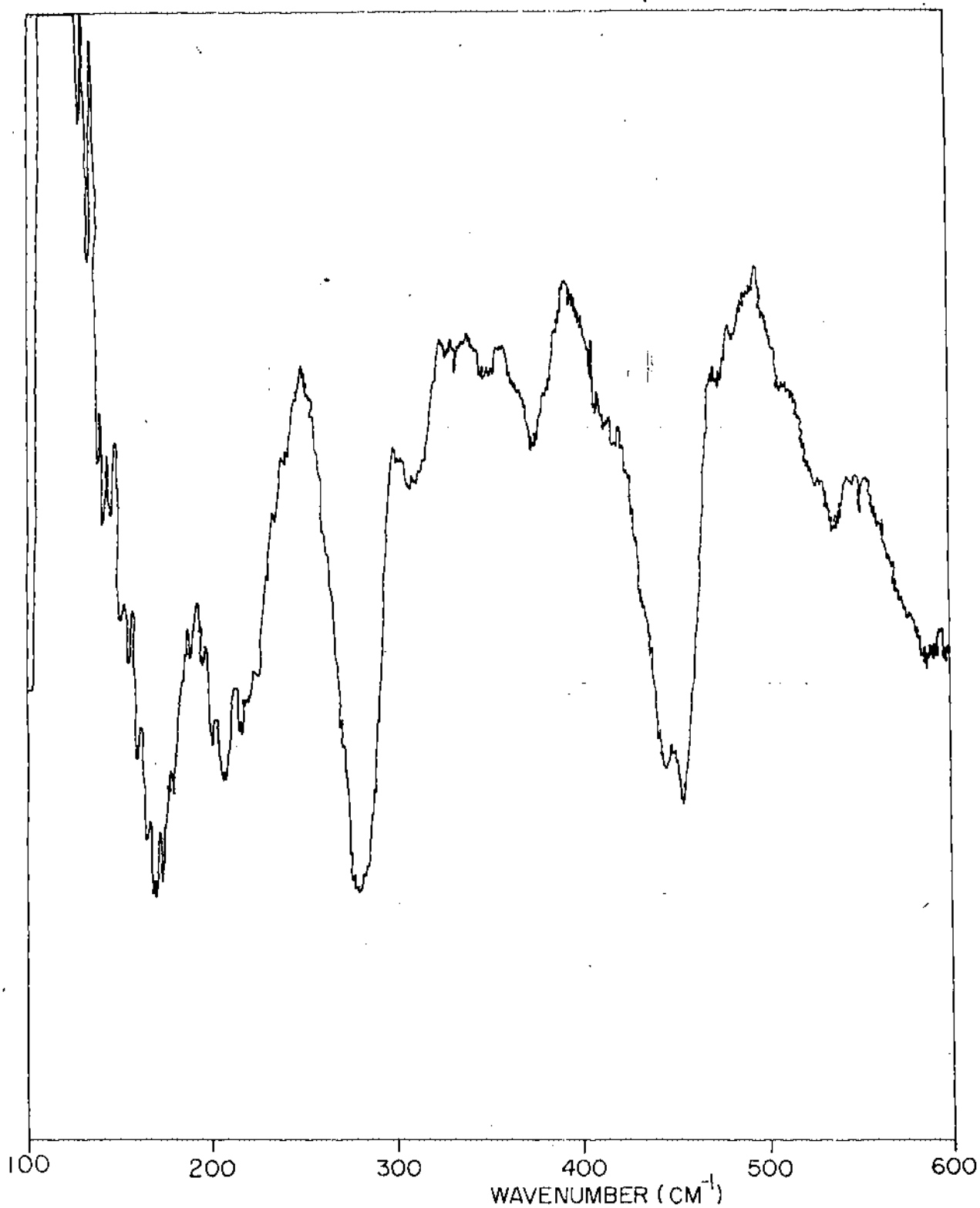


Fig.13b . FAR IR (FOURIER-TRANSFORM) SPECTRUM

OF Ph_3SnL_3

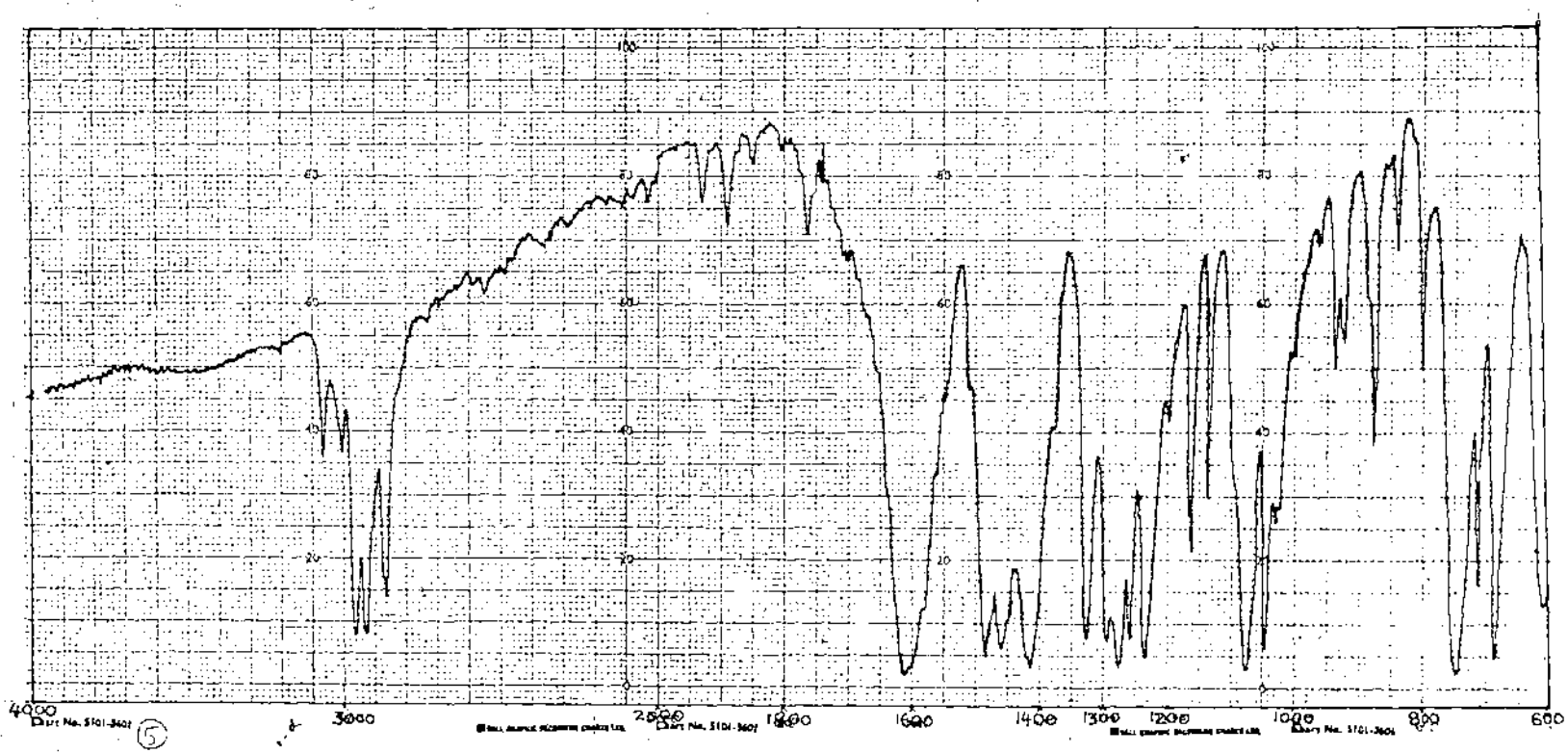


Fig.14. IR SPECTRUM OF $Bu_2Sn(L_3)_2$ IN KBr

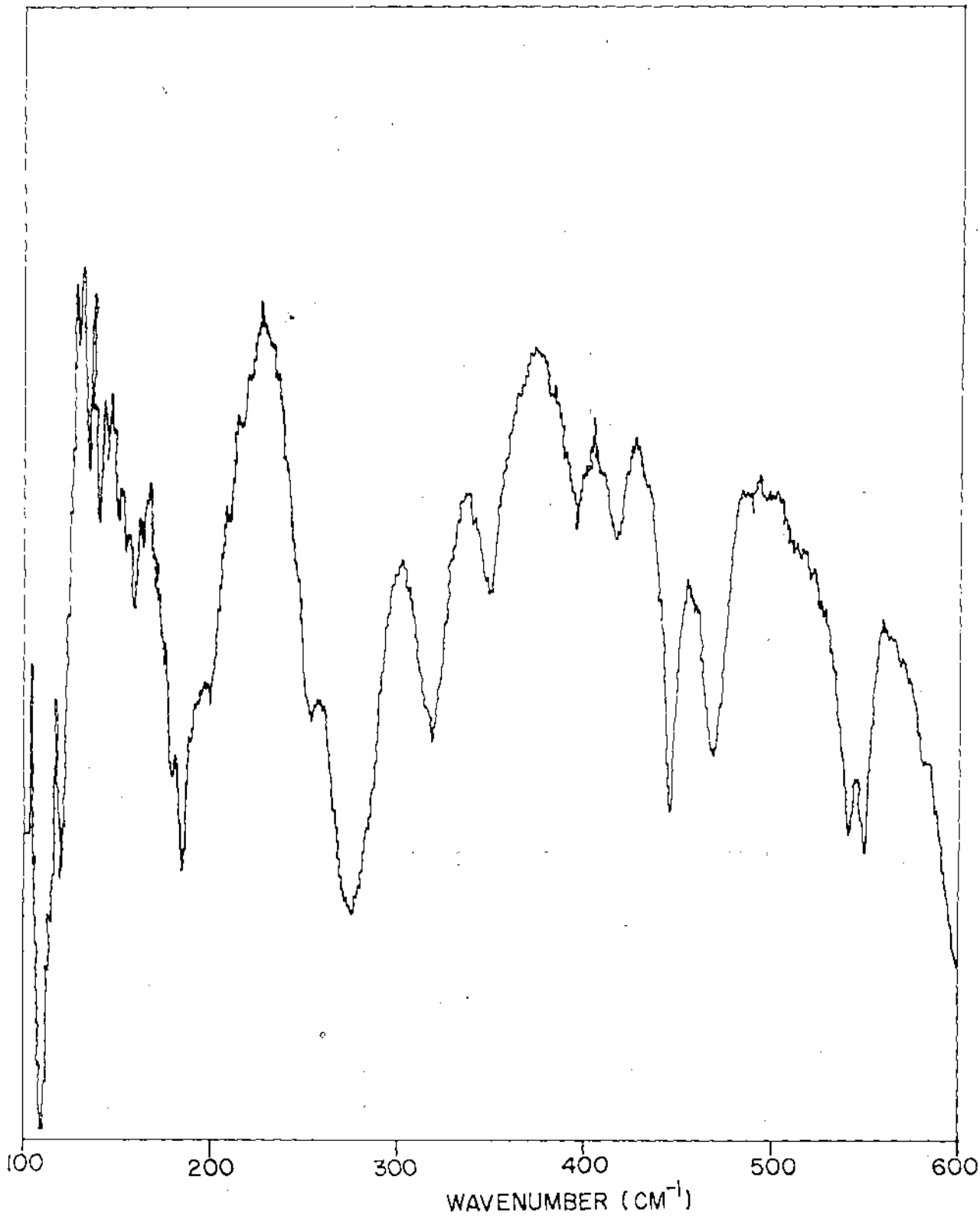


Fig.14a. FAR IR (FOURIER-TRANSFORM) SPECTRUM OF $Bu_2Sn(L_3)_2$

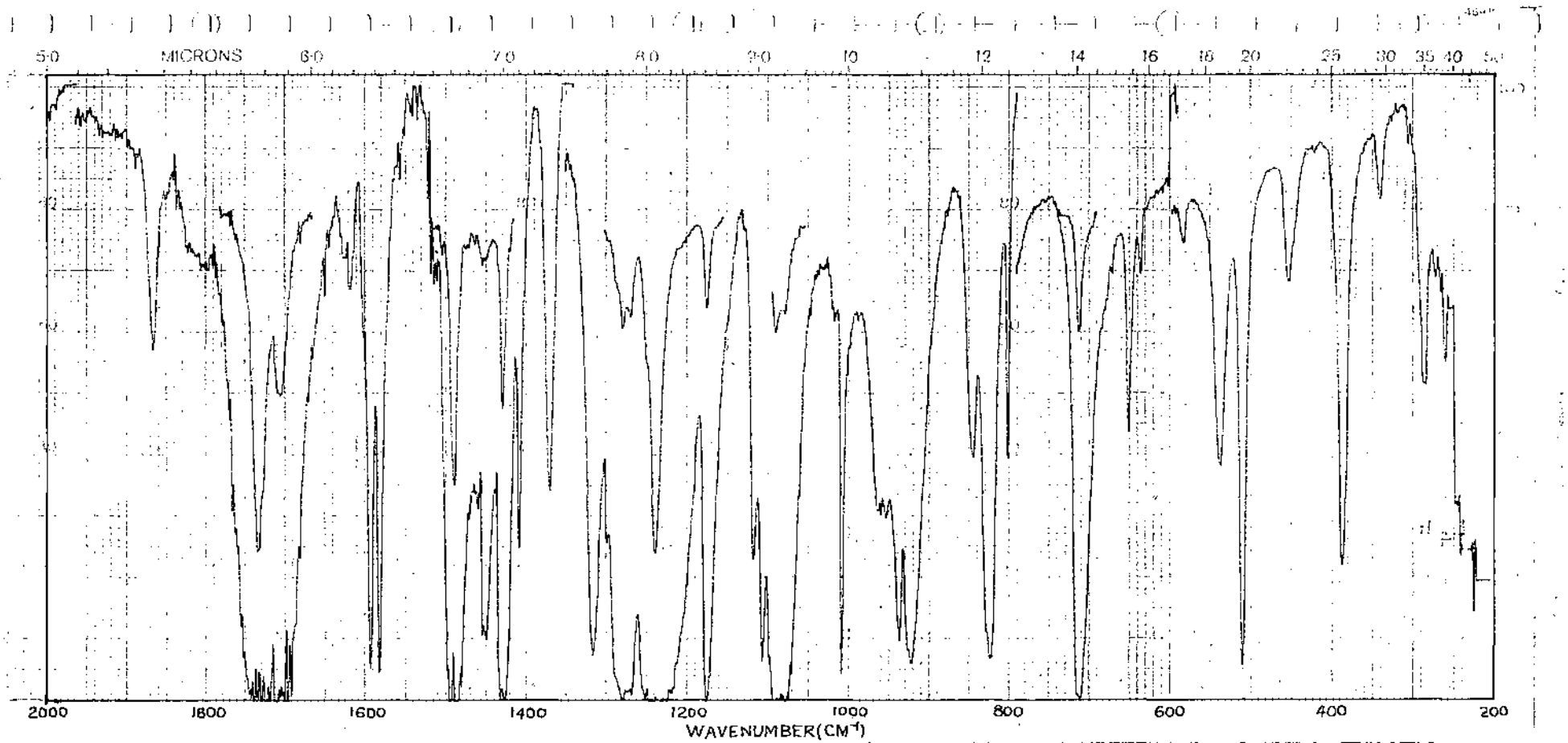


Fig.15. IR SPECTRUM OF L_4H IN KBr

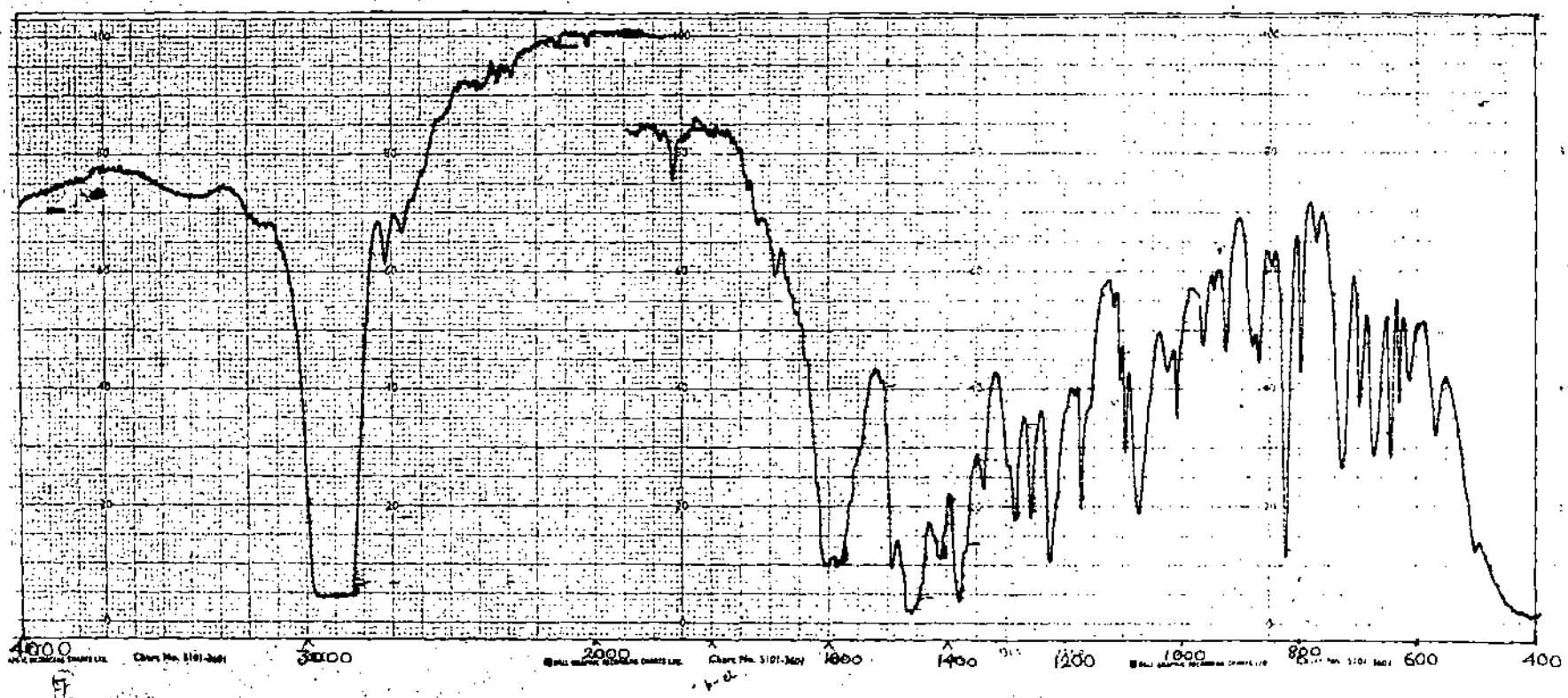


Fig.16. IR SPECTRUM OF Bu_3SnL_4 IN NUJOL

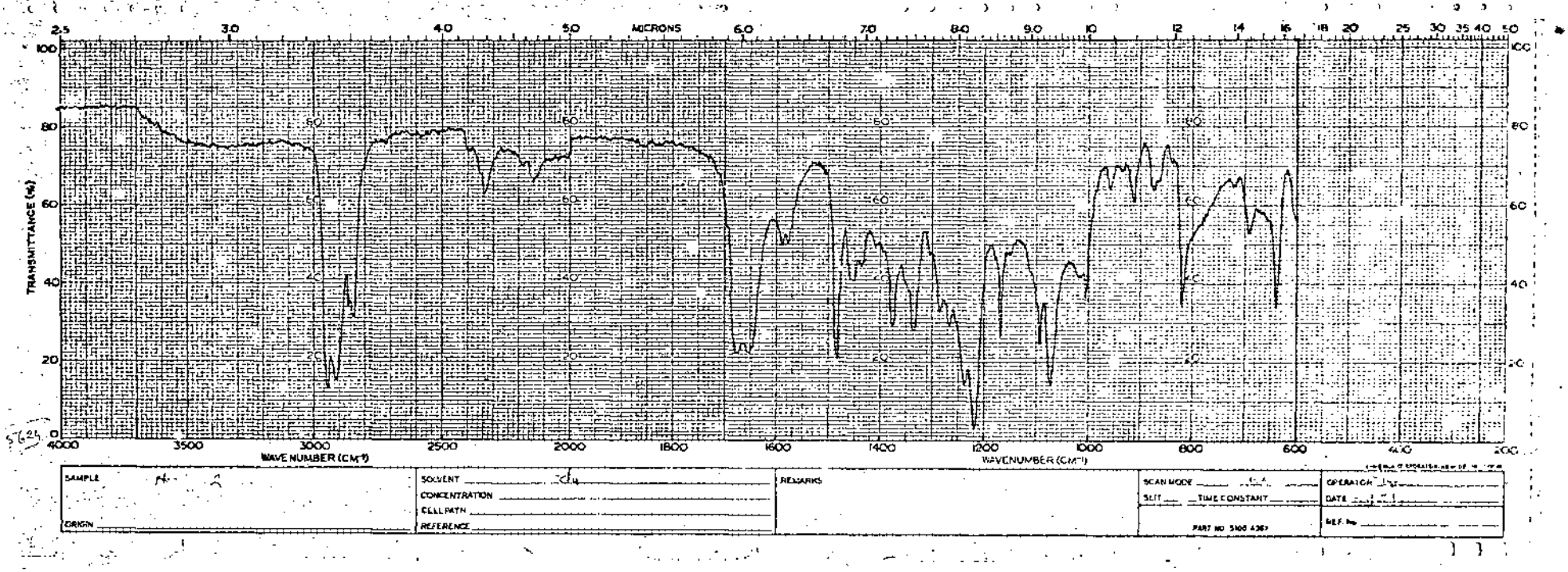


Fig.16a. IR SPECTRUM OF Bu_3SnL_4 IN CCl_4

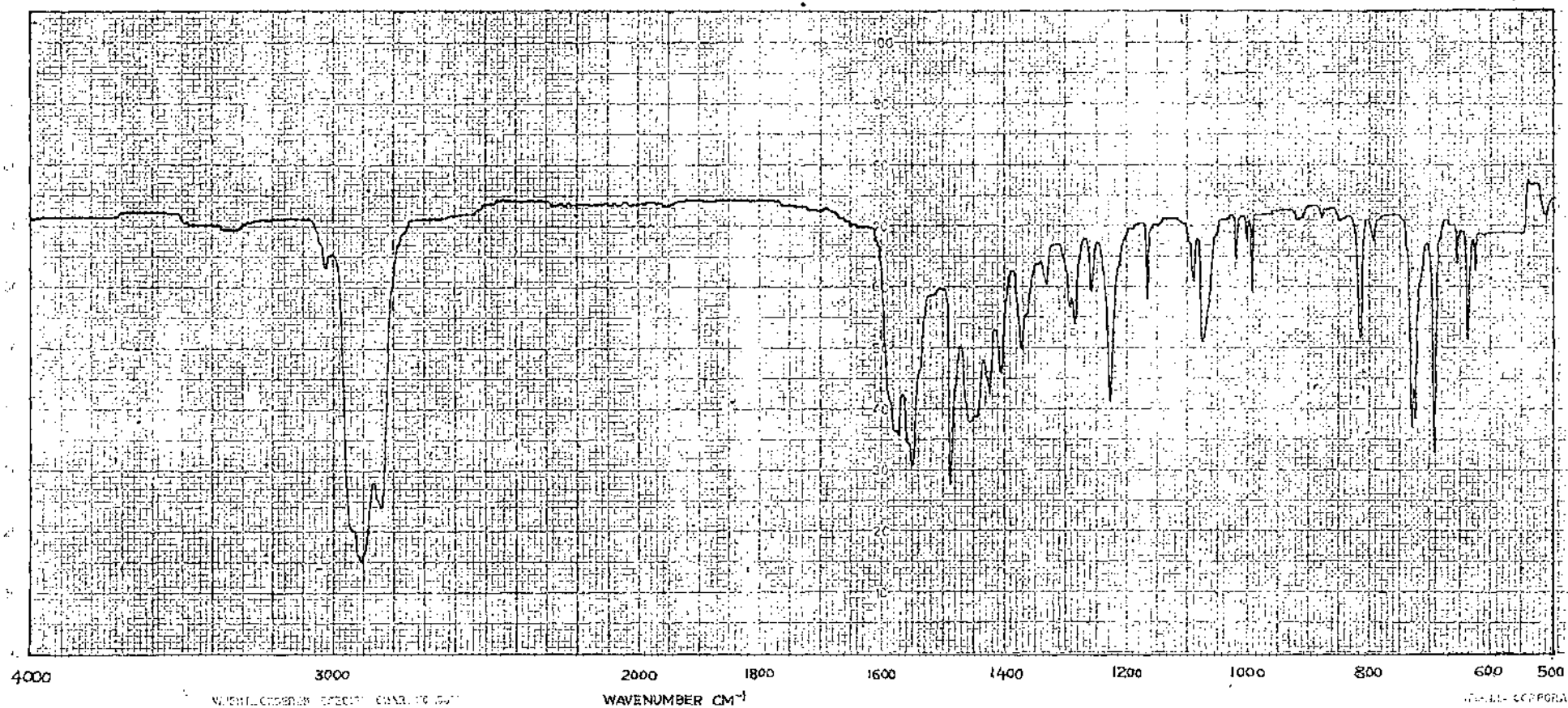


Fig.17 : IR SPECTRUM OF Ph_3SnL_4 IN NUJOL

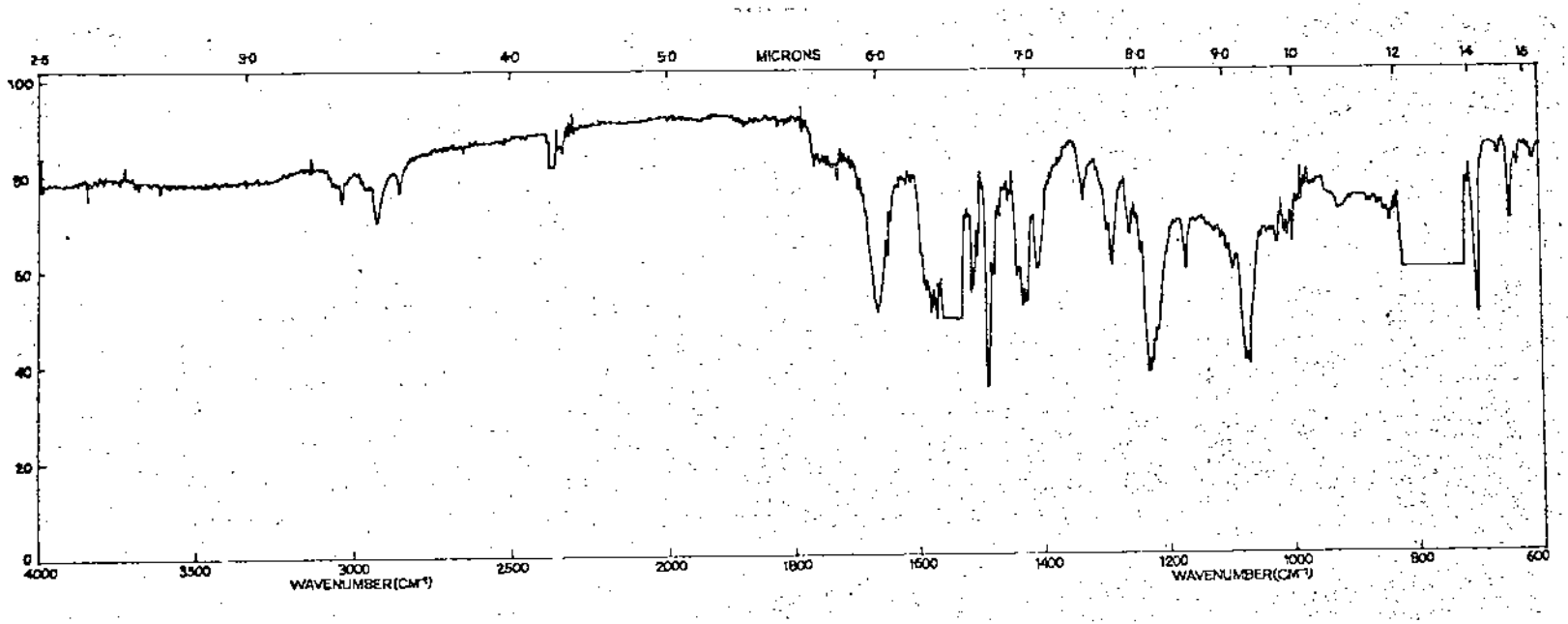


Fig.17a . IR SPECTRUM OF Ph_3SnL_4 IN CCl_4

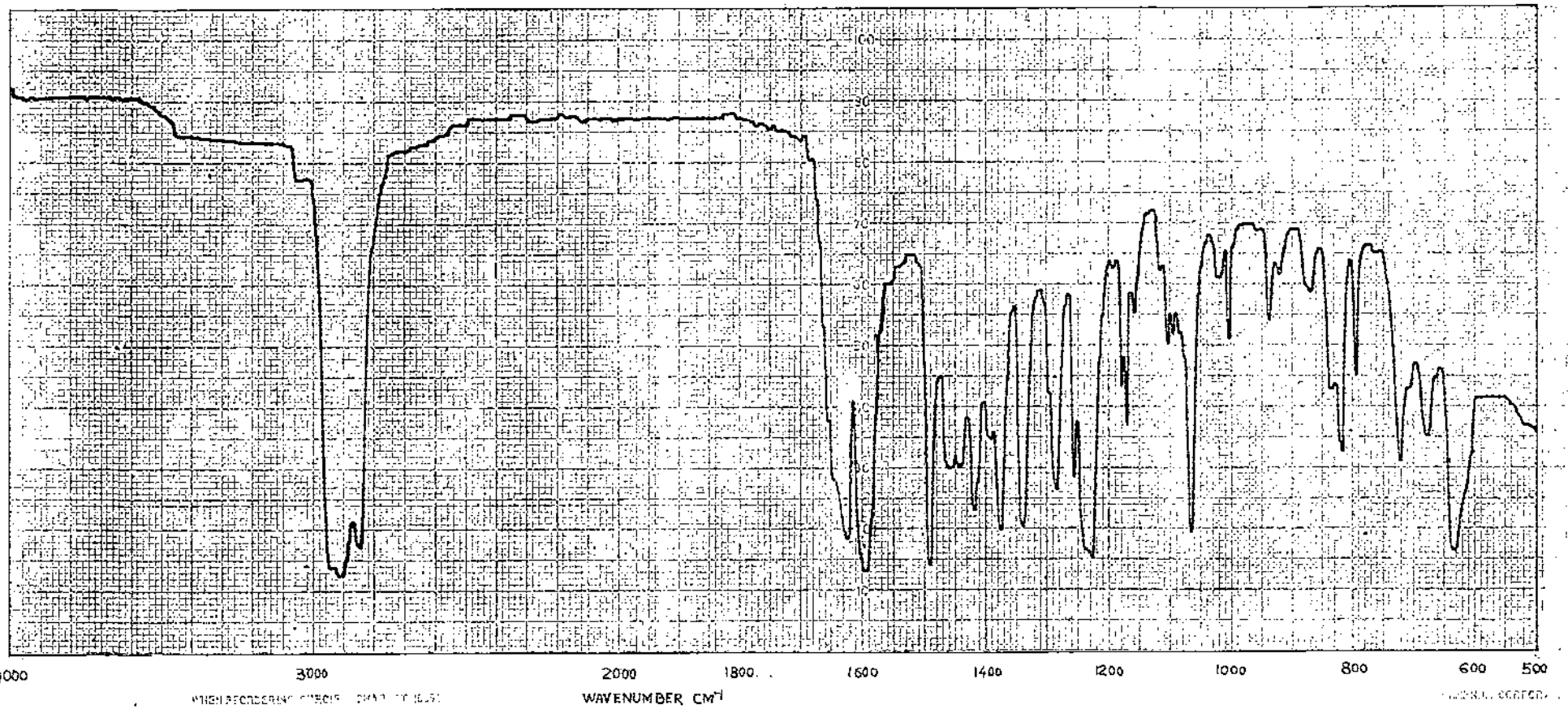


Fig. 18. IR SPECTRUM OF $Bu_2Sn(L_{42})_2$ IN NUJOL

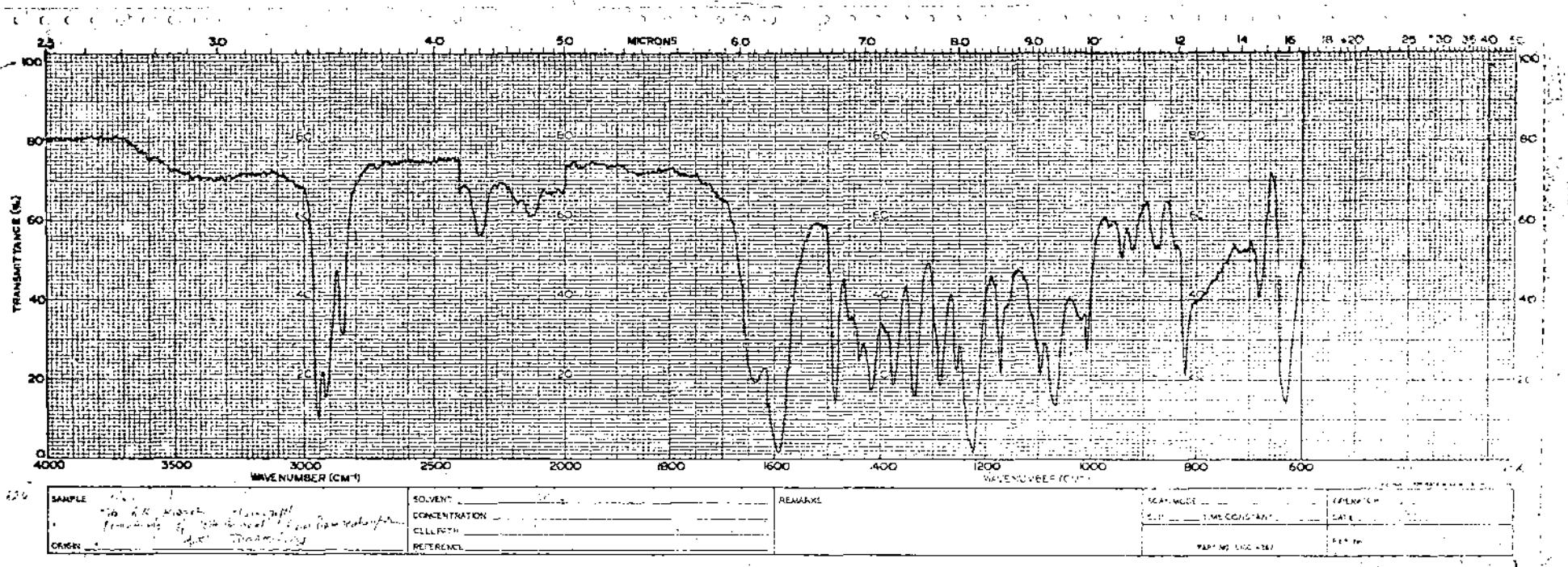


Fig.18a. IR SPECTRUM OF $Bu_2Sn(L_4)_2$ IN CCl_4

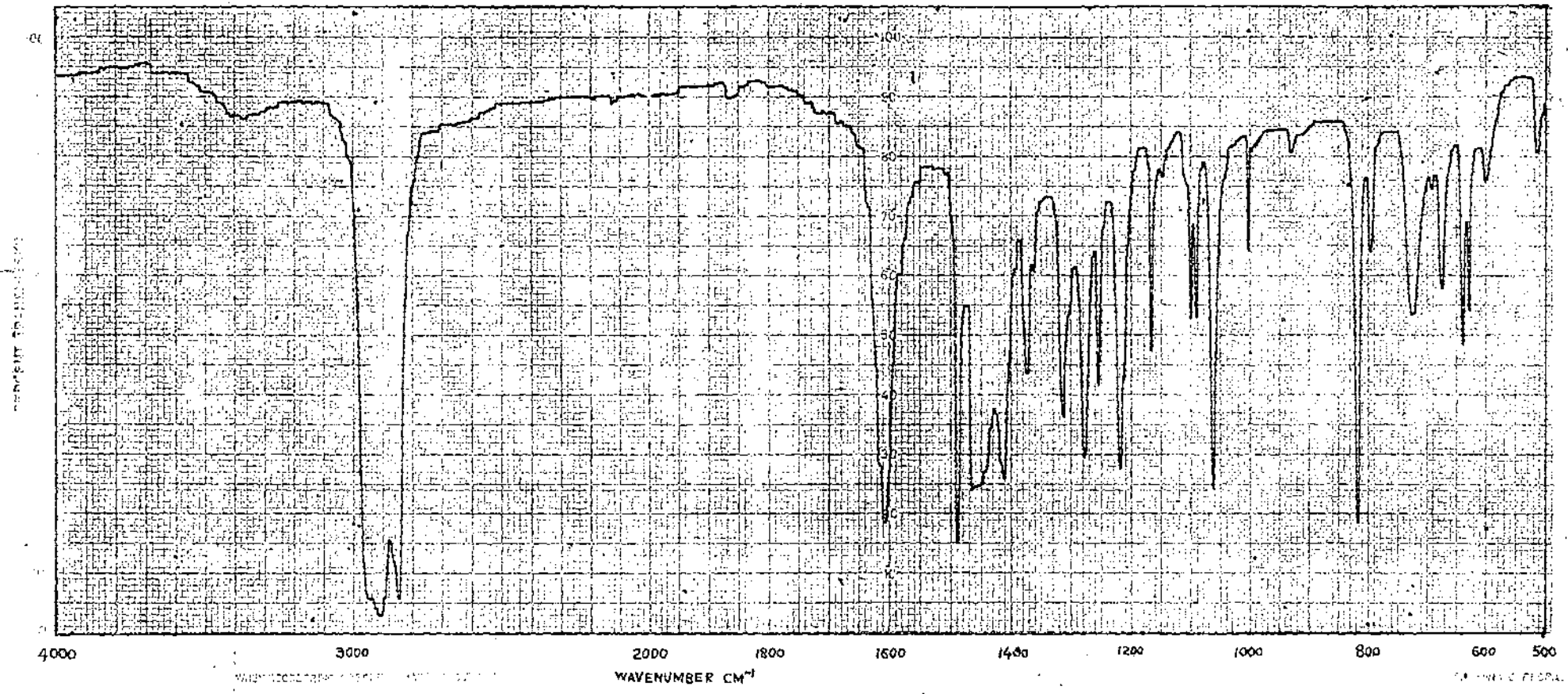


Fig.19. IR SPECTRUM OF $Oct_2Sn(L_4)_2$ IN NUJOL

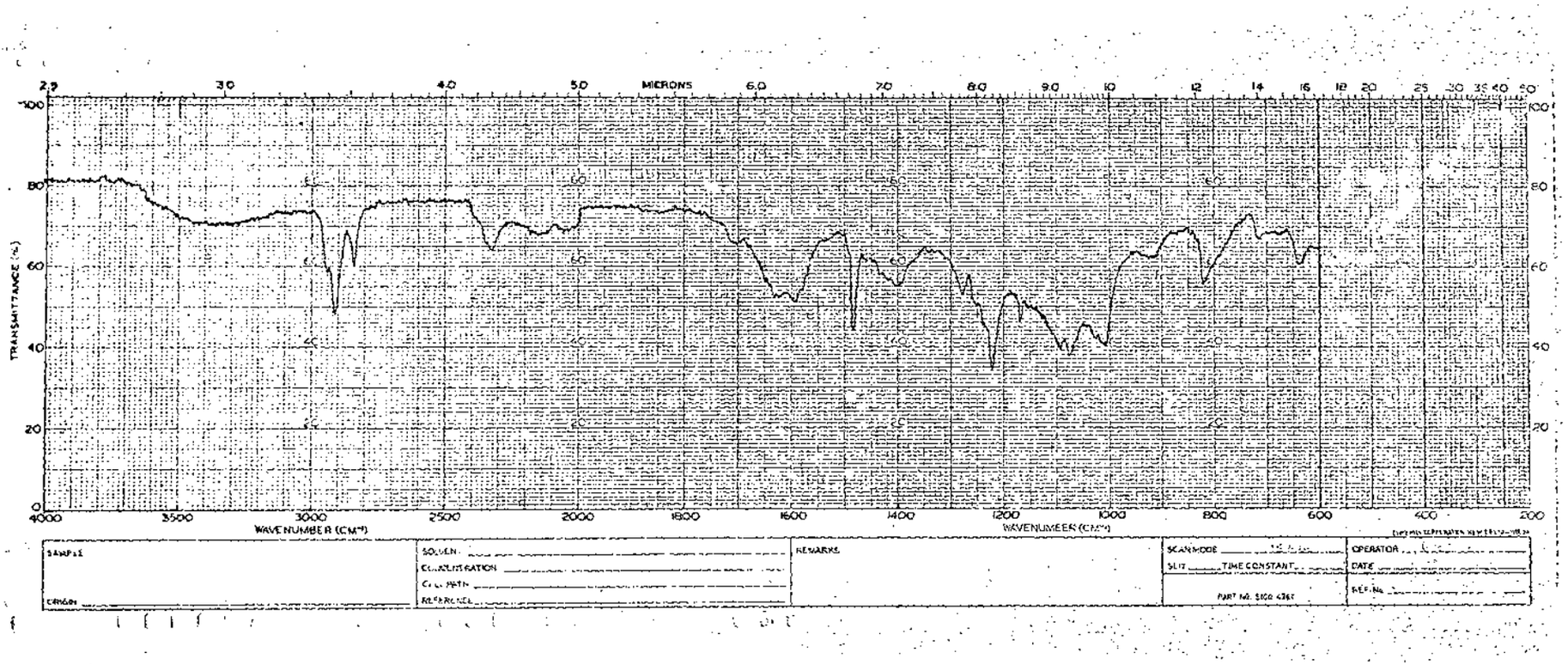


Fig.19a. IR SPECTRUM OF $Oct_2Sn(L_4)_2$ IN CCl_4

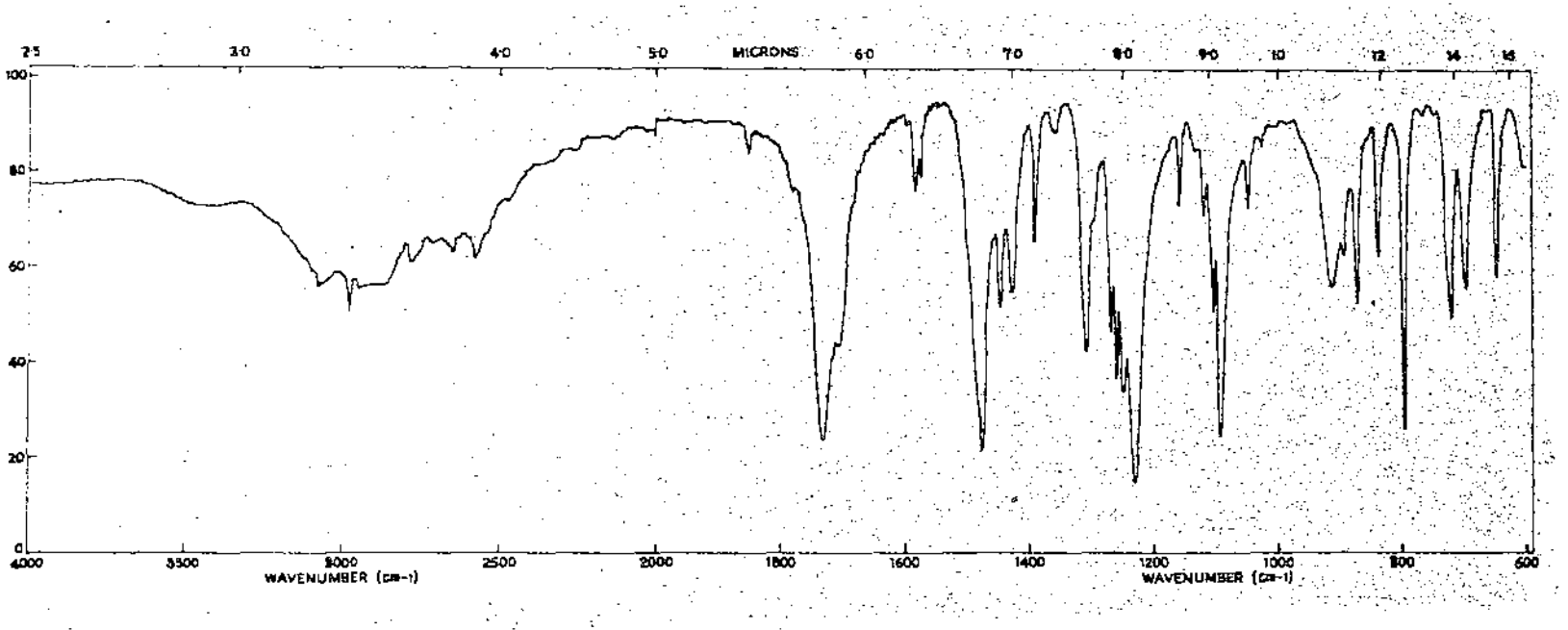


Fig.20. IR SPECTRUM OF L_5H IN KBr

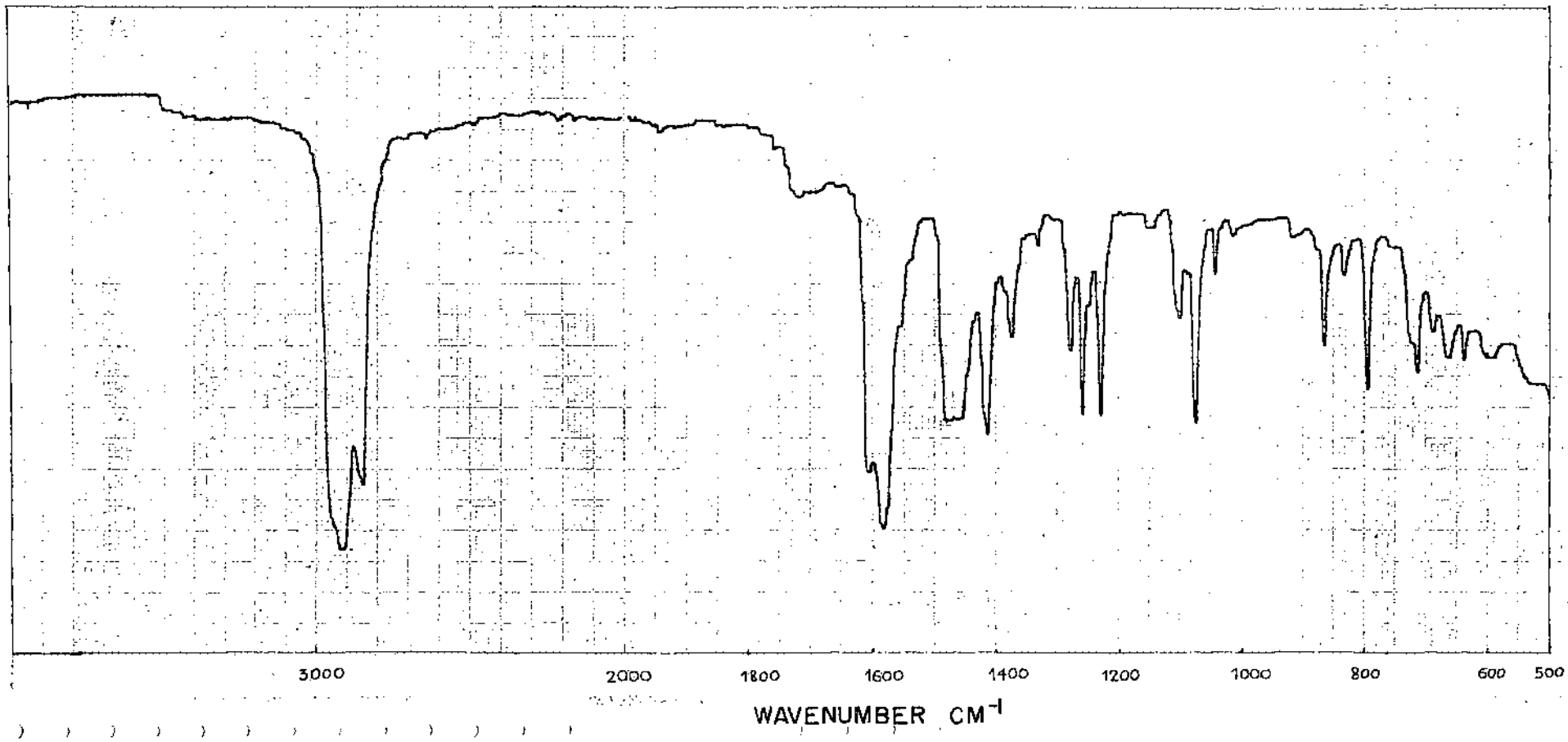


Fig.21. IR SPECTRUM OF Bu_3SnL_5 IN NUJOL

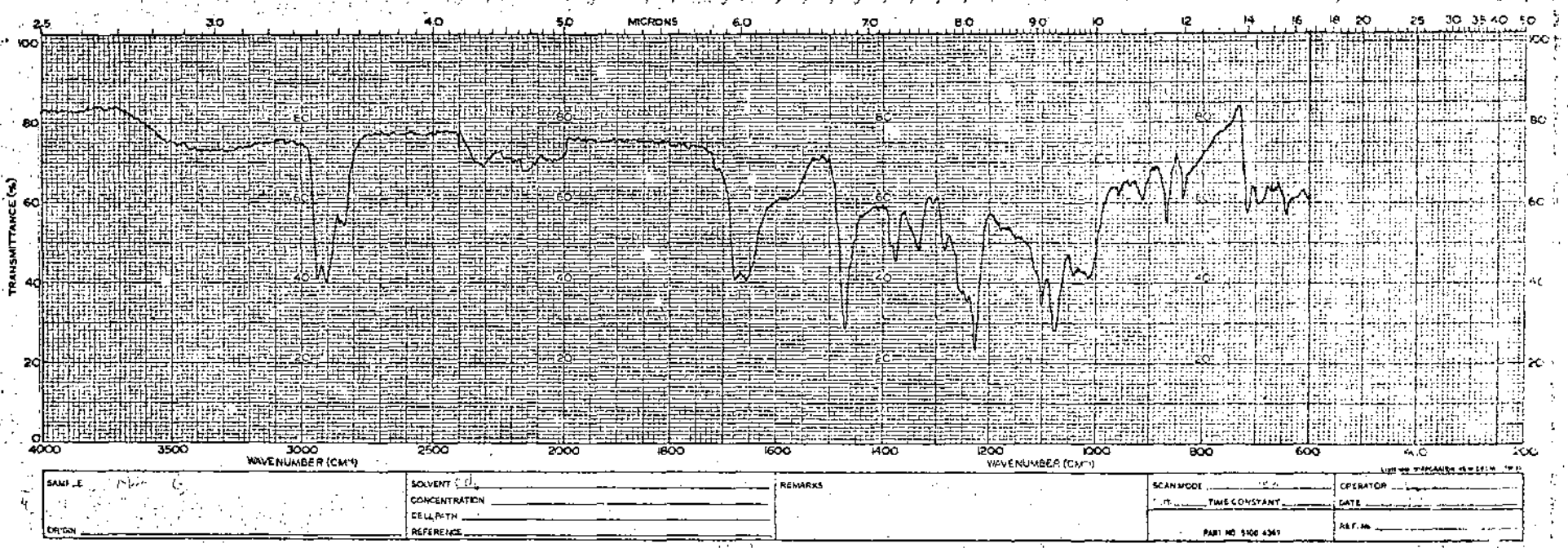


Fig.2Ia . IR SPECTRUM OF Bu_3SnL_5 IN CCl_4

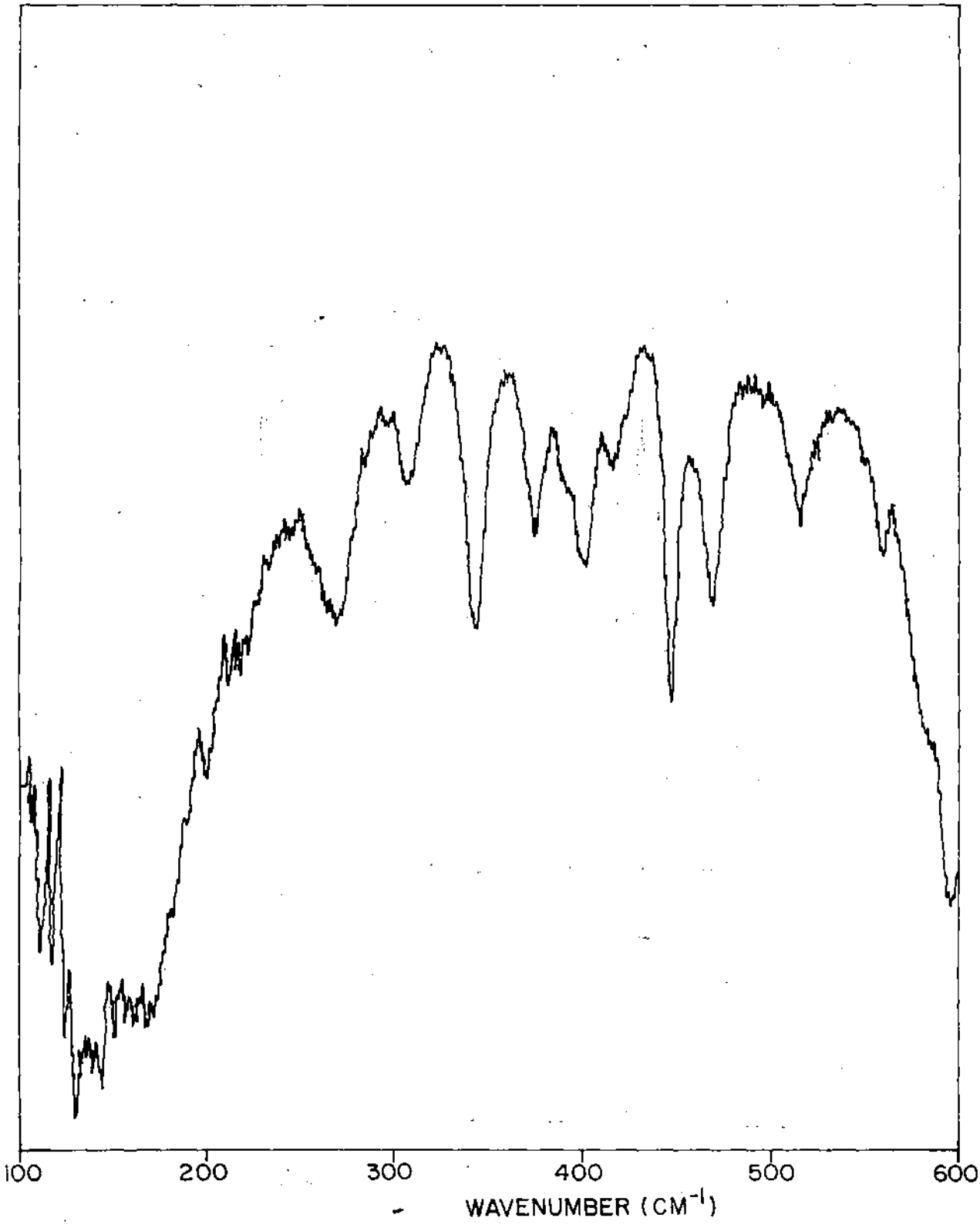


Fig.21b . FAR IR (FOURIER-TRANSFORM) SPECTRUM OF Bu_3SnL_5

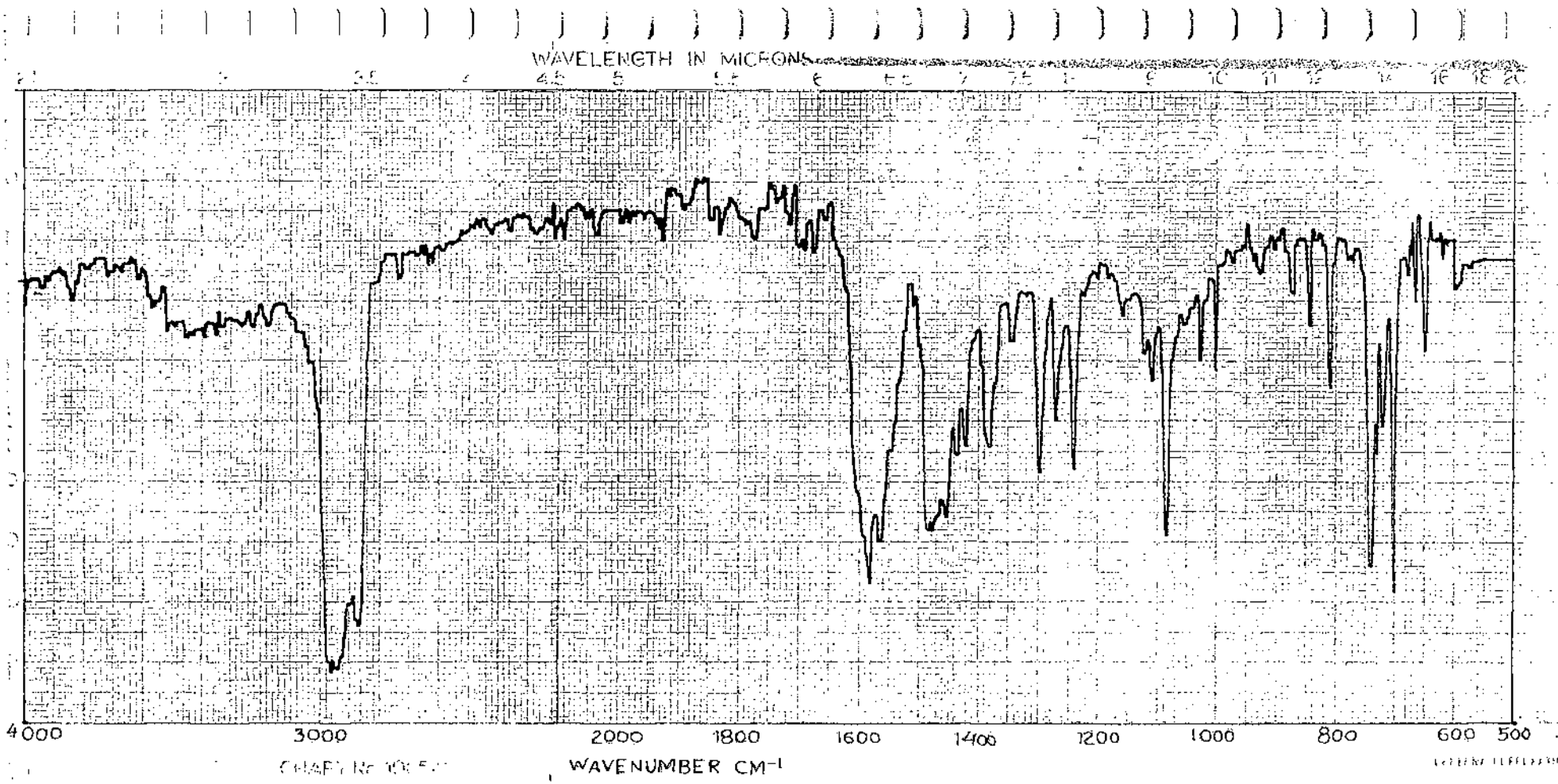


Fig.22. IR SPECTRUM OF Ph_3SnL_5 IN NUJOL

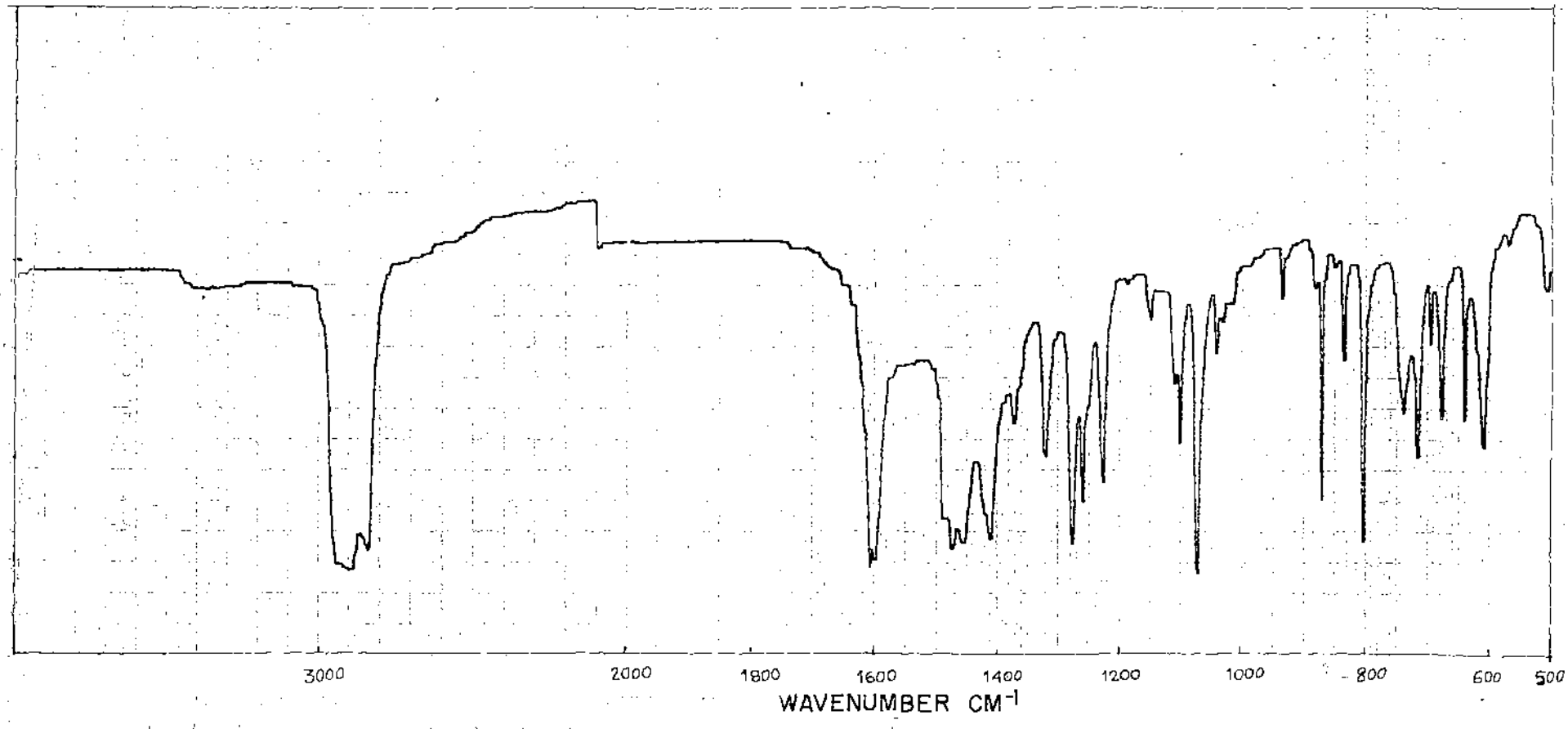


Fig.23. IR SPECTRUM OF $Bu_2Sn(L_5)_2$ IN NUJOL

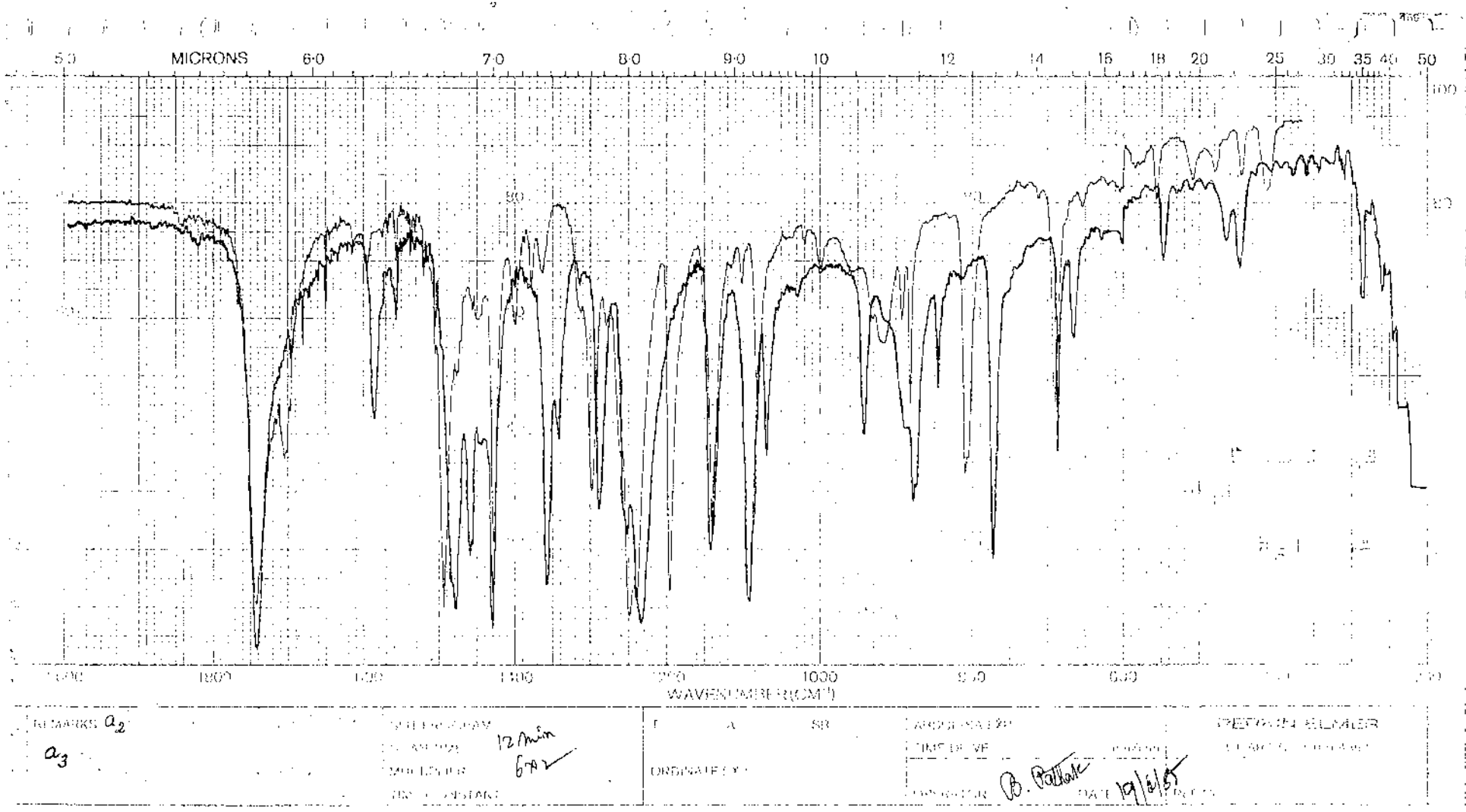


Fig.24 . IR SPECTRA OF L_6H (Deep Line) & L_7H (Light Line) IN KBr

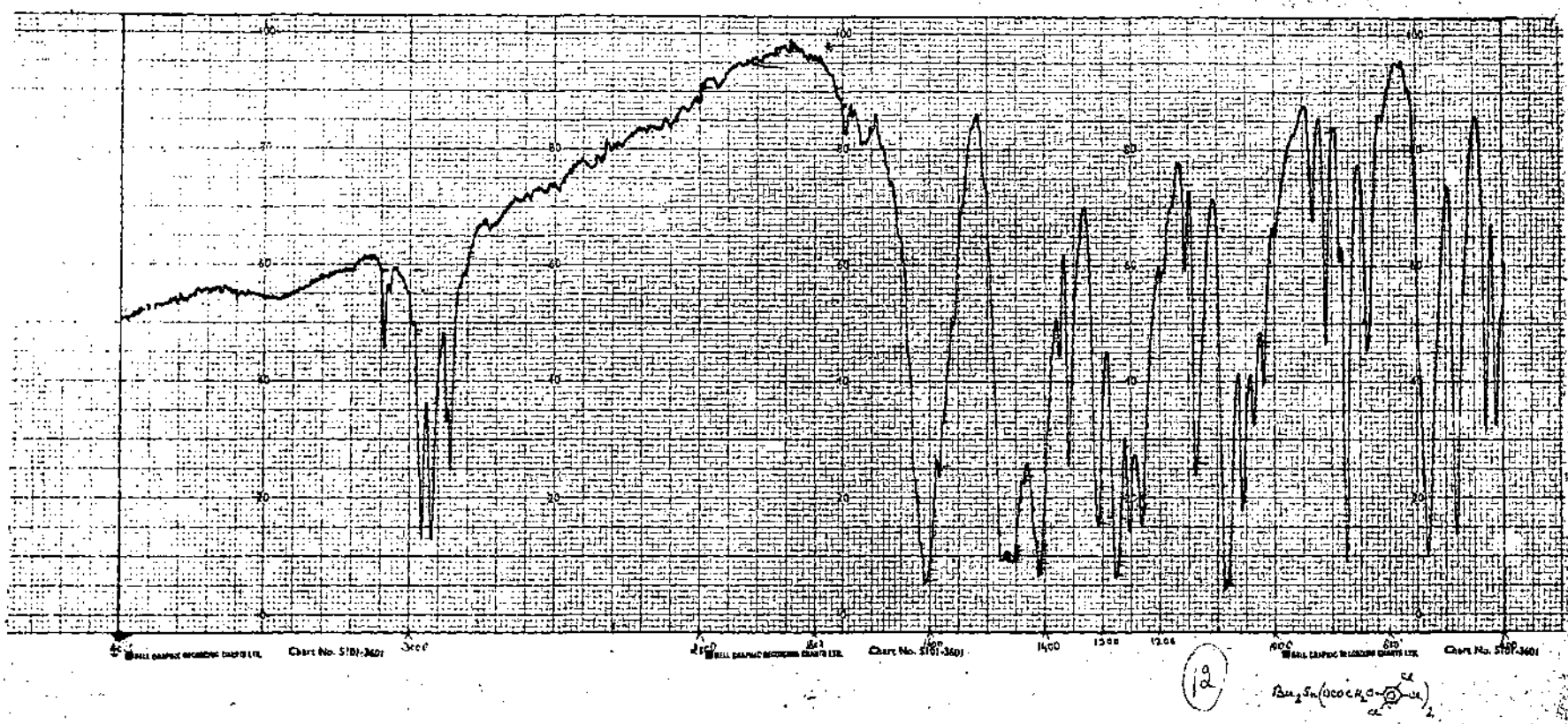


Fig.25 . IR SPECTRUM OF $Bu_2Sn(L_6)_2$ IN KBr

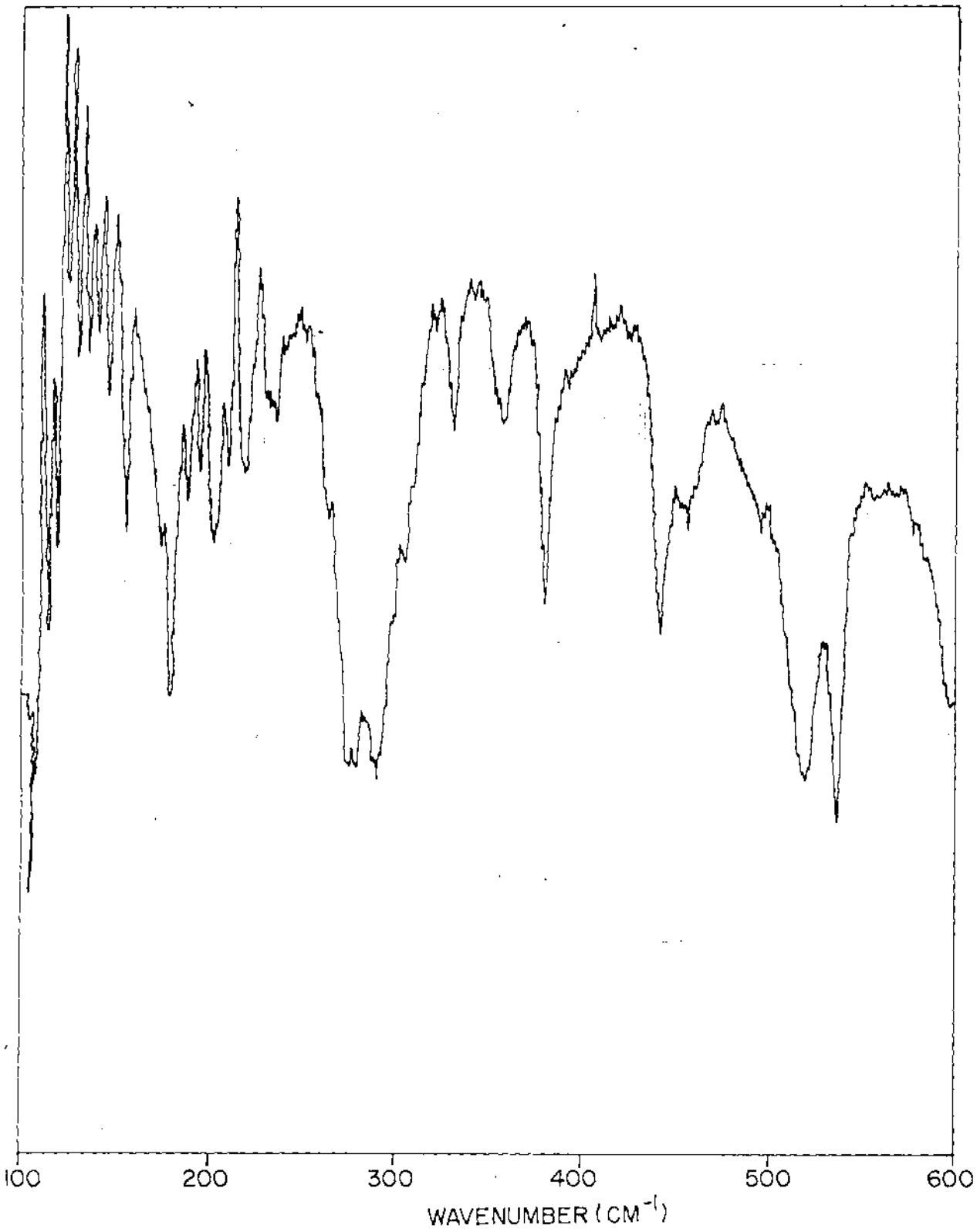


Fig.25a. FAR IR (FOURIER-TRANSFORM) SPECTRUM OF $Bu_2Sn(L_6)_2$

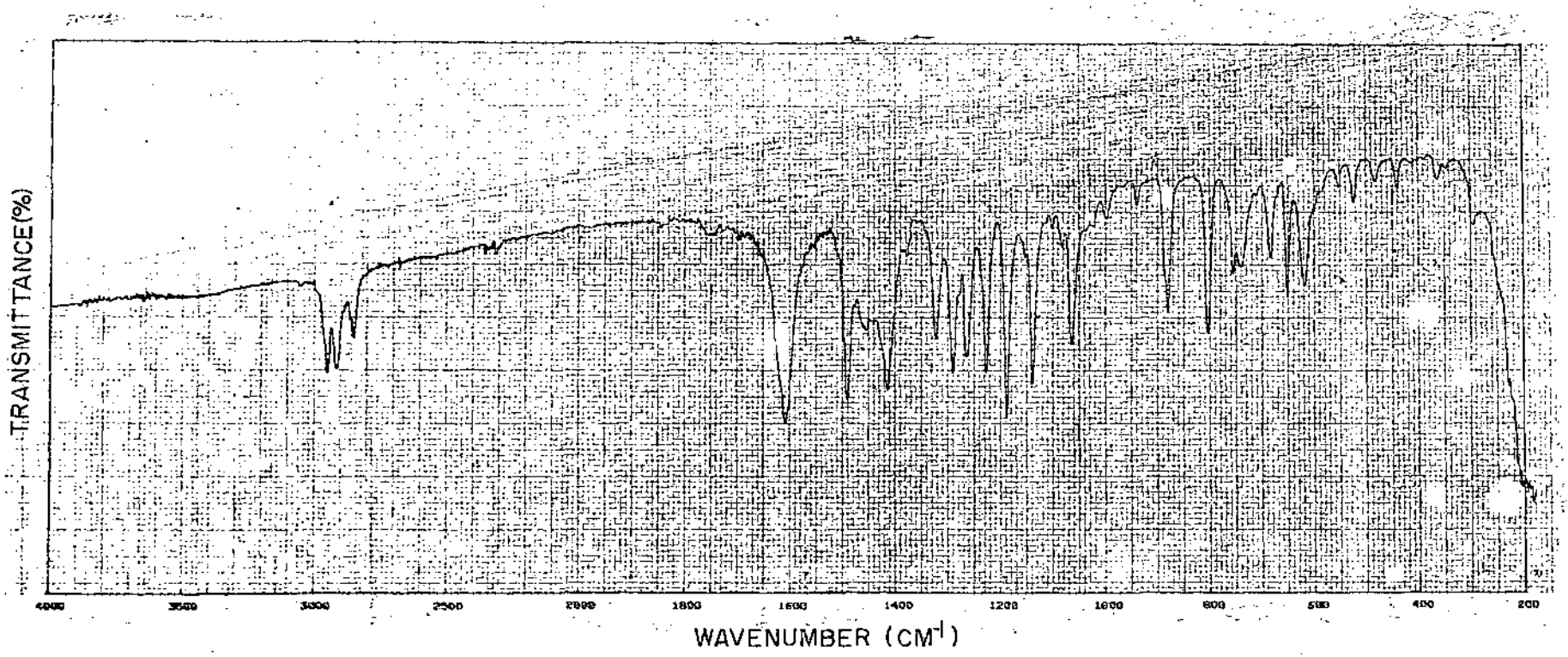


Fig.26. IR SPECTRUM OF $Bu_2Sn(L_7)_2$ IN KBr

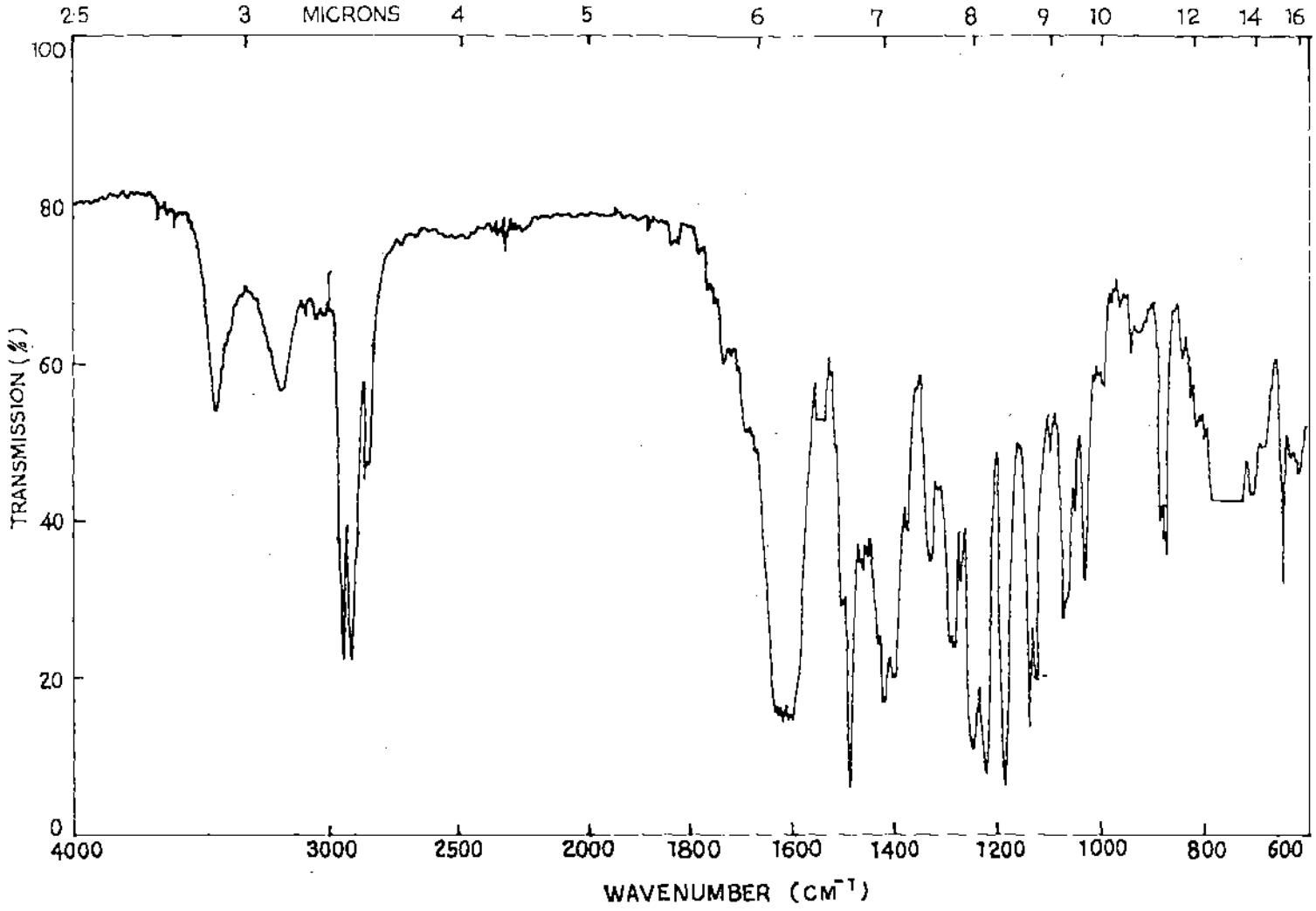


Fig.26a . IR SPECTRUM OF $Bu_2Sn(L_7)_2$ IN CCl_4

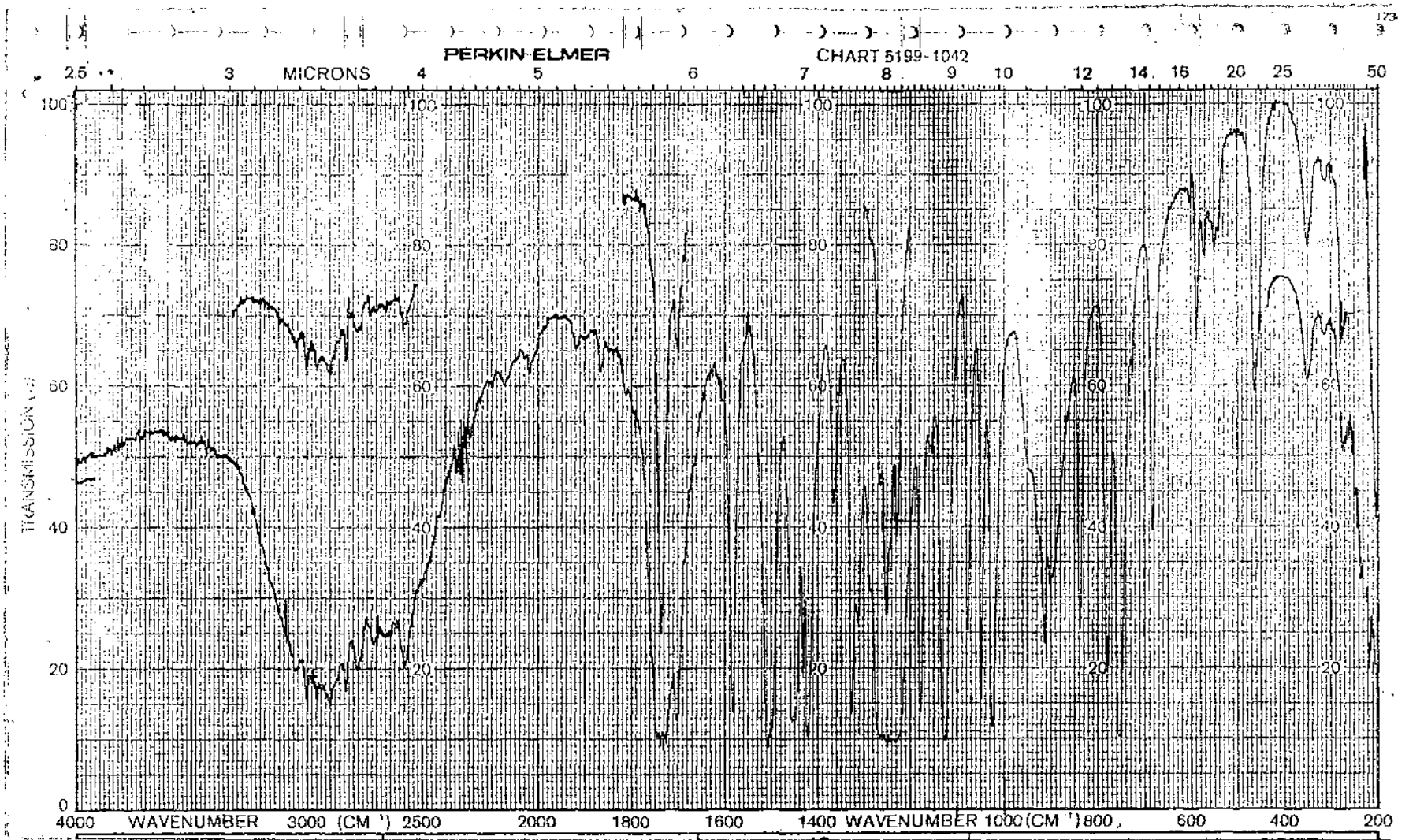
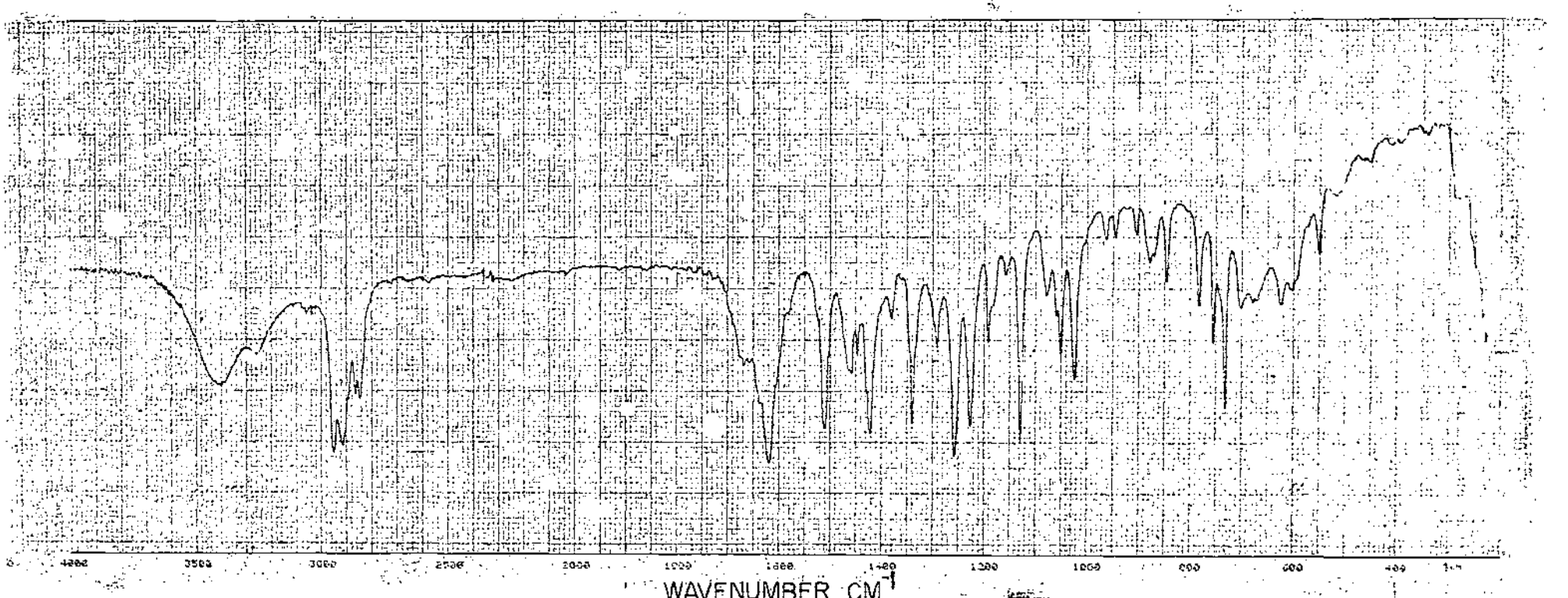


Fig.27. IR SPECTRUM OF L_8H IN KBr



WAVENUMBER CM^{-1}

Fig.28 . IR SPECTRUM OF Bu_3SnL_8 IN KBr

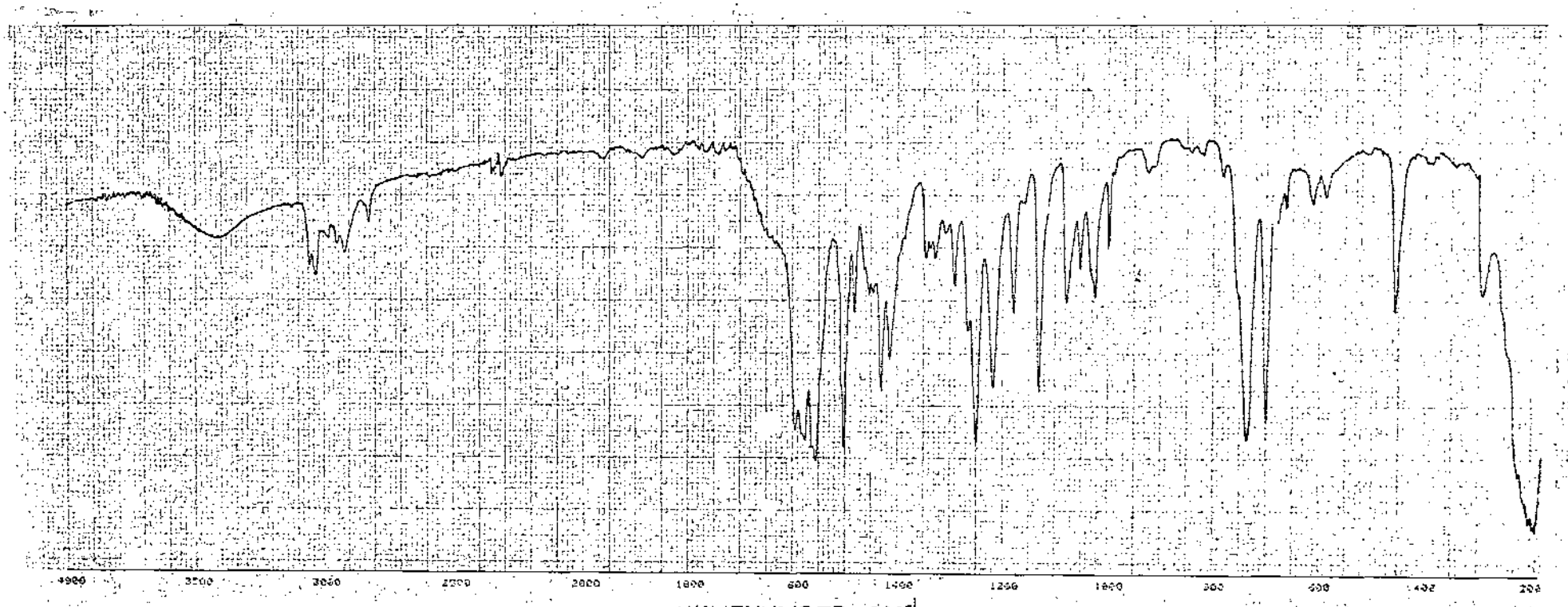


Fig.29. IR SPECTRUM OF Ph_3SnL_8 IN KBr

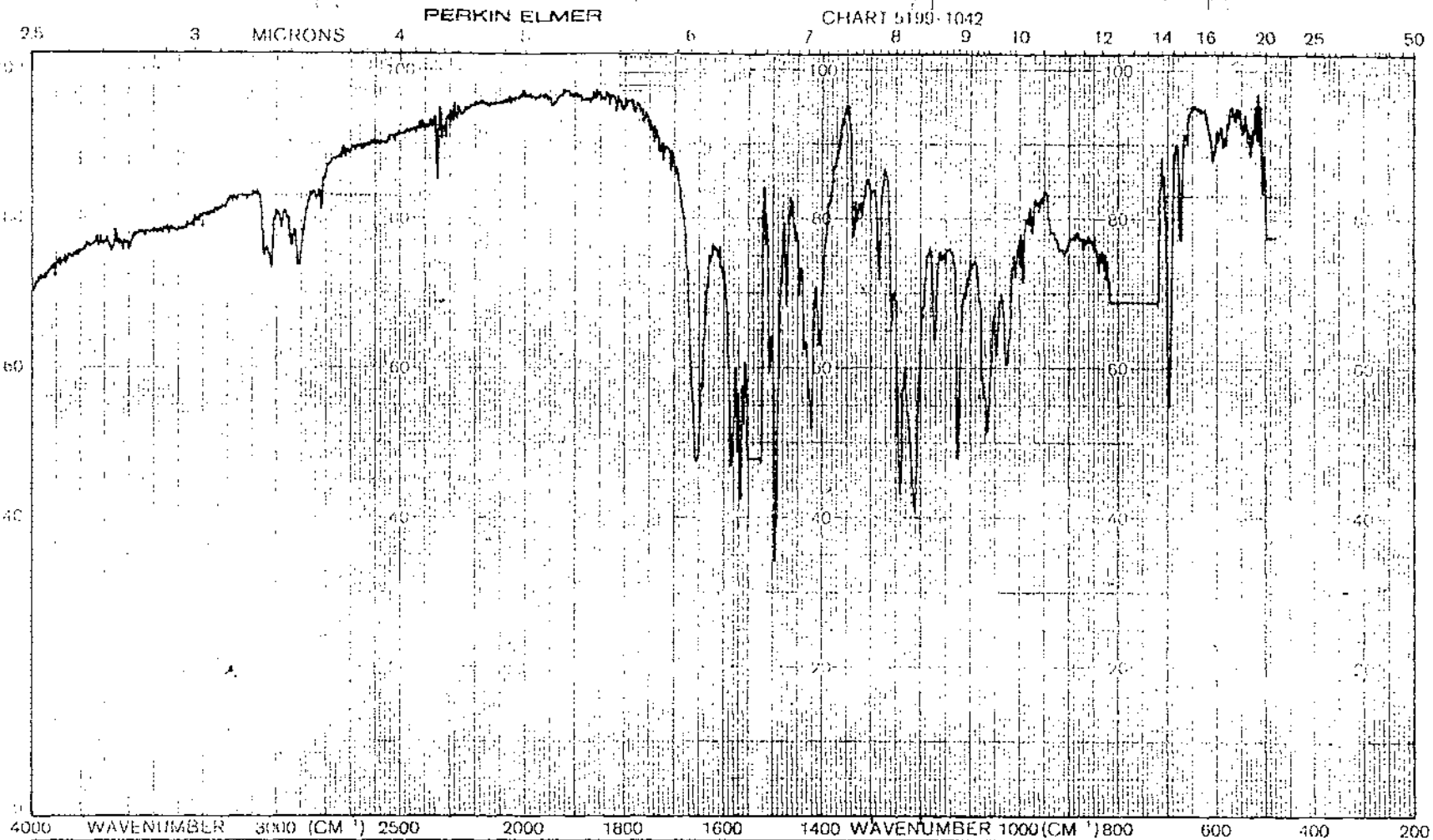


Fig.29a. IR SPECTRUM OF Ph_3SnL_8 IN CCl_4

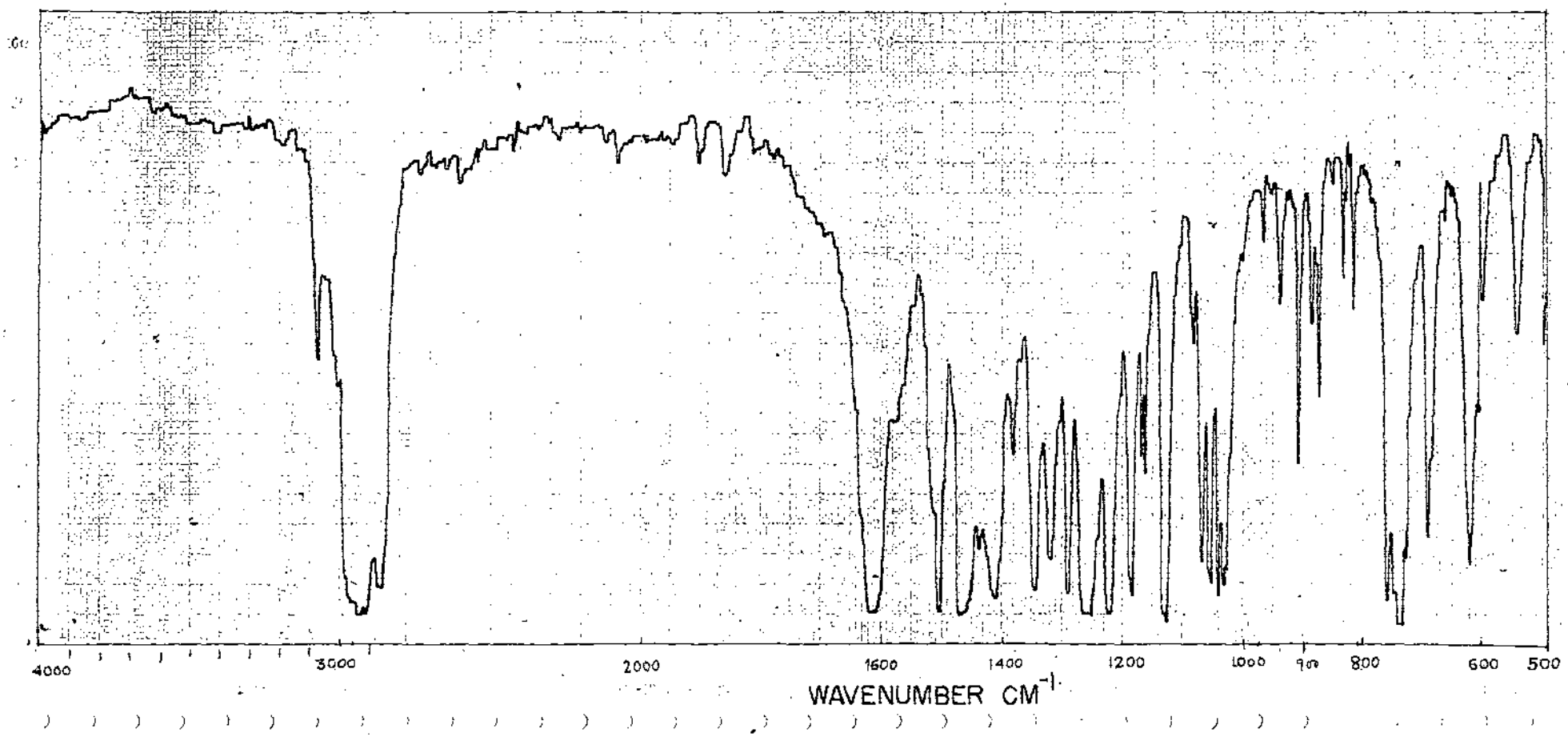
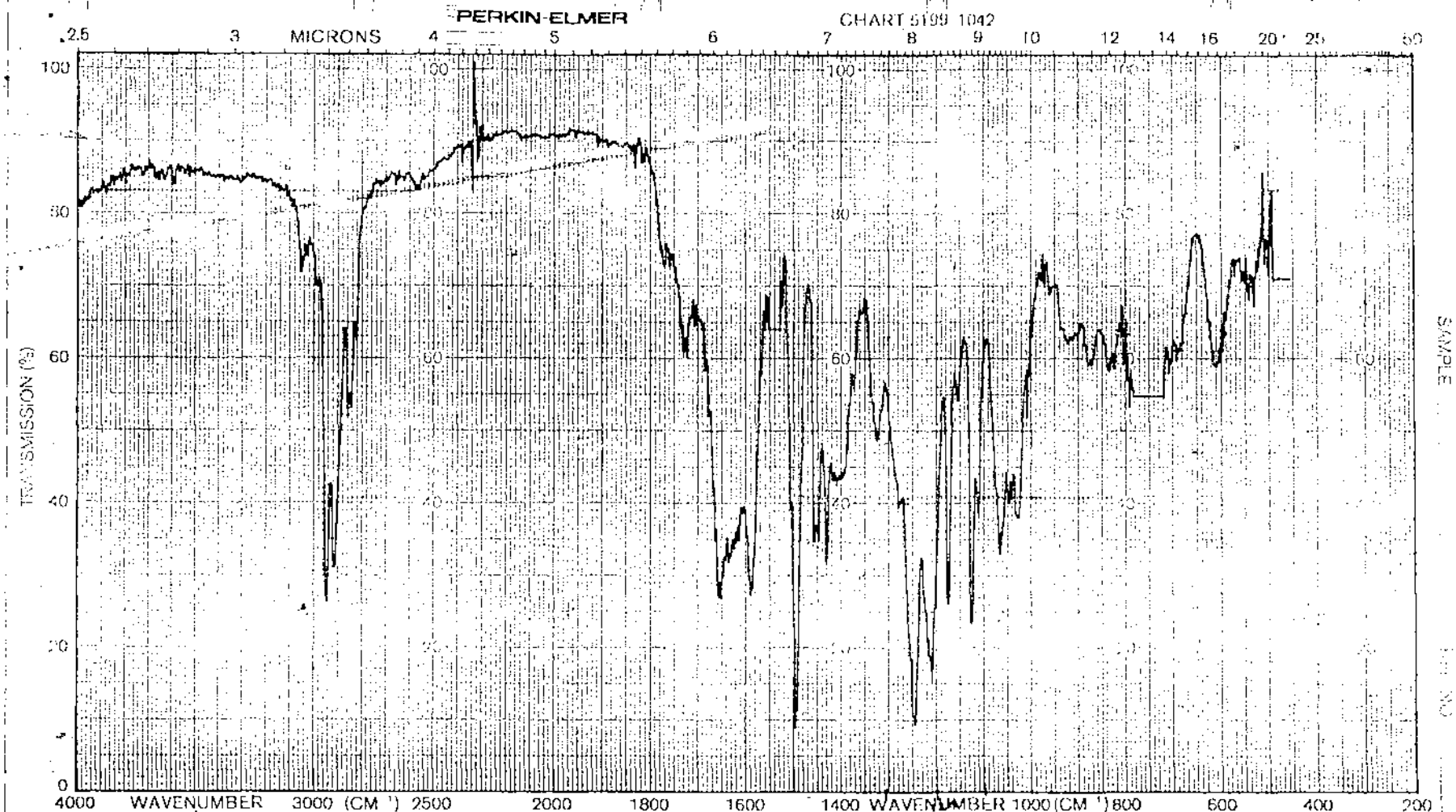
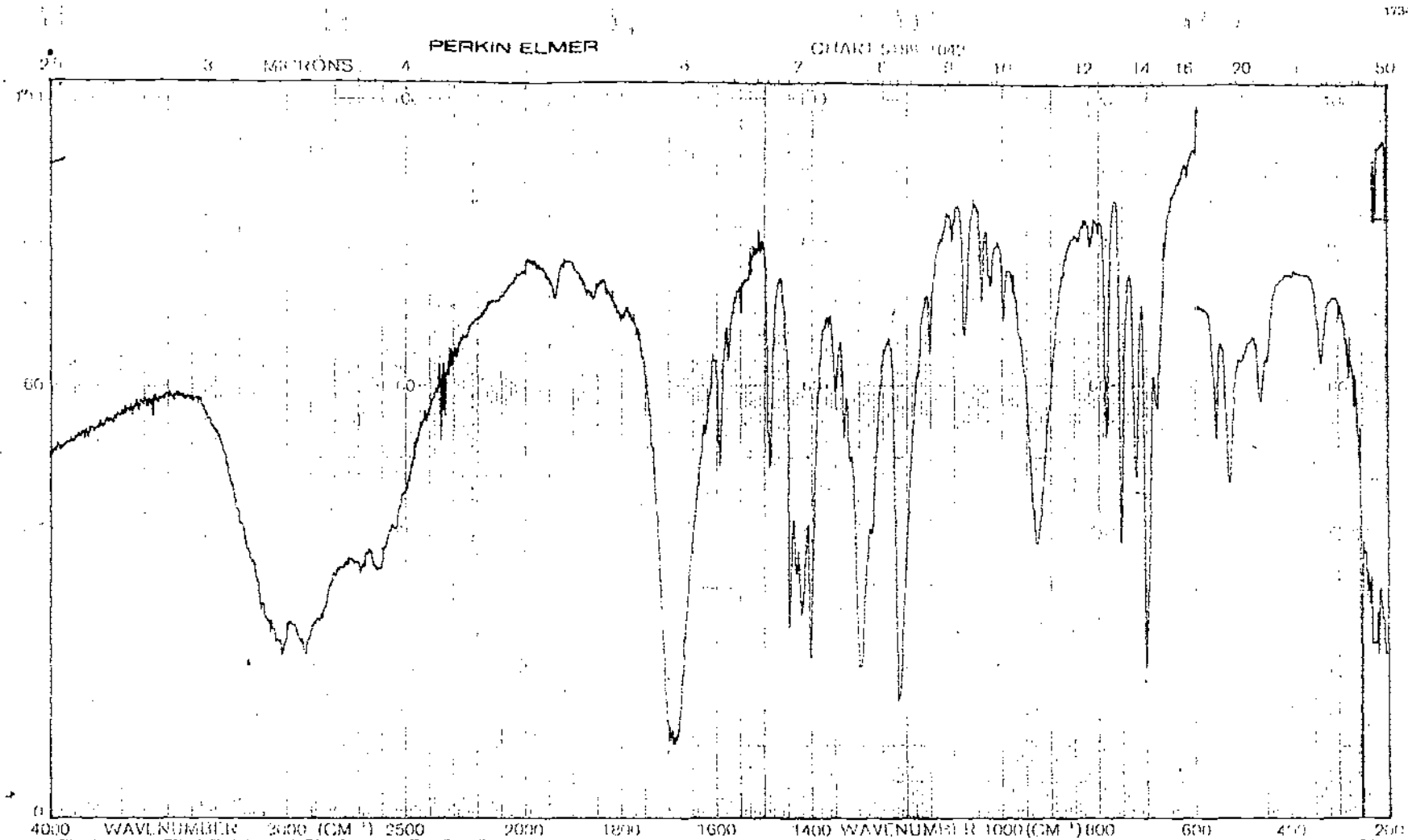


Fig.30 . IR SPECTRUM OF $Bu_2Sn(L_8)_2$ IN NUJOL



ABSCISSA'	ORDINATE	SCAN TIME 12 min	REP. SCAN ____ SINGLE BEAM ____
EXPANSION ____	EXPANSION ____	MULTIPLIER ____	TIME DRIVE ____
SUPPRESSION ____	% T ____ ABS ____	SLIT PROGRAM ____	OPERATOR S.Chaudhary DATE 25.3.85
SAMPLE 46	REMARKS ____	SOLVENT ____	CELL PATH ____
ORIGIN D.K. Banerjee		CONCENTRATION ____	REFERENCE CCl_4

Fig.30a . IR SPECTRUM OF $Bu_2Sn(L_8)_2$ IN CCl_4



ABSCISSA	ORDINATE	SCAN TIME 12 min	REP. SCAN _ SINGLE BEAM
EXPANSION	EXPANSION	MULTIPLIER	TIME DRIVE
SUPPRESSION	%T ABS	SLIT PROGRAM	OPERATOR Schaarschmidt DATE 14.2.84
SAMPLE AK6 (-)	REMARKS	SOLVENT	CELL PATH
ORIGIN L. Bandobustlingen		CONCENTRATION	REFERENCE KBr

Fig.31. IR SPECTRUM OF L_9H IN KBr

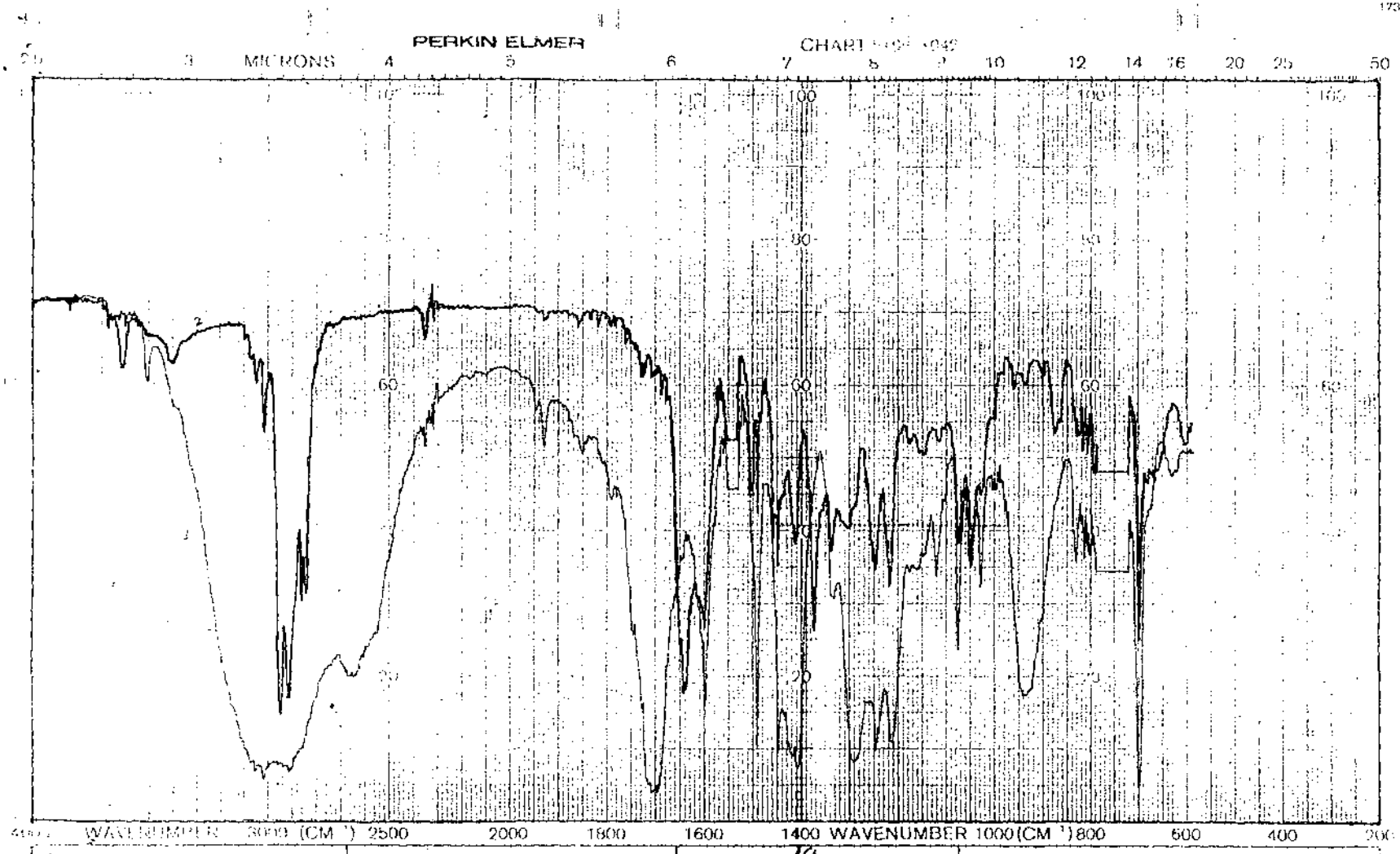
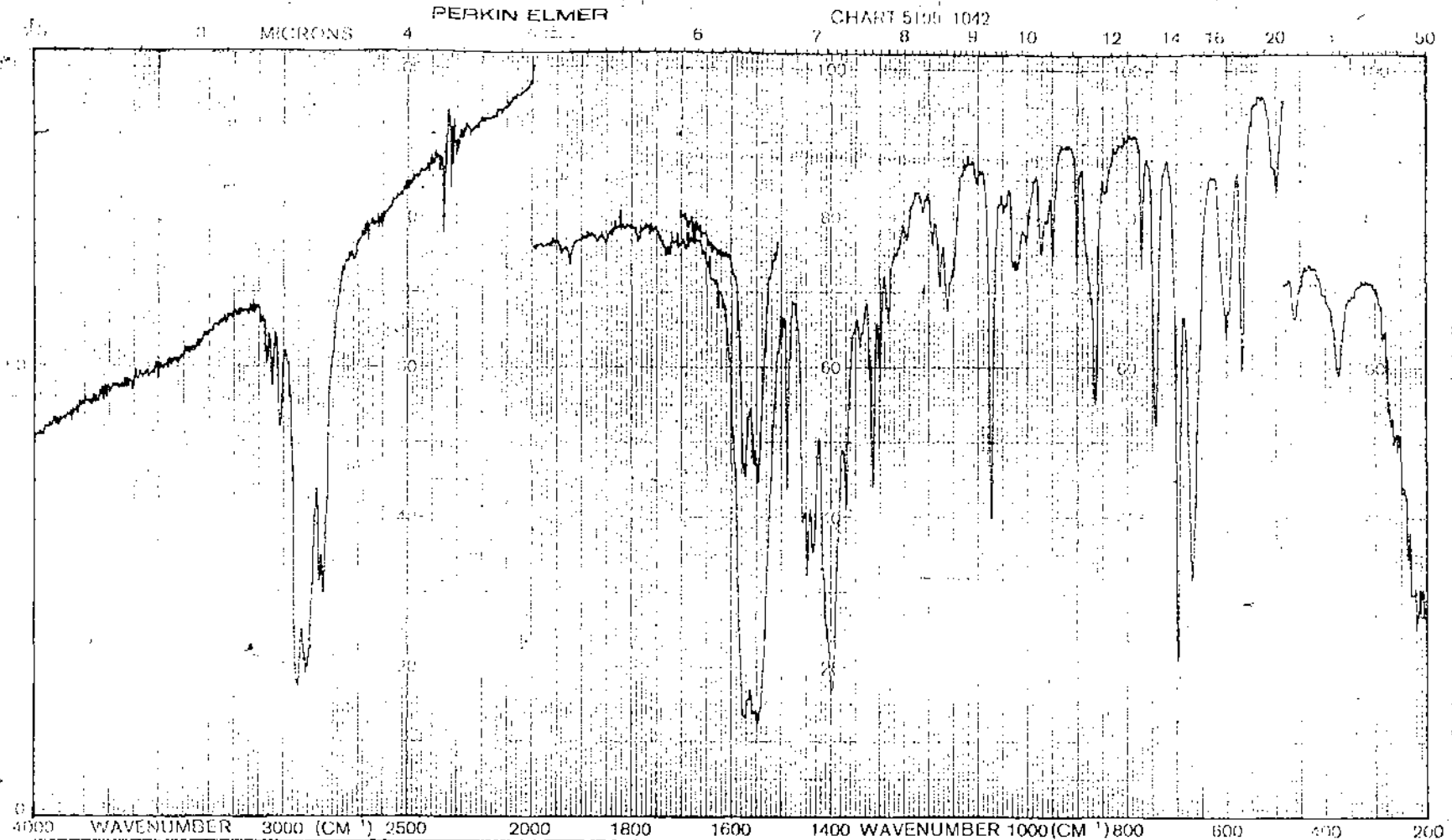


Fig.31a . IR SPECTRA OF L_9H (Light Line) & Bu_3SnL_9 (Deep Line) IN CCl_4



ABSCISSA	ORDINATE		
EXPANSION	EXPANSION	SCAN TIME 12 min	REP. SCAN ____ SINGLE BEAM
SUPPRESSION	% T ____ ABS	MULTIPLIER	TIME DRIVE
		SLIT PROGRAM	OPERATOR Schwarzbach DATE 14.2.85

SAMPLE AK7 (=)	REMARKS	SOLVENT	CELL PATH
ORIGIN L. Bandobadhyay		CONCENTRATION	REFERENCE KBr

Fig.32. IR SPECTRUM OF Bu_3SnL_9 (IN KBr)

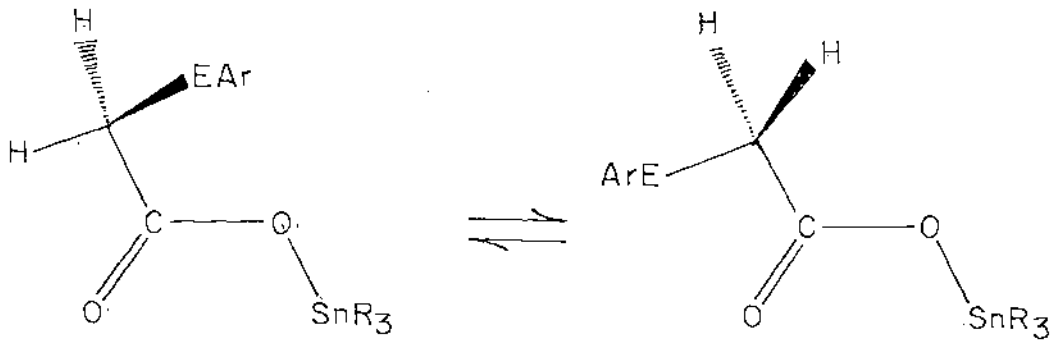
Some typical IR spectra are given in Figs. 1-32.

Dominant bands of the spectra of the tri- and di- organotin carboxylates (Table - 5) both in solid state and in solution are intense broad absorption bands ν_{as} and ν_{s} of carboxylic group and ν_{as} and ν_{s} of the phenoxymethyl group. For the latter group, $\nu_{as}(COC)$ is frequently denoted as the vibration of the phenyl-oxygen bond and $\nu_{s}(COC)$ is ascribed on the $O-CH_2$ bond vibration[16].

Data in Table - 5 show that in the parent aryloxyacetic acids, $\nu_{as}(COO)$ appear at $\sim 1740\ cm^{-1}$ and $\sim 1710\ cm^{-1}$ while $\nu_{s}(COO)$ appear at $\sim 1240\ cm^{-1}$. Although single crystal X-ray diffraction of phenoxyacetic acid revealed a hydrogen-bonded dimeric cyclic structure[21], the presence of the doublet points to the presence of intermolecular H-bonded dimer structure $[\nu_{as}(COO) = \sim 1710\ cm^{-1}]$ in addition to the normal structure with (ester-like) "free" -COOH groups $[\nu_{as}(COO) = \sim 1740\ cm^{-1}]$. This postulate is supported by the IR spectrum of methyl phenoxyacetate where only one $\nu_{as}(COO)$ is found at $1770\ cm^{-1}$. In the organotin derivatives, the asymmetric and symmetric carboxyl stretching vibrations appear at frequencies far removed from the corresponding frequencies in the parent acids indicating organo-stannylation[22]. Moreover, both ν_{as} and $\nu_{s}(COO)$ are dependent on the phase state of the sample.

From Table - 5 it is seen that for the R_3Sn - derivatives, $\nu_{as}(COO)$ and $\nu_{s}(COO)$ appear in the regions 1575-1590 cm^{-1} and 1410-1425 cm^{-1} respectively in solid state recorded either as KBr pellets or nujol mulls. The difference $\Delta\nu[\nu_{as}(COO) - \nu_{s}(COO)]$

is $\sim$170 cm^{-1} and suggests bidentate bridging carboxyl groups[23-25]. On the other hand, in case of the tri butyl tin (IV) derivatives in solution in non-polar solvents like CCl_4 and CS_2, $\nu_{as}(COO)$ is found as a pair of bands in the region 1660-1690 cm^{-1}, the pair of $\nu_s(COO)$ bands being shifted to the region of 1340-1360 cm^{-1}. In case of the triphenyltin phenoxyacetates, however, only one ν_{as} and $\nu_s(COO)$ are found in solution in non-coordinating solvents. In solution, therefore, $\Delta\nu$ is always >250 cm^{-1} indicating that the compounds break down to monomeric molecules in solution having unidentate carboxyl groups. This result is also compatible with the molecular weights measured in non-polar solvents (Table - 4). The coupling of bands in solution is presumably due to the presence of two rotamers (S-cis and S-trans), the magnitude of splitting of the bands ($\sim$20 cm^{-1}) being comparable with similar phenomenon observed with organic and organosilicon phenoxyacetates[26,27]. The two rotamers in equilibrium may be represented[27] as:



(VIIA)
Less Stable;
Low ν(COO)

(VIIB)
More Stable;
High ν(COO)

[R = Bu, Ph & E = O, S]

For the triphenyltin (IV)-derivatives we find that there is only one band with a shoulder appearing as the ν(COO). This fact, i.e., appearance of one major band as ν(COO) may be the result of either conformational homogenity or close resemblence of the carboxylate group frequency of both types of conformers.

Data in Table - 5 also show that in the triorganotin carboxylates ν_{as}(COC), i.e., $\nu_{as}(C_{Aryl}-O)$ and ν_s(COC), i.e., $\nu_s(O-CH_2)$ occur in the regions 1215-1250 cm^{-1} and 1070-1090 cm^{-1} respectively. The positions of these bands are not dependent on the phase state of the sample although their intensities change in going from solid to solution. The intensity changes may also be connected with presence of rotamers[26,27] discussed above. A comparison of these absorption frequencies with the corresponding absorption frequencies in the parent carboxylic acids do not suggest an intramolecular O⟶Sn coordination in the carboxylates in either phase.

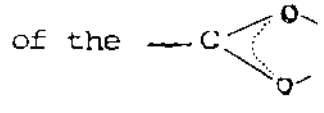
For the R_3Sn - derivatives, the deformation vibrations of the carboxylic group are less distinct than the valence vibrations. The Scissoring vibration is found as a band of medium intensity in the region of 700-712 cm^{-1} while the out-of-plane and in-plane deformation vibrations appear as weak bands in the regions of 603-615 and 500-515 cm^{-1} respectively.

The dominant vibrations in the spectra of the diorganotin carboxylates (mostly dibutyltin compounds) in both solid and solution phases are also those due to valence vibrations of the carboxyl and phenoxymethyl groups. Data in Table - 5 show that the bands due to

$\nu_{as}(C_{Aryl} - O)$ and $\nu_s(O - CH_2)$ are found in spectra in both solid phase and solution in the regions 1210-1260 cm^{-1} and 1075-1090 cm^{-1} respectively, i.e., practically the same as those of the R_3Sn- compounds discussed above. Again, the position of the bands of valence vibrations of carboxylic group depends, even though to a lesser extent, on the phase state. In solid state, the $\nu_{as}(COO)$ bands are found in the region of 1605-1625 cm^{-1} (1645 cm^{-1} for the compound $Me_2Sn(L_1)_2$) and $\nu_s(COO)$ at 1415-1425 cm^{-1}. The difference $\Delta\nu\left[\nu_{as} - \nu_s(COO)\right]$ is ~ 200 cm^{-1}. An exception is provided by the compound $Bu_2Sn(L_2)_2$ in which $\nu_{as}(COO)$ and $\nu_s(COO)$ occur at 1553 cm^{-1} and 1416 cm^{-1} respectively ($\Delta\nu = 137$ cm^{-1}). In solution (CCl_4), $\nu_{as}(COO)$ is raised to ~ 1640 cm^{-1} whereas $\nu_s(COO)$ is slightly shifted to lower wave numbers of ~ 1405 cm^{-1} ($\Delta\nu \sim 235$ cm^{-1}). These data are typical of bidentate chelating carboxyl group[1,4,5,23] and hence the diorganotin (IV) derivatives in solid phase may be ascribed an octahedral coordination around the tin atom with two bidentate chelate forming carboxyl groups. In solution, since $\Delta\nu$ is found to be less than 250 cm^{-1}, the situation is between monodentate and chelate functions of the carboxylic groups. With compound $Bu_2Sn(L_2)_2$ it is necessary to presume a bridge arrangement of -COO- group in solid state like the triorganotin derivatives.

The other vibrations of the carboxylic group lie in regions identical with those of the R_3Sn (IV) derivatives discussed above. An intensive band of the Scissoring vibration occurs in the region

of 720-750 cm^{-1} while weak bands of out-of-plane and in-plane deformation vibrations appear at 610-625 cm^{-1} and 495-512 cm^{-1} respectively.

In Table - 5 are also given the IR data of the two phenyl thio acetates. The data compare to a considerable extent with their oxygen analogues, i.e. compounds Bu_3SnL_1 and $Bu_2Sn(L_1)_2$. As expected, the intensive ν(CCC) bands disappear in the spectra of Bu_3SnL_{10} and $Bu_2Sn(L_{10})_2$. It is also found that the carboxyl group frequencies, ν_{as}(COO) and ν_s(COO), have similar values as those of the oxygen analogues. Therefore, the same conclusions can be made about their structures inclusive of the existence of two rotamers of tributyltin (IV) phenylthioacetate (VIIA and VIIB). Slight shifts of ν_{as}(COO) and ν_s(COO) to the region of lower wave numbers observed with the two phenylthioacetates (as compared to their phenoxyacetate counterparts) are, presumably, connected with the more distinct donor properties of the $C_6H_5SCH_2COO^-$ anion as compared with $C_6H_5OCH_2COO^-$. As a result of this, the bond order of the  group is relatively low in

the two phenylthioacetates. The difference in the donor properties of the $C_6H_5ECH_2COO^-$ anions (E = O or S) is also confirmed by values of the dissociation constants of their conjugate acids[28].

The vibrations due to Sn-C and Sn-O bonds are given in Table - 6. The identification of the bands, made by comparison of the IR spectra of the organotin carboxylates with those of the parent acids, is, however, only tentative. Further, in a few cases, the

ν(Sn-O) could not be assigned because FIR spectra were not available and/or the spectra were not well resolved for accurate identification of the band. It is found that both ν_{as}(Sn-C) and ν_{s}(Sn-C) bands are identified as weak to moderate bands in the region of 560-620 cm^{-1} and 500-540 cm^{-1} respectively for the R_3Sn - derivatives other than Ph_3Sn - derivatives while for the R_2Sn - derivatives the bands occur in the region of 580-615 cm^{-1} and 500-560 cm^{-1} respectively[17,29]. In case of the triphenyltin derivatives, ν_{as}(Sn-C) and ν_{s}(Sn-C) appear as weak bands at 280-295 cm^{-1} and 250-260 cm^{-1} respectively[17]. The occurrence of both ν_{as}(Sn-C) and ν_{s}(Sn-C) implies that the SnC_3 group in the R_3Sn (IV) derivatives is not perfectly planar and the SnC_2 group in the R_2Sn (IV) derivatives is not perfectly linear. The perfect planarity or linearity of the SnC_3 or SnC_2 groups respectively would cause absence of ν_{s}(Sn-C) in the spectra[17]. Reasons for the apparent deviation from planarity or linearity would become more clear as we discuss the NMR data in Section IIIG. The ν(Sn-O) vibration is ascribed to a band of medium to weak intensity in the region of 265-290 cm^{-1} in accordance with reference 18.

IIIF. ^{119m}Sn Mössbauer data of only two compounds, namely Ph_3SnL_1 and Bu_3SnL_1, could be secured by us. The data are as folow

	δ	ΔE_q
Ph_3SnL_1	1.58 ± 0.03 mm/sec	3.86 ± 0.06 mm/sec
Bu_3SnL_1	1.37 ± 0.03 mm/sec	3.43 ± 0.06 mm/sec

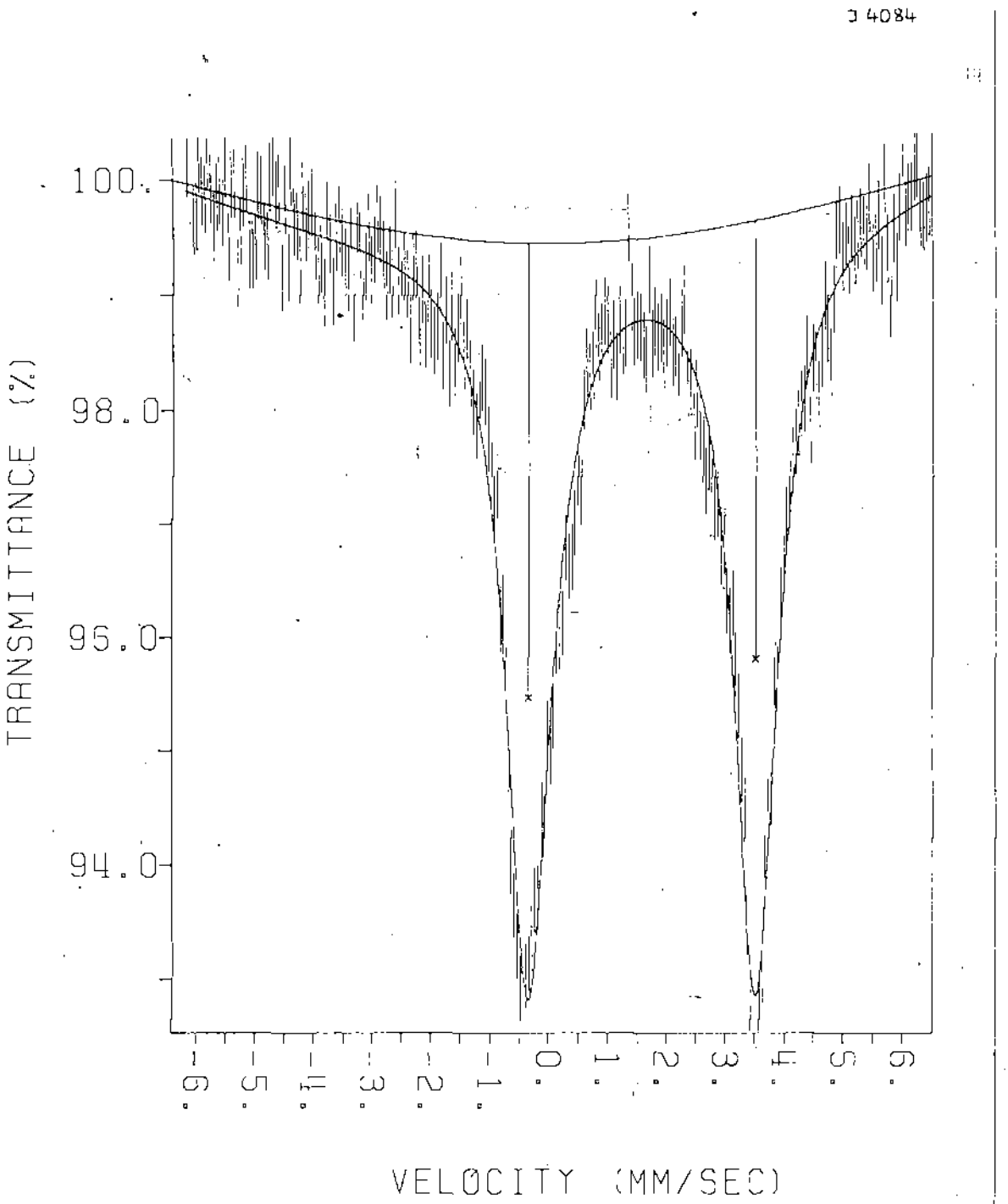


Fig.33. ^{119m}Sn - Mössbauer spectrum of Bu_3SnL_1 at 80 K

At 80 K : Is ± 0·03mm/s =1·58

□s ± 0·06mm/s = 3·86

Γ_1 ± 0·03mm/s = 0·94, Γ_2 ± 0·03mm/s = 0·89

At RT : No Signal

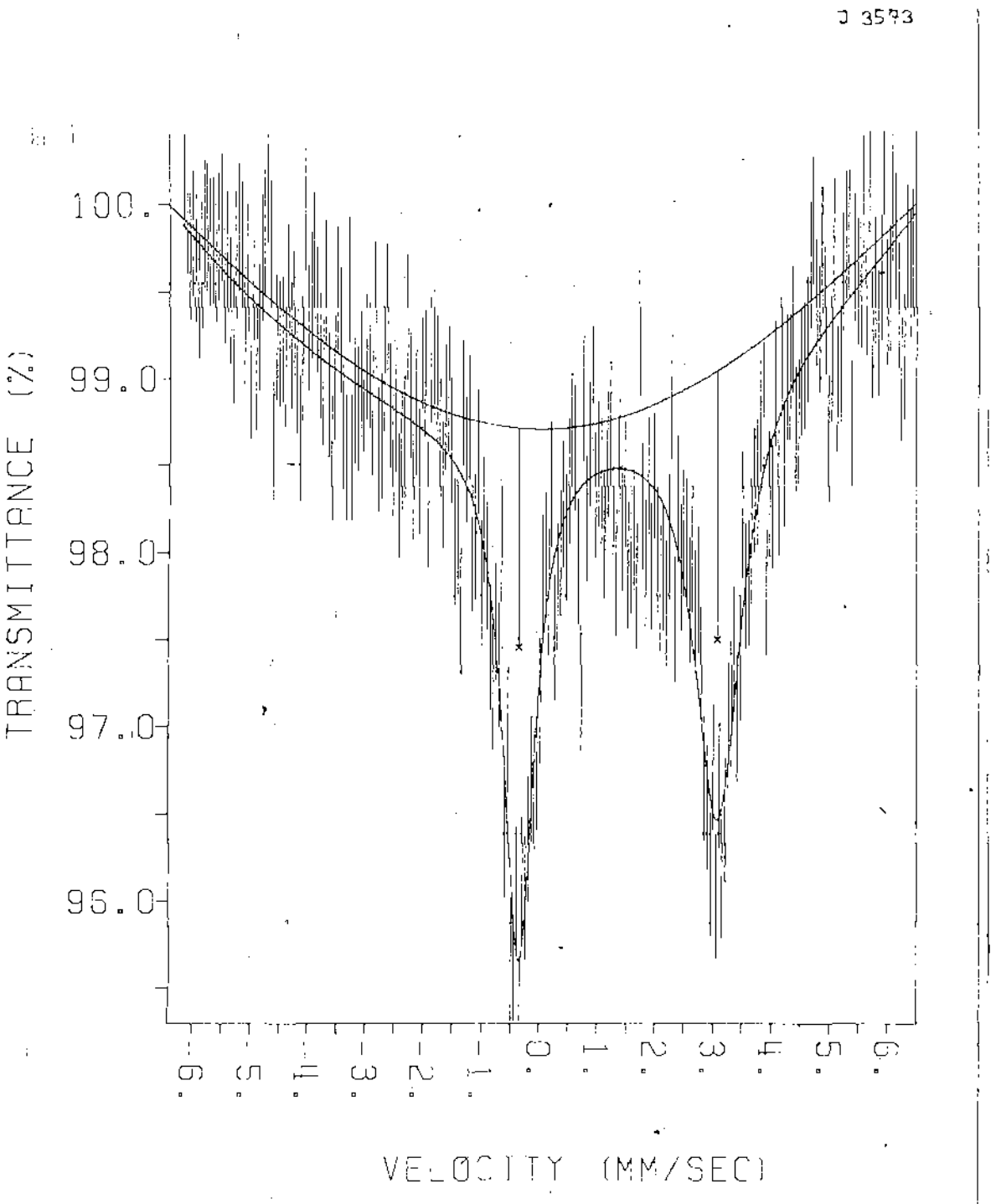


Fig. 34 . ^{119m}Sn - Mössbauer spectrum of Ph_3SnL_1 at 80 K

At 80 K: IS ± 0·03mm/s = 1·37

QS ± 0·06mm/s = 3·43

Γ_1 ± 0·03mm/s = 0·66, Γ_2 ± 0·03mm/s = 0·98

At RT : No Signal

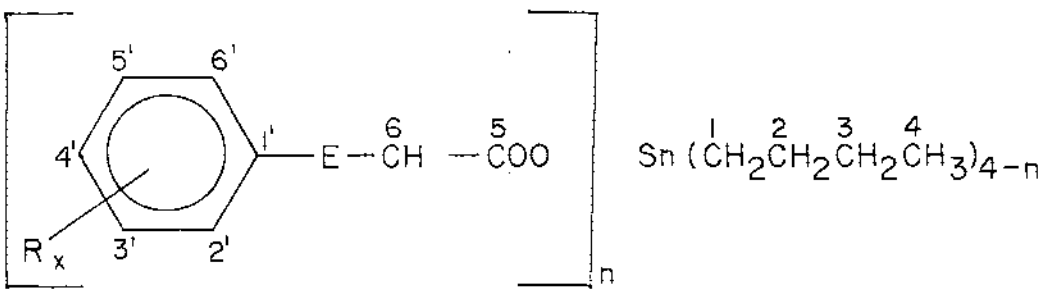
The values are consistent[15,30] with structures having penta-coordinated tin atoms and is compatible with results already revealed by the IR data in solid state. The Herber's ratio ($\rho = \Delta Eq/\delta$) of 2.44 and 2.5 for Bu_3SnL_1 and Ph_3SnL_1 respectively are also consistent with this[31].

The Mössbauer spectra are shown in Fig. 33 and Fig. 34.

IIIG. ^{13}C, ^{17}O and ^{119}Sn NMR Spectral data:

It was possible to get the ^{13}C, ^{17}O and ^{119}Sn NMR spectra of a few tri- and dibutyl tin aryloxyacetates and the pair of phenylthioacetates. NMR spectra of the triphenyltin carboxylates could not be done due to their poor solubility in the solvents used. The NMR parameters are given in Tables - 7 and 8.

From the Tables it can be seen that in $CDCl_3$ solutions, the compounds exhibit a single signal at 300°K in the ^{119}Sn spectrum. The number of signals in the ^{13}C spectrum corresponds to the number of magnetically non-equivalent cabon atoms in the structural formula suggested for the respective compound (VIII).



(VIII: R is the respective substituent in the phenyl ring; E = O or S; n & x = 1 or 2)

Table - 7

Chemical shifts $\delta(^{119}Sn)$ and $\delta(^{17}O)$ and coupling constants $^{n}J(^{119}Sn\,^{13}C)$ of some tri and di-butyltin carboxylates

Compound	$\delta(^{119}Sn)$[a], ppm	$\delta(^{17}O)$[b], ppm/$w_{\frac{1}{2}}$[c], Hz	$^{n}J(^{119}Sn\,^{13}C)$[d], Hz		
			n=1	n=2	n=3
Bu_3SnL_1	130.9	258/700	352.2	20.8	64.7
Bu_3SnL_1[e]	- 61.3		511.5	29.0	80.6
Bu_3SnL_2	127.7		352.0	20.8	64.7
Bu_3SnL_4	132.9		350.3	20.8	64.7
Bu_3SnL_3	132.2		351.6	20.8	64.7
$Bu_2Sn(L_1)_2$[f]	-117.4	249/900	549.3	36.0	100.1
$Bu_2Sn(L_1)_2$[e]	-298.3		811.8	34.2	140.4
$Bu_2Sn(L_2)_2$	-117.1		548.1	36.6	101.3
$Bu_2Sn(L_4)_2$	-114.4		545.7	36.0	100.1
$Bu_2Sn(L_5)_2$	-110.5		544.4	36.6	102.5
$Bu_2Sn(L_8)_2$	-119.7		556.6	36.6	105.0

Contd..

Table - 7 (Contd..)

Compound	$\delta(^{119}Sn)^a$, ppm	$\delta(^{17}O)^b$, ppm/$w_{\frac{1}{2}}{}^c$, Hz	$^nJ(^{119}Sn^{13}C)^d$, Hz		
			n=1	n=2	n=3
Bu_3SnL_{10}	125.5	276/500	352.8	20.8	67.1
$Bu_2Sn(L_{10})_2$	-135.8	272/1000	559.7	34.8	102.5

[a] 300K, deuteriochloroform; [b] 330K, chloroform, saturated solution, ± 3 ppm; [c] the signal half-width, ± 10%; [d] $^4J(^{119}Sn^{13}C) < 5$ Hz; [e] solution in hexamethylphosphoric triamide; [f] 220K, two signals (-116.4 and -200.9 ppm) with the integral intensity ratio of 4:1.

Table - 8

Chemical shifts $\delta(^{13}C)$ in deuteriochloroform at 300K of some tri and dibutyltin carboxylates.

Compound	$\delta(^{13}C)$, ppm									
	$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	$C_{(1')}$	$C_{(2')}$	$C_{(3')}$	$C_{(4')}$
Bu_3SnL_1	16.52	27.53	26.85	13.45	173.45	65.32	157.90	114.33	129.15	120.96
Bu_3SnL_1 [a]	18.89	27.62	26.69	13.24	170.56	65.97	158.67	114.08	128.46	119.54
Bu_3SnL_2 [b]	16.52	27.63	26.90	13.50	173.79	65.84	156.30	126.91	130.66	120.72
Bu_3SnL_4	16.57	27.58	26.85	13.50	173.21	65.65	156.59	115.70	129.05	125.88
Bu_3SnL_3 [c]	16.60	27.53	26.85	13.45	172.77	66.28	153.71	122.81	130.27	121.64
$Bu_2Sn(L_1)_2$	25.44	26.17	26.02	13.21	178.18	64.72	157.37	114.19	129.20	121.35
$Bu_2Sn(L_1)_2$ [a]	28.54	26.59	26.06	13.19	172.61	65.34	158.23	114.18	128.65	120.02
$Bu_2Sn(L_2)_2$ [d]	25.39	26.26	26.07	13.26	178.33	65.25	155.81	127.00	130.86	121.15
$Bu_2Sn(L_4)_2$	25.73	26.36	26.17	13.40	177.79	65.21	156.15	115.70	129.30	126.52
$Bu_2Sn(L_5)_2$ [e]	25.87	26.50	26.26	13.44	177.11	66.39	152.30	124.23	130.42	127.00
$Bu_2Sn(L_8)_2$	25.53	26.17	25.97	13.21	177.79	65.83	f	f	111.75	g

Contd..

Table - 8 (Contd..)

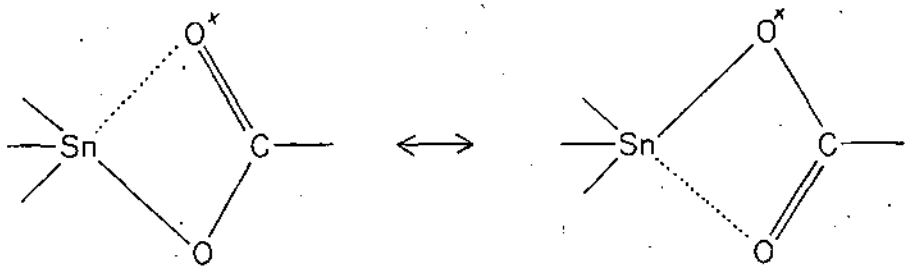
Compound	$\delta(^{13}C)$, ppm									
	$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	$C_{(1')}$	$C_{(2')}$	$C_{(3')}$	$C_{(4')}$
Bu_3SnL_{10}	16.52	27.58	26.90	13.50	174.13	36.70	136.07	128.66	128.66	125.93
$Bu_2Sn(L_{10})_2$	25.19	26.12	26.02	13.21	179.25	35.72	135.00	h	h	126.33

[a]Solution in hexamethylphosphoric triamide; [b-h]further values $\delta(^{13}C)$, ppm; [b]126.37 ($C_{(5')}$), 110.87 ($C_{(6')}$), 16.18 ($C_{(CH_3)}$); [c]127.25 ($C_{(5')}$), 131.21 ($C_{(6')}$); [d]126.32 ($C_{(5')}$), 110.73 ($C_{(6')}$), 15.98 ($C_{(CH_3)}$); [e]127.40 ($C_{(5')}$), 114.50 ($C_{(6')}$); [f]149.23 or 146.84; [g]122.08 or 120.28 ($C_{(4')}$) and ($C_{(5')}$); 113.50 ($C_{(6')}$), 55.46 ($C_{(OCH_3)}$); [h]128.86 or 128.71.

The small numbers in the formula in VIII denote the carbon atoms for assignment of the signals in the ^{13}C NMR spectra.

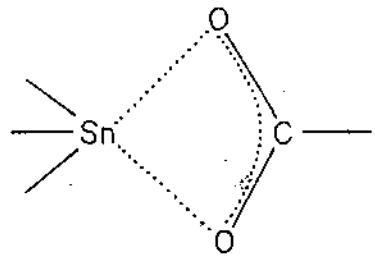
The chemical shifts $\delta(^{119}Sn)$ of the Bu_3Sn compounds in $CDCl_3$ solutions have the values 125.5 - 132.9 ppm, the coupling constants ^1J ($^{119}Sn^{13}C$) of these compounds vary within the limits from 350.3 - 352.8 Hz. Both these parameters, which are significant for evaluation of structures, possessthe values typical of quasi tetrahedral arrangement around the tin atom in this type of compounds[32]. With the Bu_2Sn compounds, the values of chemical shifts $\delta(^{119}Sn)$ and coupling constants ^1J ($^{119}Sn^{13}C$) in $CDCl_3$ solutions vary within the limit from -110.5 to -135.8 ppm and from 544.4 to 559.7 Hz, respectively, which values for the dibutyltin compounds are typical of a penta coordinated tin atom[33,34]. Thus it is obvious that in compounds $Bu_2Sn(L_1)_2$, $Bu_2Sn(L_2)_2$, $Bu_2Sn(L_4)_2$, $Bu_2Sn(L_5)_2$, $Bu_2Sn(L_8)_2$ and $Bu_2Sn(L_{10})_2$ in $CDCl_3$ solutions, the aryloxyacetate group, $ArOCH_2COO$ and the phenylthioacetate group, $PhSCH_2COO$ must act as multi-donor chelate-forming ligands. The chemical shift $\delta(^{17}O)$ was measured for Bu_3SnL_1 and Bu_3SnL_{10} and for the pair $Bu_2Sn(L_1)_2$ and $Bu_2Sn(L_{10})_2$. In each of these cases, one signal was only found for the two oxygen atoms of carboxylic group, its position being approximately in the middle of the interval containing the signals of the two oxygen atoms of -COO group of organic esters. Similar phenomenon was also encountered with other types of tri- and di- butyltin (IV) carboxylates and was explained[35] by a rapid exchange of the oxygen atom in the -COOSn fragment in

the NMR time scale as (IX):



(IX)

which from the point of view of the NMR time scale, is equivalent to the arrangement (X):



(X)

Structure X indicates a bonding affinity of the tin atom of di- and tri- butyltin (IV) compounds to both the oxygen atoms of the carboxyl group. Hence, it seems likely that both the oxygen atoms contribute (to different extents) to the bonding interactions of the -COO group with the central tin atom. The donor-acceptor bond formed with the oxygen atom of the carbonyl group (>C=O) is, of course, much weaker than a simple covalent Sn-O bond in the Sn-O-C grouping and thus the -COO group acts, in this respect, as an asymmetrical bidentate chelate-forming ligand in the two types of compounds. Such a role of the carboxyl group in the dibutyltin (IV) carboxylates is perfectly in accordance with the IR results discussed

earlier (Section III E). The idea of asymmetrical chelation as envisaged in structures (IX), however, compels us to accord a coordination number of six to the dibutyltin derivatives contrary to experimental facts. The idea, therefore, brings certain troubles with determination of the coordination number. It seems best to assign a structure in solution phase in the non-coordinating solvents such that in dibutyltin (IV) carboxylates, both carboxyl groups are weakly chelating to the tin atom such that the over-all coordination number of the central tin atom becomes five. It should be remembered that the IR data give only one $\nu_{as}(COO)$. This rules out a classically penta-coordinated structure, i.e., one carboxyl group chelating and the other being monodentate. In the tributyltin (IV) compound examined by ^{17}O NMR spectroscopy, the interaction of the oxygen atom of the carbonyl group with the tin atom is, obviously, very weak because of the much lower Lewis acidity of the Bu_3Sn group as compared to the Bu_2Sn group. Consequently, these compounds behave as quasitetrahedral in non-coordinating solvents in accordance with ^{13}C, ^{119}Sn NMR and IR spectra. Therefore, presence of an asymmetrically chelated carboxyl group in the Bu_3Sn compound can not be discounted. That there is weak interaction between the carbonyl oxygen atom and tin atom is also proved by the occurrence of $\nu_s(Sn-C)$ in both solid state and solution in the IR spectra (Section III E) which is caused by a distortion from planarity of the SnC_3 group.

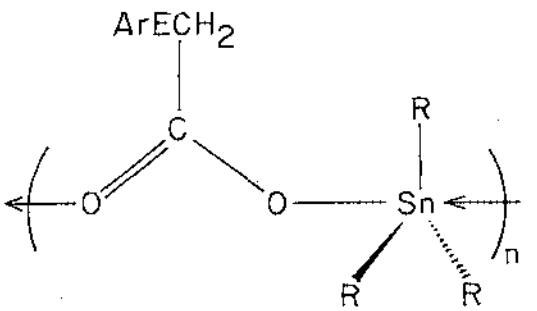
In both the types of compounds, the tin atom is distinctly incompletely saturated in its coordination, which is indicated by marked differences in the ^{13}C and ^{119}Sn NMR spectral parameters of compounds Bu_3SnL_1 and $Bu_2Sn(L_1)_2$ when going from $CDCl_3$ to hexamethylphosphoric triamide. The distinct shift of the $\delta(^{119}Sn)$ values to higher field (Table - 7) and the increase in $^1J(^{119}Sn^{13}C)$ and $\delta(^{13}C_{(1)})$ as shown in Table - 7 and Table - 8 are due to formation of much stronger complexes with one or two solvent molecules molecules for the tri- and di-butyltin phenoxyacetates respectively. The stereochemical arrangement at the central tin atom must be trans-trigonally bipyramidal[32] and trans-octahedral[33,34] respectively. In these complexes, the original chelate function of carboxyl group disappears, which is manifested in a down-field shift of the $\delta(^{13}C_{(5)})$ value[36]. The magnitude of these changes correlates with the strength of the original chelate complexes.

As indicated in Table -7, the ^{119}Sn spectrum of compound $Bu_2Sn(L_1)_2$ at 220°K in $CDCl_3$ exhibits a new signal at a higher field (-200.9 ppm) besides the original signal at 300°K. We do not have enough data for interpretation of this signal yet. It may only be stated that this signal is due to a new particle with a higher coordination number at the tin atom (probably six) and with a stronger connection of the central tin atom with the coordination partners. The interaction is, probably, caused through the phenoxy oxygen atom. No analogous phenomenon was observed with the similar dibutyltin (IV) bis-phenylthioacetate which could be connected with the well known reluctance of the sulfur atom (in contrast to the oxygen atom) to form additional donor-acceptor bonds[37].

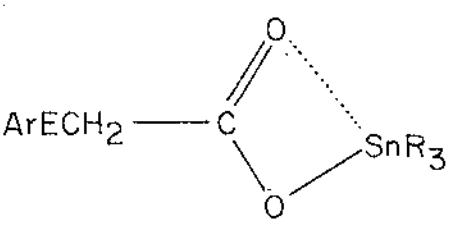
III H. Probable Structures of the aryloxy and phenylthioacetates.

The data (IR and NMR) presented in Sections III F and III G suggest the following structures.

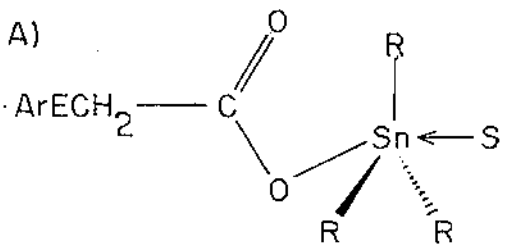
a) $ArECH_2COOSnR_3$: The compounds form polymers in solid phase with bridging bidentate carboxyl groups connecting the R_3Sn groups (XIA). The triorganotin (IV) moiety is quasi-planar (perfect planarity would necessitate the absence of ν_s(Sn-C) in IR spectra) and, therefore, the geometry around the central tin atom is a slightly deformed trans-trigonal bipyramid. In non-coordinating solvents, these compounds are present in the form of isolated molecules with deformed tetrahedral structure (XIB). The deformation is caused by the weak interaction of the carbonyl oxygen atom with the central tin atom. In coordinating solvents, stronger complexes are formed with one solvent molecule and with trans-trigonally bipyramidal coordination sphere around the tin atom (XIC).



(XIA)

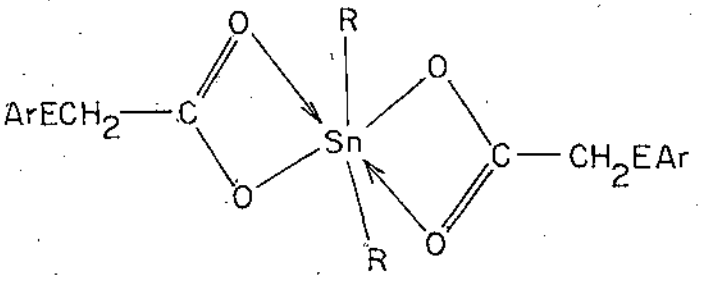


(XIB)

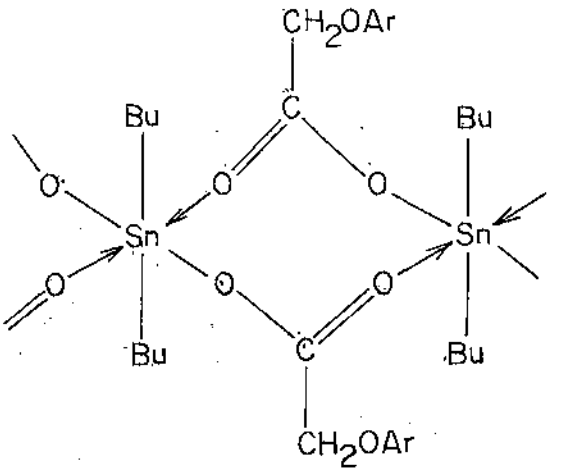


(XIC)

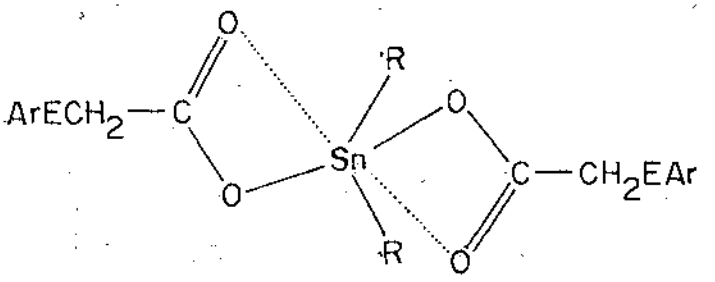
b) $(ArECH_2COO)_2SnR_2$: The compounds form, in both solid state (XIIA) and in non-coordinating solvents (XIIB), chelate complexes with considerable asymmetrical function of the two oxygen atoms of the carboxyl group. The structures are, therefore, deformed octahedral in both cases. The compounds are, thus, monomeric even in solid state. As stated earlier, the compound $Bu_2Sn(L_2)_2$ is an exception among the diorganotin (IV) derivatives and possesses the carboxyl-bridged polymeric structure (XIIC) in solid phase. In coordinating solvent, the complexes formed contain two molecules of the solvent (XIID) and only monodentate carboxylic groups. The



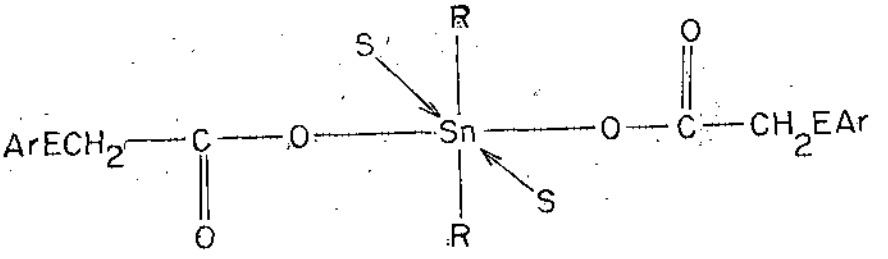
(XIIA)



(XIIC)



(XIIB)



(XIID)

molecules are octahedral and according to the high $^{1}J(^{119}Sn^{13}C)$ values, they contain the n-butyl groups in trans-position.

In none of the structures given above (XI and XII), we could observe an intramolecular connection of the O or S atom of $ArECH_2$ group with the central tin atom of the type (VI). ^{17}O NMR did not come to our aid because no signal due to oxygen atom of phenoxymethyl group was found for the tri- and dibutyl phenoxy acetates. However, the reason for not getting the desired signal may also be due to its large width, because even in the case of methylphenoxyacetate, the half-width of the signal of the oxygen atom of the phenoxymethyl group is roughly twice as large as that of both oxygen atoms of carboxyl group. The absence of intramolecular O⟶Sn bond is presumed from the fact that there is a perfect corollary in the IR and NMR data of the aryloxyacetates and those of the phenylthioacetates. In the latter case, intramolecular S⟶Sn bond is indeed unlikely[37]. It, therefore, appears that the Lewis basicity of the carbonyl oxygen atom is much greater than the phenoxy oxygen atom. The latter can not compete with the carbonyl oxygen atom in the matter of forming coordinate linkage to the tin atom resulting in formation of the usual type of carboxyl bridged polymeric triorganotin carboxylates in solid phase.

III I. Electronic Absorption Spectra of the organotin aryloxyacetates.

Absorption spectra in ultra-violet region of the ligands and their organotin derivatives are shown in Figs. 35-49. The spectral data in polar and non-polar solvents in the 200-300 nm

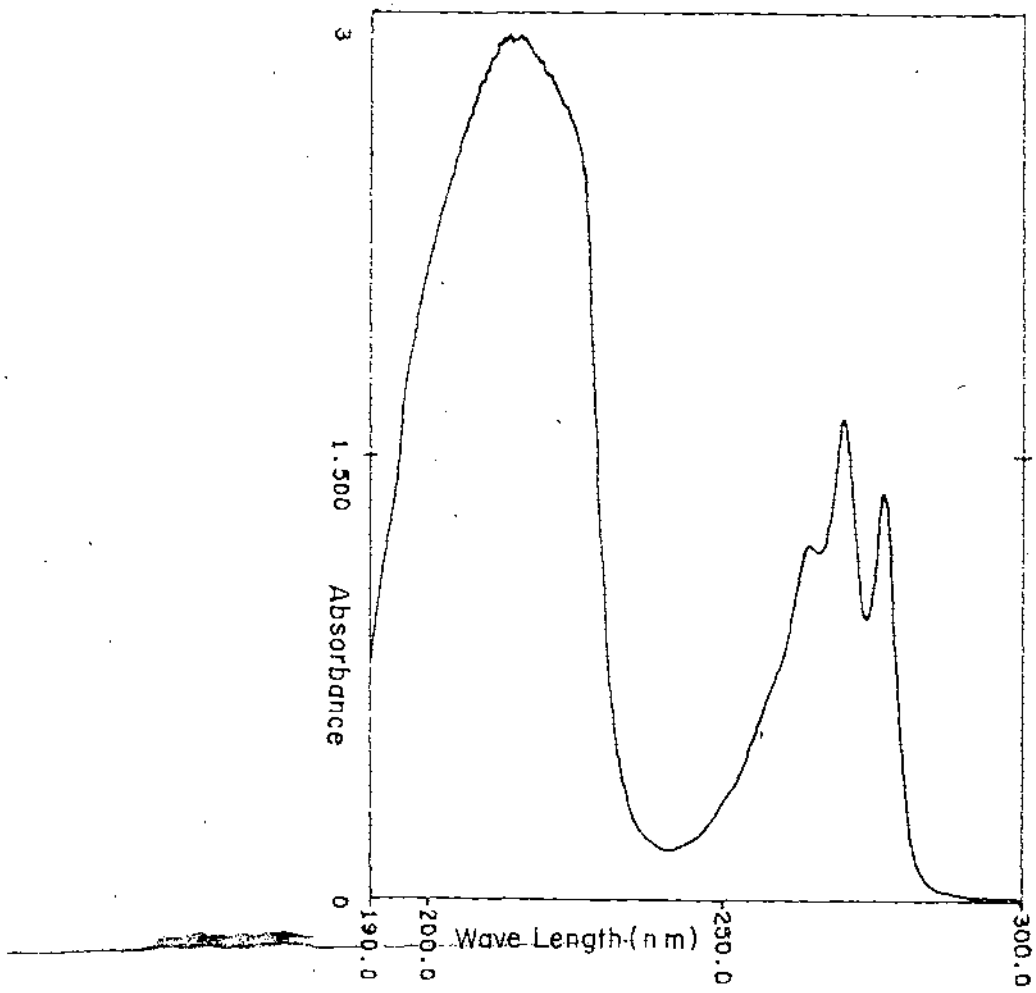


Fig.35. Absorption spectrum of Bu_3SnL_1 (0.998×10^{-3}M) in n-heptane

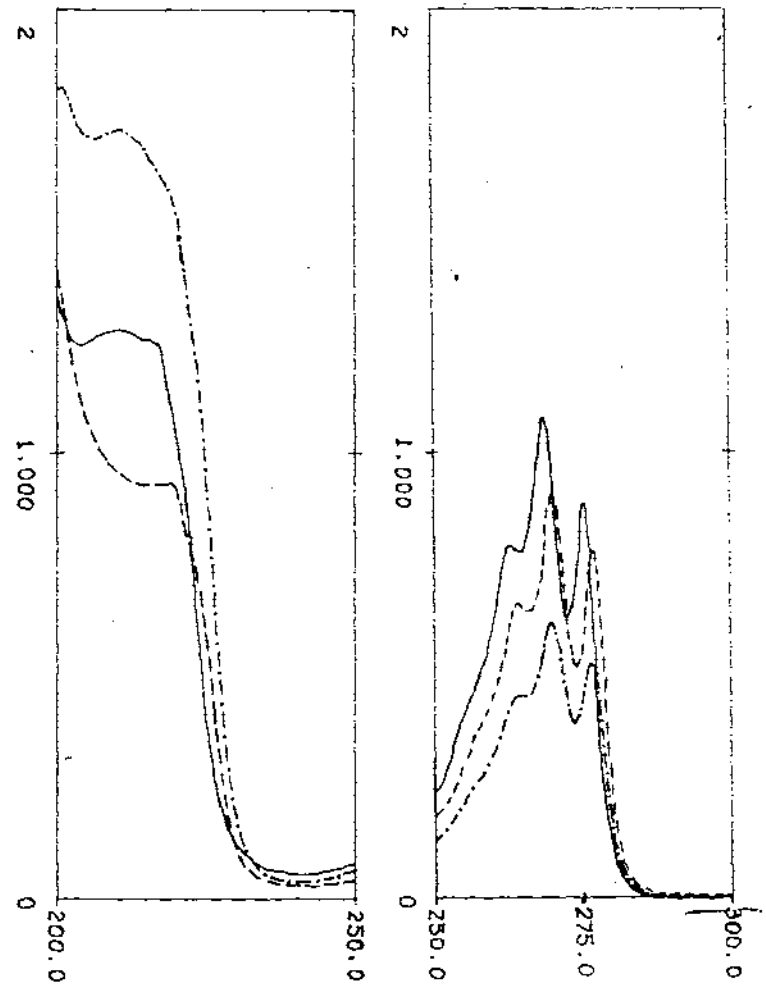


Fig.36. Absorption spectra of L_1H [——], Bu_3SnL_1 [- - - -] & $Bu_2Sn(L_1)_2$ [—·—·—] in n-heptane

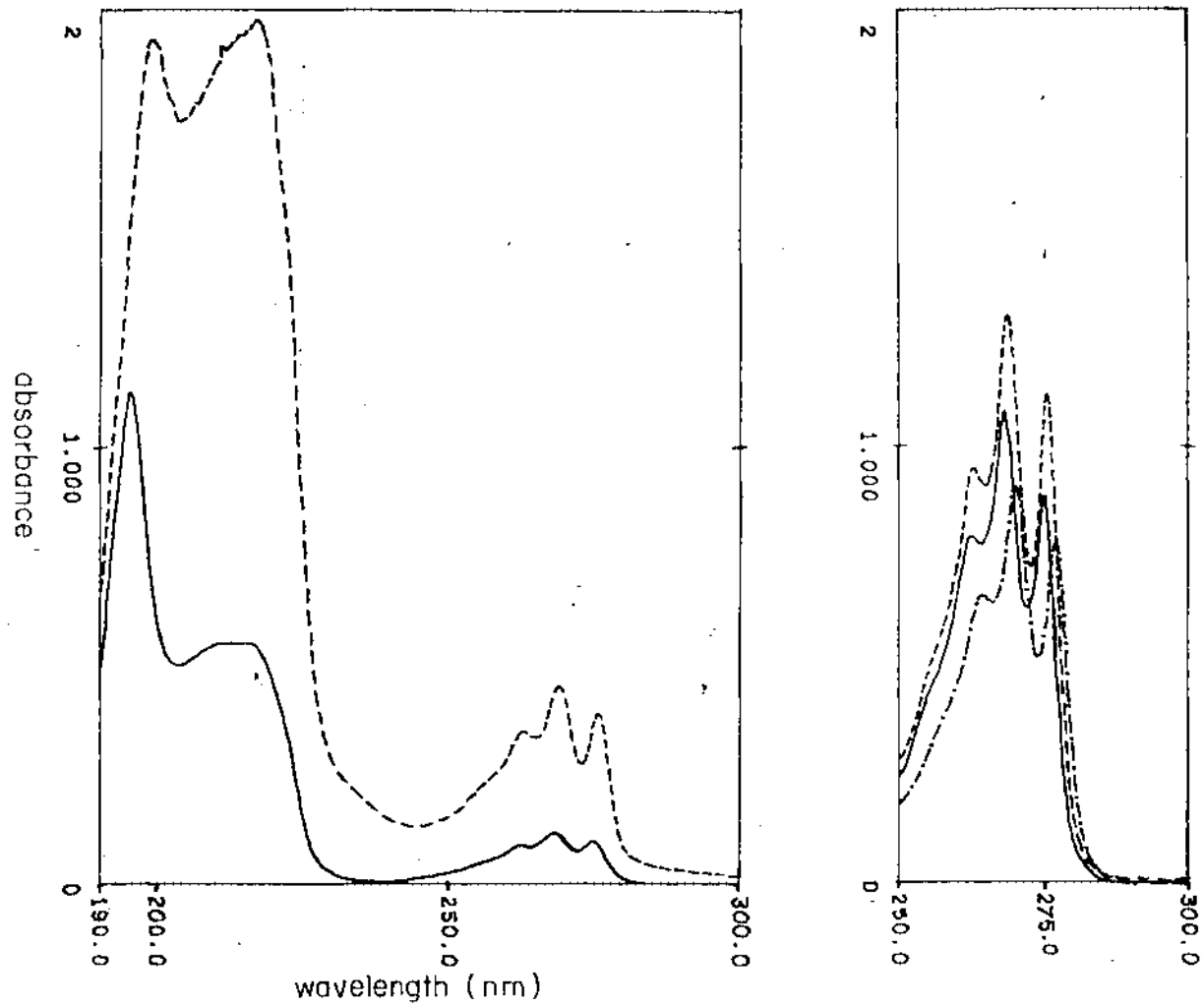


Fig.37. Absorption spectra of L_1H [——], L_1Me [- - -] & Bu_3SnL_1 [—·—]
in n-heptane

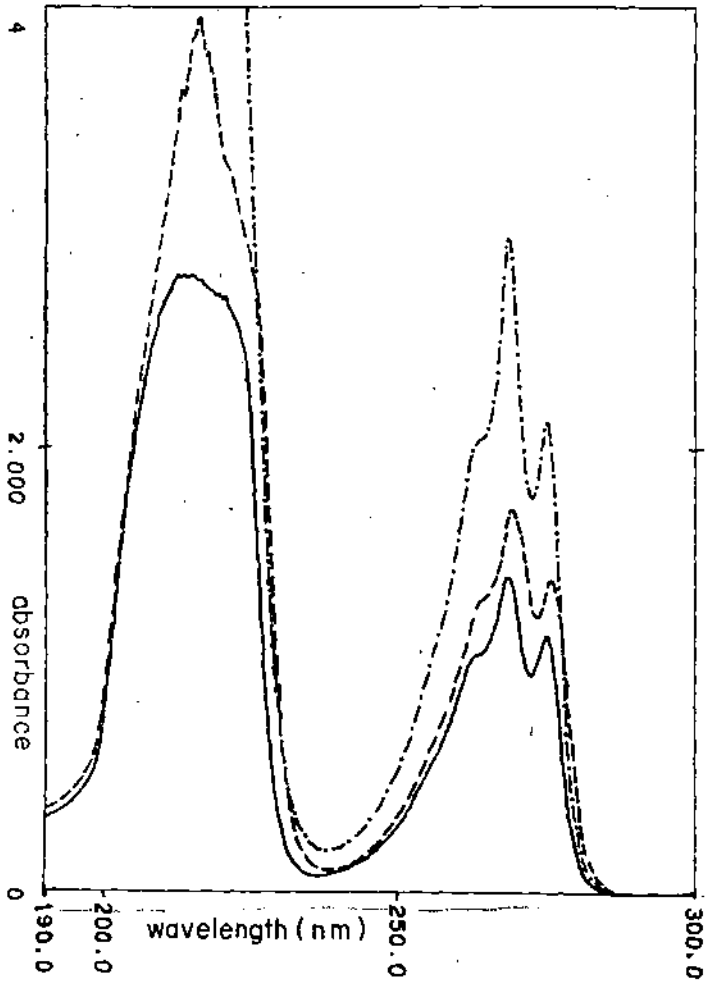


Fig.38. Absorption spectra of L_1H(1.06×10^{-3}M) [——], Bu_3SnL_1(1.13×10^{-3}M) [- - - -] & $Bu_3Sn(L_1)_2$ (0.99×10^{-3}M) [—·—] in MeOH

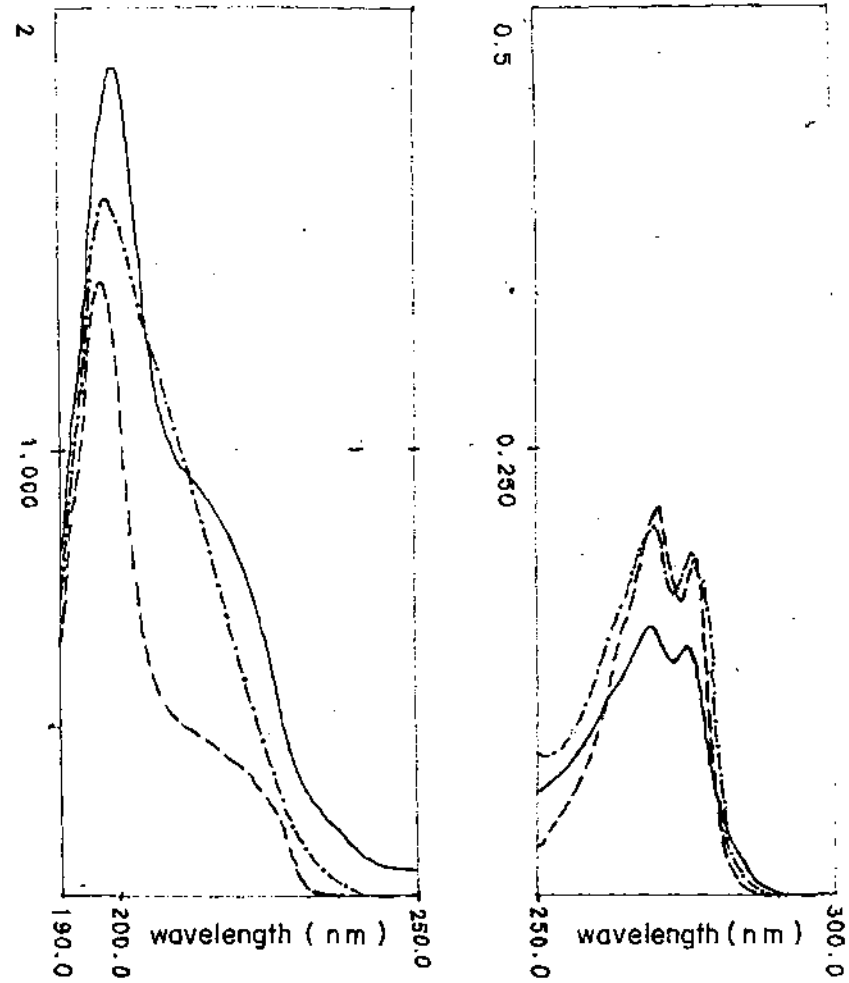


Fig.39. Absorption spectra of L_2H [——], Bu_3SnL_2 [- - - -] & $Bu_2Sn(L_2)_2$ [—·—] in n-hexane

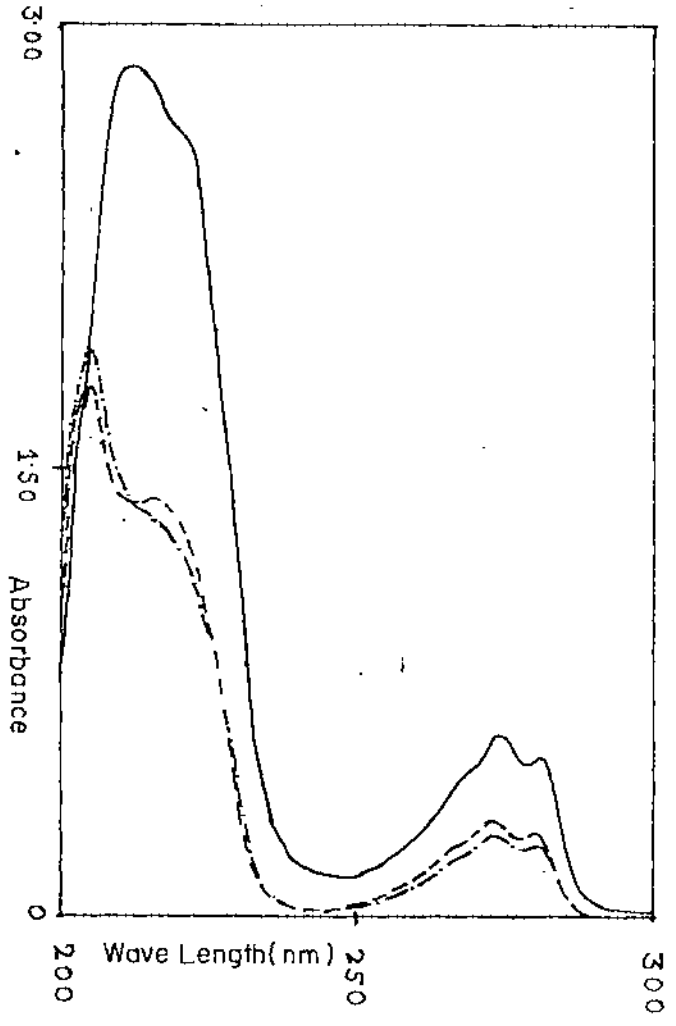


Fig.41. Absorption spectra of L_3H [----], Bu_3SnL_3 [——] & $Bu_2Sn(L_3)_2$ [—·—] in MeOH.

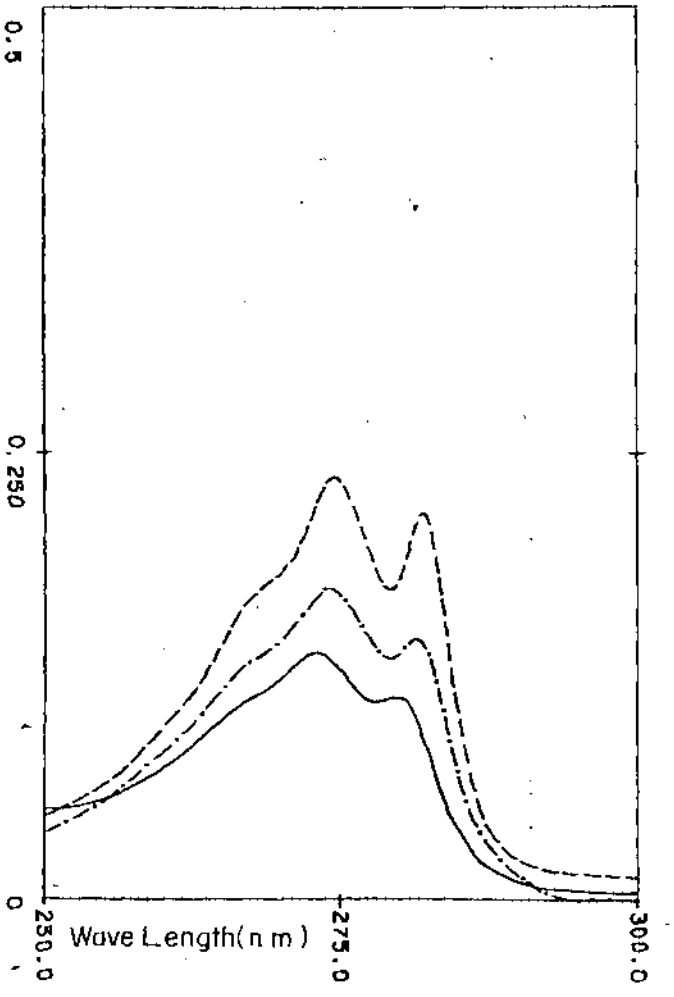


Fig.40. Absorption spectra of L_3H [——], Bu_3SnL_3 [----] & $Bu_2Sn(L_3)_2$ [—·—] in n-hexane

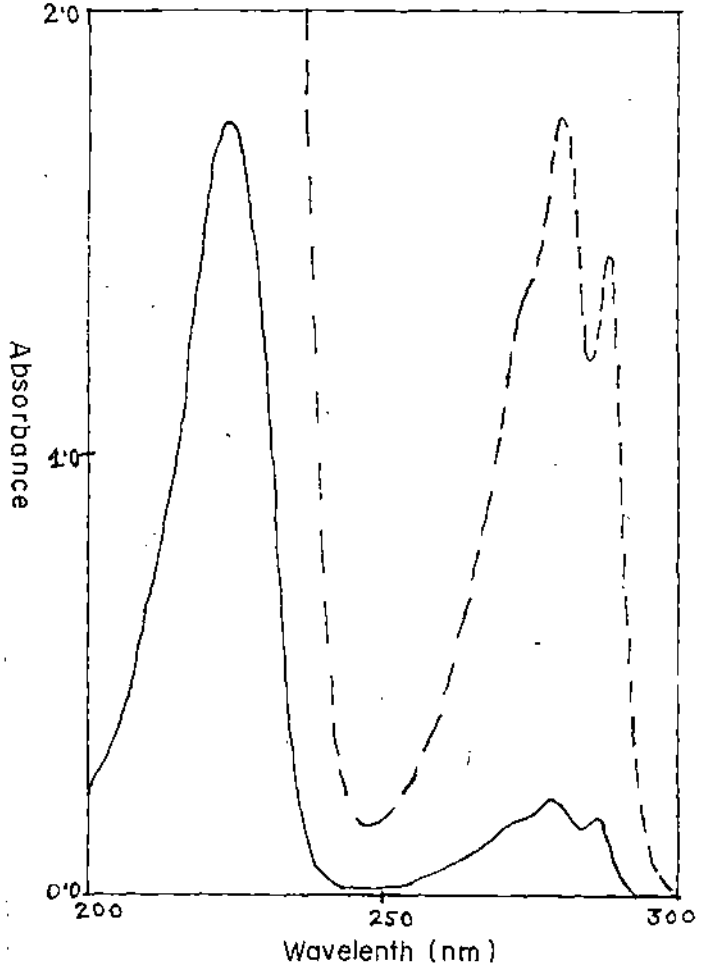


Fig.42. Absorption spectra of L_4H [——] & Bu_3SnL_4 [- - -] in n-hexane

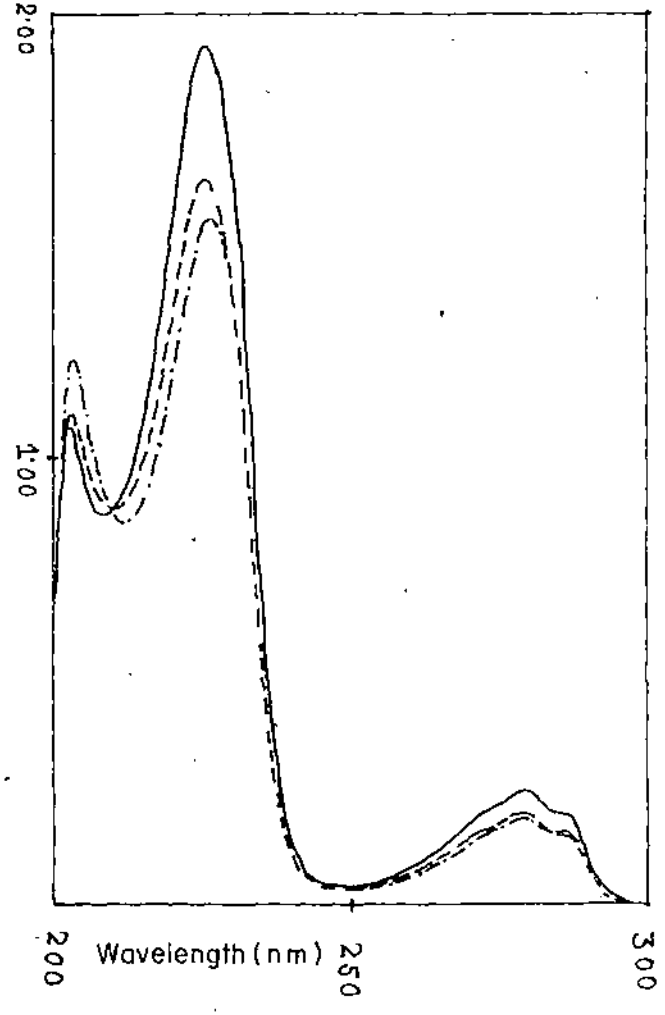


Fig.43. Absorption spectra of L_4H [——], Bu_3SnL_4 [- - -] & $Bu_2Sn(L_4)_2$ [-·-·-] in MeOH

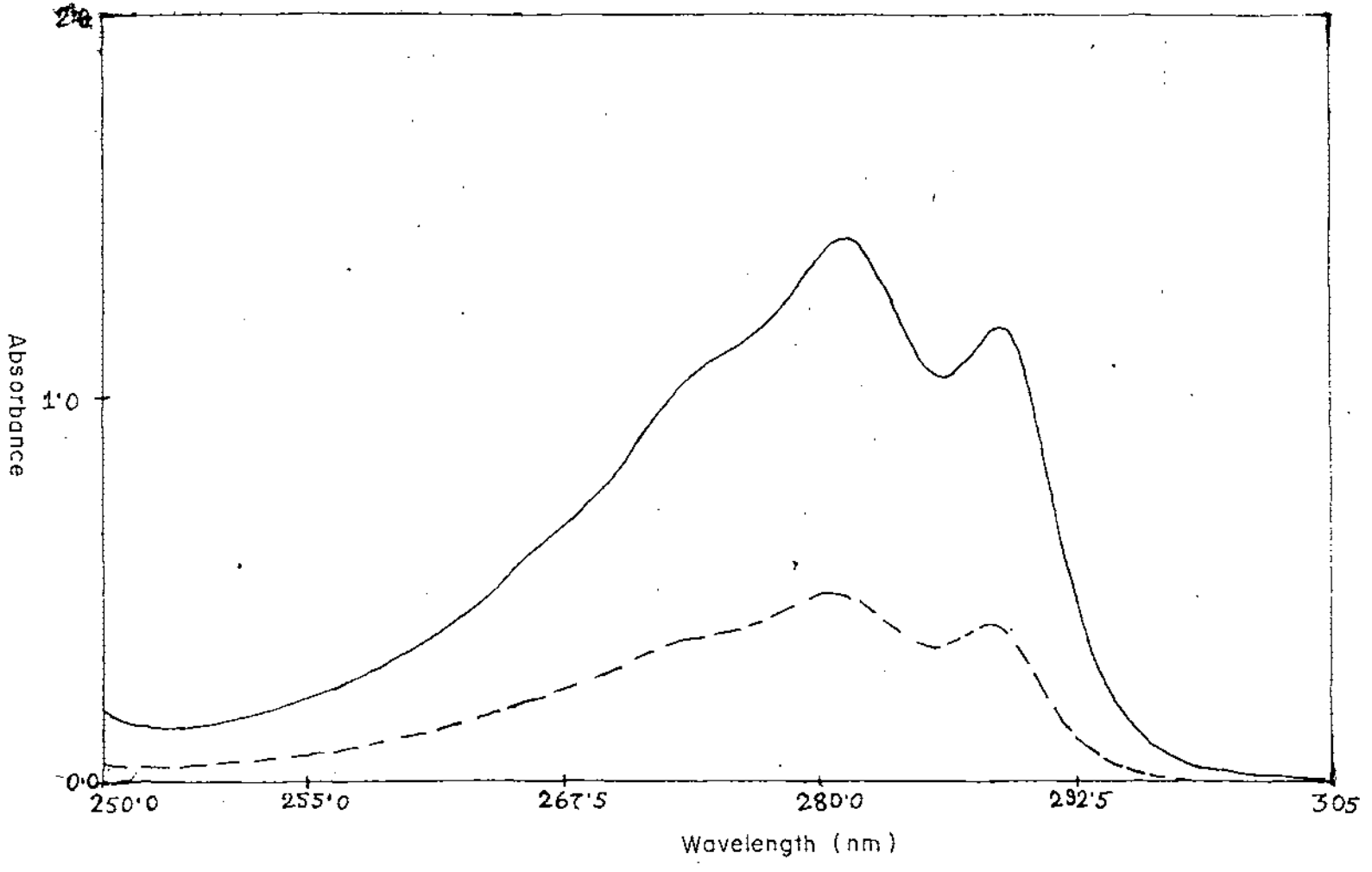


Fig. 44. Absorption spectra of $Bu_2Sn(L_4)_2$ ⊏——⊐ & $Oct_2Sn(L_4)_2$ ⊏- - -⊐ in n-hexane

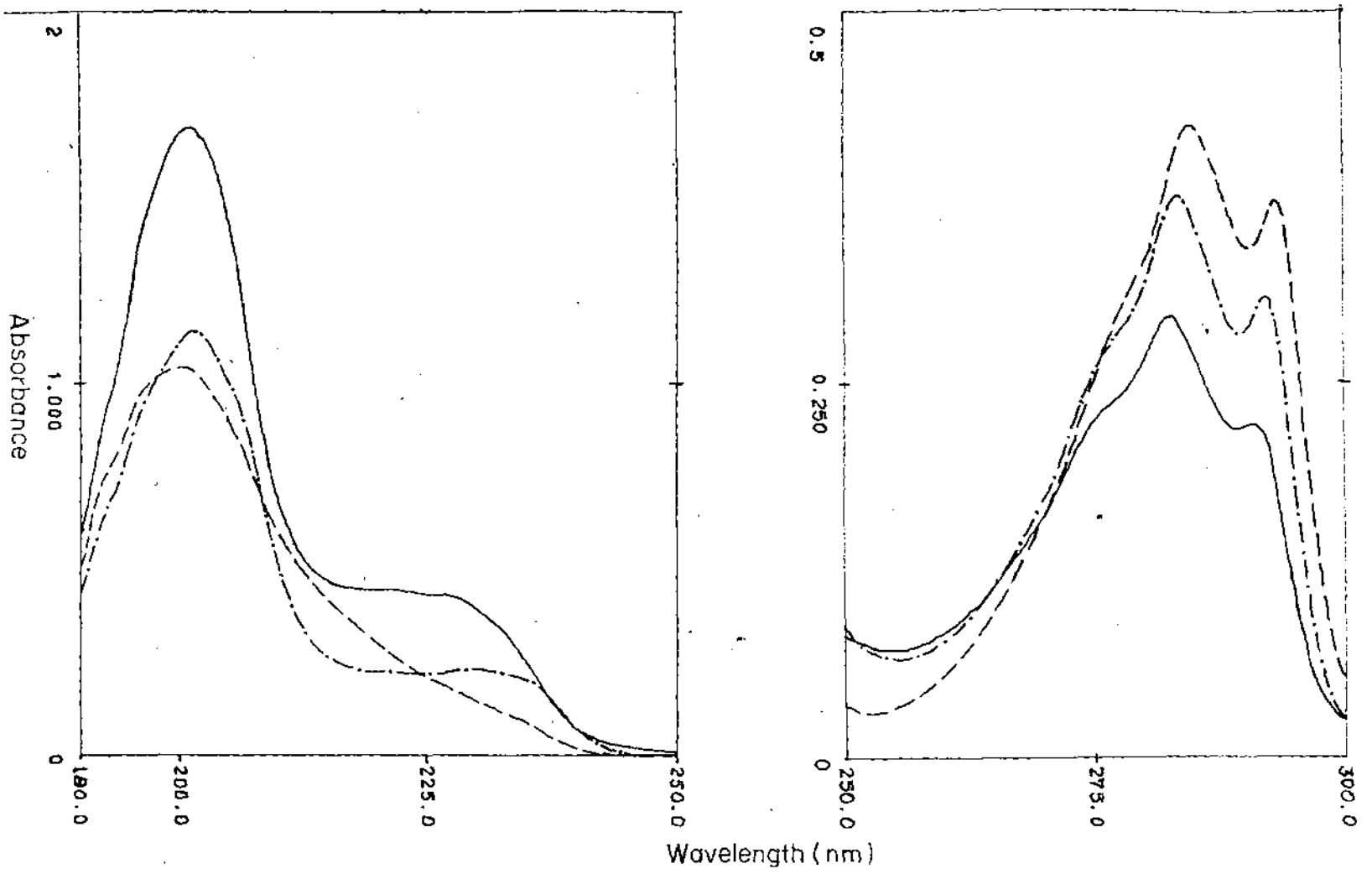


Fig.45. Absorption spectra of L_5H ⊏—⊐, Bu_3SnL_5 ⊏- -⊐ & $Bu_2Sn(L_5)_2$ ⊏- - -⊐ in n-hexane(in the range 250-300nm)

Absorption spectra of L_5H ⊏—⊐, Bu_3SnL_5 ⊏- · -⊐ & $Bu_2Sn(L_5)_2$ ⊏- - -⊐ in n-hexane(in the range 190-250nm)

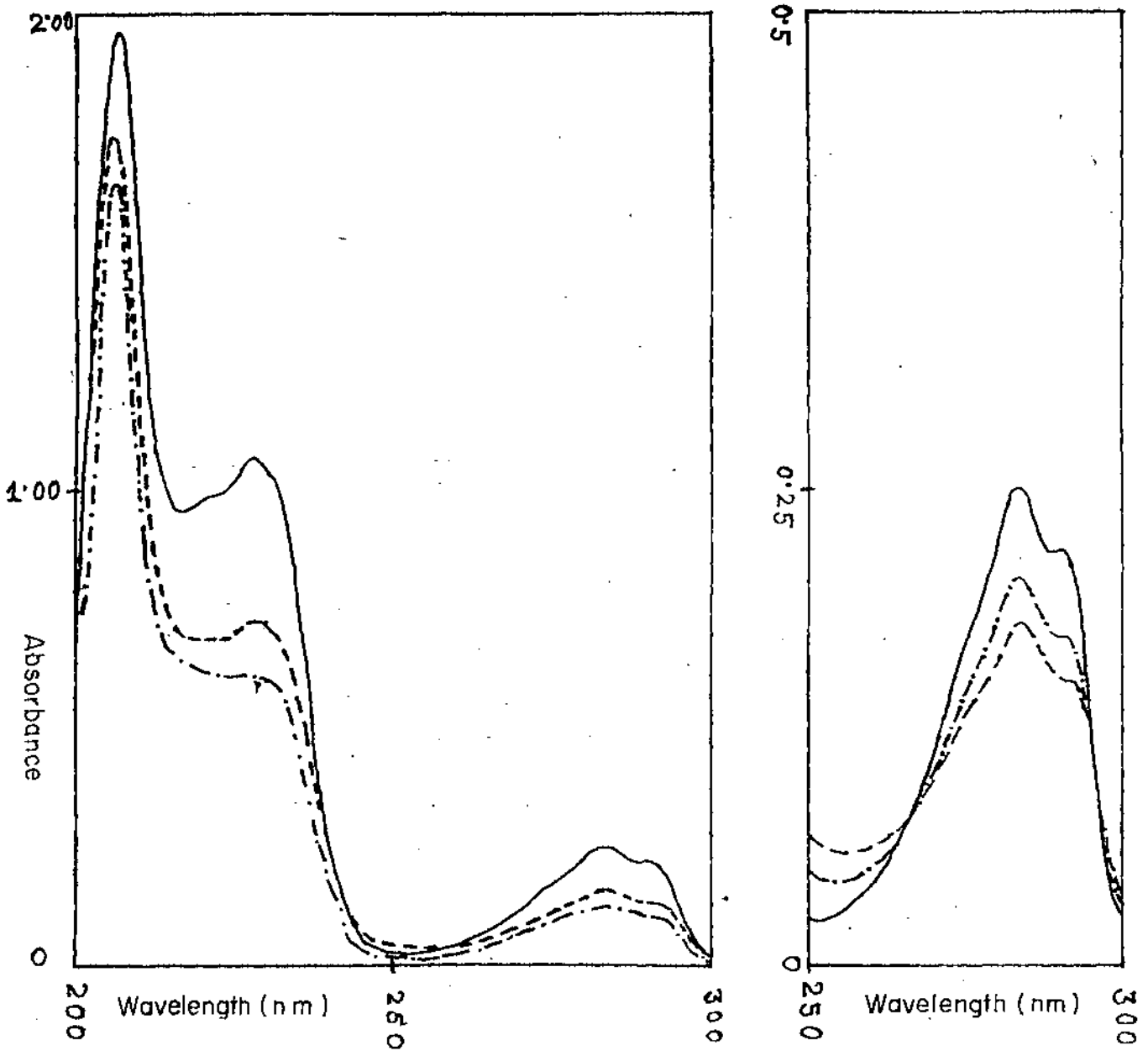


Fig.46. Absorption spectra of L_5H [—], Bu_3SnL_5 [- - -] & $Bu_2Sn(L_5)_2$ [- · -]
in MeOH

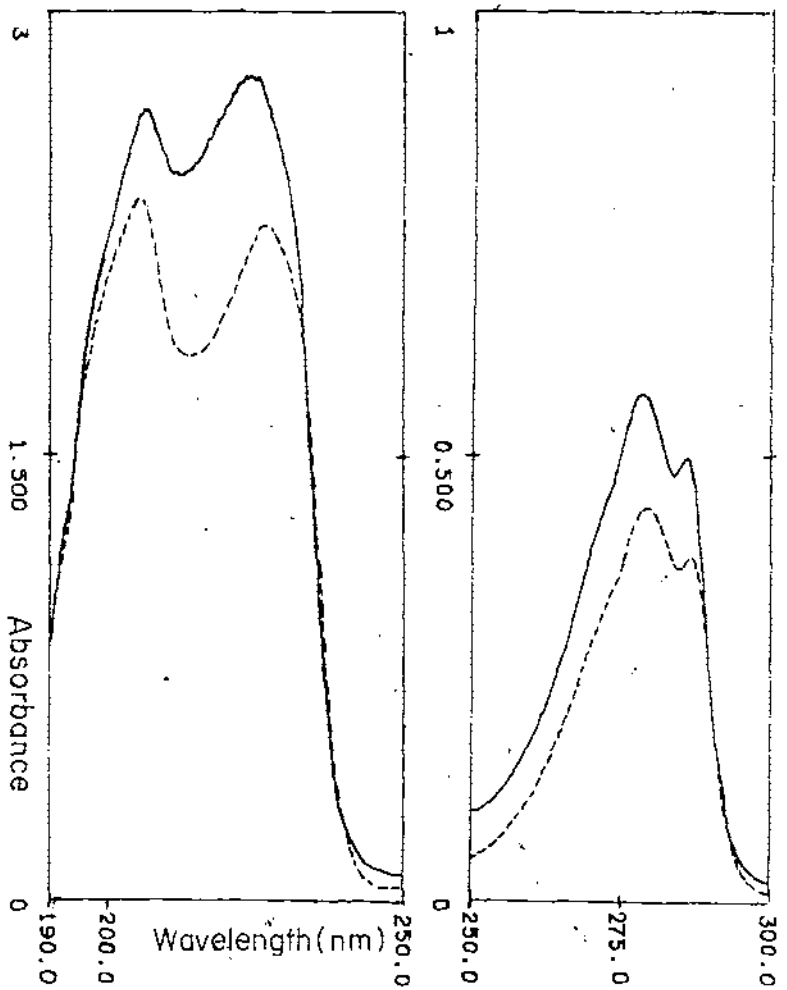


Fig.47. Absorption spectra of L_7H ⊏—⊐ & $Bu_2Sn(L_7)_2$ ⊏---⊐ in n-hexane

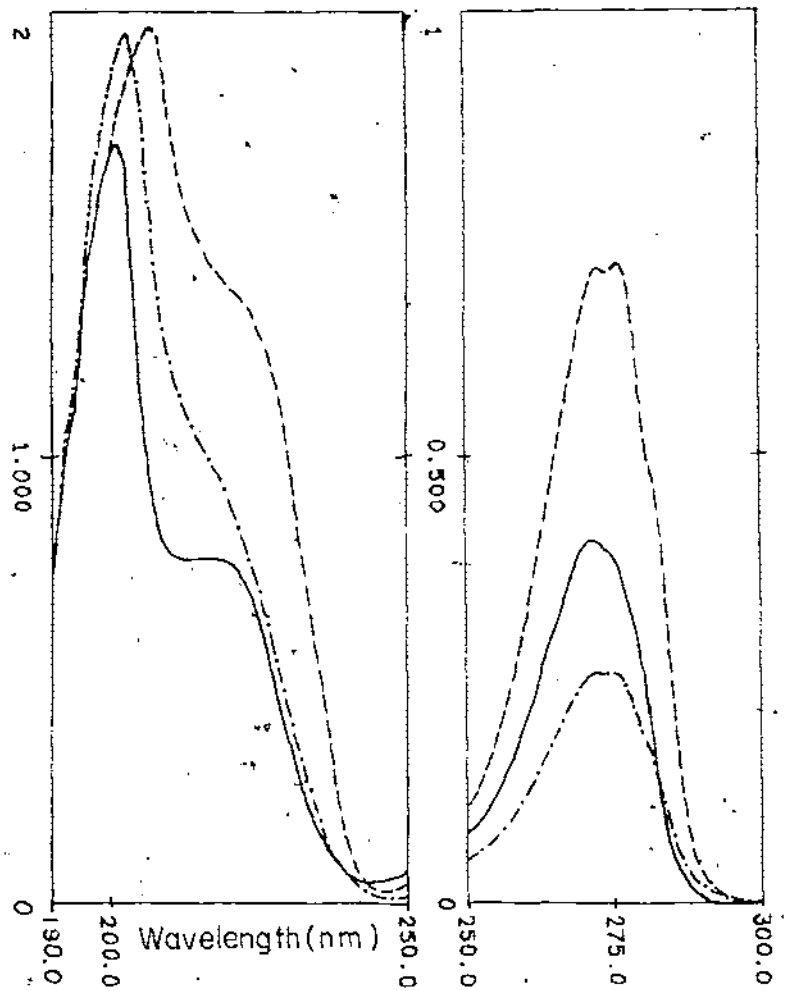


Fig.48. Absorption spectra of L_8H ⊏—⊐, Bu_3SnL_8 ⊏-·-⊐ & $Bu_2Sn(L_8)_2$ ⊏--⊐ in n-hexane

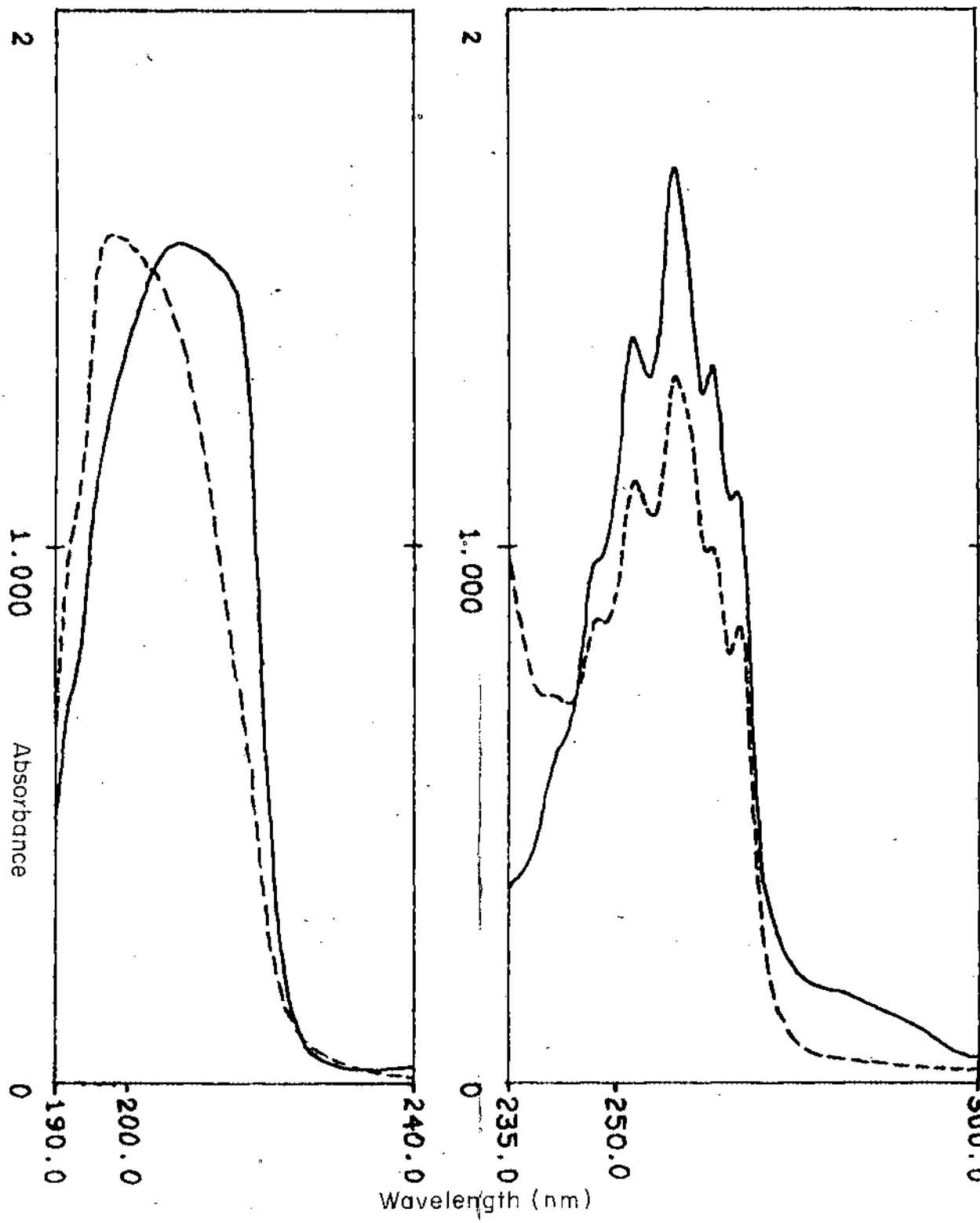


Fig. 49. Absorption spectra of L_9H E—E & Bu_3SnL_9E---E in n-hexane

region have been collected in Table - 9.

The data show that the ligands have identical spectra in polar as well as non-polar solvents. The absorption bands are attributed to the $\pi \longrightarrow \pi^*$ transitions of the phenyl ring which mask the very weak (forbidden) $n \rightarrow \pi^*$ transitions of the carbonyl group (the allowed $\pi \longrightarrow \pi^*$ transition of the carbonyl group occurs near 180 nm and is, therefore, not accessible except in vacuum UV). In benzene, three electronic transitions take place from the ground state (A_{1g}) to excited states : (i) the allowed second primary band at 184 nm ($A_{1g} \longrightarrow E_{1u}$) having $\epsilon = 4.7 \times 10^4$; (ii) the forbidden first primary band at 202 nm ($A_{1g} \longrightarrow B_{1u}$) having $\epsilon = 7.4 \times 10^3$ and (iii) the secondary band at 260 nm corresponding to a symmetry forbidden transition ($A_{1g} \longrightarrow B_{2u}$) having $\epsilon = 230$ only. The longest wavelength secondary band, although forbidden, appears as a result of interaction of the electronic energy levels with vibrational modes and bears a great deal of fine structure depending on substitutions on the ring[38,39]. In the benzene derivatives, these bands undergo bathochromic and hyperchromic shifts depending on the number and nature of the substituents[38,39]. The absorption bands in the 200-225 nm region (Table - 9) are due to the first primary bands of the phenyl ring ($A_{1g} \longrightarrow B_{1u}$) while the bands in the region of 260-290 nm are due to the secondary transitions from $A_{1g} \longrightarrow B_{2u}$. The latter absorption bands always appear in the form of three peaks with exception of LgH (two peaks) and LyH (a larger number of peaks and shoulders) due to fine splittings of the secondary band.

In Table - 9, spectral data of the triphenyltin derivatives have not been given because presence of additional phenyl groups make the spectra more complicated and do not throw any substantially new information. The data in the Table show that in all the organotin carboxylates, the long wavelength absorption bands (secondary band of the phenyl ring) always undergo small bathochromic shifts in non-polar solvents. Moreover, the intensity of all the bands are also changed relative to those of the ligands. The red shift is fully absent in the spectra of the methyl esters (L_1Me and L_4Me). The shift is also absent in the spectrum of Bu_3SnL_9 which is exactly similar to that of L_9H (β-phenyl propionic acid, in which the phenoxy oxygen atom stands replaced by a methylene group).

Table - 9

Electronic absorption spectra in polar and non-polar solvents.

Sl. No.	Compound	λ_{max} Hexane/heptane (nm)	λ_{max} MeOH (nm)
1.	L_1H/L_1Me	217.5, 262.5 (sh), 270, 275	215, 220 (sh), 262.5 (sh), 270, 275.
2.	Bu_3SnL_1	215, 225 (sh), 265 (sh), 270.6, 277.5	215, 225 (sh), 262.5 (sh), 270, 275

Contd..

Table - 9 (Contd..)

Sl. No.	Compound	λ_{max} Hexane/heptane (nm)	λ_{max} MeOH (nm)
3.	$Bu_2Sn(L_1)_2$	197.5, 215 (sh), 262.5 (sh), 270, 276.5	215, 225 (sh), 262.5 (sh), 270, 275
4.	L_2H	200, 220 (sh), 262.5 (sh), 269, 275	
5.	Bu_3SnL_2	197.5, 220 (sh), 262.5 (sh), 270.5, 277.5	
6.	$Bu_2Sn(L_2)_2$	197.5, 220 (sh), 262.5 (sh), 270, 275.5	
7.	L_3H	200, 220 (sh), 265 (sh), 273, 280	205, 220 (sh), 265 (sh), 272.5, 280
8.	Bu_3SnL_3	202.5, 225 (sh), 267.5 (sh), 274.5, 282	210, 225 (sh), 265 (sh), 272.5, 280
9.	$Bu_2Sn(L_3)_2$	200, 225 (sh), 267.5 (sh), 274, 281.25	205, 225 (sh), 265 (sh), 272.5, 280
10.	L_4H/L_4Me	225, 272 (sh), 279.4, 287.5	225, 272 (sh), 279, 287
11.	Bu_3SnL_4	227.5, 273.75 (sh), 281.25, 288.75	226, 272 (sh), 279, 287
12.	$Bu_2Sn(L_4)_2$	231.9, 273.75 (sh), 281.25, 288.75	225, 272 (sh), 289, 287
13.	$Oct_2Sn(L_4)_2$	221.25, 273.75 (sh), 280, 288.12	
14.	L_5H	200, 220 (sh), 275 (sh), 282.5, 291.25	

(Contd..)

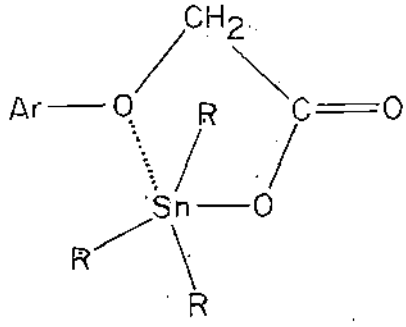
Table - 9 (Contd..)

Sl. No.	Compound	λ_{max} Hexane/heptane (nm)	λ_{max} MeOH (nm)
15.	Bu_3SnL_5	201.25, 230(sh), 277.5(sh), 285, 293.5	
16.	$Bu_2Sn(L_5)_2$	200, 235(sh), 275(sh), 283.5, 292.5	
17.	L_7H	206.25, 225, 270(sh), 278.75, 286	
18.	$Bu_2Sn(L_7)_2$	205, 226.25, 270(sh), 278.75, 286.5	
19.	L_8H	202, 220(sh), 270, 275(sh)	
20.	Bu_3SnL_8	206, 220(sh), 272, 276.25, 280(sh)	
21.	$Bu_2Sn(L_8)_2$	202, 220(sh), 272, 276.25, 280(sh)	
22.	L_9H	200(sh), 240(sh), 247(sh), 252, 257.5, 263.75, 266.25, 290(sh)	
23.	Bu_3SnL_9	200(sh), 240(sh), 247(sh), 252, 257.5, 263.75, 266.25, 290(sh)	

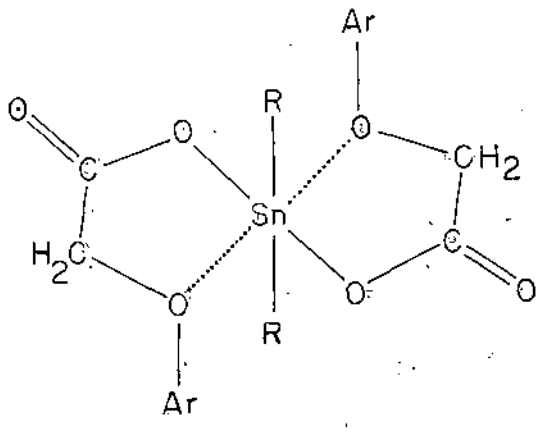
sh = shoulder in the absorption curve.

The bathocrhomic shift of the $\pi \rightarrow \pi^*$ transition of the phenyl ring in going from L_nH (n = 1-8) to its organotin derivative can not be accounted for unless on intramolecular coordination between the phenoxy oxygen atom and the organotin group is presumed. Electron withdrawal from the phenoxy oxygen atom is likely to stabilize the π^* orbital of the phenyl ring to some extent causing a red shift. Since the intramolecular O$\longrightarrow$Sn bond is expected to be rather weak, the red shift is of such small magnitude. This postulate is supported by the spectra of the compounds in a polar and protic solvent like methanol. In this solvent, the O$\longrightarrow$Sn bonds break down with consequent solvation at the central tin atom[11]. The spectra of the organotin compounds in methanol are, therefore, identical with those of the ligands in methanol. Further, the shift is absent wherever possibilities of the O$\longrightarrow$Sn coordination does not exist, for example, spectra of the methyl esters and of Bu_3SnL_9 are identical to those of the parent acids.

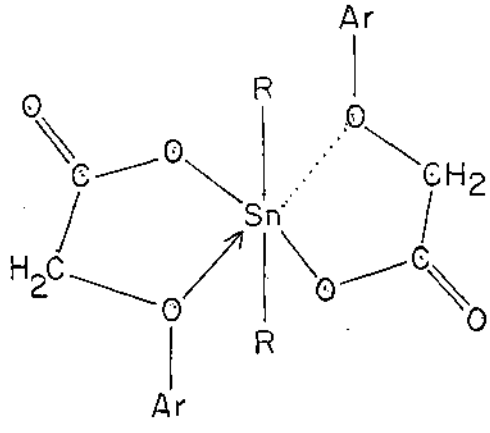
The solution structures of the organotin aryloxyacetates (XIB and XIIB, E = O or S atom) discussed in Section III H were deduced from IR spectra in non-coordinating solvents like CCl_4 and NMR (^{13}C, ^{17}O, ^{119}Sn) data in $CDCl_3$. These solutions were, necessarily, quite concentrated. The UV spectra were taken in very dilute solutios ($\sim 10^{-3}$ - 10^{-5} M) and it is quite possible that the bonding situations undergo change on going from concentrated to dilute solutions. In particular, the asymmetrically chelating bidentate carboxyl group may become unidentate in a dilute solution.



(XIII)



(XIV A)



(XIV B)

We may then assign structure XIII to the triorganotin compounds and either XIVA or XIVB to the diorganotin compounds involving intramolecularly coordinated O→Sn bonds and monomeric molecules in dilute solutions. If this interpretation of the experimental fact is held valid, then the aryloxyacetic acids are indeed potential ligands for the formation of intramolecularly coordinated monomeric organotin carboxylates.

In conclusion, we can state that although the aryloxyacetic acids are potential ligands for the formation of monomeric organotin carboxylates, this potential is not realised in solid state and in concentrated solutions in non-coordinating solvents. The reason lies in the much greater Lewis basicity of the carbonyl oxygen atom in comparison to that of the phenoxy oxygen atom making the latter incapable of competing with the former in forming coordinate bonds with the tin atom unless the solution is very dilute. In a few transition metal complexes of the aryloxyacetic acids, intramolecular O→M bond has been demonstrated to be present[21]. The situation is different in the organotin derivatives because in this case we have d-orbitals very different in energy and in spatial orientation. Steric factors are also not favourable. We, however, believe that intramolecularly coordinated organotin carboxylates can be realised once we design a ligand in which the coordinating ability of the carbonyl oxygen atom is inhibited.

The work presented in this chapter was first published in the form of a 'note' (Ref. 40). This 'note' was, however, a preliminary communication and many of the conclusions arrived at that point of time had to be revised after more detailed investigations including the NMR spectroscopic studies were carried out. The final results were published as in Ref. 41 (Annexure). The electronic absorption spectra of some of the compounds and interpretation of the spectral data as explained above were reported in Ref. 40.

III J. Experimental

The organotin compounds used for preparing the carboxylates were purchased from Fluka and Aldrich and were used without further purification except Ph_3SnCl which was used after recrystallisation from petroleum ether (m.p. 105-106°C). Unless otherwise stated, petroleum ether used refers to the fraction with B.P. 60-80°C. when necessary other solvents used were purified and dried by standard methods of purification. All melting points are uncorrected.

(a) Preparation of the ligands

In most of the cases, the method of preparation as described by Vogel[42] was used with slight modifications.

1. Preparation of L_1H (Phenoxyacetic acid):

20 gm phenol and 25 gm chloroacetic acid were dissolved in 300 ml. water containing 23 gm sodium hydroxide and slowly boiled down to small volume in an open flask. The resulting liquid was diluted with water and acidified faintly to Congo red with hydrochloric acid, on chilling the phenoxyacetic acid was separated as a voluminous mass of long, thin, needles. This was filtered and washed with cold water. On concentrating the filtrate a further crop was obtained. This total yield was dried in air and finally in vacuum at room temperature. After recrystallizing twice from benzene the yield was 24 gm (74%) and m.p. was 98-100°C.

2. Preparation of L_2H (o-Methylphenoxyacetic acid):

23 gm ortho-cresol, 20 gm monochloroacetic acid, 34 gm 50% aqueous sodium hydroxide, and about 200 ml water were slowly

boiled to small volume in an open flask. To get neutral reaction, one-half of the above quantities of chloroacetic acid, alkali, and water were then added and the solution again boiled down to small bulk. After diluting with water, hydrochloric acid (1:1) was added in excess, the o-methyl phenoxyacetic acid separating as a thick slurry. This was filtered off, washed with water and dried in the air. The yield was 30 gm (85%). Recrystallized several times from 85% methanol, it forms long, narrow, leaflets which melts at 152°C.

3. Preparation of L_3H (o-Chlorophenoxyacetic acid):

27 gm of o-chlorophenol, 20 gm monochloroacetic acid, 18.5 gm sodium hydroxide, and 400 ml water, were slowly boiled down to small bulk in an open flask and diluted with water. The resulting o-chlorophenoxyacetic acid was precipitated by acidification with hydrochloric acid (1:1) to Congo red. This was filtered off, washed with water and dried in the air. The yield was 32 gm (82%). Recrystallized successively from 95% ethanol and benzene, it forms long, thin, needle-shaped white crystals, m.p. 148-149°C.

4. Preparation of L_4H (p-Chlorophenoxyacetic acid):

By following the same procedure as described under 3, but using p-chlorophenol instead of o-chlorophenol, crystals of p-chlorophenoxyacetic acid (m.p. 156-157°C) was obtained.

5. Preparation of L_5H (2,4-Dichlorophenoxyacetic acid):

L_5H was collected from Sigma Chemical Co., USA and was purified by repeated crystallization from benzene to the melting point 140°C.

6. Preparation of L_6H (2,4,5-Trichlorophenoxyacetic acid):

It was prepared by the procedure reported in the reference J. Am. Chem. Soc., 63, (1941), 1768.

Equimolecular quantities of 2,4,5-Trichlorophenol (10 gm) and monochloroacetic acid (4.8 gm) were with a slight excess (4.4 gm) of sodium hydroxide, and 100 ml of water, until the solution was evaporated almost to dryness. The residue was then dissolved in 400 ml of hot water, the solution cooled to room temperature and acidified with hydrochloro acid. A heavy oil separated which soon crystallized. The mixture was extracted with ether, the ether extact washed with water and evaporated to dryness on water-bath. The yield of 2,4,5-trichlorophenoxyacetic acid was 9 gm (70%). Recrystallised from benzene, it forms white odourless crystals, m.p. 153°C.

7. Preparation of L_7H (4-Chloro-2-methylphenoxyacetic acid):

7.2 gm 4-chloro-2-methylphenol and 4.8 gm monochloroacetic acid were dissolved in 200 ml water containing 4.4 gm sodium hydroxide and gently boiled down almost to dryness. The residue was then dissolved in 200 ml of hot water and cooled to room temperature. The 4-chloro-2-methylphenoxyacetic acid was precipitated by acidification with hydrochloric acid to Congo red. This was separated, washed with water and dried in air. The yield was 7.8 gm (77%).

Recrystallized from benzene, it forms plate like crystals whose m.p. was 119-120°C.

8. Preparation of L_8H (o-Methoxyphenoxyacetic acid):

26.2 gm guaiacol, 20 gm monochloroacetic acid, 34 gm 50% aqueous sodium hydroxide, and about 400 ml water were gently boiled to small volume in an open flask. For neutral reaction to occur, one-half of the above quantities of chloroacetic acid, alkali, and water were then added and the solution again boiled down to small bulk. This was then diluted with water and acidified to Congo red with hydrochloric acid (1:1) to give white precipitate of o-methoxy-phenoxyacetic acid. This was filtered off, washed with water and recrystallized from water. The filtrate was decanted and the long, needle-like crystals was dried in the air. The yield was 28 gm (77%). To get the acid in pure form it was recrystallized several times from alcohol-ether mixture. The m.p. was 119-123°C.

9. Preparation of L_9H (β-Phenylpropionic acid):

This compound was prepared by the method described in page 768 of reference 42.

(b) Preparation of the Organotin aryloxyacetates and phenylthioacetates (and one organotin phenylpropionate): In each reaction described below, the carboxylic acid (L_nH) was dried in vacuum at 80°C to remove any associated water molecule, if present.

1. Reaction of Bis-(tributyltin)oxide with L_1H :

A mixture of 1.9 gm (0.003 mole) bis-(tributyltin)oxide and 1 gm (.006 mole) L_1H in 100 ml dry benzene was refluxed for

6 hrs. with a Dean and Stark apparatus and then cooled to room temperature. To remove unreacted acid, the mixture was shaken with powdered anhydrous $NaHCO_3$ (~0.5 mg) and filtered off. The solvent was evaporated and the liquid mass was dissolved in about 100 ml pet. ether and kept in refrigerator for solidification of the product. The liquid unreacted $(Bu_3Sn)_2O$ was remained in the solution. The solid was again dissolved in pet. ether and the procedure was repeated several times to completely remove all unreacted $(Bu_3Sn)_2O$. Finally, the product was recrystallized from pet-ether. Needle shaped crystals of the product (2.2 gm) was obtained

Yield = 78%

M.P. of the product = 53-54°C.

2. Reaction of Bis(tripropyltin)oxide with L_1H :

A mixture of 1.7 gm (.003 mole) bis-(tripropyltin) oxide and 1 gm (.006 mole) L_1H in 100 ml dry benzene was stirred at r.t. for 10 hrs. and then filtered off. The filtrate was concentrated and cooled. Crystals of unreacted phenoxyacetic acid (m.p. 99°C) appeared and removed by filtration. The solvent from the filtrate was removed completely; the solid mass dissolved in minimum quantity of pet-ether and kept at r.t. The desired product appeared as needle-shaped crystals (1.5 gm).

Yield = 60%

M.P. of the product = 50-52°C.

3. Reaction of Bis(tri-phenyltin) oxide with L_1H :

A solution of 1 gm (0.006 mole) L_1H in 50 ml dry benzene was slowly added with shaking to a solution of 2.3 gm (0.003 mole) bis-(tri-phenyl)tin oxide in 50 ml dry benzene; the clear solution turned milky-white. To get neutral reaction, the mixture was stirred at room temperature for 30 minutes when white precipitate separated and it was filtered off. Recrystallization was accomplished by dissolving the product in hot acetone and precipitating with benzene. The yield was 2.8 gm and the m.p. was 158°C.

Yield = 88%.

3(a) Reaction of tri-phenyltin chloride with L_1Na:

A mixture of 2 gm (0.005 mole) tri-phenyl tin chloride and L_1Na in excess (2 gm) in 200 ml spectral grade acetonitrile was stirred overnight at r.t. and filtered. The solvent was removed completely from the filtrate and the residue was extracted with hot dry benzene. To the concentrated benzene soln. pet-ether was added when a white solid, m.p. 150°C, separated which on repeated recrystallisation from benzene-pet. ether mixture yielded the desired product.

Yield = 72%

M.P. = 158°C.

4. Reaction of Di-methyl tin oxide with L_1H :

A mixture of 1 gm (0.006 mole) di-methyl tin oxide and 1.85 gm (0.012 mole) L_1H in 100 ml dry benzene was refluxed for 1 hour with a Dean and Stark apparatus. The benzene soln. was concentrated and kept at r.t.,a white crystalline solid appeared. This was recrystallized from benzene.

Yield = 95%

M.P. = 218° C.

4(a) Reaction of Di-methyl tin di-chloride with L_1H :

A mixture of 2 gm (0.009 mole) dimethyl tin dichloride, 2.8 gm (0.018 mole) L_1H and 3 drops of pyridine in 200 ml dry benzene was refluxed for 6 hrs. The mixture was cooled to r.t. and filtered. The filtrate was shaken with ~1 gm dry powdered $NaHCO_3$ for 10 mins. to remove unreacted acid. On addition of pet. ether to the concentrated filtrate, a white solid separated out and it was filtered off. The residue was dissolved in minimum quantity of hot benzene and allowed to stand at r.t. when rectangular plate like crystals appeared. This was recrystallised from benzene.

Yield of the product = 35%

M.P. of the product = 218°C.

5. Reaction of Di-butyl tin oxide with L_1H :

2 gm (0.008 mole) Bu_2SnO was dispersed in 100 ml dry benzene. A hot dry benzene soln. of 2.5 gm (0.016 mole) L_1H was

added slowly to the suspension of Bu_2SnO in benzene with constant stirring at $\sim 60^{o}C$. It was seen that the soln. was clear after complete addition of L_1H solution. This was stirred at $\sim 60^{o}C$ for another 3 hrs. for the completion of the reaction. To the concentrated solution, a few drops of hot pet. ether was added and kept at r.t. White crystalline product was obtained, which after several recrystallisation from benzene-pet. ether mixture afforded the desired product (3.4 gm).

Yield = 80%

M.P. = 133-134.5^{o}C.

6. Reaction of Di-octyl tin dichloride with L_1H :

A mixture of 2 gm (0.005 mole) di-octyl tin di-chloride, 1.5 gm (0.01 mole) L_1H and 2 drops of pyridine in 100 ml dry benzene was refluxed for 10 hours and then after cooling was filtered. The filtrate was shaken with $\sim$1 gm powdered $NaHCO_3$ for 10 mins. to remove unreacted acid. This was then filtered and the filtrate was concentrated. To the hot solution few drops of hot pet. ether was added and kept at r.t. After about fifteen minutes the product appeared as colourless crystals. This was separated and after repeated crystallisation from benzene-pet. ether mixture, white needle shaped crystals of the organotin carboxylate (1.2 gm) was obtained.

Yield = 40%

M.P. = 114-116^{o}C.

7. Reaction of Bis-(tri-butyl tin) oxide with L_2H :

A mixture of 2 gm (0.0033 mole) Bis-(tri-butyl tin) oxide and 1.1 gm (0.0066 mole) L_2H in 150 ml dry benzene was refluxed for 6 hrs. with a Dean and Stark apparatus and cooled to r.t. To remove unreacted acid, the mixture was shaken with dry powdered $NaCHO_3$ ($\sim$1 gm) for 10 mins. and filtered. The solvent was completely evaporated from the filtrate and the residue was dissolved in about 150 ml pet. ether and kept in a refrigerator. After 30 mins. it was found that white solid deposited on the bottom of the container and this was separated from the supernatant liquid which contained unreacted Bis-(tri butyl tin) oxide. Again the solid was dissolved in pet. ether and the procedure was repeated several times to remove all unreacted $(Bu_3Sn)_2O$ completely. Finally, the solid was dissolved in minimum quantity of hot pet. ether. After keeping the solution for 2 days at r.t. white crystals of the desired product appeared which was filtered and dried in vacuum.

Yield = 81%

M.P. = 70.5 - 71.5^{o}C.

8. Reaction of Dibutyl tin oxide with L_2H :

A mixture of 1 gm (0.006 mole) L_2H and 0.75 gm (0.003 mole) di-butyl tin oxide in 100 ml dry benzene was refluxed for 3 hours with a Dean and Stark apparatus, cooled to r.t. and filtered. To the hot concentrated solution, a few drops of hot pet. ether was added. On keeping the solution for 1 to 2 hrs. at r.t., white crystalline solid (m.p. 110^{o}C) appeared. This was separated out

which after recrystallisation from benzene-pet. ether mixture afforded the dibutyl tin derivative (1.5 gm).

Yield = 85%

M.P. = 112-114°C.

9. Reaction of Bis-(tri-butyltin) oxide with L_3H :

A mixture of 1 gm (0.0053 mole) L_3H and 1.6 gm (0.0027 mole) bis-(tri-butyltin) oxide in 200 ml dry benzene was refluxed for 6 hours with a Dean and Stark apparatus and then cooled. Unreacted acid was removed from the reaction mixture by shaking it with powdered $NaHCO_3$ (~1 gm) for 10 minutes and filtered. The solvent in the filtrate was completely evaporated and the residue was dissolved in about 150 ml pet. ether and cooled in a refrigerator. White solid separated. The liquid containing unreacted $(Bu_3Sn)_2O$ was decanted off. The solid mass was again dissolved in pet ether and the process was repeated several times for complete removal of all unreacted $(Bu_3Sn)_2O$. The desired product was recrystallised from pet ether.

Yield = 88%
M.P. = 68.5-69.5°C.

10. Reaction of tri-phenyltin chloride with L_3Na.

A mixture of 2 gm (0.005 mole) tri-phenyltin chloride and excess powdered L_3Na (2 gm, 0.009 mole) in 200 ml dry acetonitrile (or absolute ethanol) was stirred overnight at r.t. The solvent was removed completely and the residue was extracted several times

with hot dry benzene. All the benzene fractions were collected in a conical flask and concentrated. Then to this hot solution pet. ether was gradually added until a white precipitate, m.p. 170°C, separated. Filtered; the residue was dissolved in minimum volume of hot benzene and then reprecipitated with pet ether. Purification was achieved by repeating this process. The m.p. of the purified compound was 174°C. The yield of the product was 70%.

10(a) Reaction of Bis (tri-phenyl tin) oxide with L_3H :

A mixture of 2 gm (0.0027 mole) bis-(triphenyl tin) oxide and 1 gm (0.005 mole) L_3H in 200 ml dry benzene was stirred at room temperature for 10 mins. At first the solution was clear but gradually white turbidity appeared on stirring. This was allowed to stand for 1 hour. White precipitate (m.p. 174°C) appeared. The mixture containing the ppt. was refluxed for 15 mins. The clear solution was then concentrated and allowed to stand at r.t. when a gelatinous white ppt. appeared. This was separated and dissolved in minimum quantity of hot benzene and reprecipitated by cooling. Purification was achieved by repeating this process several times.

Yield = 92%

M.P. = 174°C.

11. Reaction of Dibutyltin oxide with L_3H :

A mixture of 2 gm (0.008 mole) di-butyl tin oxide and 3 gm (0.016 mole) L_3H in 200 ml dry benzene was refluxed for 3 hours with a Dean and Stark apparatus. This was allowed to stand overnight. Needle-shaped crystals (m.p. 154°C) came out and was filtered. The filtrate on concentration followed by addition of few drops pet. ether furnished an additional quantity of the same compound. Recrystallisation from benzene-pet. ether mixture afforded the desired product (4.1 gm).

Yield = 85%

M.P. = 156°C.

12. Reaction of Bis (tri-butyl tin) oxide with L_4H :

A mixture of 1 gm (0.0053 mole) L_4H and 1.6 gm (0.0027 mole) bis-(tri-butyl tin) oxide in 200 ml dry benzene was refluxed for 6 hrs. with a Dean and Stark apparatus. Unreacted acid was removed from the reaction mixture by shaking it with dry powdered $NaHCO_3$ (~1 gm) and filtered off. The solvent was completely evaporated and the residue was dissolved in about 150 ml pet. ether and cooled in the refrigerator when a white solid separated. The liquid containing the unreacted $(Bu_3Sn)_2O$ was decanted immediately. The solid mass was again dissolved in pet. ether and this procedure was repeated several times to get pure product. On recrystallising the product from pet. ether needle shaped crystals of Bu_3SnL_4 was obtained.

Yield of the product = 70%

M.P. = 74-76°C.

13. Reaction of Bis (tri-phenyltin) oxide with L_4H :

To a solution of 2 gm (0.0027 mole) bis-(triphenyl tin) oxide in 200 ml dry benzene 1 gm (0.005 mole) L_4H was added with stirring at r.t. A clear solution was obtained. The solution was refluxed for 15 mins. and cooled to r.t.; filtered, the concentrated filtrate was allowed to stand at r.t. for 2 hrs. when a white precipitate (m.p. 144°C) was settled down and filtered off. The filtrate on concentration followed by addition of few drops of pet. ether furnished an additional quantity of the same compound. The product was again dissolved in minimum quantity of hot benzene and reprecipitated by adding pet. ether. Purification was achieved by repeating this process. The m.p. of the purified product was 146°C and yield was 90%.

14. Reaction of Dibutyltin oxide with L_4H :

A mixture of 2 gm (0.008 mole) di-butyltin oxide and 3 gm (0.016 mole) L_4H in 200 ml dry benzene was refluxed for 3 hrs. and then cooled to r.t. Unreacted acid was removed from the reaction mixture by shaking it with dry powdered $NaHCO_3$ ($\sim$1 gm) and filtered off. To the hot concentrated filtrate few drops of hot pet. ether was added and allowed to stand when needle-shaped crystalline product obtained. This was separated out which after several recrystallisation from benzene-pet. ether mixture afforded the dibutyl tin derivative, m.p. 125-126°C. Yield of the desired product was 82%.

15. Reaction of Di-octyl tin di-chloride with L_4H :

A mixture of 2 gm (0.0048mole) di-octyl tin dichloride, 1.8 gm (0.0096 mole) L_4H and 3 drops pyridine in 200 ml dry benzene was refluxed for 36 hrs. Unreacted acid was removed from the reaction mixture by shaking it with dry powdered $NaHCO_3$ ($\sim$ 1 gm) and filtered off. The filtrate was concentrated and pet. ether was added when a white solid separated. This was filtered; the solid dissolved in minimum quantity of hot pet. ether and allowed to stand till needle-shaped crystals appeared. The m.p. of the product was 133°C and yield of the product was 45%.

15(a) Reaction of Di-Octyl tin oxide with L_4H :

A mixture of 1 gm (0.0027 mole) di-octyl tin oxide and 1 gm (0.0054 mole) L_4H in 100 ml dry benzene was stirred at r.t. for 1 hr. The clear solution was concentrated and allowed to stand overnight. A beautiful needle-shaped crystals appeared. It was recrystallized from light petroleum as needle-shaped crystals, m.p. 133°C. The yield of the product was quantitative.

16. Reaction of Bis-(tri-butyl tin) oxide with L_5H

To 200 ml dry benzene in a 250 ml round-bottom flask was added 2 gm (0.0034 mole) bis-(tributyl tin) oxide and 1.5 gm (0.0068 mole) L_5H. The flask was fitted with a Dean-Stark moisture trap and a water-cooled condenser. The mixture was refluxed at 80°C for 6 hrs. The unreacted acid was removed by powdered anhydrous $NaHCO_3$ and filtered. The solvent in the filtrate was completely

removed by evaporation, the liquid residue dissolved in about 150 ml pet. ether and the solution was placed in a refrigerator. The desired product solidified and was separated by immediate decantation of the supernatant liquid. All the unreacted bis-(tributyl tin) oxide was removed by repeating the process several times. Recrystallization from pet. ether produced long, clear needle like crystals; m.p. 82-84°C. The yield of the desired product was 86%.

17. Reaction of bis(triphenyltin) oxide with L_5H :

To a solution of 2.4 gm (0.0032 mole) bis-(triphenyltin) oxide in 50 ml dry benzene, a solution of 1.5 gm (0.0068 mole) L_5H in 50 ml dry benzene was slowly added with shaking. After complete addition with continuous shaking the solution turned milky-white. The solution was stirred for further 30 minutes at room temperature when white solid precipitated and this was filtered off. The yield was quantitative. Recrystallization was accomplished by dissolving the product in hot ethanol and precipitating with benzene.

M.P. of the pure product was 175°C.

18. Reaction of Di-butyl tin oxide with L_5H :

A mixture of 2 gm (0.008 mole) dibutyltin oxide and 3.55 gm (0.016 mole) L_5H in 200 ml dry benzene was refluxed for 2.5 hrs. and allowed to stand overnight. A needle-shaped compound (m.p. 166°C) was crystallised out, which was filtered off. The filtrate on concentration furnished an additional quantity of the same

crystalline compound. This was separated out which after several recrystallisation from benzene afforded the desired product of m.p. 167-170°C. The yield was quantitative.

19. Reaction of Di-butyl tin oxide with L_6H :

A mixture of 2 gm (0.008 mole) di-butyl tin oxide and 4.1 gm (0.016 mole) L_6H in 200 ml dry benzene was refluxed for 2 hrs. and allowed to stand overnight. Needle-shaped compound (m.p. 158°C) was crystallised out, which was filtered off. The filtrate on concentration furnished a further crop of the same crystalline compound (m.p. 158°C). Both the compounds were mixed and recrystallised several times from benzene. The m.p. of the purified compound was 160°C and the yield of the product was quantitative.

20. Reaction of di-butyl tin oxide with L_7H :

A mixture of 2 gm (0.008 mole) di-butyl tin oxide and 3.2 gm (0.016 mole) L_7H in 200 ml dry benzene was refluxed for 4 hrs and filtered. To the hot concentrated filtrate few drops of hot pet. ether was added and allowed to stand when a needle-shaped crystals separated. This was filtered and recrystallised from the benzene-pet mixture. The m.p. of the desired product was 122°C and the yield of the product was quantitative.

21. Reaction of Bis(tributyltin) oxide with L_8H :

To 200 ml dry benzene in a 250 ml round-bottom flask was added 2 gm (0.0034 mole) bis (tributyltin) oxide and 1.2 gm (0.0068 mole) L_8H. The flask was fitted with a Dean-Stark moisture trap and a water-cooled condenser. The mixture was refluxed at 80°C for 8 hrs. The unreacted acid was removed by shaking with powdered anhydrous $NaHCO_3$ and filtered off. The solvent in the filtrate was completely

evaporated, the liquid residue dissolved in about 150 ml pet. ether and the solution was placed in a refrigerator. The desired product solidified and was separated by quick decantation of the supernatant liquid. All the unreacted bis (tributyltin)oxide was removed by repeating the process several times. Recrystallization from pet. ether produced long, clear needle-like crystals; m.p. 68-70°C. Yield of the desired organotin ester was 72%.

22. Reaction of Bis(triphenyltin)oxide with L_8H :

To a solution of 2 gm (0.0027 mole) bis (triphenyltin) oxide in 200 ml dry benzene, 1 gm (0.0054 mole) L_8H was gradually added with stirring at r.t., a clear solution was obtained. This was refluxed for 15 minutes. The clear solution was concentrated and allowed to stand at r.t. A white gelatinous precipitate settled down. This was separated and purified by several recrystallization from benzene. The m.p. of the product was 145-148°C and the yield was 88%.

23. Reaction of dibutyltin oxide with L_8H :

A solution of 2.9 gm (0.016 mole) L_8H and 2 gm (0.008 mole) dibutyltin oxide in dry benzene (150 ml) was refluxed for 3 hrs. using Dean-Stark moisture trap and was allowed to stand overnight. The resulting slightly cloudy solution was filtered. The product obtained as rectangular plate-like crystals (m.p. 120-122°C) by crystallization of the concentrated filtrate and were recrystallized from benzene. The yield was 79%.

24. Reaction of bis(tri-butyltin) oxide with L_9H :

A mixture of 2 gm (0.0033 mole bis-(tributyltin) oxide and 1 gm (0.0066 mole) L_9H in ~100 ml dry benzene was refluxed for 4 hrs. and then cooled to room temperature. The unreacted acid was

removed by shaking with powdered anhydrous $NaHCO_3$ ($\sim$0.5 gm); the reaction mixture filtered, the filtrate concentrated in vacuo and the liquid residue dissolved in pet. ether and cooled in ice. The desired product solidified and was quickly removed by decantation. The solid material was again dissolved in pet. ether and the procedure was repeated to completely removed all unreacted bis-(tri-butyltin) oxide. Finally the product appeared as needle-shaped crystals (m.p. 64-66°C) by recrystallization from pet. ether. The yield was 74%.

25. Reaction of bis (tributyltin) oxide with $L_{10}H$

A solution of 1 gm(0.0017 mole) bis (tributyltin) oxide and 0.6 gm (0.0035 mole) $L_{10}H$ in about 100 ml dry benzene was refluxed for 8 hours. The unreacted acid was removed by shaking the solution with powdered anhydrous $NaHCO_3$; the reaction mixture filtered, the filtrate concentrated in vacuo and the liquid mass dissolved in pet. ether and cooled in ice. The desired product solidified and was quickly removed by decantation. All the unreacted bis (tributyltin) oxide was removed by repeating the process several times. The solid product was recrystallized from pet. ether to elongated needles (m.p. 63-67°C). The yield was 1.4 gm (90%).

26. Reaction of dibutyltin oxide with $L_{10}H$

A mixture of 1 gm (0.004 mole) dibutyltin oxide and 1.4 gm (0.008 mole) $L_{10}H$ in $\sim$100 ml dry benzene was heated to reflux for 5 hours. The product obtained by crystallization of the concentrated

solution. This was recrystallized from a mixture of benzene and pet. ether. The m.p. of the colourless crystalline product was 88-89°C and the yield was 1.8 gm (80%).

(c) The molecular weights were determined using a Mechrolab Vapour Pressure Osmometer (Model 301A) calibrated with benzene solutions of benzil. In a few cases, cryoscopic method in benzene was also employed to determine the molecular weights.

The IR spectra were measured with a Perkin-Elmer Spectrophotometer in solid state (KBr disc or suspension in Nujol oil) and in solution (CCl_4, CS_2) in the region of 4000-200 cm^{-1}. Most of the IR spectra were recorded at R.S.I.C. of C.D.R.I., Lucknow and I.I.T., Madras and also at the I.A.C.S. at Jadavpur, Calcutta.

The NMR spectra were recorded as described in Ref. 41.

The UV absorption spectra were recorded with a SHIMADZU Spectrophotometer (Model UV 240) using 1 cm quartz cells. All solvents used were of UVASOL (E. Merck) grade.

The Mössbauer spectra were recorded by Prof. J.J. Zuckerman at the University of Oklahoma, U.S.A.

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CHAPTER – IV

Biological Properties Of The Organotin Aryloxyacetates

CHAPTER - IV

Biological properties of the Organotin(aryloxy)acetates.

IV A. Introduction

The biological properties of the organotin compounds and their potential for application in industry and agriculture are mainly responsible for the unusual increase in their production in recent years. Organotin compounds are now the active components in a number of biocidal formulations, finding application in such diverse areas as fungicides, miticides, molluscicides, marine antifouling paints, surface disinfectants and wood preservatives.[1-3]

In view of the characteristic biological activities encountered in the organotin compounds, it is of interest to prepare compounds of the type R_nSnX_{4-n} in which the active organotin moiety (R_nSn) is bound to a substrate (X) which is itself active, in the hope that a combination of complementary properties might enhance the biological effectiveness of the whole unit.

In the context of a systematic study of preparation, properties and structures of a series of substituted di- and tri-organotin (IV) aryloxy and thioacetates (described in Chapter - III), we investigated some biological properties of the organotin compounds. In this connection, it may be noted that the biological properties of the phenoxyacetic acid and its substituted derivatives as well as those of phenylthioacetic acid are known[4]. A survey of literature

shows one example[5] where these properties were also examined in the compound tricyclohexyltin (IV) phenoxy acetate.

For the sake of convenience of presentation of results and their discussion, this chapter is divided into the following Sub-Sections.

IV B. The Fungitoxicity of the Organotin(aryloxy)acetates and Structure - Activity relationships.

The role of organotin compounds as antifungal agents was worked out by Van der Kerk and Luijten[6,7]. These compounds were found to be effective because of their high potency and favourable toxicological and environmental properties[8].

Phenoxyacetic acid and some of its derivatives are known to have growth inhibitory effect on dermatophytes and yeast-like fungi[4,9]. The purpose of the present study is to evaluate the antifungal activity of the organotin(aryloxy)acetates on a few dermatophytes and plant pathogens and to compare their fungitoxicity with the parent acids in order to elucidate structure-activity relationships.

Results and Discussion

Table 1 and 2 show the antifungal effect of different aryloxyacetic acids and their organotin derivatives on various plant and animal skin pathogens and Table 3 shows the relationship between the organotin content of different organotin compounds and their fungitoxicity.

Table -1

Minimum inhibitory concentration (MIC) of different aryloxyacetic acid and their organotin derivatives for some plant pathogens.

*Compound	% Organotin content	MIC in mg litre^{-1}			
		A. brassica	C. lunata	F. oxysporum	A. flavus
L_1H	0	400	>500	> 500	>500
L_2H	0	400	500	> 500	>500
L_3H	0	100	300	>500	>500
L_4H	0	>500	>500	>500	>500
L_5H	0	300	500	500	500
$Bu_2Sn(L_1)_2$	43	30	>150	125	150
$Bu_2Sn(L_2)_2$	41	100	70	120	>150
$Bu_2Sn(L_3)_2$	38	30	>150	50	>150
$Bu_2Sn(L_4)_2$	38	100	>150	>150	>150
$Bu_2Sn(L_5)_2$	35	150	100	150	150

Contd..

Table - 1 (Contd..)

*Compound	% Organotin content	MIC in mg litre^{-1}			
		A. brassica	C. Tunata	F. oxysporum	A. flavus
Bu_3SnL_1	66	20	20	20	10
Bu_3SnL_2	64	5	1	10	10
Bu_3SnL_3	61	4	6	1	6
Bu_3SnL_4	61	1	6	5	20
Bu_3SnL_5	57	10	10	20	20

* For abbreviation see the Chap. III.

Table - 2

Fungitoxicity of different aryloxyacetic acids and their organotin derivatives for some animal skin pathogens

Compound	% Organotin content	MIC in mg litre^{-1}				
		N. incurvata	A. simii	T. mentagrophytes	A. vanbreuseghemii	T. rubrum
L_1H	0	>500	>500	500	500	500
L_2H	0	500	500	>500	500	>500
L_3H	0	150	100	300	300	300
L_4H	0	>500	>500	500	>500	500
L_5H	0	500	500	500	>500	500
$Bu_2Sn(L_1)_2$	43	125	125	15	150	40
$Bu_2Sn(L_2)_2$	41	50	60	100	100	150
$Bu_2Sn(L_3)_2$	38	>150	50	10	150	50
$Bu_2Sn(L_4)_2$	38	150	50	>150	>150	125
$Bu_2Sn(L_5)_2$	35	>150	>150	120	>150	120

Contd..

Table - 2 (Contd..)

Compound	% Organotin content	MIC in mg litre^{-1}				
		N. incurvata	*A. simii*	*T. mentagrophytes*	*A. vanbruseghemii*	*T. rubrum*
Bu_3SnL_1	66	10	10	4	1	4
Bu_3SnL_2	64	8	1	1	1	1
Bu_3SnL_3	61	3	1	1	2	4
Bu_3SnL_4	61	2	4	1	1	2
Bu_3SnL_5	57	20	10	1	20	2

Table - 3

Relationships between organotin content and antifungal activity of phenoxyacetic acid and some organotin compounds

Compound	% Organotin content	MIC in mg litre^{-1}				
		Plant pathogens			Dermatophytes	
		A. brassica	C. lunata	A. flavus	A. vanbreuse-ghemii	T. mentagro-phytes
L_1H	0	400	>500	>500	500	500
$Bu_2Sn(L_1)_2$	43	30	>150	150	150	15
Bu_3SnL_1	66	20	20	10	1	4
Bu_3SnL_9	66	20	30	10	1	5
$(Bu_3Sn)_2O$	97	1	5	5	1	1

Free phenoxyacetic acid exhibited very little fungitoxicity. Substitution of a Cl atom in the 2-position of the phenyl ring slightly enhanced the antifungal property in certain cases, while substitution of a Cl atom in the 4-position, or a CH_3 group in the 2 position, or two Cl atoms in both 2- and 4-positions failed to improve mycotoxicity.

Dibutyltin derivatives are much more effective as antifungal agents than the free acids while the tributyltin derivatives showed still higher antifungal character. This is consistent with the findings of van der Kerk and Luijten[7] who claim that maximum fungitoxicity is associated with a total number of 9-12 C atoms in the alkyl groups. However, as shown in Table 1, 2 and 3 this enhancement of fungitoxicity may be dependent on the organotin content of these compounds.

It has been found that among the tributyltin compounds of the type Bu_3SnX, depending on the nature of X, the fungistatic concentrations differed considerably. Also some of these compounds displayed selectivity towards one or the other of the test fungi. Similar observations were also made by other workers[10].

It may be recalled that the primary mode of action of dibutyltin compounds is quite different from that of the triorganotin compounds. While diorganotin compounds function through their ability to combine with enzymes or coenzymes possessing vicinal dithiol groups thereby inhibiting α-keto acid oxidation,

the tributyltin compounds inhibit mitochondrial oxidative phosphorylation and also bind to the cysteine or histidine residues of certain proteins[8]. In this context, it may be interesting to note that in case of substituted diorgano- or triorganotin phenoxyacetates the MIC values cannot be directly correlated to their organotin contents.

Introduction of an electron-withdrawing chloro group in the 2- or 4-position of the phenyl ring of the tributyltin phenoxyacetates resulted in enhancement of fungitoxic character of the parent compound. The very high mycotoxicity of the monohalogenated analogues may be associated with the action of two active centres in the molecule - the tributyl stannyl fragment and the substrate containing the halogen atom at the C:C bond. Further increase in the number of Cl groups led to diminished mycotoxicity as compared to the monosubstituted compound which indicated that the steric factor and molecular size were also important in deciding fungitoxicity. Substitution of a CH_3 group in the 2-position markedly improved the antifungal activity which may be due to its special steric configuration.

It is apparent from Table 3 that Bu_3SnL_1 and Bu_3SnL_9 having identical organotin content are almost equally fungitoxic suggesting that the phenoxy oxygen atom in phenoxyacetic acid has no role in deciding antifungal properties. $(Bu_3Sn)_2O$ was most active in this group which may be due to its higher organotin content and

also to its capacity to combine with certain amino acids of cell proteins[11].

IV C. Antibacterial activity of the organotin (aryloxy)acetates.

The bactericidal activity of organotin compounds, especially the tri-n-propyl and tri-n-butyltin derivatives, have been reported by many workers[12-14]. In the present study, the antibacterial activity of some organotin(aryloxy)acetates have been worked out and compared to that of the parent acids.

Results and Discussion

Table 4 shows the antibacterial property of the aryloxy-acetic acids and their organotin derivatives.

Table - 4

Antibacterial activity of different organotin compounds

Compound	% organotin content	Concentration (μg/ml)	Mean diameter of the zone of inhibition (mm)	
			E. coli	S. typhi
L_1H	0	50	11.6	12
$Bu_2Sn(L_1)_2$	43	50	21	16
Bu_3SnL_1	66	50	12.6	19

Contd..

Table - 4 (Contd..)

Compound	% organotin content	Concentration (μg/ml)	Mean diameter of thezone of inhibition (mm)	
			E. coli	S. typhi
Bu_3SnL_2	64	50	12	23.3
Bu_3SnL_3	61	50	13.6	17.6
Bu_3SnL_4	61	50	13.6	20
Bu_3SnL_5	57	50	12	16
Alcohol (control)	0	0	0	0

It is found that organostannylation increases the bactericidal activity of the free acid L_1H. In case of E. coli, $Bu_2Sn(L_1)_2$ is more toxic than Bu_3SnL_1 and its chlorinated or methylated analogues. But when the test organism was S. typhi, the tributyltin compounds showed more pronounced antibacterial activity. It is, however, difficult to correlate the activities with organotin content of the compounds.

IV D. Acute Oral Toxicity of tributyltinphenoxyacetate against mice.

The acute oral LD_{50} value with a single administration of Bu_3SnL_1 to mice has been determined.

Results and Discussion

The LD_{50} value of Bu_3SnL_1 is 251.2 mg/kg of body weight when administered orally to mice. As regards the mode of toxic action, it is believed that the Bu_3Sn compounds produce an interstitial oedema of the white matter of the brain and spinal cord without a histologically detectable change in the nerve tissues[15]. The mechanism of poisoning has been considered to be associated with membrane damage and inhibition of oxidative phosphorylation[16-18].

The oral toxicity of Bu_3SnL_1 is fairly low. The maximum tolerable dose (MTD) is 100 mg/kg which is fairly high compared with the in vitro antifungal dose (1-20 μg/ml). The compound, therefore, appears to have potential as a useful drug in combating superficial and systematic mycoses.

IV E. Phytotoxicity of the organotin(aryloxy)acetates.

The effect of inorganic tin compounds on some herbaceous plants have been studied by Cohen[19] who showed that 0.05 ppm tin as $SnCl_4$ and $SnCl_2$ stimulates root growth. $SnCl_2$ or $SnSO_4$ in concentration of 5 ppm or more have toxic effects upon corn, pea and sunflower. Alkyltin (IV) compounds have found limited use in agriculture, because of their high phytotoxicity. Corresponding phenyl and cyclohexyltin (IV) compounds which are less phytotoxic are now widely used in agriculture. The problem of toxic residues

is the least in organotin compounds due to their degradation to non-toxic products.

In this section we present results of studies on the phytotoxicity of different triorganotin(aryloxy)acetates on the growth of rice and mung bean seedlings (Table -5 and 6, pages-131&132).

All the compounds show inhibitory effects on the growth of both rice and mung bean seedlings at concentrations of 1, 10 and 50 ppm. But they are only moderately phytotoxic at the concentrations at which they suppress fungal growth. The least phytotoxic of all these compounds studied is Bu_3SnL_5 (tributyltin-2,4-dichloro phenoxyacetate) in the case of mung bean seedling. One interesting observation was the stimulation of root growth of rice seedlings by very low concentration (1 ppm) of Bu_3SnL_1, Bu_3SnL_3 and Bu_3SnL_4. This effect may be due to some hormonal action of these compounds.

IV F. Experimental

The preparation of the aryloxyacetic acids and their organotin derivatives with their abbreviations have been given in Chapter - III.

a) Studies of Fungitoxicity:

The test organisms used were animal skin pathogens, namely, Trichophyton rubrum, T. mentagrophytes, Nannizia incurvata, Arthroderma simii and A. vanbreuseghemii. T. rubrum and T. mentagrophytes were collected from the School of Tropical Medicine, Calcutta. The other skin pathogens were kind gifts from Dr. Irene

Table - 5

Effect of different tributyltin aryloxyacetates on the growth of rice seedling.

Treatment Compound	Concentration	Length of shoot (cm.)	% inhibition of shoot length	Length of root (cm)	% inhibition of root length
Aq. Acetone (Control)	6%	3	0	4.7	0
Bu_3SnL_1	1 ppm	2.5	16.66	4.9	-
	10 ppm	2.5	16.66	3.9	17.02
	50 ppm	1.69	43.67	0.8	82.98
Bu_3SnL_3	1 ppm	2.88	4	5.80	-
	10 ppm	2.65	11.67	1.3	72.34
	50 ppm	0.8	73.33	0	100
Bu_3SnL_4	1 ppm	2.67	11	5.07	-
	10 ppm	2.3	23.33	3.84	18.3
	50 ppm	0.5	83.33	0	100
Bu_3SnL_5	1 ppm	2.2	26.67	4	14.89
	10 ppm	1.71	43	1.56	66.81
	50 ppm	0.8	73.33	0	100

Table - 6

Effect of different tributyltinaryloxyacetates on the growth of Mung bean seedling.

Treatment		Length of shoot (cm)	% inhibition of shoot length	Length of root (cm)	% inhibition of root length
Compound	Concentration				
Aq. acetone (Control)	6%	18.24	0	6.99	0
Bu_3SnL_1	1 ppm	13.82	24.23	5	28.47
	10 ppm	11.2	38.6	2.9	58.51
	50 ppm	7.70	57.79	1.01	85.55
Bu_3SnL_3	1 ppm	14.41	21	5.5	21.32
	10 ppm	12.12	33.55	3.27	53.22
	50 ppm	7.5	58.88	1.02	85.41
Bu_3SnL_4	1 ppm	13.9	23.79	0.92	86.84
	10 ppm	12.22	33	0.5	92.85
	50 ppm	3. 65	79.99	0-0.5	100-92.85
Bu_3SnL_5	1 ppm	16.30	10.64	6.10	12.73
	10 ppm	13.15	27.91	3.25	53.51
	50 ppm	6.1	66.56	0.7	89.99

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The test organisms also included the plant pathogens like Curvularia lunata, Alternaria brassica, Aspergillus flavus and Fusarium oxysporum. All these fungi were obtained from the Department of Botany, Calcutta University.

The test fungi were maintained on Sabouraud's agar slants.

The minimum Inhibitory Concentration (MIC) of the test compounds were determined by Serial agar streak dilution method[20].

b) Studies of Antibacterial Activity:

Organisms used: The test organisms were Escherichia Coli and Salmonella typhi, both of which are gram-negative bacteria. They were maintained on tryptone-agar slants containing 1% tryptone, 0.5% yeast extract, 2% agar, pH 7.2.

0.2 ml of the bacterial suspensions were taken in sterile petri-dishes and 20 ml molten tryptone agar medium (45°C) was poured on each of them and mixed well for uniform distribution of bacteria. The agar was allowed to set. In each plate, three cups were bored with a heat-sterilized cork-borer. In each plate, 0.05 ml of the alcohol-solution of the test compounds containing 50 µg of the test material was added to two cups. The third cup in all the plates was filled with 0.05 ml of control solution (alcohol). All the plates were kept at refrigeration temperature for uniform diffusion of the bactericide in the agar medium. Then the plates

were incubated at 37°C for 24 hrs. At the end of the incubation period the mean diameter of the zone of inhibition formed by test compounds were measured.

(c) Studies of Acute oral toxicity against mice:

Animals : Albino Swiss mice, purchased from M/S Satya Charan Ghosh, Calcutta, was used in the experiment. The mice were maintained on standard laboratory diets.

Chemicals : Bu_3SnL_1 was used as solution in double refined ground nut oil.

Method : Male albino mice weighing 15-18 gms were used in these studies.

Each of the dose was administered orally to a group of ten mice. The mortality was determined after 24 hrs.

(d) Studies of Phytotoxicity:

In this experiment the following variety of seeds have been used:

(i) Rice (Oryza sativa L. Cv. Rupsail) supplied by State Agricultural Reseadh Institute, Chinsurah, West Bengal. (ii) Mung bean (Phaseolus aureus Cv. N P23) supplied by Agricultural Research Institute, Bihar.

Germinating condition of the seeds: Rice seeds were sterilized with 0.1% mercuric chloride solution and was washed with distilled water several times. Seeds were spread in hatches over filter papers in Petri dishes containing the test solutions. They were germinated

in dark at a constant temperature of 30°C for the stipulated periods. 6% aqueous acetone controls were run parallel to each experiment.

In case of mung bean the germinating conditions were similar to those of rice.

Throughout the experiment, solutions of the triorganotin aryloxyacetates in 6% aqueous acetone were used.

Harvesting period of seeds: The germinating seedlings were harvested after 4 days for growth analysis of rice and mung bean seedlings. For both the seedlings shoot and root length elongation was measured.

In conclusion, it may be stated that organostannylation enhances the biocidal properties of the parent aryloxyacetic acids. In order to account for the quite large increase of activity, we presume that the biocidal activity of both the organotin component (R_3Sn/R_2Sn) and the carboxylic acid substrate are mutually complemented in the compounds examined.

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ANNEXURE

PREPARATION AND INFRARED AND ^{13}C, ^{17}O, AND ^{119}Sn NMR SPECTRA OF SOME SUBSTITUTED DI- AND TRI(1-BUTYL)TIN PHENOXYACETATES AND PHENYLTHIOACETATES

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The paper describes preparation and basic physical and chemical properties of a group of substituted di- and tri(1-butyl)tin(IV) phenoxyacetates and phenylthioacetates of the general formula $(R_xC_6H_{5-x}ECH_2CO_2)_nSn(1\text{-}C_4H_9)_{4-n}$, where R = H, 2-Cl, 4-Cl, 2-CH_3, and 2-OCH_3, E means oxygen or sulphur atoms, n = 1 or 2, and x = 1 or 2. From IR spectral data, ^{13}C, ^{17}O, and ^{119}Sn NMR spectra, and from other physico-chemical methods, conclusions are drawn about structure of the compounds in solid state and in solutions of coordinating (hexamethylphosphoric triamide) and non-coordinating solvents (chloroform, carbon tetrachloride, carbon disulphide, benzene). In solid state the tri(1-butyl)tin(IV) compounds form polymeric chains with bidentate bridge carboxylic groups. In non-coordinating solvents these compounds are present as isolated pseudotetrahedral molecules, whereas in hexamethylphosphoric triamide they form complexes with one solvent molecule, the central tin atom exhibiting the *trans*-trigonally bipyramidal coordination. The di(1-butyl)tin(IV) compounds form, both in solid state and in non-coordinating solvents, monomeric particles containing bidentate chelate carboxylic groups. In hexamethylphosphoric triamide they form complexes with octahedral coordination around the tin atom containing monodentate carboxylic groups and the butyl groups at trans position. In none of the cases studied evidence was obtained for interaction of the oxygen or sulphur atoms of $C_6H_5ECH_2$ group with the tin atom.

An unusual increase is observed in production of organotin compounds during the past few years. This fact is particularly due to their biocidal properties and the consequent application to the pest control, ecology problems, veterinary medicine and human medicine, etc. For these purposes especially suitable are the compounds type R_nSnX_{4-n}, where R means an organic substituent and X is a polar group (anion of an acid). Out of the most frequently wanted are such compounds whose biocidal properties are due not only to the R_nSn group but also to the X group, because in these cases the effects are mutually combined and complemented. The organotin(IV) compounds of this type in which the X group is formed by phosphate or its organo-

-analogues and sulphur analogues were studied in more detail both from physical and from chemical points of view[1-4].

In the context of a systematic study of synthesis, properties and structure of organotin(IV) compounds, we prepared a series of substituted di- and tri(1-butyl)tin(IV) phenoxyacetates and phenylthioacetates of the general formula $(R_xC_6H_{5-x}ECH_2.CO_2)_nSn(1\text{-}C_4H_9)_{4-n}$, where R stands for H, 2-Cl, 4-Cl, 2-CH_3, and 2-OCH_3, E means oxygen or sulphur atom, n is 1 or 2, and x is 1 or 2. Biocidal properties of phenoxyacetic acid and its derivatives as well as those of phenylthioacetic acid are sufficiently known[5]. They were also reexamined in combination with the organotin-(IV) component[6]. There is no doubt, either, that structure of these compounds is significantly connected with their biocidal properties and/or ways of their practical application[7].

EXPERIMENTAL

All the compounds studied (Table I) were prepared in the yields of 78 to 92% by azeotropic dehydration of the stoichiometric mixture of the respective phenoxyacetic or phenylthioacetic acid and bis tri(1-butyl)stannyl oxide or di(1-butyl)stannyl oxide in benzenic solution. The products obtained by crystallization of the concentrated solutions were recrystallized from a mixture of benzene and petroleum ether (60–80°C). Table I summarizes the results of elemental analyses and melting points. The molecular masses of the compounds were determined by cryoscopy in benzene or by osmometry in carbon tetrachloride. In both the solutions, the values measured correspond to monomeric character of the compounds. The infrared spectra were measured with a Perkin–Elmer apparatus type 684 in solid state (KBr disc or suspension in paraffine oil) and in solution (carbon tetrachloride, carbon disulphide) in the range from 4 000 to 200 cm^{-1}. The cells used were made of KBr (4 000–300 cm^{-1}) and polyethylene (600–200 cm^{-1}). The ^{13}C, ^{17}O, and ^{119}Sn NMR spectra were measured with a JNM-FX 100 apparatus (JEOL, Japan) at 25·047, 13·50, and 37·14 MHz, respectively. The ^{13}C and ^{119}Sn NMR spectra were measured in solutions of deuteriochloroform and hexamethylphosphoric triamide at 300 K (if not otherwise stated), the ^{17}O NMR spectra were measured in saturated solutions in chloroform at 330 K. The chemical shifts $\delta(^{13}C)$ are related to a suitable signal of the solvent ($\delta(C^2HCl_3) = 77{\cdot}00$ ppm, $\delta((CH_3)_6.N_3PO) = 36{\cdot}00$ ppm) and transformed to the δ scale, the $\delta(^{17}O)$ and $\delta(^{119}Sn)$ values are related to external neat deuterium oxide and tetramethylstannane, respectively. The details of measurement and interpretation of the NMR spectra were described earlier[8,9].

RESULTS

Preparation and Identification of Compounds

All the compounds investigated (prepared by esterification of the respective acids with bis tri(1-butyl)stannyl oxide or di(1-butyl)stannyl oxide) are colourless crystalline solids with well-defined melting points (usually relatively low). Their analyses results agree well with theory (Table I). Moreover, the compounds were identified by their IR and ^{13}C and ^{119}Sn NMR spectra (see below). All the data obtained agree with the

TABLE I

Chemical analysis and melting points of compounds *I*–*IV*

No	Compound	Elemental analysis (calculated/found), %				Melting point, °C
		C	H	Sn	others	
Ia	$C_6H_5OCH_2COOSn(C_4H_9)_3$	54·59	7·59	26·79		53·0–54·0
		54·45	7·77	26·90		
Ib	$2\text{-}CH_3C_6H_4OCH_2COOSn(C_4H_9)_3$	55·84	8·07	25·97		70·5–71·5
		55·41	7·97	26·07		
Ic	$4\text{-}ClC_6H_4OCH_2COOSn(C_4H_9)_3$	50·42	7·08	24·65	7·75[a]	74·0–76·0
		50·51	6·99	24·95	7·45	
Id	$2\text{-}ClC_6H_4OCH_2COOSn(C_4H_9)_3$	50·75	7·03	24·53	7·57[a]	68·0–68·5
		50·51	6·99	25·95	7·45	
IIa	$(C_6H_5OCH_2COO)_2Sn(C_4H_9)_2$	54·09	6·14	21·98		133·0–134·5
		53·86	6·03	22·18		
IIb	$(2\text{-}CH_3C_6H_4OCH_2COO)_2Sn(C_4H_9)_2$	55·76	6·42	21·37		112·0–114·0
		55·44	6·44	21·07		
IIc	$(4\text{-}ClC_6H_4OCH_2COO)_2Sn(C_4H_9)_2$	47·71	5·07	19·69	11·93[a]	125·0–126·0
		47·72	5·00	19·65	11·74	
IIe	$(2,4\text{-}Cl_2C_6H_3OCH_2COO)_2Sn(C_4H_9)_2$	42·97	4·38	17·94	20·83[a]	167·0–170·0
		42·83	4·19	17·64	21·07	
IIf	$(2\text{-}CH_3OC_6H_4OCH_2COO)_2Sn(C_4H_9)_2$	52·32	6·23	20·08		120·0–122·0
		52·46	6·10	19·94		
III	$C_6H_5SCH_2COOSn(C_4H_9)_3$	52·80	7·36	26·10	6·87[b]	63·0–67·0
		52·54	7·50	25·96	7·01	
IV	$(C_6H_5SCH_2COO)_2Sn(C_4H_9)_2$	50·69	6·12	21·15	11·03[b]	88·0–89·0
		50·81	5·69	20·92	11·30	

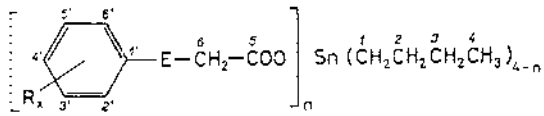
[a] Cl; [b] S.

TABLE II

The band frequences of carboxylic and phenoxymethyl groups in compounds *I*—*IV* (cm^{-1})

Compound	Solid phase				Solution			
	ν_a(COO)	ν_s(COO)	ν_a(COC)	ν_s(COC)	ν_a(COO)	ν_s(COO)	ν_a(COC)	ν_s(COC)
Ia	1 587 vs	1 421 s	1 243 s 1 220 sh	1 085 s	1 690 vs 1 665 vs	1 358 m 1 340 s	1 245 s 1 218 s	1 085 s
Ib	1 577 vs	1 413 s	1 243 vw 1 224 vs	1 085 s	1 690 vs 1 666 vs	1 358 w 1 340 s	1 245 vs 1 225 vs	1 085 s
Ic	1 585 vs	1 415 vs	1 245 sh 1 225 vs	1 075 vs	1 690 vs 1 663 vs	1 358 sh 1 342 s	1 243 s 1 225 vs	1 078 vs
Id	1 583 vs	1 417 vs	1 235 vs	1 082 vs	1 690 vs 1 667 vs	1 355 w 1 340 s	1 245 m 1 228 vs	1 080 vs
IIa	1 615 vs	1 416 vs	1 240 sh 1 217 vs	1 083 vs	1 637 vs	1 407 vs	1 240 s 1 218 vs	1 090 vs
IIb	1 553 vs	1 416 vs	1 245 sh 1 228 vs	1 075 vs	1 640 vs	1 405 vs	1 247 vs 1 226 vs	1 080 vs
IIc	1 623 vs	1 420 s	1 245 vs 1 220 m	1 082 vs	1 645 vs	1 405 vs	1 247 s 1 230 vs	1 082 vs
IIe	1 608 vs	1 418 vs	1 235 vs 1 220 sh	1 080 vs	1 643 vs	1 405 s	1 232 vs 1 220 sh	1 080 vs
IIf	1 615 vs	1 412 s	1 255 vs 1 228 vs	1 073 m 1 055 vs	1 640 vs	1 405 s	1 255 vs 1 215 vs	1 070 vs 1 055 s
III	1 575 vs	1 370 vs			1 665 vs 1 655 vs	1 340 sh 1 327 vs		
IV	1 592 vs	1 370 vs			1 612 vs	1 360 vs		

presumed constitution which is schematically represented by the formula:



where R is the respective substituent of the phenyl ring, E means an oxygen or sulphur atom, and n, x are 1 or 2. The small numbers in the formula denote the carbon atoms for assignment of the signals in ^{13}C NMR spectra (Table IV).

Infrared Spectra

All the spectral bands were found at practically identical wavenumber values in solid phase and in solutions of the compounds. This is true especially of the frequences due to the 1-butyl group and most frequences due to the phenyl ring. These bands as well as those of the other *i.e.* X-sensitive vibrations of the phenyl ring (out of which some are identical with the vibrations of the C—O—C or C—S—C grouping), vibrations of carboxylic group, vibrations of substituents in the phenyl ring, of the methylene group in the phenoxyacetates or phenylthioacetates, and of the Sn—O and/or Sn—C bonds were assigned on the basis of comparison of the spectra of the compounds studied with those of the original acids, their methyl esters, further di- and tri-(1-butyl)tin(IV) compounds, and literature data [10–13].

The bands of valence vibrations of carboxylic group, those due to Sn—C bonds, and the bands of phenoxymethyl or phenylthiomethyl group are fundamentally important for discussion of structure of the compounds studied and shape of the coordination polyhedron around the tin atom. The other bands, although they have their informative value (serving for identity proof of the compounds studied), are of minor importance for the discussion of structure (Table II).

Dominant bands of the spectra of tri(1-butyl)tin(IV) phenoxyacetates (*Ia–Id*), both in solid state and in solvents, are intensive broad absorption bands ν_a and ν_s of carboxylic group and ν_a and ν_s of phenoxymethyl group (ν_a(COC) is frequently denoted as the vibration of phenyl-oxygen bond, ν_s(COC) being ascribed to the O—CH_2 bond vibration)[13]. In contrast to the ν_a(COC) and ν_s(COC) bands, whose position in the regions of 1 245–1 218 and 1 085–1 075 cm^{-1}, respectively, does not depend on the phase state of the sample (the intensity changes of these bands in solid state and in solution are connected with the presence of rotamers, as it is shown below), the position as well as number of ν_a(COO) and ν_s(COO) bands depend markedly on the phase state. In solid state, ν_a(COO) and ν_s(COO) are found in the regions of 1 587–1 577 and 1 421–1 413 cm^{-1}, respectively ($\Delta\nu \sim 170\ cm^{-1}$). In solution, on the contrary, ν_a(COO) is found as a pair of bands in the region of 1 690–1 663 cm^{-1}, the pair of ν_s(COO) bands being shifted to the region of 1 358

to 1 340 cm^{-1}. The ν_a and ν_s values in the solid state are characterical for a bridge bidentate carboxylic group, the same values in solutions correspond to a monodentate carboxylic group[14]. The coupling of bands in solution is obviously due to the presence of two rotamers (*s-cis* and *s-trans*), the magnitude of splitting of the bands ($\sim$20 cm^{-1}) being comparable with the similar phenomenon observed with organic[15] and organosilicon[16] phenoxyacetates.

The deformation vibrations of carboxylic group are less distinct than the valence vibrations. The scissoring vibration is found as a band of medium intensity in the region of 712–700 cm^{-1}, the out-of-plane and in-plane deformation vibrations forming weak bands in the regions of 615–603 and 515–500 cm^{-1}, respectively. The ν_a(SnC) and ν_s(SnC) vibrations make themselves felt as weak spectral bands at 580–570 and 530–520 cm^{-1}, respectively. The ν(SnO) vibration is ascribed (in accordance with ref.[10]) to a band of medium to weak intensity in the region of 286–268 cm^{-1}.

The bands due to valence vibrations of carboxylic and phenoxymethyl groups are also dominant in the spectra of di-(1-butyl)tin(IV) phenoxyacetates (*IIa–IIf*). The vibration bands of phenoxymethyl group ν_a(COC) and ν_s(COC) are found in spectra of both the solid phase and solution in the regions of 1 255–1 215 and 1 090–1 080 cm^{-1}, respectively, *i.e.* practically the same as those of the tri(1-butyl)-tin(IV) compounds. Again, the position of the bands of valence vibrations of carboxylic group depends (even though to a lesser extent) on the phase state, *i.e.* whether the sample is crystalline or in solution. In solid state the ν_a(COO) bands are found in the region of 1 623–1 608 cm^{-1} (except the compound *IIb*) and ν_s(COO) at 1 420 to 1 416 cm^{-1} ($\Delta\nu \sim 200$ cm^{-1}). In carbon tetrachloride solutions, ν_a(COO) is shifted to higher wavenumbers ($\sim$ 1 640 cm^{-1}), whereas ν_s(COO) is slightly shifted to lower wavenumbers ($\sim$ 1 405 cm^{-1}) ($\Delta\nu \sim 235$ cm^{-1}). The positions of bands of the compounds in solid state are typical of bidentate chelate function of carboxylic group (with compound *IIb* it is necessary to presume a bridge arrangement of COO group), in solutions the situation is between the monodentate and chelate functions of carboxylic group. The other vibrations of carboxylic group lie in the regions identical with those of compounds *Ia–Id* (an intensive band of the scissoring vibration in the region of 750–720 cm^{-1}, weak bands of out-of-plane and in-plane deformation vibrations at 625–610 and 512–495 cm^{-1}, respectively). The vibrations of Sn–C bonds are manifested as weak bands in the regions close to those of the deformation vibrations of carboxyl (610–580 and 532–495 cm^{-1}, respectively). The ν(SnO) vibrations are ascribed to the bands of medium to weak intensity in the region of 280–270 cm^{-1}.

The infrared spectra of the two phenylthioacetates *III* and *IV* can be compared to a considerable extent with their oxygen analogues (compounds *Ia* and *IIa*), taking, of course, as self-evident that the intensive ν(COC) bands disappear and the position of X-sensitive bands is changed, too. It is important to find that ν_a(COO) and ν_s(COO)

(and, hence, also their difference) have similar values as those of the oxygen analogues. Therefore, the same conclusions can be made about their structure inclusive of the existence of two rotamers of compound *III*. Slight shifts of $\nu_a(COO)$ and $\nu_s(COO)$ to the region of lower wavenumbers observed with compounds *III* and *IV* (as compared with *Ia* and *IIa*) are connected with the more distinct donor properties of the $C_6H_5S.CH_2CO_2^-$ anion as compared with $C_6H_5OCH_2CO_2^-$, which is confirmed, *inter alia*, also by values of the dissociation constants of their conjugated acids[17].

NMR Spectra

The parameters of ^{13}C, ^{17}O, and ^{119}Sn NMR spectra of compounds *I*–*IV* are given in Tables III and IV. From the tables it can be seen that the deuteriochloroform solutions exhibit a single signal at 300 K in the ^{119}Sn spectrum; the number of signals in the ^{13}C spectrum corresponds to the number of magnetically non-equivalent carbon atoms in the structural formula suggested for the respective compound.

The chemical shifts $\delta(^{119}Sn)$ of the tri(1-butyl)tin(IV) compounds in deuteriochloroform solutions have the values 125·5 to 132·9 ppm, the coupling constants $^1J(^{119}Sn^{13}C)$ of these compounds vary within the limits from 350·3 to 352·8 Hz.

TABLE III
Chemical shifts $\delta(^{119}Sn)$ and $\delta(^{17}O)$ and coupling constants $^nJ(^{119}Sn^{13}C)$ of compounds *I*–*IV*

Compound	$\delta(^{119}Sn)^a$, ppm	$\delta(^{17}O)^b$, ppm/$w_{1/2}{}^c$, Hz	$^nJ(^{119}Sn^{13}C)^d$, Hz		
			n = 1	n = 2	n = 3
Ia	130·9	258/700	352·2	20·8	64·7
Ia[e]	− 61·3		511·5	29·0	80·6
Ib	127·7		352·0	20·8	64·7
Ic	132·9		350·3	20·8	64·7
Id	132·2		351·6	20·8	64·7
IIa[f]	−117·4	249/900	549·3	36·0	100·1
IIa[e]	−298·3		811·8	34·2	140·4
IIb	−117·1		548·1	36·6	101·3
IIc	−114·4		545·7	36·0	100·1
IIe	−110·5		544·4	36·6	102·5
IIf	−119·7		556·6	36·6	105·0
III	125·5	276/500	352·8	20·8	67·1
IV	−135·8	272/1 000	559·7	34·8	102·5

[a] 300 K, deuteriochloroform; [b] 330 K, chloroform, saturated solution, ±3 ppm; [c] the signal half-width, ±10%; [d] $^4J(^{119}Sn^{13}C) < 5$ Hz; [e] solution in hexamethylphosphoric triamide; [f] 220 K, two signals (−116·4 and −200·9 ppm) with the integral intensity ratio of 4 : 1.

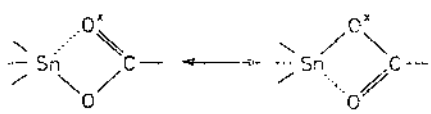
TABLE IV

Chemical shifts $\delta(^{13}C)$ of compounds *I*–*II'* in deuteriochloroform at 300 K

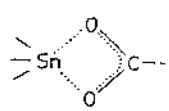
Compound	$\delta(^{13}C)$, ppm									
	$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	$C_{(1')}$	$C_{(2')}$	$C_{(3')}$	$C_{(4')}$
Ia	16·52	27·53	26·85	13·45	173·45	65·32	157·90	114·33	129·15	120·96
Ia[a]	18·89	27·62	26·69	13·24	170·56	65·97	158·67	114·08	128·46	119·54
Ib[b]	16·52	27·63	26·90	13·50	173·79	65·84	156·30	126·91	130·66	120·72
Ic	16·57	27·58	26·85	13·50	173·21	65·65	156·59	115·70	129·05	125·88
Id[c]	16·60	27·53	26·85	13·45	172·77	66·28	153·71	122·81	130·27	121·64
IIa	25·44	26·17	26·02	13·21	178·18	64·72	157·37	114·19	129·20	121·35
IIa[a]	28·54	26·59	26·06	13·19	172·61	65·34	158·23	114·18	128·65	120·02
IIb[d]	25·39	26·26	26·07	13·26	178·33	65·25	155·81	127·00	130·86	121·15
IIc	25·73	26·36	26·17	13·40	177·79	65·21	156·15	115·70	129·30	126·52
IIe[e]	25·87	26·50	26·26	13·44	177·11	66·39	152·30	124·23	130·42	127·00
IIf	25·53	26·17	25·97	13·23	177·79	65·83	[f]	[f]	111·75	[g]
III	16·52	27·58	26·90	13·50	174·13	36·70	136·07	128·66	128·66	125·93
IV	25·19	26·12	26·02	13·21	179·25	35·72	135·00	[h]	[h]	126·33

[a] Solution in hexamethylphosphoric triamide; [b–h] further values $\delta(^{13}C)$, ppm: [b] 126·37 ($C_{(5')}$), 110·87 ($C_{(6')}$), 16·18 ($C_{(CH_3)}$); [c] 127·25 ($C_{(5')}$), 131·21 ($C_{(6')}$); [d] 126·32 ($C_{(5')}$), 110·73 ($C_{(6')}$), 15·98 ($C_{(CH_3)}$); [e] 127·40 ($C_{(5')}$), 114·50 ($C_{(6')}$); [f] 149·23 or 146·84; [g] 122·08 or 120·28 ($C_{(4')}$) and ($C_{(5')}$), 113·50 ($C_{(6')}$), 55·46 ($C_{(OCH_3)}$); [h] 128·86 or 128·71.

Both these parameters, which are significant for evaluation of structure, possess the values typical of quasitetrahedral arrangement around the tin atom in this type of compounds[18]. With the di(1-butyl)tin(IV) compounds, the values of chemical shifts $\delta(^{119}Sn)$ and coupling constants $^{1}J(^{119}Sn^{13}C)$ (in deuteriochloroform solutions) vary within the limits from −110·5 to −135·8 ppm and from 544·4 to 559·7 Hz, respectively, which values (with the di(1-butyl)tin(IV) compounds) are typical of a pentacoordinated tin atom[19,20]. Thus it is obvious that in compounds *II* and *IV* in chloroform solutions (with regard to monomeric character of these compounds), phenoxyacetate and phenylthioacetate must act as multi-donor chelate-forming ligands. With selected representatives of the tri(1-butyl)tin(IV) compounds (compounds *Ia* and *III*) and di(1-butyl)tin(IV) compounds (compounds *IIa* and *IV*) we could measure the chemical shifts $\delta(^{17}O)$. In each of the cases, one signal was only found for the two oxygen atoms of carboxylic group, its position being approximately in the middle of the interval containing the signals of the two oxygen atoms of carboxyl group of organic esters (no signal due to oxygen atom of phenoxymethyl group was found in compounds *Ia* and *IIa*; the reason obviously lies in its large width, because even in the case of methyl phenoxyacetate the half-width of the signal of oxygen atom of the phenoxymethyl group is roughly twice as large as that of both oxygen atoms of carboxyl group). Similar phenomenon was encountered also with other tri- and di(1-butyl)tin(IV) carboxylates and was explained in ref.[9] by a rapid exchange of the oxygen atom in the COOSn fragment in the NMR time scale as follows:



which, from the point of view of the NMR time scale, is equivalent to the arrangement:



and indicates a bonding affinity of the tin atom of di- and tri(1-butyl)tin(IV) compounds to both the oxygen atoms of the carboxyl group. Hence, it seems likely that both the oxygen atoms contribute (even though to different extents) to the bonding interactions of the carboxyl group with the central tin atom. The donor–acceptor bond of the oxygen atom of carbonyl group, of course, is much weaker than a simple covalent SnO bond in the Sn—O—C grouping and thus the carboxyl group acts, in this respect, as an asymmetrical bidentate chelate-forming ligand in the two types of compounds. Such a role of carboxylic group in the di(1-butyl)tin(IV) compounds is not surprising, after all, it is in accordance with results of IR spectra. The asym-

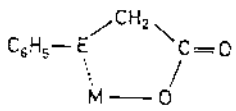
metrical chelate connection with the very weak donor–acceptor interaction of the carbonyl oxygen atom and the tin atom was also proved recently in the case of molecular crystals of some sterically hindered triphenyltin(IV) carboxylates[21,22]. The degree of asymmetry obviously depends on the strength of the donor–acceptor connection, *i.e.* on the donor ability of oxygen atom of carbonyl group and the acceptor ability of the central tin atom. Thus it can be expected that it will depend significantly on the character of the organic residue bound to the carboxyl group as well as on the character and number of organic substituents and polar groups bound to the tin atom. With the tri(1-butyl)tin(IV) compounds the interaction of the oxygen atom of carbonyl group with the tin atom obviously is very weak, and it will not distinctly affect the electronic, bonding, and geometrical relations in the other parts of the molecule; consequently, these compounds behave as tetracoordinated ones in accordance with the ^{13}C and ^{119}Sn NMR and IR spectra. The stronger Lewis acidity of the di(1-butyl)tin(IV) compounds causes a more distinct interaction of the tin atom with oxygen atom of carbonyl group, which results in the parameters of the ^{13}C and ^{119}Sn NMR spectra being consistent with a pentacoordinated tin atom. If, however, the idea of asymmetrical four-membered chelate connection of carboxyl group with tin atom is considered to be justified, it will not be improper to characterize the number of the partners bound to the tin atom in tri- and di(1-butyl)tin(IV) compounds by the coordination numbers five and six, respectively. The idea of asymmetrical chelate connection thus brings certain troubles with determination of the coordination number of the central tin atom, on the contrary, however, it allows a unified and logical explanation of apparently contradictory experimental facts.

In both the types of compounds the tin atom is distinctly incompletely saturated in its coordination, which is indicated by marked differences in the ^{13}C and ^{119}Sn NMR spectral parameters of compounds *Ia* and *IIa* when going from deuteriochloroform solutions to hexamethylphosphoric triamide. The distinct shift of the $\delta(^{119}Sn)$ values to higher field and the increase in $^1J(^{119}Sn^{13}C)$ and $\delta(^{13}C_{(1)})$ are due to formation of much stronger complexes with one and two solvent molecules, resp., and with trans-trigonally bipyramidal[18] and trans-octahedral[19,20] (with respect to the $C_{(1)}$ atoms) coordination, respectively, of the central tin atom. In these complexes the original chelate function of carboxyl group disappears, which is manifested in a down-field shift of the $\delta(^{13}C_{(5)})$ value[23]. The magnitude of these changes correlates with the strength of the original chelate complexes.

The ^{119}Sn NMR spectrum of compound *IIa* measured at 220 K exhibits, besides the original signal (at 300 K) a new one at higher field (~ -200 ppm). We have not enough data for interpretation of this signal yet; it could only be stated that this signal is due to a new particle with a higher coordination number at the tin atom (probably six) and with a stronger connection of the central tin atom with the coordination partners.

DISCUSSION

A characteristical structural feature usually found in molecules and crystals of phenoxyacetates and phenylthioacetates of metals (transition metals in particular) is a five-membered chelate cycle



(M stands for the metal atom) in which an important part is played by the donor–acceptor intramolecular connection of the E atom and the central metal atom M[24]. In the structures of the compounds studied by us this feature is not observed.

At room temperatute, the compounds studied behave like most tri- and diorganotin(IV) carboxylates. The tri(1-butyl)tin(IV) compounds form polymers in solid phase, the quasi-planar $(1\text{-}C_4H_9)_3Sn$ groups (their perfect planarity would necessitate the absence of ν_s(SnC) from the IR spectra) being mutually connected by the oxygen atoms of carboxyl groups. Then the $O—Sn(1\text{-}C_4H_9)_3\cdots O$ grouping has a shape of slightly deformed *trans*-trigonal bipyramid. In non-coordinating solvents these compounds are present in the form of isolated molecules with deformed tetrahedral structure. The deformation is caused by the heterogeneity of the coordination sphere and by the weak interaction of the carbonyl oxygen atom with the central tin atom. In coordinating solvents, stronger complexes are formed with one solvent molecule and with *trans*-trigonally bipyramidal coordination sphere around the tin atom. The di(1-butyl)tin(IV) compounds form, obviously in both solid state and non-coordinating solvents, chelate complexes with considerably asymmetrical function of the two oxygen atoms of carboxyl group and, hence, with a deformed octahedral structure. In hexamethylphosphoric triamide the complexes formed contain two molecules of the solvent. These complexes only contain the monodentate carboxylic groups, they are octahedral, and according to the high $^1J(^{119}Sn^{13}C)$ values they contain the 1-butyl groups in *trans* position.

In none of the structures given we could observe an intramolecular connection of the oxygen or sulphur atom of $C_6H_5ECH_2$ group with the central tin atom. Of course, intermolecular interactions of oxygen atoms of $C_6H_5OCH_2$ groups with tin atoms of other molecules (with formation of dimers or higher associates) cannot be completely excluded. The parameters of the second signal of the ^{119}Sn NMR spectrum which was found with compound *IIa* at low temperatures at higher field (Table III, footnote *f*) could indicate formation of such associates[25]. No analogous phenomenon was observed with the similar compound *IV*, which could be connected with the well-known reluctance of the sulphur atom (in contrast to the oxygen atom) to form additional donor–acceptor connections[26].

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