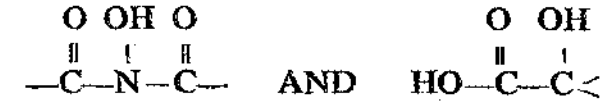
ORGANOTIN DERIVATIVES OF SOME SELECTED LIGANDS CONTAINING



AND SOME RELATED GROUPS

THESIS

SUBMITTED FOR THE DEGREE OF DOCTOR OF PHILOSOPHY (SCIENCE) OF THE UNIVERSITY OF NORTH BENGAL

ASIS ADHIKARI

DEPARTMENT OF CHEMISTRY

UNIVERSITY OF NORTH BENGAL

1990

Dedicated
to the memory
of my
father

A C K N O W L E D G E M E N T

The present thesis contains the results of research work performed by the author in the Department of Chemistry, University of North Bengal, Darjeeling, India.

The author takes the pleasure to express his gratefulness to Dr. A.K.Ghosh, D.Phil, Professor of Chemistry, University of North Bengal, for his guidance and continuous inspiration all through the investigation.

The author is indebted to Dr. S.K. Saha, Senior Lecturer in Chemistry and Dr B. Basu, Lecturer in Chemistry, University of North Bengal for their kind cooperation in obtaining some spectral data and for some useful discussions.

The author is thankful to Dr A.K. Majumder, Scientific Officer, University of North Bengal, for his kind help in the investigation.

He would like to thank his co-workers Mr. T. Pandit and Dr. A. Samad for their valuable help during the investigation for biological studies.

He is also very much thankful to Miss C. Deb for her cordial cooperation in preparing the manuscript. Specific thanks are also due to Mr. M. Chakraborty for typing the manuscript.

The author is also thankful to the Department of Environment, Government of India, for providing the research fellowship and to

the authorities of the North Bengal University for all kind of facilities regarding research work.

Thanks are due to RSIC, Chandigarh and RSIC, NEHU, Shilong for the analysis of the samples and also for some spectral data.

Finally, the author likes to express his deep sense of gratitude to his mother and family members for their constant inspiration.

Department of Chemistry
University of North Bengal
Darjeeling, West Bengal,
INDIA

Asis Adhikari
(ASIS ADHIKARI)

August 1990.

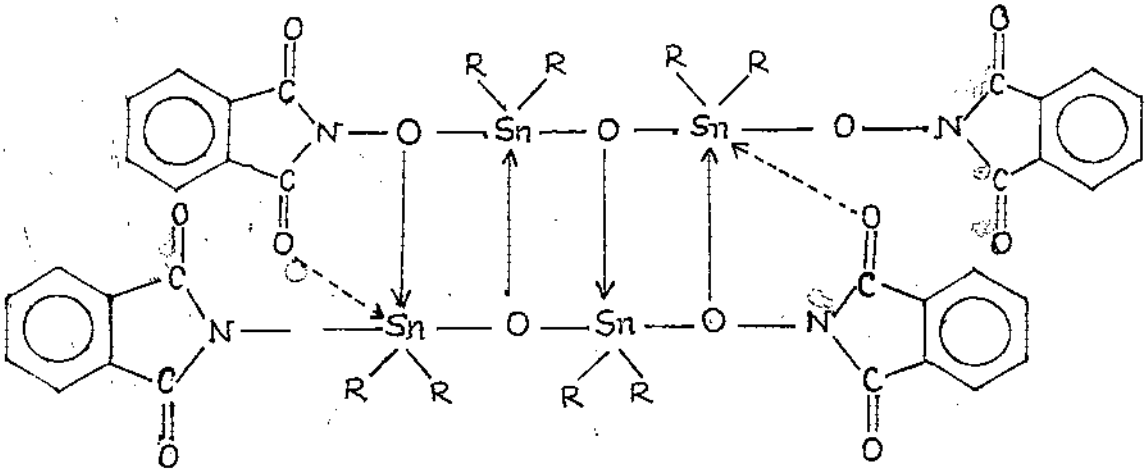
S U M M A R Y

Organotin Chemistry during the last few decades has become very important for its diverse applications. Both from theoretical consideration and practical applications, organotin chemistry has assumed a very significant role in the study of organometallic chemistry.

The present investigation has been divided into three parts. The Part I of this investigation described the preparation and characterisation of few organotin derivatives of N-hydroxy phthalimide and N-hydroxy succinimide. A brief review of the earlier literature relevant to current investigations has been attempted in the beginning of each part of this thesis. As indicated earlier, the first part described the organotin derivatives of N-hydroxy, phthalimide and N-hydroxy succinimide. The triorganotin derivatives of these hydroxamic acids gave monomeric compounds, as indicated from their molecular weight. The elemental analyses and ^{1}H NMR spectral data indicate the molecular composition of these compounds as described later. The IR spectra together with ^{13}C NMR spectra suggest these compounds are of ester type. The carbonyl groups do not significantly coordinates with tin atom. The ^{119}Sn NMR spectra also support the tetra coordinating nature of tin atom in these compounds.

During the preparation of di organotin derivatives of the above mention hydroxamic acids, it was found the diorganotin moieties contain Sn-O-Sn bonds. Moreover, these compounds are probably polymeric in nature. The presence of Sn-O-Sn bond has been indicated from a

band around 576 cm^{-1} in the infrared spectra. The elemental analyses and ^{1}H and ^{13} NMR spectra suggest the diorganotin derivatives of the following type, e.g.



The carbonyl groups may form intermolecular coordination of the tin atoms, making some tin atoms penta coordinate while some tin atoms are hexa coordinate. The contention has been supported by the ^{119}Sn NMR data e.g. in Tetrabutyl 1:3 di-N-hydroxy phthalimido distannoxane, there are two ^{119}Sn peaks at δ -164.46 and -218.87. Attempts have been made to discuss the structures of these type of diorganotin derivatives. The IR spectra and ^{13}C NMR spectra of these compounds probably exclude the possibility of intramolecular carbonyl coordination.

In the second part of these few organotin derivatives diphenyl glycolic acid have been prepared. It was not possible to prepare any triorganotin derivatives of diphenyl glycolic acid. When the reactions of tri organotin chloride were carried out with diphenyl glycolic acid under suitable conditions, only diorganotin derivatives could be obtained. Dimethyltin, dibutyl tin, di propyl tin, dibenzyl tin, diphenyl tin and dicyclohexyl tin derivatives of diphenyl glycolic acids have been prepared. These compounds have been characterised by elemental analyses, IR, NMR (^{1}H, ^{13}C, ^{119}Sn) spectra. The IR spectra indicate both the hydroxylic protons are replaced by organotin moieties. The shifting of carbonyl band indicates strong coordination from $\overset{\overset{O}{\|}}{C} - OH$ group in addition of the replacement of the proton. The ^{13}C NMR spectra also support this contention. The ^{119}Sn spectra suggest the penta coordinating nature of tin in these compounds. But only in case of dimethyl tin derivative of diphenyl glycolic acid, elemental and spectral data suggest that two diphenyl glycolic acid molecule reacted with one molecule of dimethyl tin oxide giving Dimethyl tin bis (diphenyl glycolate). Carbonyl absorption band in the IR spectra is less shifted compared to other diorganotin derivative, suggesting no coordination from the $>C = O$ group of carboxylic acid. ^{119}Sn signal also indicates hexa coordinating tin atom. In absence of X-ray data, for which there was no facility, the structures suggested may be considered somewhat tentative.

The third part of this dissertation described some preliminary results of fungicidal, seed germination studies and acaricidal properties of some of the compounds described in earlier part. It is well known that tri organotin compounds, particularly the tributyl and tri phenyl tin compounds show excellent fungicidal properties. Tri phenyl tin N-hydroxy succinimide and Tributyl tin N-hydroxy phthalimide have tested against two commercially important fungi, Alternaria solani and Helminthosporium oryzae . All these compounds showed excellent fungicidal properties against these two fungi. The ED_{95} values ranged between 0.69 - 1.90 μg/ml (72 hrs) for Alternaria solani, compared to Tributyl tin acetate which has ED_{95} value of 0.96 μg/ml (72 hrs). In case of Helminthosporium oryzae the ED_{95} values were 2.22 - 6.38 μg/ml (72 hrs) compared to Tributyltin acetate 0.96 μg/ml (72 hrs).

The effect of these compounds on the germination of rice seeds have also been studied on a preliminary scale.

The acaricidal properties of Tricyclohexyl tin N-hydroxy phthalimide. Tetra cyclohexyl 1:3 di N-hydroxy succinimido distannoxane, dicyclohexyl tin diphenyl glycolate were studied against some green mite. Compared to 'Plictran (active ingredient Tricyclohexyl tin hydroxide), these showed reduced acaricidal properties.

C O N T E N T S

PART - II

PART - III

***

P A R T - I

I N T R O D U C T I O N

Tin either as a metal or as alloys and chemical compounds, has diverse applications. Organotin chemicals are widely used in industry and represent a significant and growing outlet for tin. Historically, organotin compounds were among one of the first organometallic species to be investigated.

The basic studies in the field of organotin compounds have been developed due to the success of a large number of modern techniques applied to the organotin compounds. Tin possesses, for example, two spin of one half isotopes, ^{117}Sn and ^{119}Sn which become important in nuclear magnetic resonance studies. Tin has ten stable isotopes, which allow the easy identification of the tin-beering fragments in the mass spectrometer. Mossbauer resonance from the ^{119}Sn nucleide can be easily recorded. Further tin-carbon stretching frequencies in the infrared and Raman spectra can be assigned in most cases. The availability of two stable oxidation states, tin (II) and tin (IV), with contrasting chemistries and a wide variety of structural types have afforded a large scope for diverse studies in organotin compounds. Tin (IV) derivatives alone encompass four-, five-, six-, seven- and eight- coordination at tin centre in neutral, cationic and anionic species, with intra and intermolecular association to give dimer and higher polymers with one, two and three dimensional lattice in the solid states, which have provided much interest in extensive studies in these areas.

The annual industrial production of organotin compounds was less than 50 tons per annum in 1950s. But this figure (1) gradually increased to 35000 tons in 1983. The conservative estimate for the current years will be not less than 40,000 tons per annum.

Tin the element having atomic number 50, is a member of group IVA of the periodic table with an electronic configuration $[Kr]\ 4d^{10}5s^{2}5p^{2}$ in the ground state (2). The common four covalent state is derived from sp^{3} hybridisation. The four covalent state occurs far more frequently than the two covalent state and most of the organotin compounds possess a four covalent tin atom in simple compounds.

Organotin compounds were first reviewed by Krause and Van Grosse in 1937 (3). Later, Gilman et al (4) published another review of organotin compounds in 1960. In last two decades or so, innumerable reviews and books have been published in the area of organotin compounds. Mention may be made to some of the representative ones (5-27).

Tin differs from lighter group IVA element in that its d-orbitals are of sufficiently low energy for them to be frequently used in bonding so that tin can readily expand its coordination number above four. As a consequence of this, many organotin compounds exhibit considerable Lewis acid character and can form stable adducts with a number of Lewis bases. Moreover reactions involving nucleophilic attack at tin are facilitated by the formation of

coordinated intermediates which, however, unstable, lower the energy of transition state. The coordination chemistry of organotin compounds was discussed by Poller (28) in 1965 and by Gielen and Sprecher in 1966 (29).

Organotins can form a large number of complex compounds with suitable donor and chelating ligands. The presence of an organic group in a molecule usually diminishes the tendency of organotins to form complexes and hence the observed stability of the complexes should decrease as follows: $SnX_4 > RSnX_3 > R_2SnX_2 > R_3SnX > R_4Sn$. The configuration of the complex readily follows from the type of metal hybridisation involved. In R_4Sn complexes sp^3 hybrid orbital exist and tetrahedral configurations are attained. In SnX_6^{-2} the other limiting case, the six sp^3d^2 - hybrid orbitals of the metal are directed towards the ligands so that the resulting complex will be octahedral. When only one monodentate ligand adds to an organotin molecule, a trigonal bipyramidal complex (coordination number five) may be found through the participation of the sp^3d hybrid orbitals of the metal. A number of compounds have been described by Beletskaya, Butin, Ryabtsev and Reutov (30) which also show agreement with these simple rules, although in many cases, the structures mentioned are often distorted, due to the different nature of the ligands in an organotin complex.

The first organotin compound was prepared by Frankland (31, 32) in 1849 with the preparation of a few crystals of diethyl tin diiodide from the reaction of ethyliodide and metallic tin at 160°. In 1852 Lowig (33) also described the action of ethyl iodide

on a tin sodium alloy. Though he could not detect the formation of tetraethyl tin, he isolated triethyl tin iodide and hexaethyl di tin.

Organotin compounds act as Lewis acid to react with electron pair donor i.e. Lewis base to form addition compound. Stannic halides form thermodynamically stable well known adducts of the type $SnX_4.2L$ (L = ligand) with Lewis bases (34). Mono-, di- and triorganotin compounds can form adducts with mono-, di- and polydentate ligands.

In the last three decades or so, extensive work have been carried out in the area of organotin coordination compounds with bi- and polydentate- ligands. The ligands which formed coordination compounds with organotin moieties were of diverse types. These included β-diketone, diphenyl thiocarbazone, diphenyl carbazone, 8 hydroxy quinoline or its derivatives, kojic acid, Schiff bases, dithiocarbamic acid, substituted hydroxamic acids etc. As illustration of the above type of complex compounds, only few types of the above ligands will be discussed here.

Diorgandin bis acetyl acetonates, $R_2Sn(acac)_2$ have been obtained by adding acetyl acetone (acac) to a mixture of diorganotin dichloride and sodium methoxide in methanol (35). These diorganotin bis β-diketonates can also be obtained by direct reaction of the reactants in the presence of a base (36).

The isolation of several solid organotin dithizonates with mono-, di- and tri- organotin moiety have been reported (37,38).

The organotin dithizonates, $R_3Sn(HDz)$, $R_2Sn(HDz)_2$, $R_2Sn(HDz)X$ and $RSn(HDz)XY$ (R = CH_3, C_6H_5, C_4H_9, C_3H_7, p-tolyl; X = Cl, Br, I, NCS; Y = substituted benzohydroxamic acids; H_2Dz = Dithizone) have been isolated and characterised. Test of triphenyl and tributyl tin dithizonates as fungicides showed very good activity against a number of plant pathogenic fungi (39). The oxygen analogue of dithizone, 1,5-diphenyl-carbazone was also reported (40) to form organotin complexes of the type R_3SnL, R_2SnL_2, $RSnL_3$, R_2SnLX (R = CH_3, C_3H_7, C_4H_9, C_6H_5, p-tolyl, cyclohexyl; X = Cl, Br, SCN and LH_2 = diphenyl carbazone). Some of these triorganotin compounds showed good fungitoxicity (39).

Organotin oxinates of the type $R_{4-n}SnOxin_n$ (R = organic group, Oxin H = 8-hydroxy-quinoline (oxine), n = 1,2,3) (41-45) are prepared either from the organotin halides and sodium/thalium oxinate (41,42) or from organotin halides and oxine itself, the hydrogen halide formed was removed by a base such as ammonia (46) and also by reacting organotin oxide with oxine (47,48). Triorganotin oxinates have also been prepared by triorganotin chloride with a mixture of oxine and sodium methoxide (49). Preparation of bis (penta-fluorophenyl)tin bis oxinates have also been reported (50).

In the crystal structure of dimethyltin bis (8-hydroxy oxinate) which assumes a cis - dimethyl tin group, the oxygen atoms appear trans and the nitrogen atoms are cis (50).

Organotin halide bis oxinate, $RSnX(Oxin)_2$ (R = CH_3, nC_4H_9, C_6H_5 ; X = Cl, Br) have been prepared by reacting organotin trihalides with oxine (1:2 mole) in ethanol followed by neutralisation

with aqueous ammonia or sodium acetate (42,52). Datta (53) has reported phenyl tin halo bis oxinate by reacting diphenyl tin dioxinate with mercuric halides in ether at room temperature. A compound, $[n\text{-}C_4H_9Sn(Oxin)_2]_S$ was prepared from n-butyl tin sesquisulphide and oxine in boiling tolune (54).

Some of the organotin trioxinates have been prepared by using either of the following reactions (45,48):

$$R_2Sn_2O_3 + 6\ Oxin\ H \xrightarrow[benzene]{boiling} 2RSnOxin_3 + 3H_2O$$

$$RSnCl_3 + 3Na\ Oxin \longrightarrow RSn(Oxin)_3 + 3\ NaCl$$

$$(R = C_2H_5,\ C_4H_9,\ C_6H_5)$$

Mehrotra et al (55) prepared butyl tin isopropoxide oxinate by reacting butyl tin tris isopropoxide with 8-hydroxy quinoline.

Organotin derivatives of substituted oxines have also been reported. Srivastova et al (56) have prepared some diaryl tin bis oxinate/2-methyl oxinates and diaryl tin chloride oxinate/2-methyl oxinates. Sen et al (57-59) have synthesised and characterised several diorganotin bis (mono- and di- substituted oxinate). They have also reported the synthesis and spectral studies on mono and triethyl tin (IV) and tri phenyl tin (IV) chelates with substituted 8-quinolinols.

Smith et al (60) have studied the synthesis and Mossbauer spectra of some mixed chelates of diorganotin (IV) complexes of the

type $RR'SnLL'$ ($R = R' =$ Me, Ph, Bu; $R =$ Bu, $R' =$ Ph, $L,L' =$ 8-hydroxy quinolinate, 2 methyl 8-hydroxy quinolinate etc.).

Deb et al (61) prepared a number of complexes of the types R_2SnL_2, $RSnL_2Cl$, R_2SnLCl, $R_2Sn(L'H')_2$, R_2SnL'' and $R_2SnL'''Cl$ (where R = $CH_3OCOCH_2CH_2$-, $C_4H_9OCOCH_2CH_2$- and $CH_3OCOCH(CH_3)CH_2$-; LH = 5-phenyl azo-8-quinolinol, 1-nitroso-2-napthol; $L'HH'$ = 5-(2'-carboxy phenyl azo)-8-quinolinol and $L''H_2$ = 1,2 dihydroxy anthraquinone) and a thiocyanate derivative.

Deb and co-workers (62) also prepared a number of complexes of the type R_2SnL_2, R_2SnLX, R_2SnL_2X and $RSnL_3$ where R = $CH_3CO_2CH_2CH_2$, $C_4H_9CO_2CH_2CH_2$, $CH_3CO_2CH(CH_3)CH_2$ or $CH_3COCH_2C(CH_3)_2$, X = Cl or SCN and L = Oxine, 5,7-dichloro oxine and 5,7-dibromo oxine.

Kojic acid can form complex with organotin compounds. Dimethyl tin bis kojate was prepared by the reaction of $(CH_3)_2SnCl_2$ and kojic acid (1:2 mole). Methyl tin chloride and methyl tin bromide bis kojates have been prepared by Otera et al (63).

Organotin halides or oxides can react with bidentate, tridentate and tetradentate Schiff bases (64-68). Tandon and co-workers (69) have been synthesised some five and six-coordinated di- and tributyl tin (IV) complexes Bu_2SnL, Bu_2SnL_2 and Bu_3SnL (where L is the anion of a monofunctional bidentate or bifunctional tridentate Schiff bases). These complexes were shown to be highly active towards bacteria.

Organotin dithiocarbamates were prepared by reaction of organotin chloride with sodium dithiocarbamate. Organotin dithio-

carbamates with different types of alkyl and aryl groups have been prepared by Srivastava et al and others (70-82). Some of these compounds showed considerable biological activities, alkyl and aryl tin (IV) mono thio carbamates have also been reported by Majee et al (83).

A number of organotin tropolonate complexes of the type R_3SnT, R_2SnXT, R_2SnT_2 and $RSnXT_2$ (R = alkyl or Ph; X = Cl, Br, I; HT = Tropolane) have been prepared where the tropolane acts as bidentate chelating agent bonding through both oxygen atoms. Diorganotin bis tropolonates have been prepared (84,85) by the following reactions:

$$R_2SnCl_2 + 2NaT \longrightarrow R_2SnT_2 + 2NaCl$$

$$R_2SnT_2 + 2TlT \longrightarrow R_2SnT_2 + 2TlCl$$

Phenyl tin tris tropolonate and phenyl chloro tin bis tropolonate have been prepared by reacting phenyl tin tri chloride in benzene with a solution of tropolone in ether (86).

The hydroxylamine derivatives of organotin have been initiated by Harrison et al (87,88).

Diorganotin derivatives of N-substituted benzo hydroxamic acids have been prepared (89-92) by the reaction of diorganotin oxide and hydroxamic acid (liberated hydrochloric acid was neutralised by 25% aqueous ammonia).

Phenyl tin halide bis (N-phenyl benzo hydroxamates), phenyl tin thiocyanate bis (N-phenyl benzo hydroxamate have been prepared (92).

A part of the present investigation have been carried out on organotin derivatives of N-hydroxy succinimide and N-hydroxy phthalimide, which may be considered as hydroxamic acids. So detailed discussions on hydroxamic acids and their organotin compounds would be relevant here.

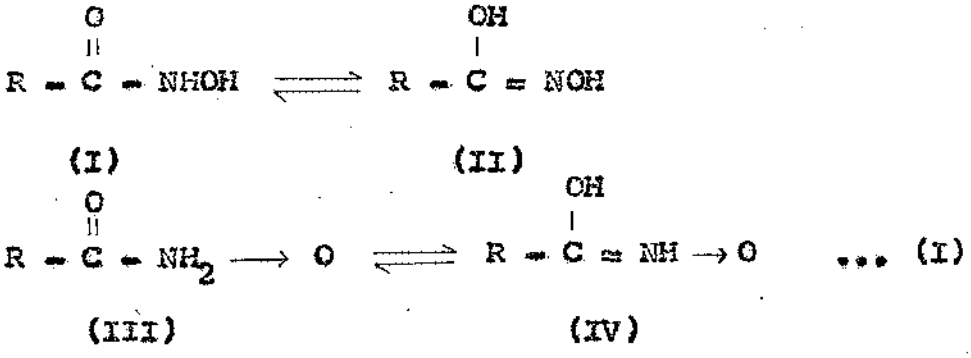
The hydroxamic acids were known for over a century (93) and a considerable body of literature exists on the subject, though the study of their chemistry and practical applications lagged for some years.

The increasing interest in hydroxamic acids has been attributed, in part, to work on cycloserine (D-4-amino-3-isoxazolidone, "oxamycin") (94), ferrichromes (93), work on the acceleration of hydrolysis of organic fluorophosphates and fluorophosphonates such as sarin (isopropyl methyl phosphono-fluoridate) by hydroxamic acids (96). Various analytical applications (based either on the characteristic colour formed on reaction of hydroxamic acids with ferric chloride solution or their ability to act as chelating agents), uses as floation agents, and biochemical or medicinal studies have been investigated. Polymeric hydroxamic acids have received some attention as ion-exchange resins (97).

Sandler and Karo have published a review on the chemistry of hydroxamic acid in 1972 (98). The first stereochemical concepts of hydroxamic acids were proposed by Werner (99) who carefully differentiated between hydroxamic acids and their tautomers, the hydroximic acids.

(I) (II)

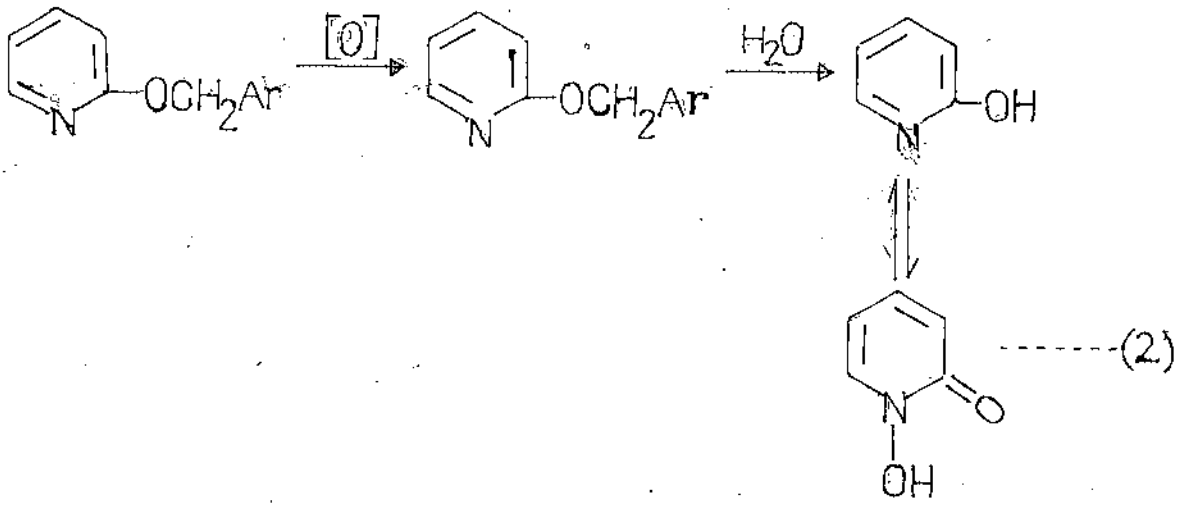
The above structure may be in equilibrium also with other tautomeric forms:



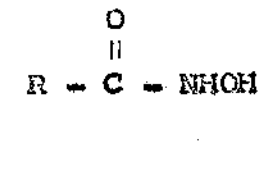
(I) (II)

(III) (IV)

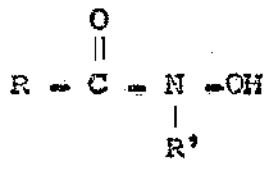
Structure (II) termed as hydroxamic acids constitute only a minor component of the tautomeric equilibrium mixture although derivatives of hydroxamic acids are well known. Structure (III) and (IV) have been added to the list of possible tautomeric forms relatively recently (100,101). Their importance becomes obvious from the standpoint of the preparation of cyclic hydroxamic acid. For example N oxidation of an appropriately constituted molecule may produce a cyclic hydroxamic acid (102):



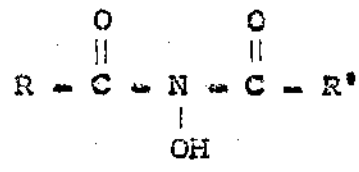
The variety of substituted hydroxamic acid is surprisingly large. If we consider only the structures which may be written upon alkylation and/or acylation of hydroxylamine but ignore the tautomeric derivatives, the following compounds result:

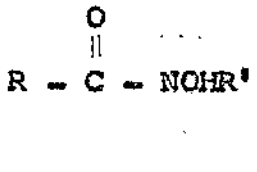


(I)

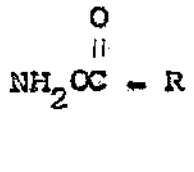


(V)

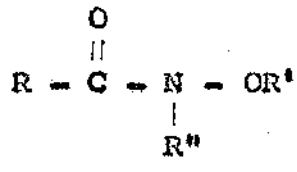




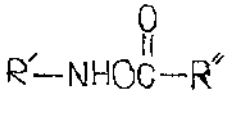
(VII)



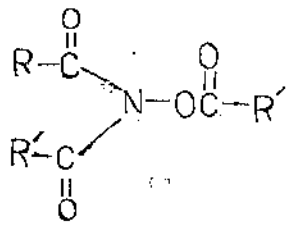
(VIII)



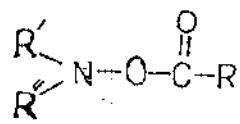
(IX)



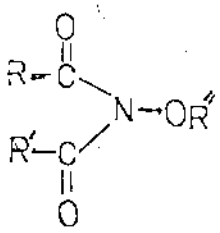
(X)



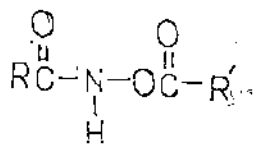
(XI)



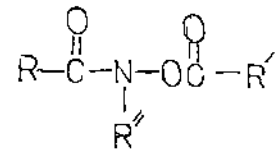
(XII)



(XIII)



(XIV)



(XV)

Compounds such as (VII), (IX) and (XIII) are esters of hydroxamic acids and in the case of structure (VII) are alkyl hydroxamates.

When the distribution of electrons of hydroxamic acid and hydroximic acids are considered it will be noted that several sites exist with which these compounds may act as neucleophilic agents.

Furthermore the hydroxamic acid may act as chelating groups. The classical colour test for hydroxamic acid with ferric chloride involves chelation. Also a common method of isolating these compounds by precipitation with cupric ions frequently referred to as a formation of copper chelates. Because of its unusual electron distribution, the chemistry of hydroxamic acid is complicated.

The acid strength of hydroxamic acids has been reported to be the same order of magnitude as that of the carboxylic acids. At least some of these acids are said to be soluble in sodium bicarbonate solution.

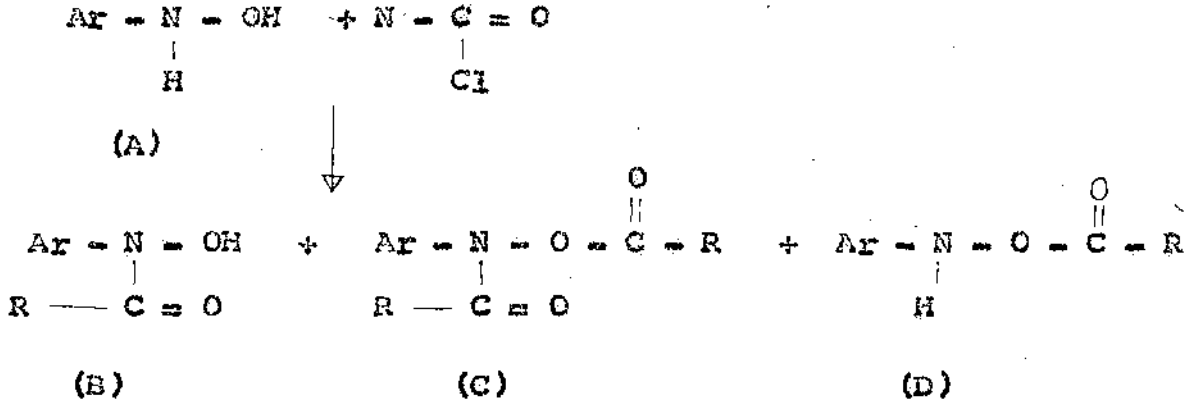
Hydroxamic acids may be prepared by treating esters, acid chlorides or acid anhydrides with hydroxylamine (103) in the presence of alkali and the free acid is obtained by the addition of acid in the appropriate quantity in cold solution.

$$RCO_2Et + NH_2OH + KOH \longrightarrow RCONHOK + EtOH + H_2O$$

$$RCONHOK + HX \longrightarrow RCONHOH + KX$$

The general method employed in the synthesis of N-aryl hydroxamic acids are outlined by Yale (103) in a review work.

One of the widely used procedures for the preparation of hydroxamic acids is based on Schotten-Baumann reaction (104). This involves the partial acylation of the N-aryl hydroxylamine (A) with acid chloride in aqueous (105) or benzene (106,107) or diethyl ether medium (108,109).



The course of acylation is very sensitive to the proper choice of experimental conditions, otherwise the concommitant formation of disubstituted hydroxamic acid (and possibly the O-acetylated aryl hydroxylamine, D) takes place.

Most of the workers isolated the desired mono derivative (B) from the crude product by tedious and repeated extraction with concentrated ammonium hydroxide, in which the di derivative (and D, if present) is insoluble. Subsequent acidification with hydrochloric acid (110) of the ammoniacal solution liberates the hydroxamic acid.

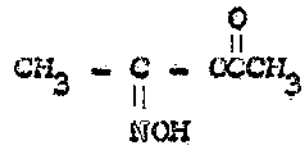
On the basis of Schotten-Baumann reaction, Tandon and co-workers (111, 112) have prepared several N-aryl hydroxamic acids by reacting phenyl hydroxylamine (PhNHOH) with acyl chloride or its derivatives ($R'COCl$) in the presence of dilute alkali.

$$RNHOH + R'COCl + NaOH \longrightarrow R-N(-OH)-C(=O)-R' + NaCl + H_2O$$

Ghosh and Sarkar have synthesised succinyl bis N-phenyl hydroxamic acid (113) and adipyl bis N-phenyl hydroxamic acid (114) with phenyl hydroxylamine and corresponding acid chlorides in ice cold diethyl ether using a base (pyridine).

The acid anhydrides and acyl halides have been used to prepare hydroxamic acids. Because of the reactivity of these reagents, frequently there is a loss of desired product because diacylation may take place to produce N, N-diacylhydroxylamines.

There is some evidence that acyl halides and anhydrides initially acylate the hydroxyl oxygen. This reaction is followed by a more or less rapid rearrangement from the O-acyl hydroxylamine to the hydroxamic acid (115). In the case of acylation with anhydrides, it has also been proposed that "diacetyl hydroxamic acid" forms initially (116).



A series of hydroxamic acid may be prepared by this method using different solvent, temperature and period of reaction.

There are many other methods for the preparation of hydroxamics beyond those are described above. These are as follows:

Acylation of hydroxylamine with amides (117-120) or nitriles (121).

The hydroxylamine derivatives of organotin has been synthesised by Harrison (87, 88) by the azeotropic removal of water from the mixture of appropriate hydroxylamine and the organotin oxides or hydroxides.

$$(R_3Sn)_2O \text{ or } R_3SnOH + HONR'R'' \longrightarrow R_3SnONR'R'' + H_2O$$

(where R = Me, R' = R'' = Et; R' = Ph, R'' = COPh;
R = N-Pr, R' = Ph, R'' = COPh; R = Ph, R' = Ph, R'' = COPh;
R = Me, R' = H, R'' = COPh; R = n-Pr, R' = H, R'' = COPh).

However, attempts to prepare $Ph_3SnONHCOPh$ by the same method only resulted in the formation of tetraphenyl tin in high yield, presumably by a disproportion reaction although no pure diphenyl tin derivatives could be isolated.

$$Ph_3SnOH + HONOHCOPh \xrightarrow{-H_2O} Ph_3SnONHCOPh$$

$$Ph_4Sn + [Ph_2Sn(ONHCOPh)_2]$$

The organotin derivatives of N-benzoyl hydroxylamines are extremely stable in moisture. The $Ph_3SnONPhCOPh$ is monomeric in both crystal and solution phases, whereas the trimethyl tin derivatives are associated in the solid (87,88).

Diorganotin derivatives of N-substituted benzo hydroxamic acids have been prepared(89-92) according to the following reaction scheme:

$$R_2SnO + 2HONR'R'' \longrightarrow R_2Sn(ONR'R'')_2 + H_2O$$

$$R_2SnCl_2 + 2HONR'R'' \longrightarrow R_2Sn(ONR'R'')_2 + HCl$$

(R,R',R'' = alkyl or aryl).

The liberated hydrochloric acid was neutralised by 25% aqueous ammonia and removed as precipitated ammonium chloride.

Phenyl tin halide bis (N-phenyl benzo hydroxamates) have been prepared by the reaction of triphenyl tin N-phenyl benzo hydroxamate with mercuric chloride, mercuric bromide and mercuric iodide (92).

Phenyl tin thiocyanate bis (N-phenyl benzohydroxamate) has been prepared (92) from the corresponding chloride by the displacement of chloride by thiocyanate.

$$PhSnCl(PBHA)_2 + KCNS \longrightarrow PhSn(CNS)(PBHA)_2 + KCl$$

(HPBHA = N-phenyl-N-benzohydroxamic acid).

Compounds of the type $R_2SnX(PBHA)$ have also been prepared by Pradhan and Ghosh (92, 123) where R = Ph, X = Cl, I, SCN; R = Bu, X = SCN) through disproportion reaction.

$$R_2SnX_2 + R_2Sn(PBHA)_2 \longrightarrow 2R_2SnX(PBHA)$$

But $Ph_2Sn(SCN)(PBHA)$ has been prepared by the reaction of corresponding chloride complex with KCNS (124).

$$Ph_2SnCl(PBHA) + KCNS \longrightarrow Ph_2Sn(SCN)(PBHA) + KCl.$$

Pradhan and Ghosh (92) have shown that penta coordinated diorganotin halide N-phenyl-N-benzo hydroxamates disproportionate to the more stable hexa coordinated tin compounds when refluxed with non polar solvent like benzene for long time.

$$Ph_2SnX(PBHA) \longrightarrow PhSnX(PBHA)_2 + Ph_3SnX$$

(where X = Cl, SCN).

However in polar solvents like methanol, $Ph_2SnX(PBHA)$ was found not to give any triphenyl tin halide and $PhSnX(PBHA)_2$ instead another hexa coordinated compound phenyltin halide. Methoxy N-phenyl benzo hydroxamate was found along with the liberation of one equivalent of benzene (92).

The methoxy compound was also obtained when phenyl tin halide bis-N-phenyl benzohydroxamate was refluxed in methanol with the liberation of one mole of ligand (92).

$$Ph_2SnX(PBHA) \xrightarrow{\text{in } CH_3OH} PhSnX(OCH_3)(PBHA) + C_6H_6$$

$$PhSnX(PBHA)_2 \xrightarrow{\text{in } CH_3OH} PhSnX(OCH_3)(PBHA) + HPBHA.$$

Some mono organotin derivatives of hydroxamic acids was prepared by Narula and Gupta (124). They have synthesised five, six and seven coordinated mono organotin derivatives of hydroxamic acid. They have isolated the compounds of the general formulae $R_2Sn_2O_2L_2 \cdot (RSnL_2)_2O$ [LH = hydroxamic acid derivatives].

Harrison et al (125) have prepared a number of organotin hydroxamates following the usual procedures (87,88). These compounds are of the types R_2SnL_2 (where R = Me, n-Bu, n-Octyl, Ph and LH = N-benzoyl N-phenyl (hydroxylamine), R_2SnXL (where R = Me, X = Cl, Br, I) and $RSnL_3$ (where R = n-Bu).

Chaudhuri, Roy and Ghosh (126) also synthesised organotin hydroxamate of the type R_2SnL_2, R_2SnXL and $RSnXL_2$ (where R = methyl, butyl; X = Cl^-, Br^-, I^-, SCN^- and LH = N-phenyl p-chloro benzo hydroxamic acid) and nine new organotin N-phenyl p-nitro benzo hydroxamates (127) of the types R_2SnL_2 and R_2SnXL (where R = methyl, butyl; X = Cl, Br, I, SCN and LH = N-phenyl-p-nitro benzo hydroxamic acid). These compounds have been characterised on the basis of their elemental analyses, molar conductance, IR and PMR spectral data.

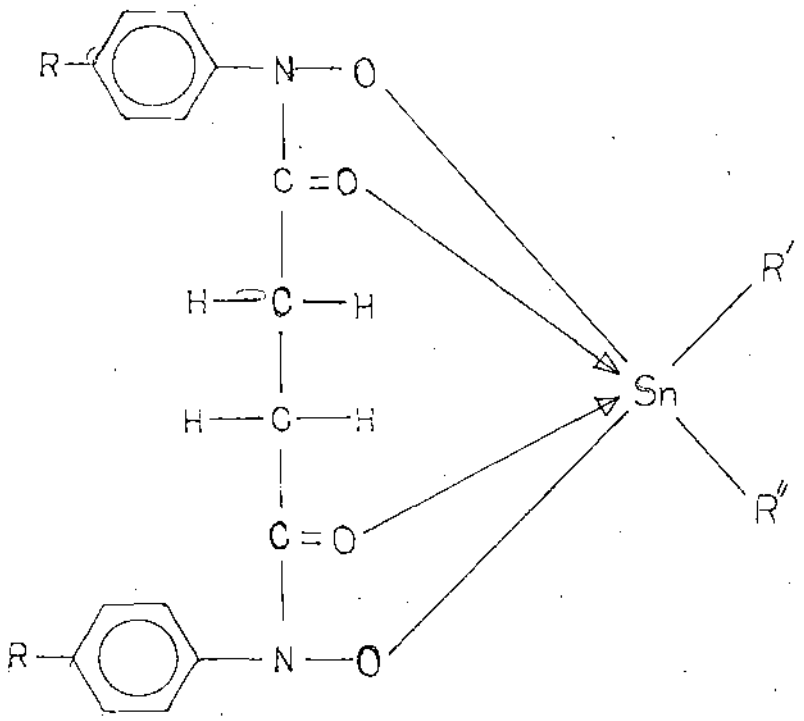
They have also synthesised (128) two new ligands viz. oxalyl bis N-phenyl hydroxamic acid (L) and oxalyl bis N-p-tolyl hydroxamic acid (L'). These have been used to prepare some new types of organotin coordination compounds.

$(R_3Sn)_2L$ (R = phenyl), $(R_3Sn)_2L'$ (R = phenyl, cyclohexyl), $(R_2SnL')_n$

(R = phenyl, butyl, benzyl), $\left[(R_2SnCl)_2L\right]_2$ and $\left[CR_2SnCl)_2L'\right]_2$ (R = p-tolyl). Some of these derivatives are polymeric in nature.

Recently a series of organotin derivatives of hydroxamic acids derived from succinyl glutaryl and adipyl chlorides have been synthesised (129).

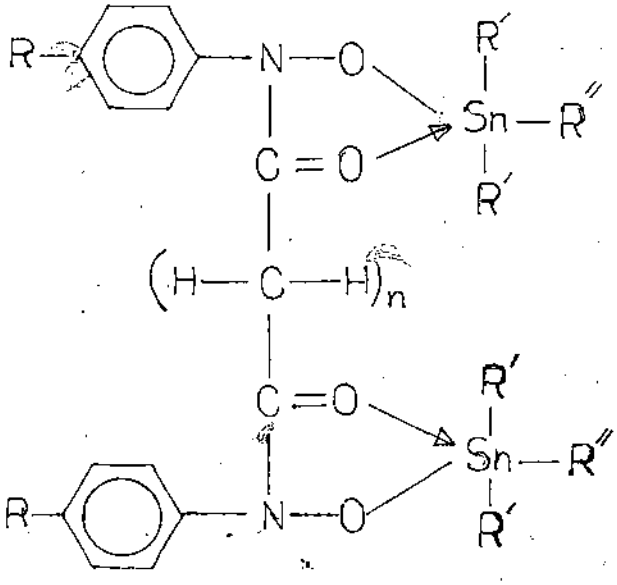
Some of these hydroxamic acids behave as tetradentate ligands



R = H, CH_3 ; R' = phenyl, benzyl, butyl

R'' = phenyl, benzyl, butyl, Cl.

while some of these behave as double bidentate ligands, e.g.



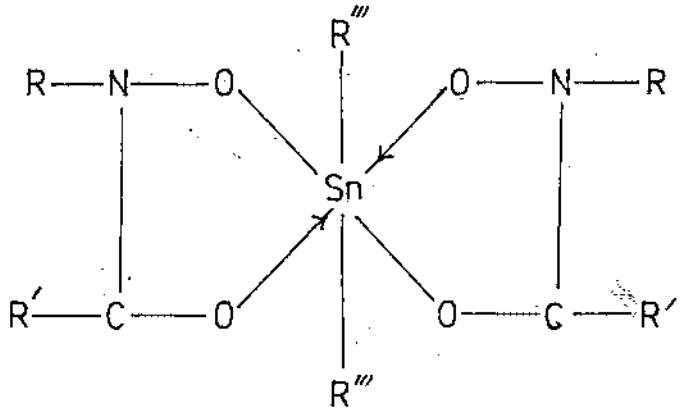
R = H, CH_3 ; R' = Cy, Me; R'' = Cy, Cl

n = 2,3.

The organotin hydroxamates have shown good biocidal properties, which will be discussed later.

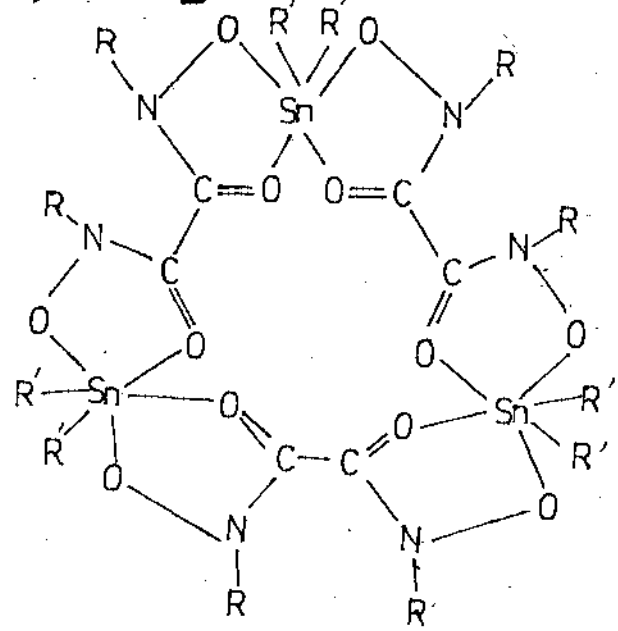
S C O P E A N D O B J E C T I V E

From earlier discussions it can be seen that substituted hydroxamic acids yield a number of organotin derivatives. In these derivatives, the hydroxamic acids behave as bidentate, doubly bidentate or tetradentate ligands, e.g.

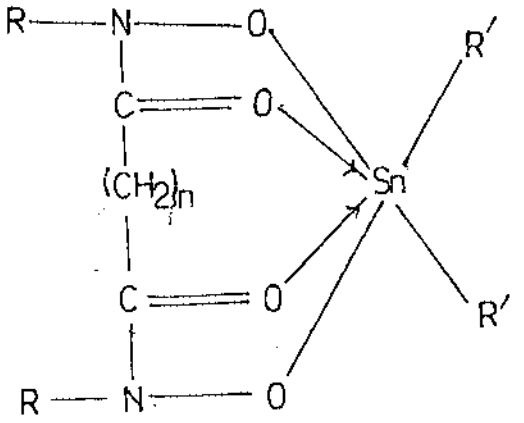


[R = R' = Ph, NO_2-C_6H_4 -, ClC_6H_4 - etc

R''' = Me, Bu, Ph, Bz etc]



R = Ph pCH_3-C_6H_4 , R' = phenyl

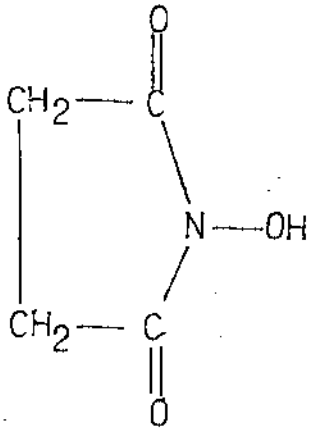


R = Phenyl, p-tolyl

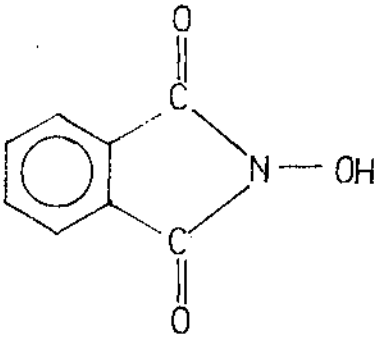
R' = phenyl, benzyl, methyl, butyl, Cl,

n = 2,3,4.

But so far no organotin hydroxamates has been isolated, where hydroxamic acids behave as tridentate ligands. N-hydroxy succinimide and N-hydroxy phthalimide have three coordinating positions available, though they may not behave for an ideal tridentate ligands due to steric reasons.



(N-hydroxy succinimide)



(N-hydroxy phthalimide)

In the present investigation, it was proposed to investigate the organotin derivatives of N-hydroxy succinimide and N-hydroxy phthalimide to see whether coordinated chelate compounds involving coordination from one of two carbonyl groups can be obtained, with simultaneous replacement of the proton of the N-OH group. In such case, one would expect, the other carbonyl group may not be involved in chelate formation. In coordination from both the carbonyl groups takes place, the resultant organotin derivative will contain a tridentate hydroxamic acid ligands. In case none of the carbonyl group coordinates with the organotin moiety, the resultant compound may result as an ester of hydroxamic acid by replacing the proton of the N-OH group. For stoichiometric reasons, there might be a possibility of the formation of distannoxyl derivative of N-hydroxy hydroxamic acids. Results so far obtained indicate monomeric tri organotin N-hydroxy succinimide or N-hydroxy phthalimide could be obtained, where as diorganotin derivatives yield polymeric stannoxane derivatives. In all cases, none of the carbonyl groups of any of these ligands provide significant intramolecular coordination.

E X P E R I M E N T A L

Tin was estimated gravimetrically by conversion to Sn(IV) oxide and finally to volatile stannic iodide, essentially by the method of Vander Kerk and Luijten (130).

Analysis of the compounds for carbon, hydrogen and nitrogen were carried out at Regional Sophisticated Instrumentation Centre, Punjab University, Chandigarh and Central Drug Research Institute, Lucknow.

UV spectral data were taken in Shimadzu UV - 160 Spectrophotometer. "Uvasol" (Merck) methanol was used as solvent.

Conductance measurement have been carried out in PYE UNICAM conductivity meter (PW 9509) using "Uvasol" methanol.

The infrared spectra have been taken in the range between 4000-500 cm^{-1} for most of the compounds using Beckmann IR-20 and Pye-Unicam-SP-300S infrared spectrophotometer equipped with KBr optics and mulling the compounds in nujol. Few IR spectra have also been recorded in the range between 4000-200 cm^{-1} at RSIC North East Hill University, Shillong, Meghalaya in PERKIN ELMER F.T. Infrared spectrophotometer (error limit = $\pm$ 5 cm^{-1}).

The following abbreviations have been used to express the intensity of the IR absorption bands:

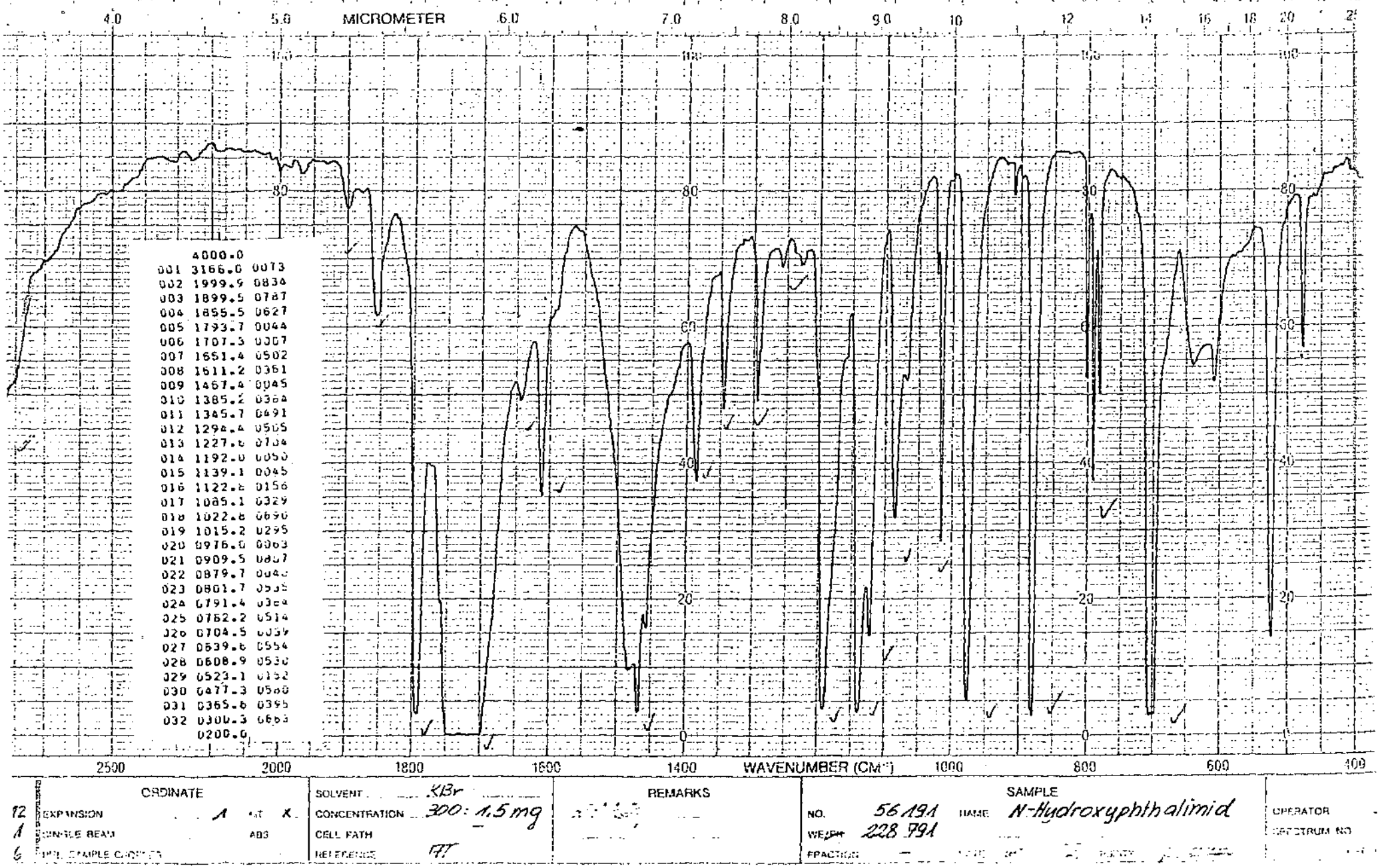
V.S. = very strong, S = strong, m = medium, w = weak, b = broad, sh = shoulder, h = hump, nujol had peaks at 3000-2800 cm^{-1} (V.S.) 1460 cm^{-1} (s), 1376 cm^{-1} (m).

Some ^{1}H NMR have been recorded in VA-EM-390; 90 MHz NMR Spectrophotometer at RSIC, North East Hill University, Shillong using $CDCl_3$ and in some cases DMSO-d_6 as solvent.

The ^{13}C, ^{119}Sn and some ^{1}H NMR spectral data were obtained (through the courtsey of Dr. D.J. Greenslade) with Bruker WP 80 SY Multinuclear 80 MHz FT NMR Spectrophotometer and JEOL PMX 60 SI CW ^{1}H Spectrophotometers at the Department of Chemistry and Biological Chemistry, University of Essex, Colchester, U.K. $CDCl_3$ was used as the solvent and TMS as reference unless otherwise mentioned. In case of ^{119}Sn NMR spectra chemical shifts were recorded against tetramethyl tin.

Preparation of Starting Materials:

All the solvents viz benzene, petroleum ether (boiling range 60°-80°C), chloroform, diethyl ether, methanol etc. used in the experiments, were purified and dried according to the methods described in Vogel's Practical Organic Chemistry (131). Tributyl tin oxide, dibutyl tin dichloride, dibutyl tin oxide, dimethyl tin oxide, triphenyl tin chloride, diphenyl tin dichloride and N-hydroxy phthalimide were Alfa/Fluka products, and were used without further purification in most cases. All the melting points reported here are uncorrected.



ORDINATE	SOLVENT KBr	REMARKS	SAMPLE
72 EXPANSION 1 %T X	CONCENTRATION 300 : 1.5 mg		NO. 56191 NAME N-Hydroxyphthalimid
1 SINGLE BEAM ABS	CELL PATH		WEIGHT 228.791
6 [illegible]	REFERENCE KBr		FRACTION

OPERATOR

SPECTRUM NO

IR spectrum of N-Hydroxy phthalimide (KBr)

1. Dibenzyl tin dichloride

Dibenzyl tin dichloride was prepared by the method of Sisido et al (132). It was recrystalised from ethyl acetate and dried in air.

mp 161 [lit (132) mp 164°C]

% Analyses for $C_{14}H_{14}SnCl_2$

Found :	C 44.95	H 3.60
Calcd :	C 45.16	H 3.76

2. Diphenyl tin Dichloride

Diphenyl tin dichloride was prepared by the method of Gilman et al (133) and was recrystalised from pet ether. It was air dried and had mp 42-44°C (lit mp 41-43°C).

3. Diphenyl tin Oxide

Polymeric diphenyl tin oxide was prepared by the reaction of diphenyl tin dichloride with 50% excess of NaOH as described by McLean. This was dried in air and finally in vacuum at room temperature for 12 hours.

4. bis (Triphenyl tin) oxide

It was prepared by the reaction of triphenyl tin chloride with 50% excess of NaOH, as described by McLean et al (134). It was dried in air and finally in vacuum at room temperature for 12 hours.

mp 122-24°C.

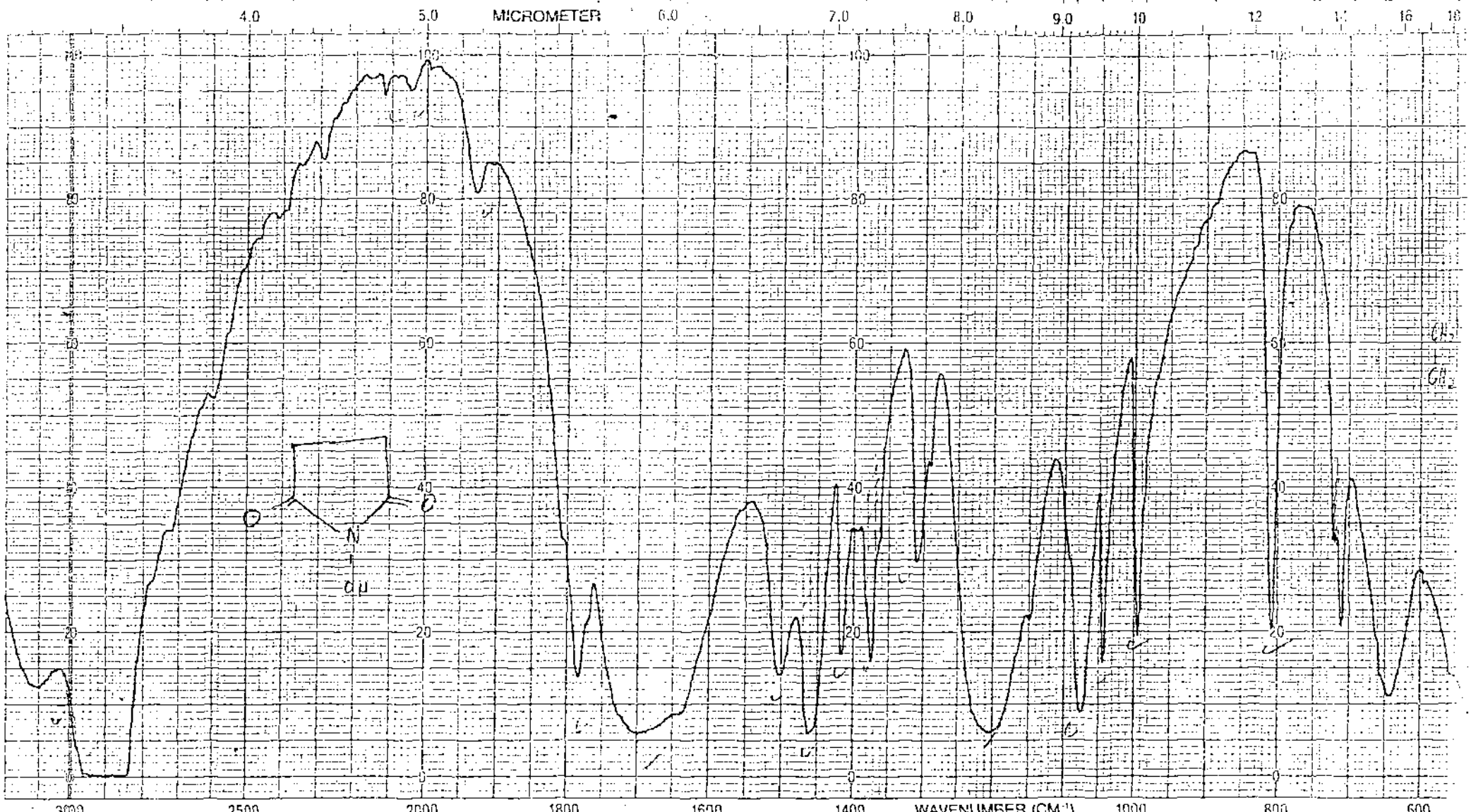
5. Succinic Anhydride

Succinic anhydride was prepared by the methanol described Sandler and Karo (135). To a flask equipped with a reflux condenser topped with a tube leading in an HCl trap is added 118 gm (1.0 moles) of succinic acid and 235 gm (215 ml, 3.0 moles) of acetyl chloride. The contents are refluxed for 2-3 hours, cooled, the anhydride filtered, washed twice with 75 ml of cold ether, and dried under reduced pressure to afford 93-95 gm (93-95%), mp 118°-119°C (lit 119-120°C).

6. N-Hydroxy succinimide

N-Hydroxy succinimide has been prepared following the method of Kung-Tsung Wang et al (136).

A freshly prepared solution of sodium (6.70g, 0.291g atom) in methanol (100 ml) was poured into a stirred suspension of finely ground hydroxylamine hydrochloride (22.2g, 0.291 mole) in methanol (100 ml). The mixture was refluxed on a steam bath for 15 minutes, chilled in an ice bath for 15 minutes and filtered to remove precipitated sodium chloride. Succinic anhydride (29.1g, 0.291 mole) was added in small portions over a several minute period to the stirred hydroxylamine filtrate and the resulting liquid was boiled for 2 hours. Excess solvent was removed by distillation, tolune (1200 ml) was mixed with the viscous N-hydroxy succinimic acid and refluxing was continued for another 4 hours. During the period, a Dean-Stark Water separator was used to collect a mixture of methanol tolune water (200 ml). The hot solvent was decanted,



SCAN TIME 17	ORDINATE	SOLVENT	REMARKS	SAMPLE
RESPONSE	EXPANSION	CONCENTRATION	richly	NO. 56480 NAME N-Hydroxysuccinimid
	SINGLE BEAM	CELL PATH		WE/PR 29035
				DATE

IRspectrum of N-Hydroxy succinimide (KBr)

and on standing deposited crude N-hydroxy succinimide, mp 86-92°C. The residual solid in the reaction flask was extracted with a combination of tolune mother liquor and methyl ethyl ketone (100 ml) and on concentration and cooling afforded a second crop of product. The compound was further crystalised from ethyl acetate to find 16.5g (49%) of white flakes mp 97-98°C. [lit (136) mp 98°C].

Important Infrared spectral data (cm^{-1}):

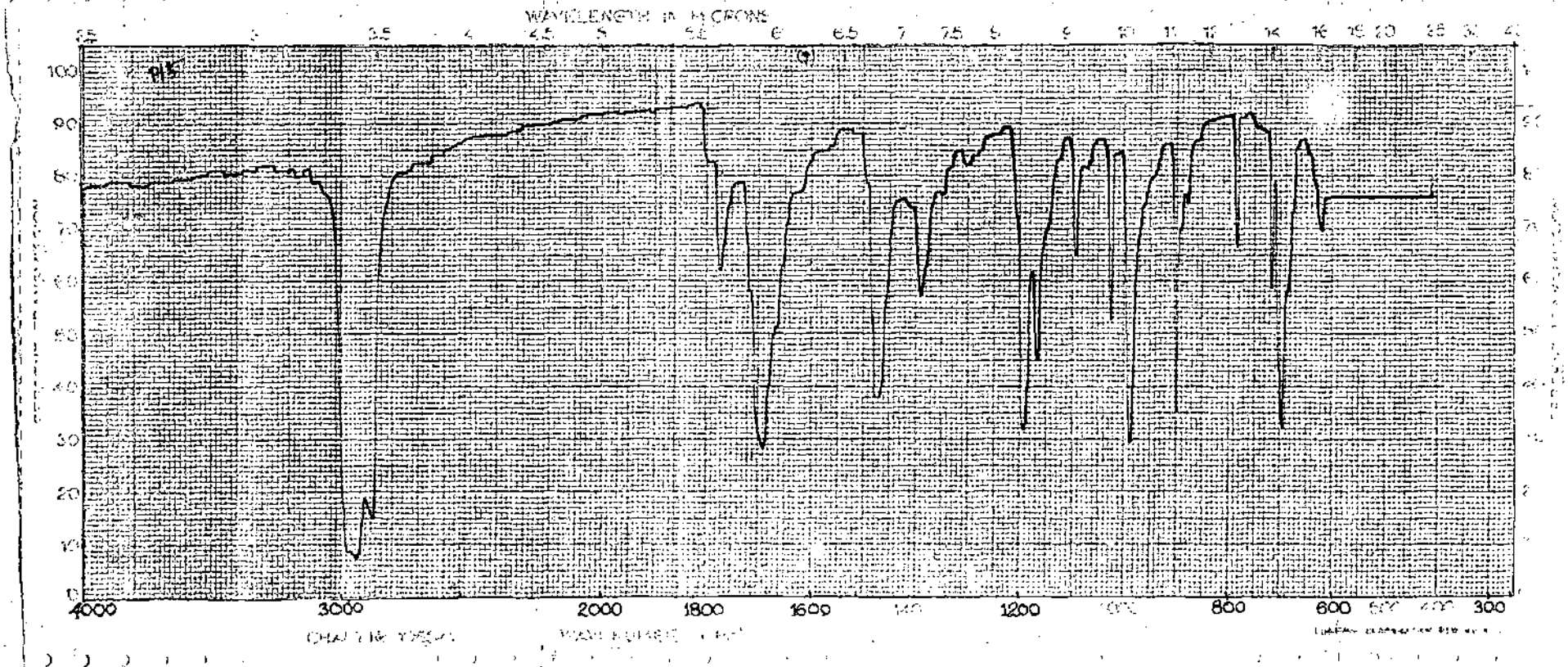
3000(b), 1775(s), 1700(b), 1420(s), 1365(s), 1310(w), 1220(b), 1070(s), 995(s), 810(s), 710(s), 645(s).

7. Tributyl tin N-hydroxy phthalimide

N-Hydroxy phthalimide (652 mg, ~ 4 m.moles) and bis tri n-butyl tin oxide (1.192g, ~ 2 m.moles) were taken in a 250 ml round bottom flask, 150 ml benzene was poured in it. The mixture was refluxed for 4 hours with a Dean Stark Water separator. The colour of the solution gradually changed to deep yellow. The reaction mixture was cooled and filtered. The clear yellow filtrate was concentrated to about 15 ml. On keeping overnight, deep yellow crystals appeared.

(Yield = ~70%)

The crystals were dissolved in minimum volume of chloroform, warmed and then a few drops of methanol were added. A yellow crystalline product appeared. The compound was further purified by repeated crystallisation from chloroform methanol mixture.



IR spectrum of Tributyl tin N-hydroxy phthalimide (nujol)

The compound melted at 86-87°C.

% Analysis for $C_{20}H_{31}O_3NSn$

Found :	C 52.21	H 6.67	N 2.89	Sn 25.84
Calcd :	C 53.09	H 6.85	N 3.09	Sn 26.32

Important Infrared Spectral data (cm^{-1}):

1770(m), 1700(s), 1300(w), 1200(s), 1170(w), 1100(m), 1030(m), 990(s), 700(s), 800(m), 710(s), 680(w), 620(w).

8. Triphenyl tin N-hydroxy phthalimide

N-Hydroxy phthalimide (652 mg; ~ 4 m.moles) and bis (triphenyl tin) oxide (1.432g, ~ 2 m.moles) were taken in 150 ml benzene in a 250 ml round bottom flask. The mixture was refluxed for 4 hours with a Dean-Stark Water Separator. The colour of the reaction mixture changed to yellow. The reaction mixture was allowed to cool and filtered. The filtrate was concentrated to about 10 ml. Yellow crystals appeared on keeping the solution overnight.

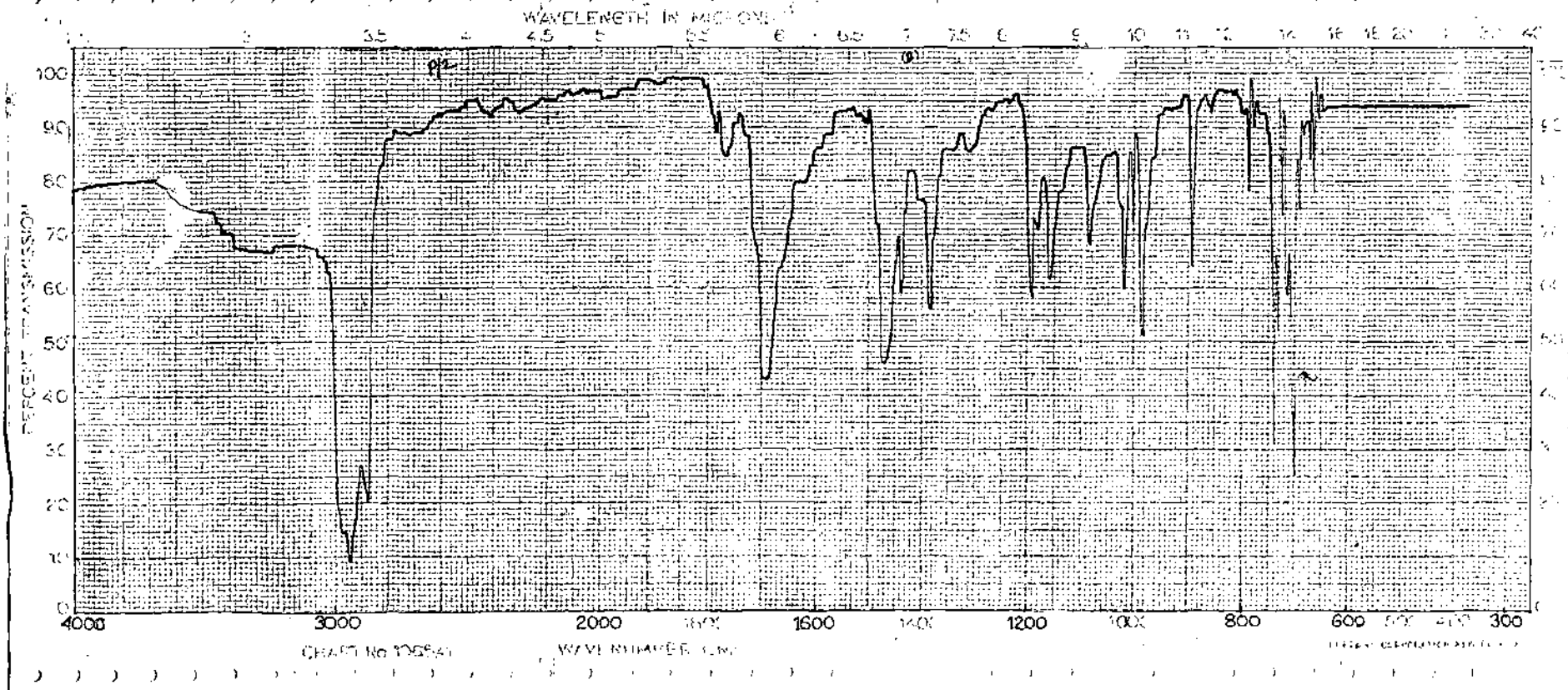
(Yield = ~55%)

The compound was purified by repeated crystallisation of the product from chloroform methanol mixture. It was dried in vacuum.

The compound was found to melt at 115-116°C.

% Analysis for $C_{24}H_{19}O_3NSn$:

Found :	C 59.95	H 3.60	N 2.55	Sn 22.86
Calcd :	C 60.93	H 3.71	N 2.73	Sn 23.24.



IR spectrum of Triphenyltin N-hydroxy phthalimide (nujol)

Important Infrared Spectral Data (cm^{-1}):

1770(w), 1690(s), 1190(m), 1160(m), 1080(m), 1020(m), 1000(w), 990(s), 890(m), 790(w), 740(s), 700(s), 660(m).

9. Tricyclohexyl tin N-hydroxy phthalimide

A mixture of tricyclohexyl tin hydroxide (1.54g; ~4 m. moles) and N-hydroxy phthalimide (652 mg; ~4 m. moles) was taken in a 250 ml round bottom flask. 150 ml benzene was poured in it. Refluxing was carried out for 4 hours as described earlier. During refluxing the colour of the solution changed to yellow. It was cooled and filtered. The filtrate was concentrated to ~ 15 ml. Pale yellow crystalline product appeared on keeping overnight. The pure compound was obtained by repeated crystallizations from the same solvent and it was dried in vacuum.

(Yield = ~60%)

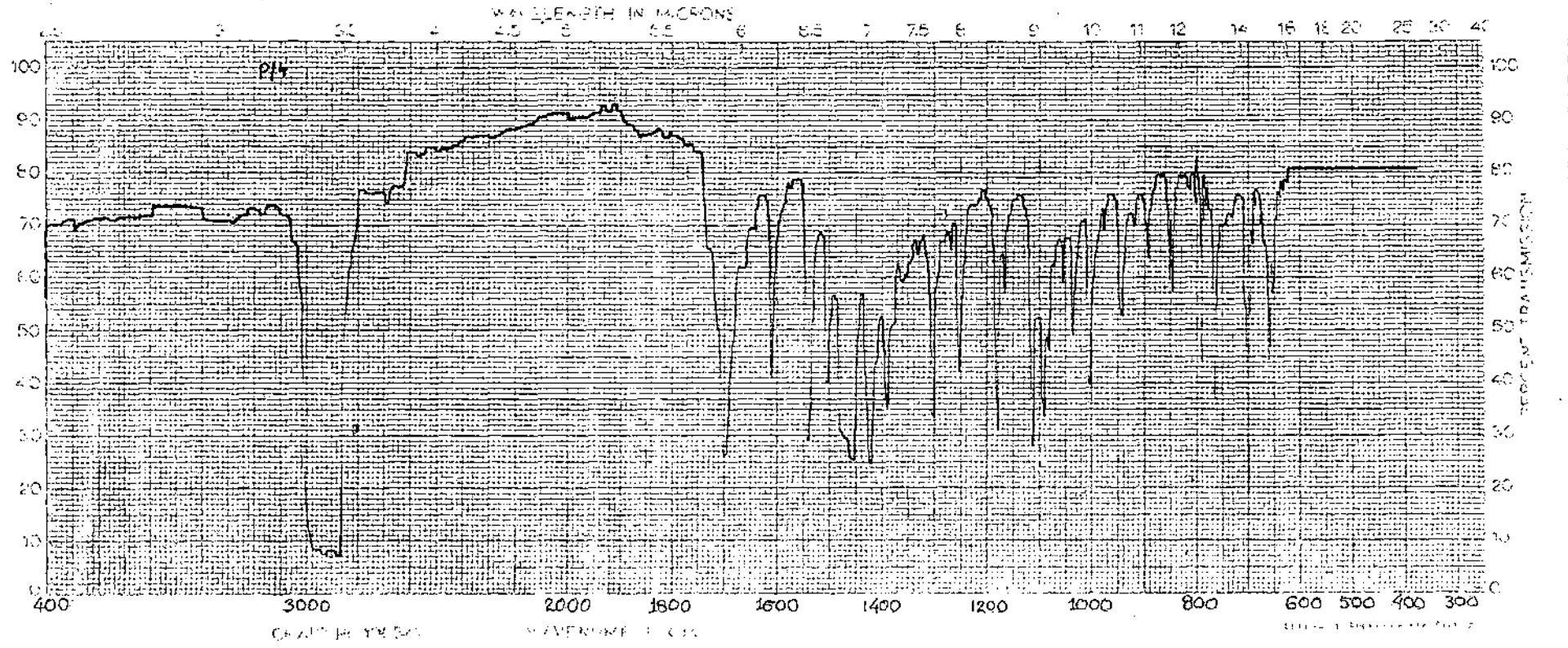
The compound melted at 195-96°C.

% Analysis for $C_{26}H_{37}O_3NSn$:

Found	:	C 57.94	H 7.04	N 2.56	Sn 22.02
Calcd	:	C 58.86	H 6.98	N 2.64	Sn 22.45

Important Infrared Spectral Data (cm^{-1}):

1700(s), 1610(m), 1540(s), 1300(m), 1250(m), 1180(s), 1110(s), 1090(m), 1050(w), 1000(m), 950(m), 900(w), 790(m), 760(m), 700(s), 660(m), 650(w).



IR spectrum of Tricyclohexyl tin N-hydroxy phthalimide (Nujol)

10. Tetramethyl 1:3 di N-hydroxy phthalimido distannoxane (Polymeric).

A mixture of dimethyl tin oxide (660 mg; ~4 m. moles) and N-hydroxy phthalimide (652 mg; ~ 4 m. moles) was taken in a 250 c.c. round bottom flask. 100 ml benzene was added to it. The mixture was refluxed for 3 hours using a water separator. The colour changed to yellow. The reaction mixture was filtered hot. The filtrate was concentrated to ~ 15 ml allowed to stand a few minutes. Yellow powdery substance appeared. The compound was practically insoluble in common organic solvents. It was washed with hot benzene several times and dried in vacuum.

(Yield = ~60%)

The compound decomposed at 280-282°C.

% Analyses for $C_{20}H_{20}O_7N_2Sn_2$:

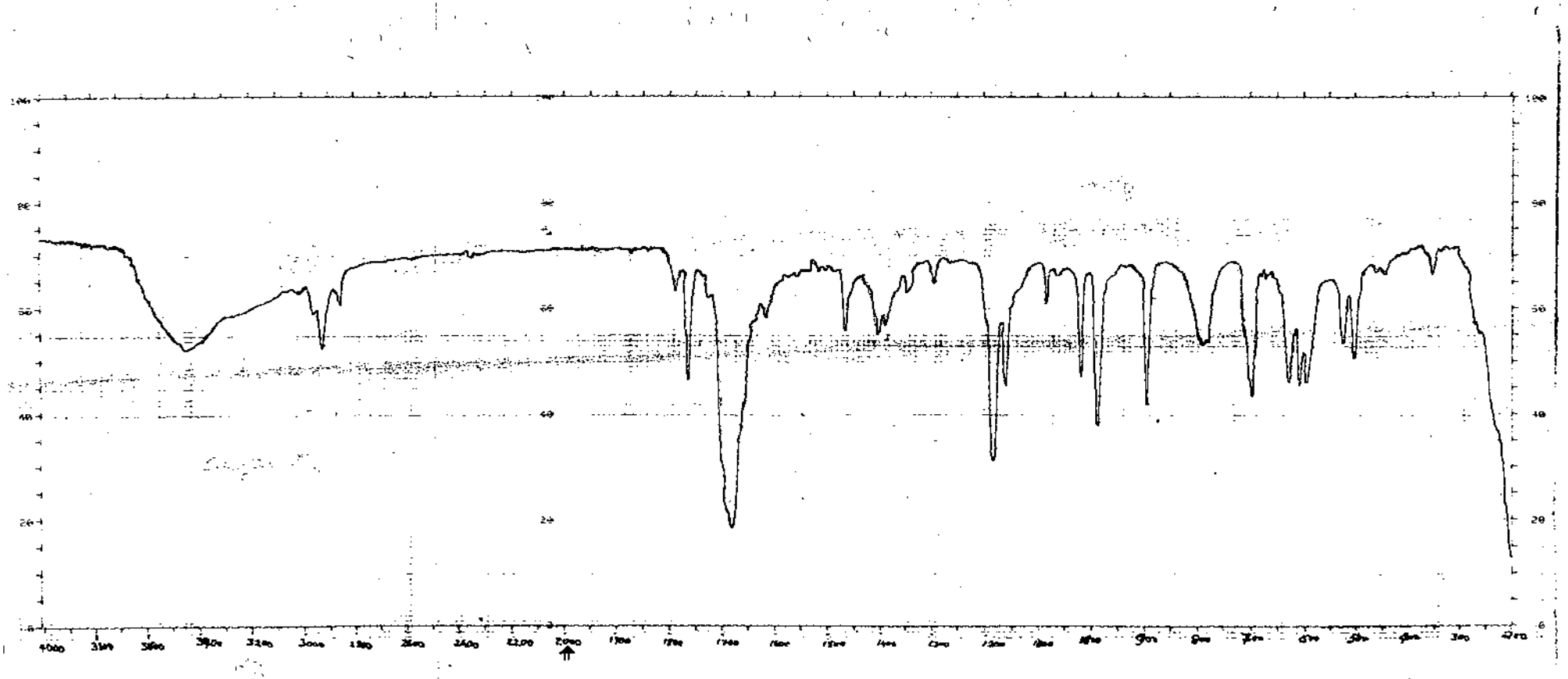
Found :	C 37.74	H 2.95	N 4.10	Sn 37.12
Calcd :	C 37.61	H 3.13	N 4.38	Sn 37.30

Important Infrared Spectral Data (cm^{-1}):

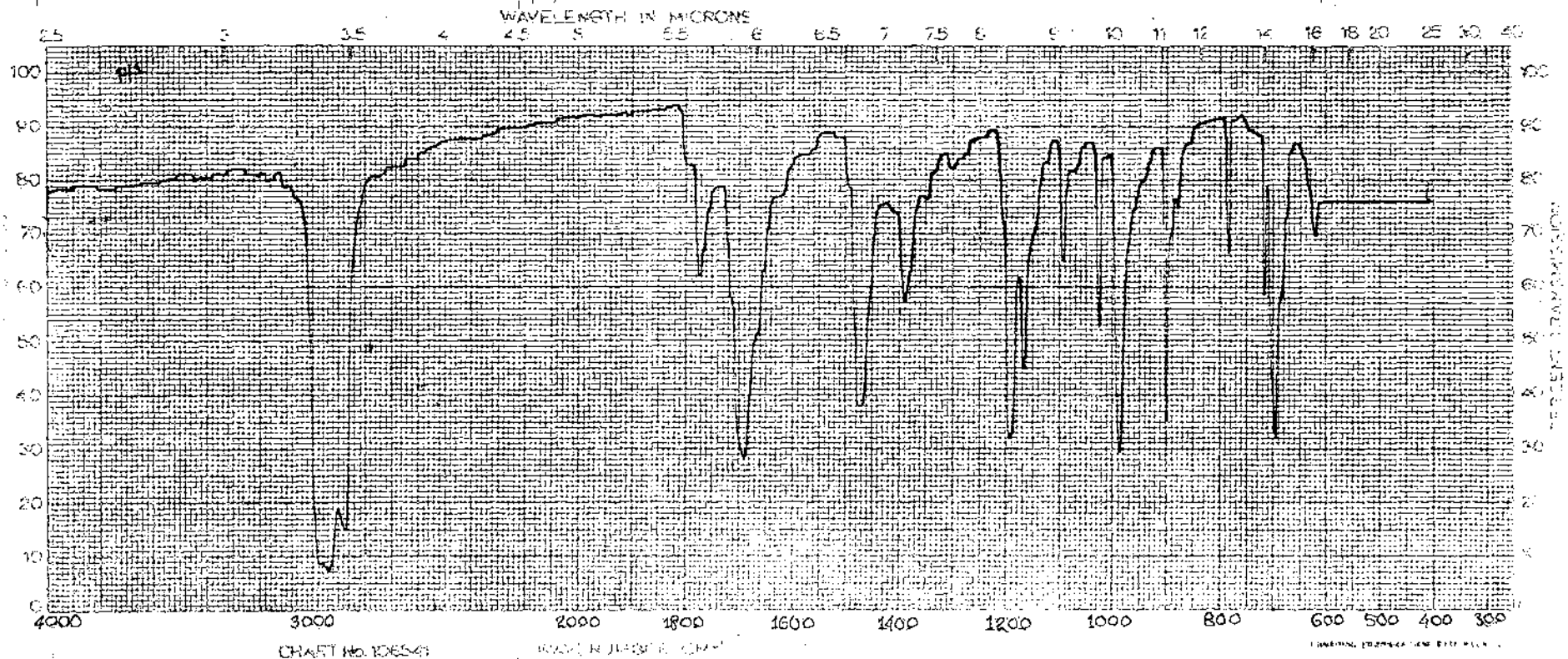
1763(m), 1677(s), 1181(s), 1158(m), 1083(w), 1077(m), 984(s), 892(s), 786(m), 776(m), 696(m), 671(m), 627(m), 607(m), 594(m), 521(m), 500(m), 496(w), 441(w), 351(w).

11. Tetrabutyl 1:3 di N-hydroxy phthalimido distannoxane (Polymeric)

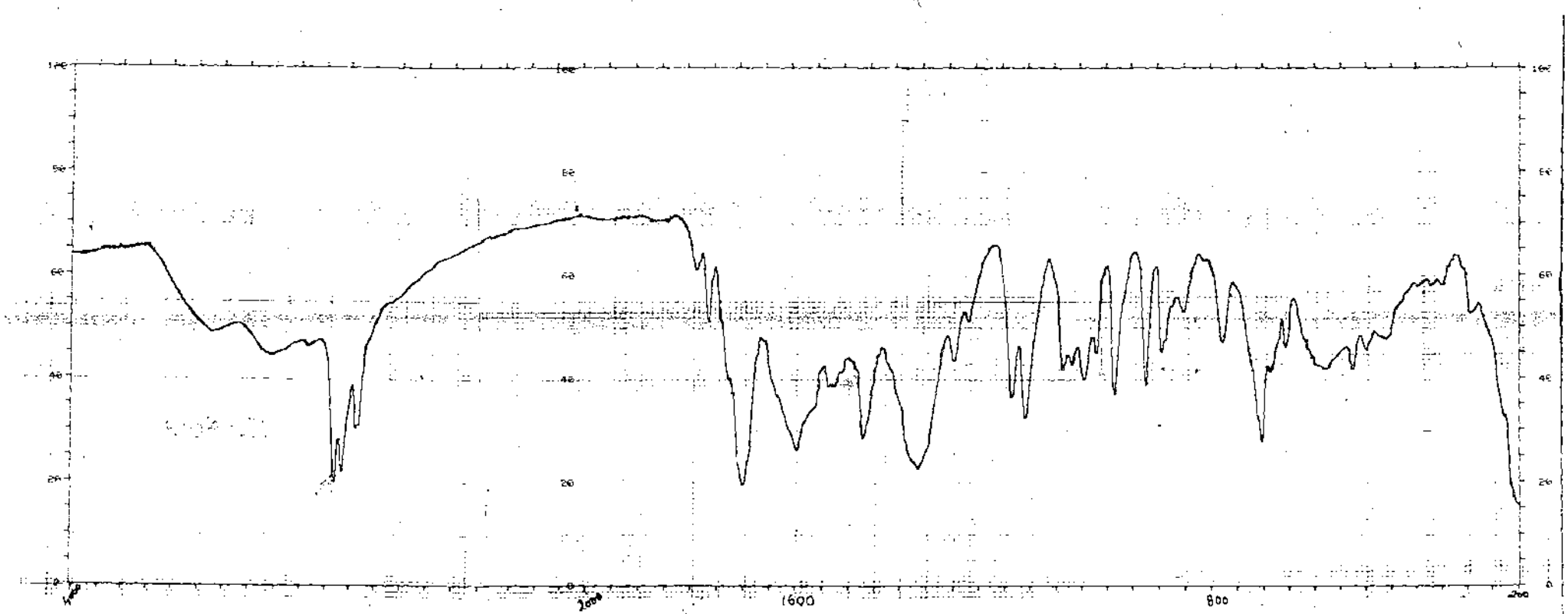
A mixture of dibutyl tin oxide (996 mg; ~4 m.moles) and N-hydroxy phthalimide (652 mg; ~ 4 m.moles) was taken in a 250 ml round bottom flask. 150 ml benzene was added to it. The mixture was refluxed for 4 hours equipped with Dean Stark Water Separator.



IR spectrum of Tetramethyl 1: 3 di N-hydroxy phthalimido distannoxane (KBr)



IR spectrum of Tetrabutyl ~~tin~~ 1:3 di N-hydroxy phthalimido distannoxane (Nujol)



IR spectrum of Tetrabutyl tin 1 : 3 di N-hydroxy phthalimido distannoxane (KBr)

Then it was cooled and filtered. The filtrate was concentrated to ~25 ml. The orange coloured solution yielded an yellow white powder (A) on standing for an hour, which was filtered. The product could not be purified and characterised. The deep orange filtrate was kept overnight, from which orange crystals (B) appeared. It was recrystallized from chloroform-methanol mixture and was dried in vacuum.

(Yield = ~ 70%)

The melting point was found 210°C.

% Analyses for $C_{32}H_{44}O_7N_2Sn_2$:

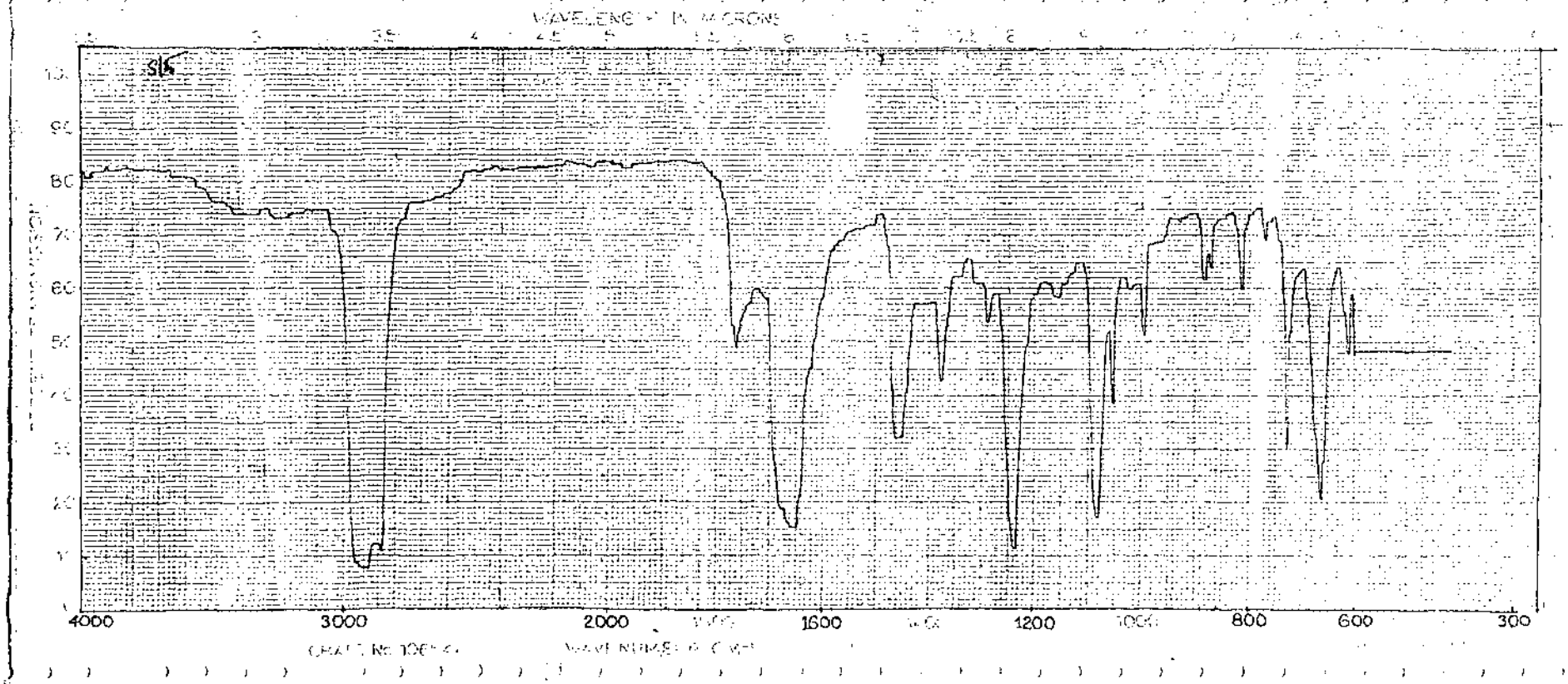
Found	:	C 47.77	H 5.65	N 3.43	Sn 29.62
Calcd	:	C 47.64	H 5.45	N 3.47	Sn 29.52

Important Infrared Spectral Data (cm^{-1}):

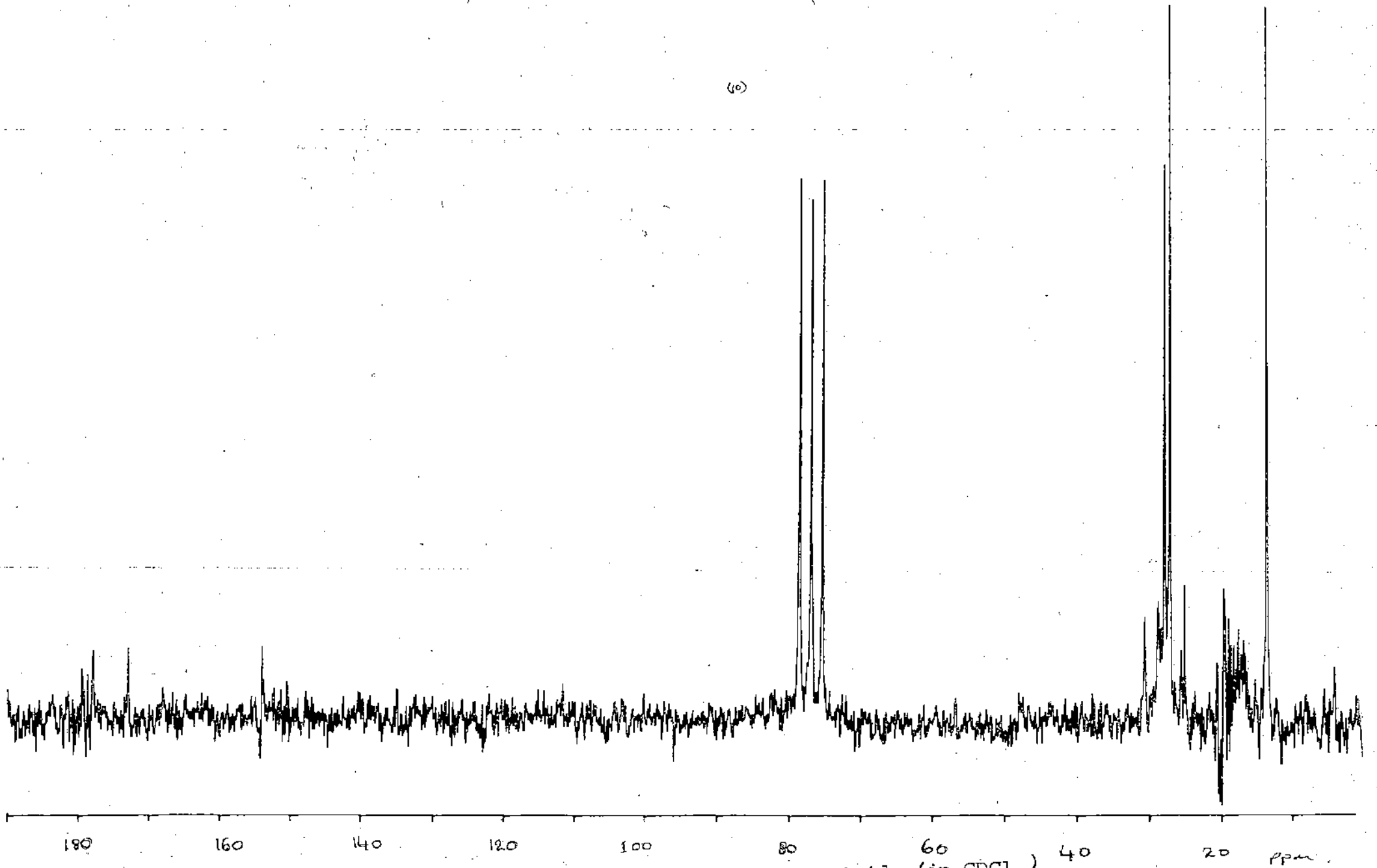
1761(m), 1697(s), 1359(s), 1292(m), 1264(w), 1182(m), 1156(s), 1082(m), 1040(m), 1016(m), 980(m), 921(m), 890(w), 776(m), 700(s), 684(m), 654(m), 576(m), 522(m), 497(w), 460(w), 397(w), 371(w), 384(w), 289(w).

12. Tri butyl tin N-hydroxy succinimide

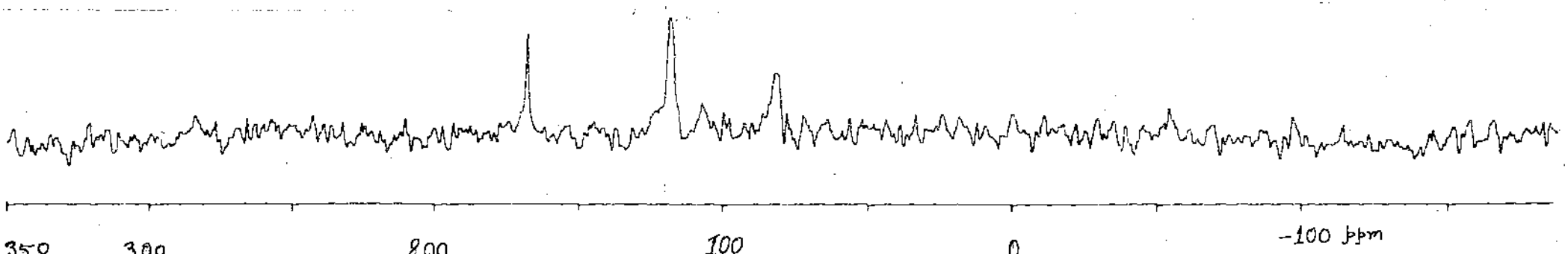
N-Hydroxy succinimide (460 mg; ~ 4 m.moles) and bis tributyl tin oxide (1.192g; ~ 2 m.moles) were taken in a round bottom flask, 150 ml benzene was poured in it. The mixture was refluxed for 4 hours with water separator. The reaction mixture was cooled and filtered. The filtrate was concentrated to about 15 ml and kept overnight. A white product appeared.



IR spectrum of reaction product of bis (Tributyltin)oxide and N-hydroxy succinimide (nujol)



^{13}C NMR spectrum of Tributyl tin derivative of N-hydroxy succinimide (in $CDCl_3$)



^{119}Sn NMR spectrum of Tributyl tin derivative of N-hydroxy succinimide (in $CDCl_3$)

The compound decomposed at $\sim 70^{o}C$.

Moreover the compound decomposed when kept even in a vacuum desiccator. The elemental analyses indicated the impure nature of the compound due to its unstable nature.

% Analyses for $C_{16}H_{31}O_3NSn$:

Found	:	C 45.60	H 6.10	N 2.18	Sn 27.33
Calcd	:	C 47.52	H 7.67	N 3.46	Sn 29.45

Important Infrared Spectral Data (cm^{-1}):

1680(s), 1570(s), 1220(m), 1100(m), 1060(w), 1040(w), 960(w), 880(m), 830(w), 780(w), 710(w), 670(s), 610(w).

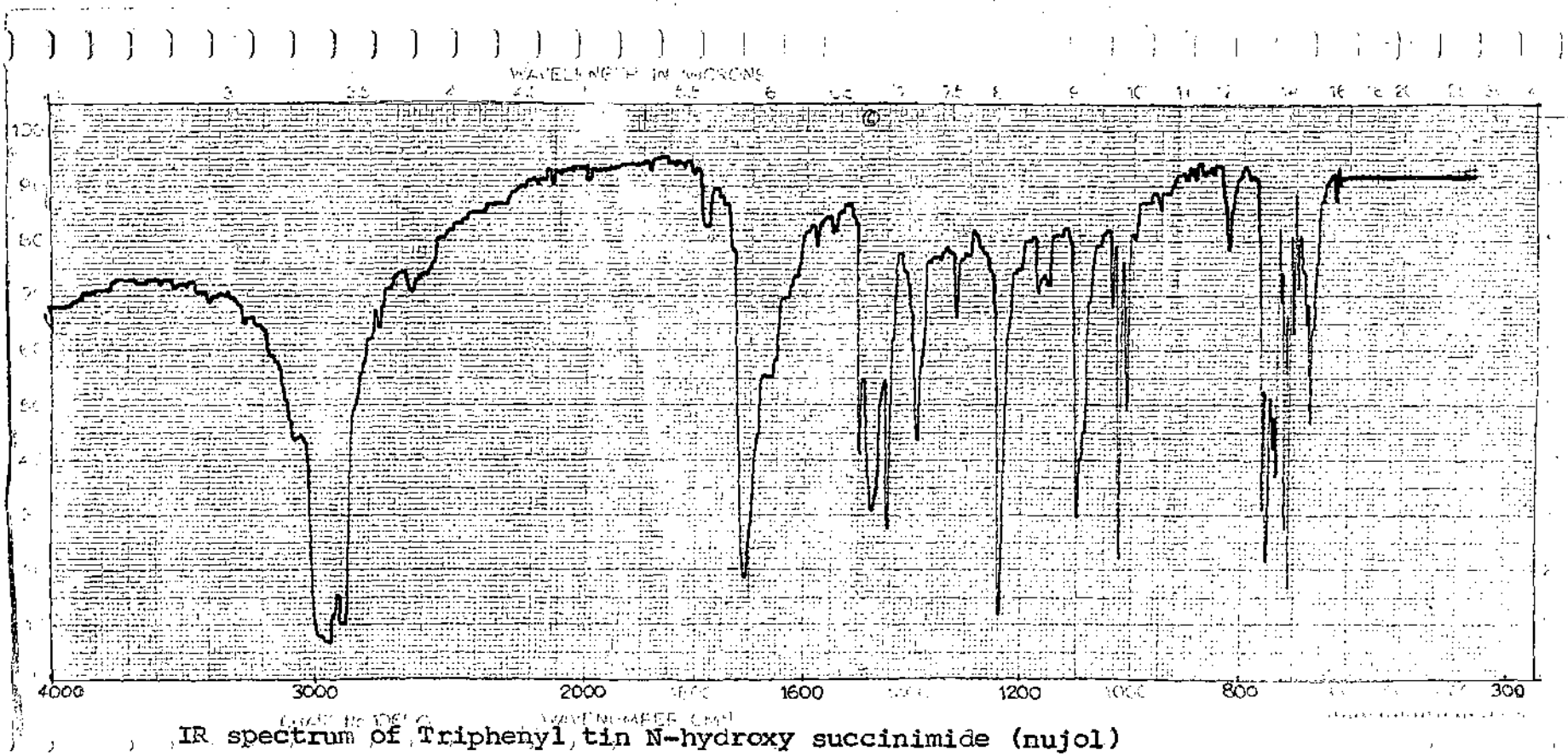
The ^{1}H, ^{13}C and ^{119}Sn NMR spectra indicated impure nature of the compound.

13. Triphenyl tin N-hydroxy succinimide

A mixture of bis (triphenyl tin oxide)(1.432g; $\sim$ 2 m.moles) and N-hydroxy succinimide (460 mg; $\sim$ 4 m. moles) was taken in a round bottom flask. 150 ml benzene was poured in it. The mixture was stirred for few minutes and then refluxed for 4 hours with a Dean Stark Water Separator. The reaction mixture was allowed to cool and then filtered. The filtrate was concentrated to about 10 ml. Kept overnight, white crystalline product appeared.

(Yield = $\sim$60%)

The compound was purified by repeated crystallization from chloroform methanol mixture. It was dried in air and finally in a vacuum desiccator.



IR spectrum of Triphenyl tin N-hydroxy succinimide (nujol)

The compound was found to melt at 112°C.

% Analyses for $C_{22}H_{19}O_3NSn$:

Found	:	C 56.15	H 4.10	N 2.87	Sn 24.98
Calcd	:	C 56.89	H 4.09	N 3.01	Sn 25.64

Important Infrared Spectral Data (cm^{-1}):

1785(w), 1705(s), 1315(w), 1290(w), 1230(s), 1150(w), 1100(s), 1020(s), 1000(m), 840(w), 750(s), 710(m), 670(m).

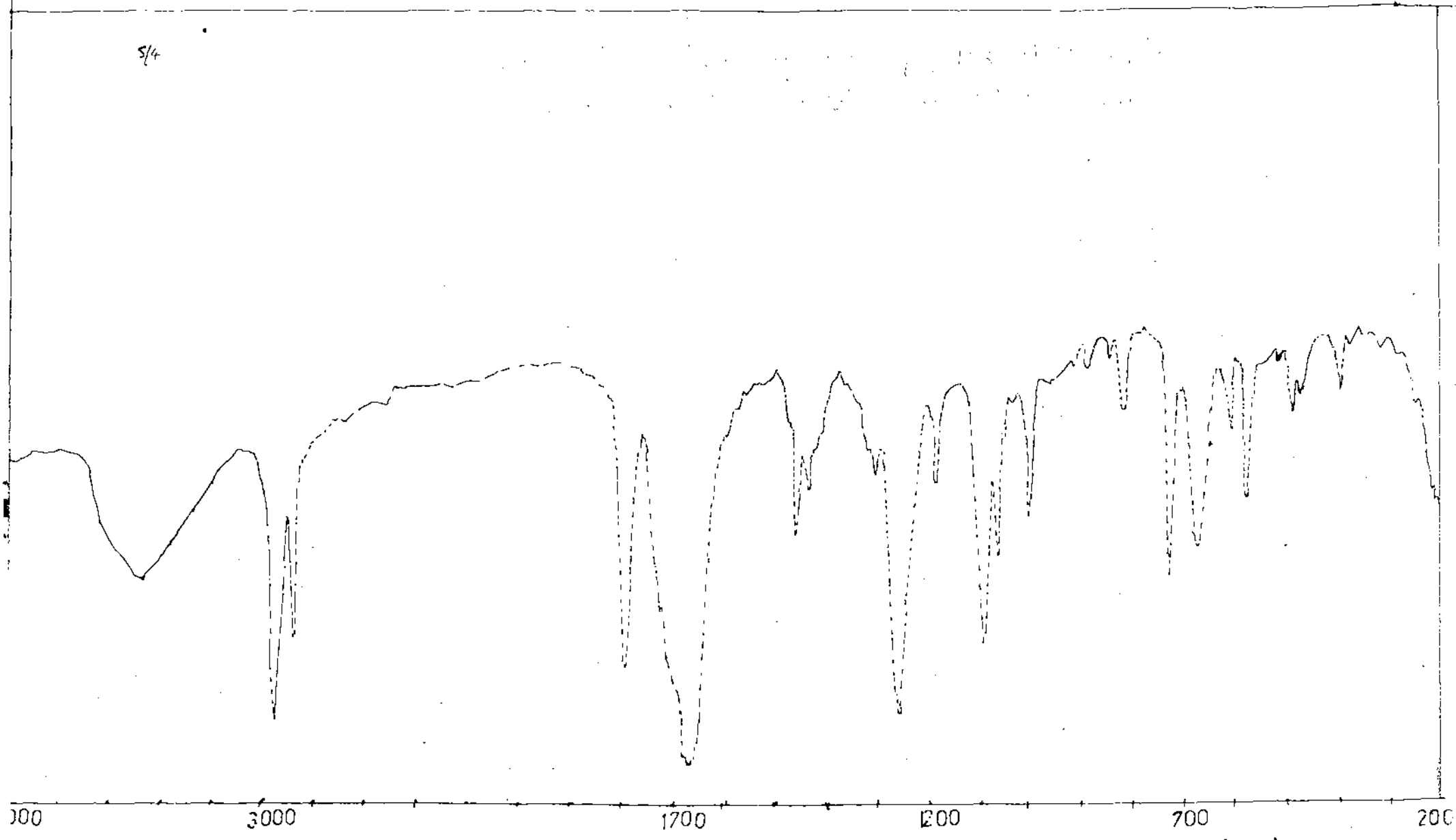
14. Tetracyclohexyl 1:3 di N-hydroxy succinimido distannoxane (Polymeric)

A mixture of tricyclohexyl tin hydroxide (1.54g; ~4 m.moles) and N-hydroxy succinimide (460 mg; ~ 4 m. moles) was taken in 250 ml round bottom flask. 150 ml benzene was poured in it and refluxed for 4 hours as described earlier. It was cooled and filtered, the filtrate was concentrated to ~15 ml, white crystalline product appeared on keeping overnight. Repeated crystallisation from chloroform-methanol mixture yielded a compound having a melting point 150°C.

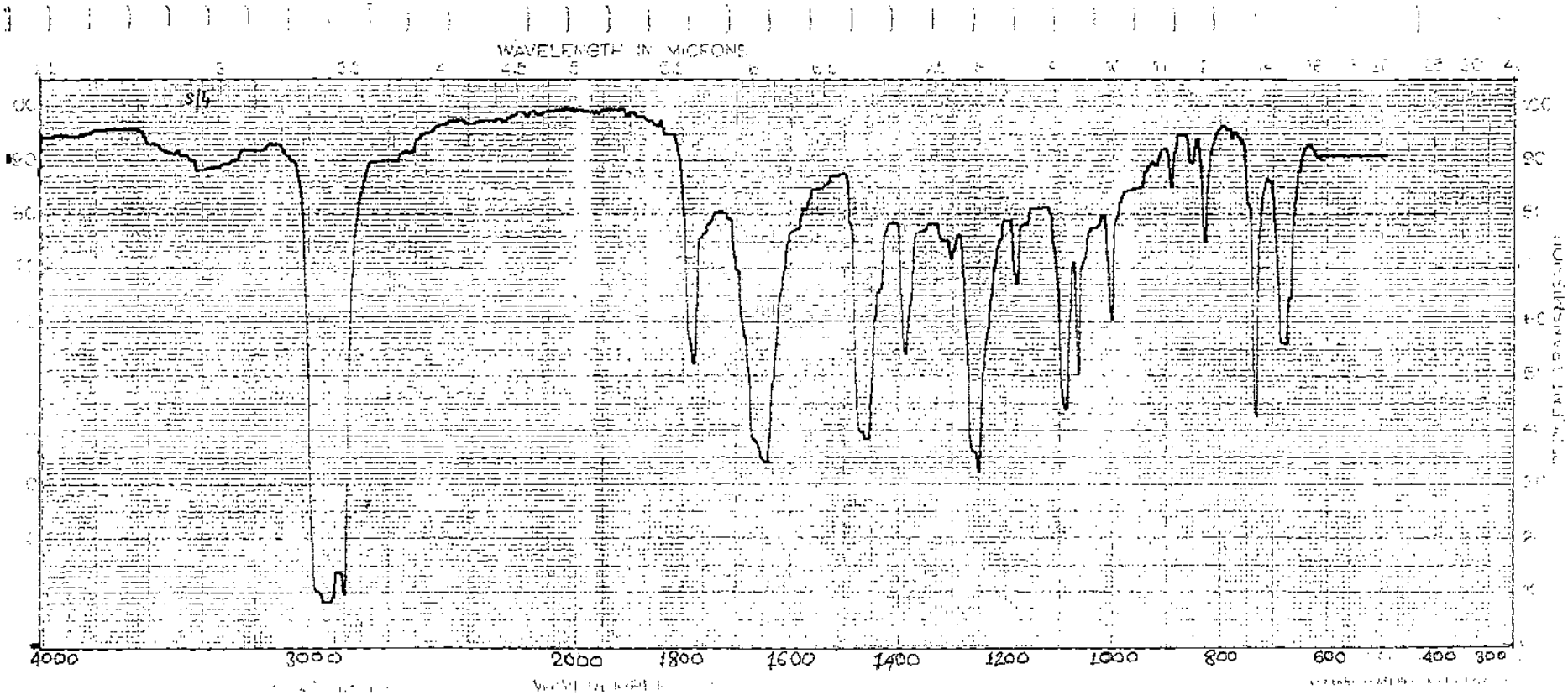
(Yield = ~50%)

% Analyses for $C_{32}H_{52}O_7N_2Sn_2$:

Found	:	C 47.10	H 6.26	N 3.60	Sn 29.39
Calcd	:	C 47.17	H 6.38	N 3.43	Sn 29.23



IR spectrum of Tetracyclohexyl 1:3 di N-hydroxy succinimido distannoxane (KBr)



IR spectrum of Tetracyclohexyl 1:3 di N-hydroxy succinimide distannoxane (Nujol)

Important Infrared Spectral Data (cm^{-1}):

1780(s), 1660(s), 1300(w), 1250(s), 1180(w), 1090(m), 1070(m), 1000(m), 890(w), 820(m), 730(s), 580(w), 490(w), 475(w), 320(w).

15. Tetramethyl 1:3 di N-hydroxy succinimide distannoxane (Polymeric)

Dimethyl tin oxide (660 mg; $\sim$ 4 m.moles) and N-hydroxy succinimide (460 mg; $\sim$ 4 m.moles) were taken in a 250 ml round bottom flask. 150 ml benzene was poured in it. The mixture was stirred for few minutes. Then it was refluxed for 4 hours with a Dean Stark Water Separator. The reaction mixture was filtered hot. The filtrate was concentrated to about 15 ml and was allowed to stand : powdery substance very light pink in colour was appeared. The solubility of the product was very poor in common organic solvent. It was washed with hot benzene and dried in vacuum.

(Yield = $\sim$ 55%)

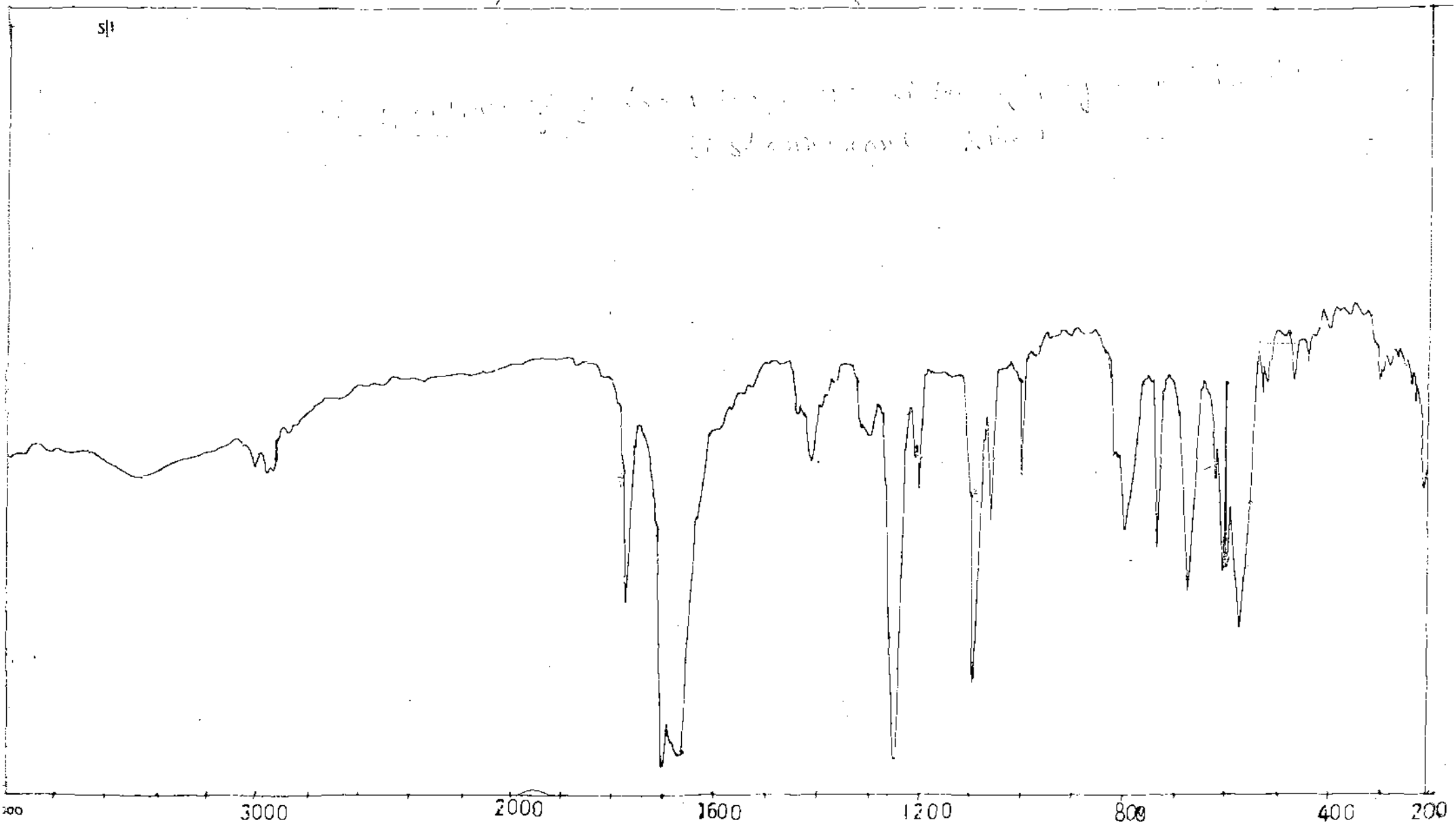
The compound decomposed at 189-90°C.

% Analyses for $C_{12}H_{20}O_7N_2Sn_2$:

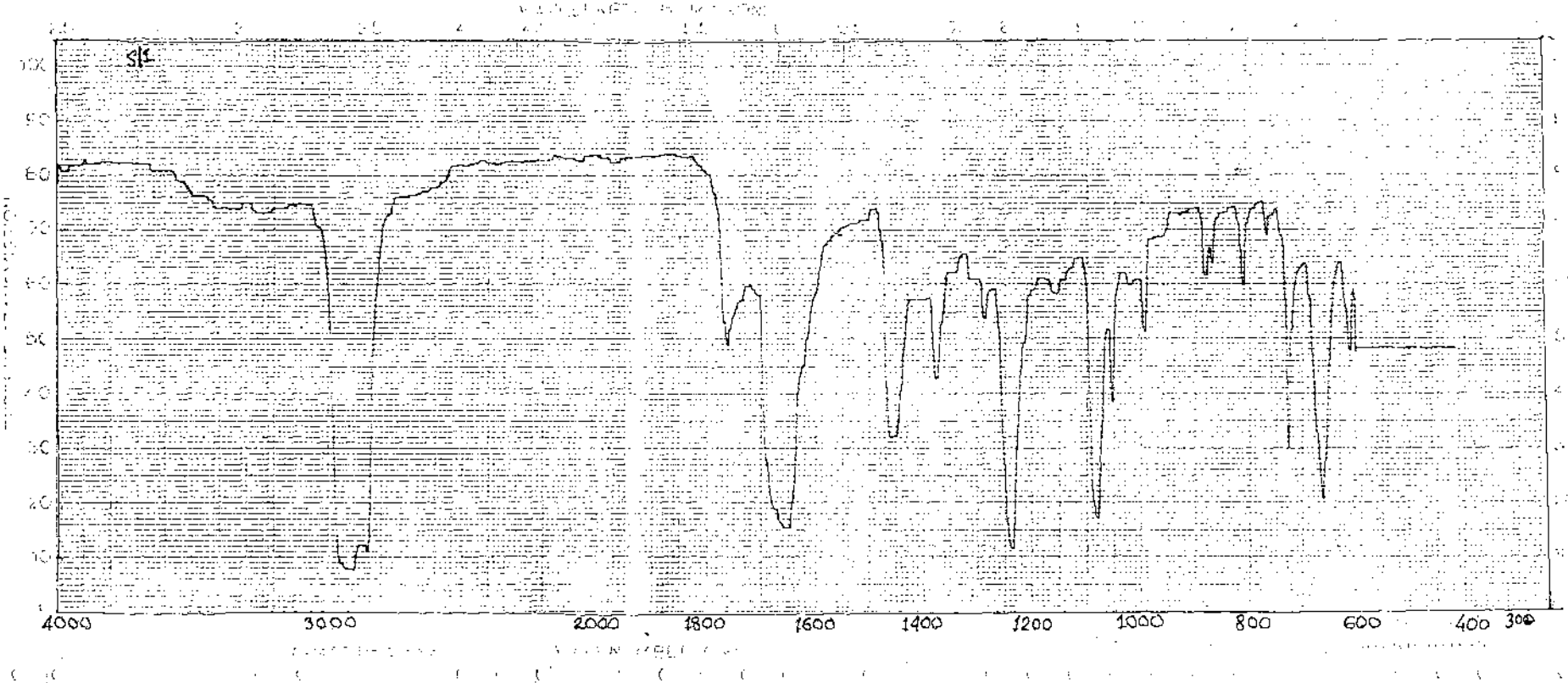
Found :	C 26.43	H 3.30	N 5.21	Sn 44.18
Calcd :	C 26.56	N 3.69	N 5.16	Sn 43.91

Important Infrared Spectral Data (cm^{-1})

1770(m), 1670(d), 1300(w), 1250(s), 1210(w), 1090(s), 1060(m), 1000(m), 800(m), 750(m), 675(m), 610(m), 576(s), 535(w), 460(w), 300(w).



IR spectrum of Tetramethyl 1:3 di N-hydroxy succinimido distannoxane (KBr)



IR spectrum of Tetramethyl 1:3 di N-hydroxy succinimido distannoxane (Nujol)

16. Tetrabutyl 1:3 di N-hydroxy succinimido di stannoxane (Polymeric)

A mixture of dibutyl tin oxide (996 mg; ~ 4 m.moles) and N-hydroxy succinimide (460 mg; ~4 m.moles) was taken in a 250 c.c. round bottom flask. 150 ml benzene was poured in it. The mixture was then refluxed for 4 hours using a water separator. It was then cooled and filtered. The filtrate was then concentrated to ~ 10 ml and kept overnight. A white crystalline product appeared. It was recrystallised from chloroform-methanol mixture. The product was dried in vacuum.

(Yield = ~ 62%)

The pure compound melted at 140°C.

% Analysis for $C_{24}H_{44}O_7N_2Sn_2$:

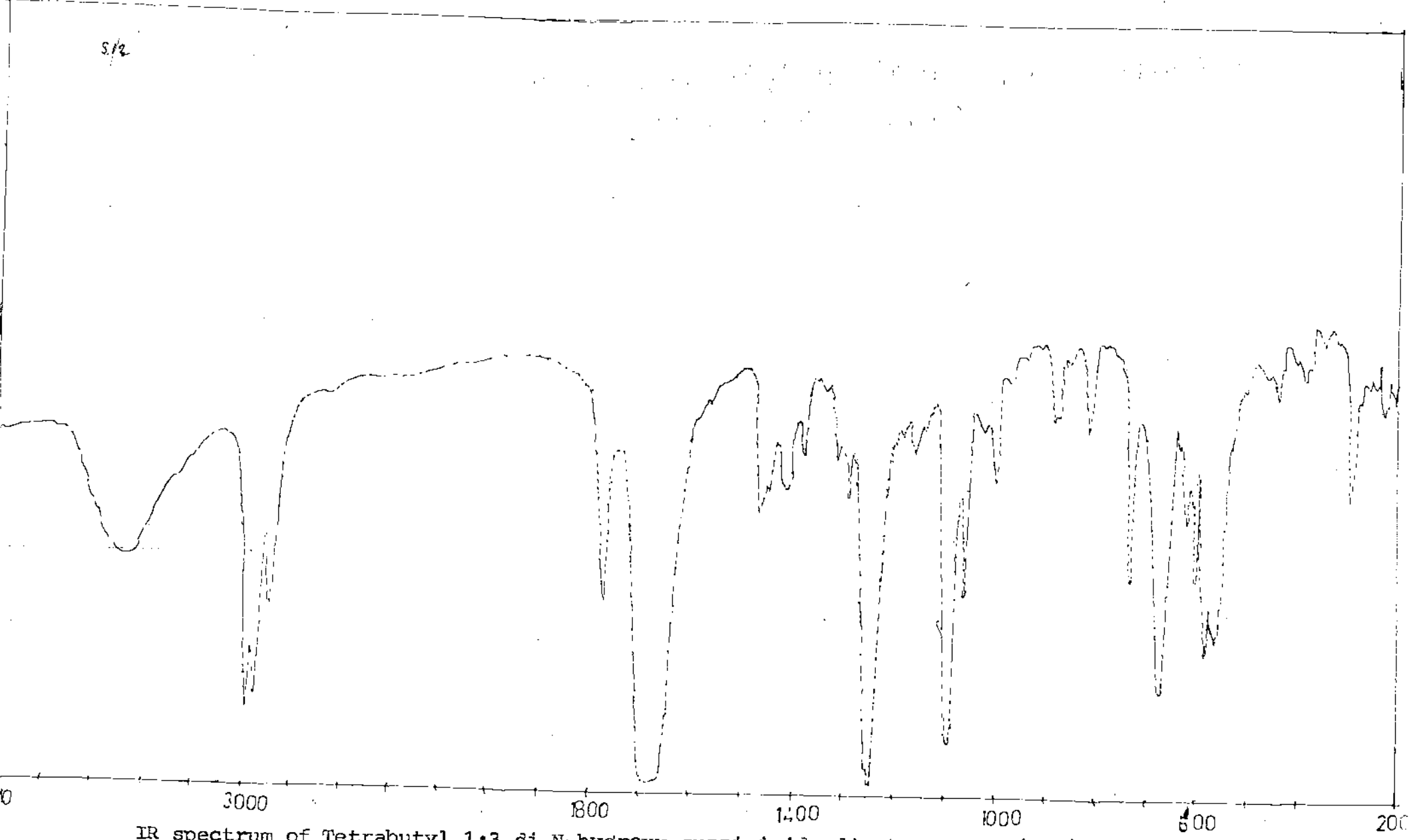
Found :	C 40.49	H 6.06	N 3.74	Sn 33.17
Calcd :	C 40.56	H 6.19	N 3.94	Sn 33.52

Important Infrared Spectral Data (cm^{-1})

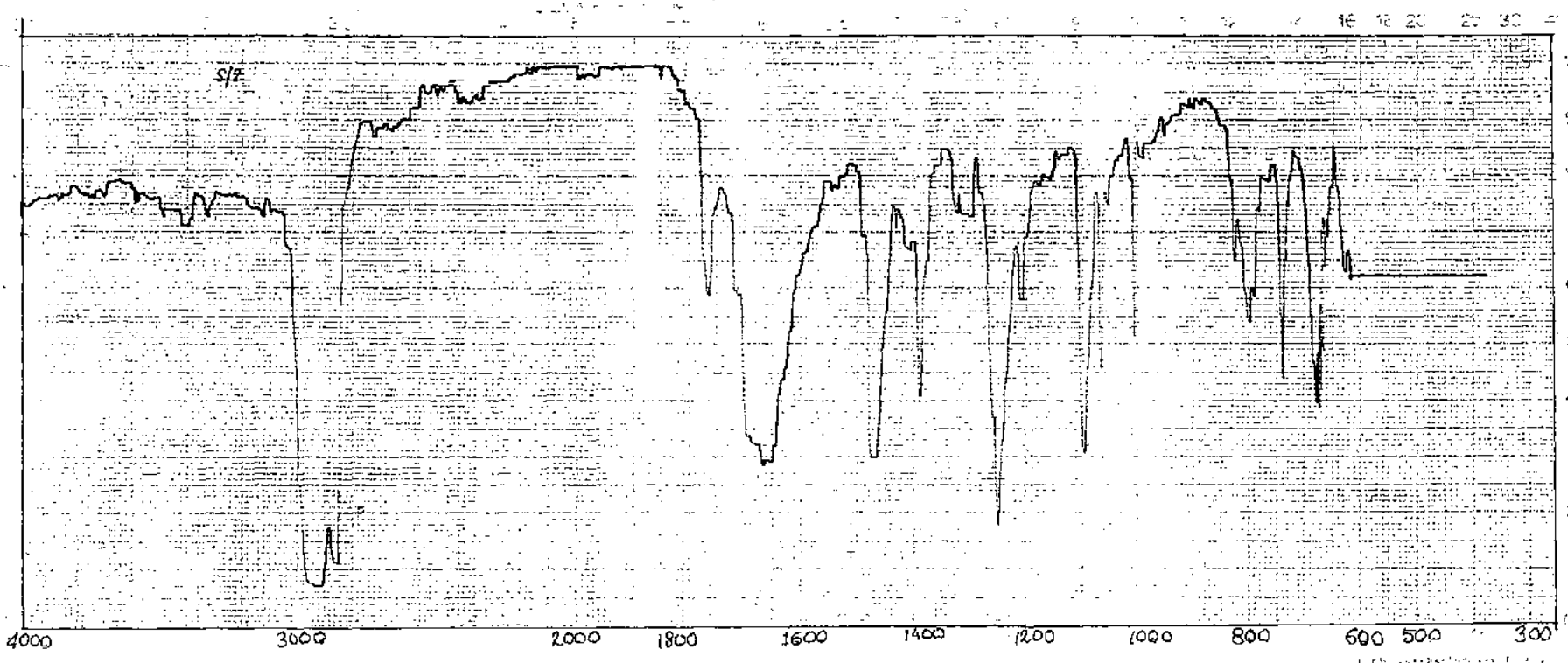
1780(s), 1690(s), 1240(s), 1090(s), 1000(m), 890(m), 820(m), 735(m), 670(s), 620(m), 580(m), 560(s), 440(w), 380(w), 300(w).

Some attempted reactions:

Reactions have also been carried out with dibenzyltin dichloride, tribenzyl tin chloride, $Cl_2Sn(CH_2CH_2COOCH_3)_2$, $C_6H_5CH(SnCl_3)CH_2COC_6H_5$ and N-hydroxy phthalimide and also with N-hydroxy succinimide separately. In most of the cases a gummy



IR spectrum of Tetrabutyl 1:3 di N-hydroxy succinimido di stannoxane (KBr)



IR spectrum of Tetrabutyl 1 : 3 di N-hydroxy succinimido distannoxane (Nujol)

product appeared, from which no pure product can so far be isolated. In some cases starting materials were recovered unchanged indicating no reaction took place.

The results of the above said reactions can be summarised in the following table :

Organotin compounds	Ligand	Result of Reaction
1. Dibenzyl tin dichloride		Gummy product
2. Tribenzyl tin chloride	N-hydroxy phthalimide	Gummy product
3. $Cl_2Sn(CH_2CH_2COOCH_3)_2$		Reactants recovered unchanged
4. $C_6H_5CH(SnCl_3)CH_2COC_6H_5$		Reactants recovered unchanged
5. Dibenzyl tin dichloride		Gummy product
6. Tribenzyl tin chloride	N-hydroxy succinimide	Gummy product
7. $Cl_2Sn(CH_2CH_2COOCH_3)_2$		Gummy product
8. $C_6H_5CH(SnCl_3)CH_2COC_6H_5$		Gummy product

TABLE I

MOLAR CONDUCTANCE OF SOME OF THE COMPOUNDS

Temp. 25°C — Solvent Methanol

Compound	Molar Conductance (λ) Mho cm^2
Triphenyl tin N-hydroxy phthalimide	21.66
Tricyclohexyl tin N-hydroxy phthalimide	24.19
Tetrabutyl 1:3 di N-hydroxy phthalimido distannoxane	25.50
Tributyl tin N-hydroxy succinimide	17.10
Triphenyl tin N-hydroxy succinimide	18.80
Tetracyclohexyl 1:3 di N-hydroxy succinimido distannoxane	15.60
Tetrabutyl 1:3 di N-hydroxy succinimido di stannoxane	15.10

These molar conductance values indicated essentially non ionic nature of these compounds.

TABLE II

^{1}H NUCLEAR MAGNETIC RESONANCE SPECTRAL DATA

Compound	Chemical shift (δ)		
	Aromatic protons	Alkyl protons	Others
N-Hydroxy phthalimide	7.64(t)		10.64(s) (OH-proton)
Tributyl tin N-hydroxy phthalimide	8.3(t)	1.36(q) 1.39 to 2.9 (comp)	
Triphenyl tin N-hydroxy phthalimide	7.8(m) 8.18(q)		
Tricyclohexyl tin N-hydroxy phthalimide	7.85(m)		1.65(comp)
Tetrabutyl 1:3 di N-hydroxy phthalimido distannoxane	7.7(q)	0.9(t) 1.36(comp) 1.80(d)	
N-Hydroxy succinimide		2.6(t)	3.8(h) (OH-proton)
Triphenyl tin N-hydroxy succinimide	7.5(q) 7.75(t)	2.46(s)	
Tetra cyclohexyl 1:3 di N-hydroxy succinimido di stannoxane		2.8(s)	1.3(d), 1.65(d) 1.8(dd)
Tetrabutyl 1:3 di N-hydroxy succinimido distannoxane		0.95(d) 1.6(t) 2.82(s)	

s = singlet, d = doublet, t = triplet, q = quartet
dd = doublet of a doublet, comp = complex, m = multiplet, h = hump

TABLE III

^{13}C NUCLEAR MAGNETIC RESONANCE SPECTRAL DATA

Compound	Chemical shift (δ)		
	Aromatic carbon	Alkyl carbon	Carbonyl carbon
N-Hydroxy phthalimide	122.86, 128.69, 134.42		164.10
Tributyl tin N-hydroxy phthalimide	122.60, 129.52, 133.62	13.62, 17.88, 27.11, 27.67	165.32
Triphenyl tin N-hydroxy phthalimide	122.74, 129.12, 129.61, 129.89, 130.51, 133.66, 136.95		
Tetrabutyl 1:3 di N-hydroxy phthalimido distannoxane	122.48, 130.05, 133.18	13.54, 26.76, 26.89, 27.52	164.84
N-Hydroxy succinimide		25.12	172.74
Triphenyl tin N-hydroxy succinimide	128.79, 130.10, 130.36, 136.75	24.25	172.90
Tetrabutyl 1:3 di N-hydroxy succinimido distannoxane		13.61, 25.02, 26.75, 26.86, 27.53	172.77

TABLE IV

^{119}Sn NUCLEAR MAGNETIC RESONANCE SPECTRAL DATA

Compound	Chemical shift (δ)
Tributyl tin N-hydroxy phthalimide	181.45
Triphenyl tin N-hydroxy phthalimide	-54.33
Tetrabutyl 1:3 di N-hydroxy phthalimido distannoxane	-164.46 & -218.87
Triphenyl tin N-hydroxy succinimide	-74.44
Tetrabutyl 1:3 di N-hydroxy succinimido distannoxane	-178.85 & -223.50

An attempt have been taken to determine the molecular weight of these compounds following Rast's method. Camphor (mp 178°C) used as solvent. Cryoscopic constant for Camphor,

$$K_f = 39.7^{\circ}C$$

In some cases molecular weight by Rast method could not be determined as those compounds were insoluble in Camphor.

TABLE V

APPARANT MOLECULAR WEIGHT DATA

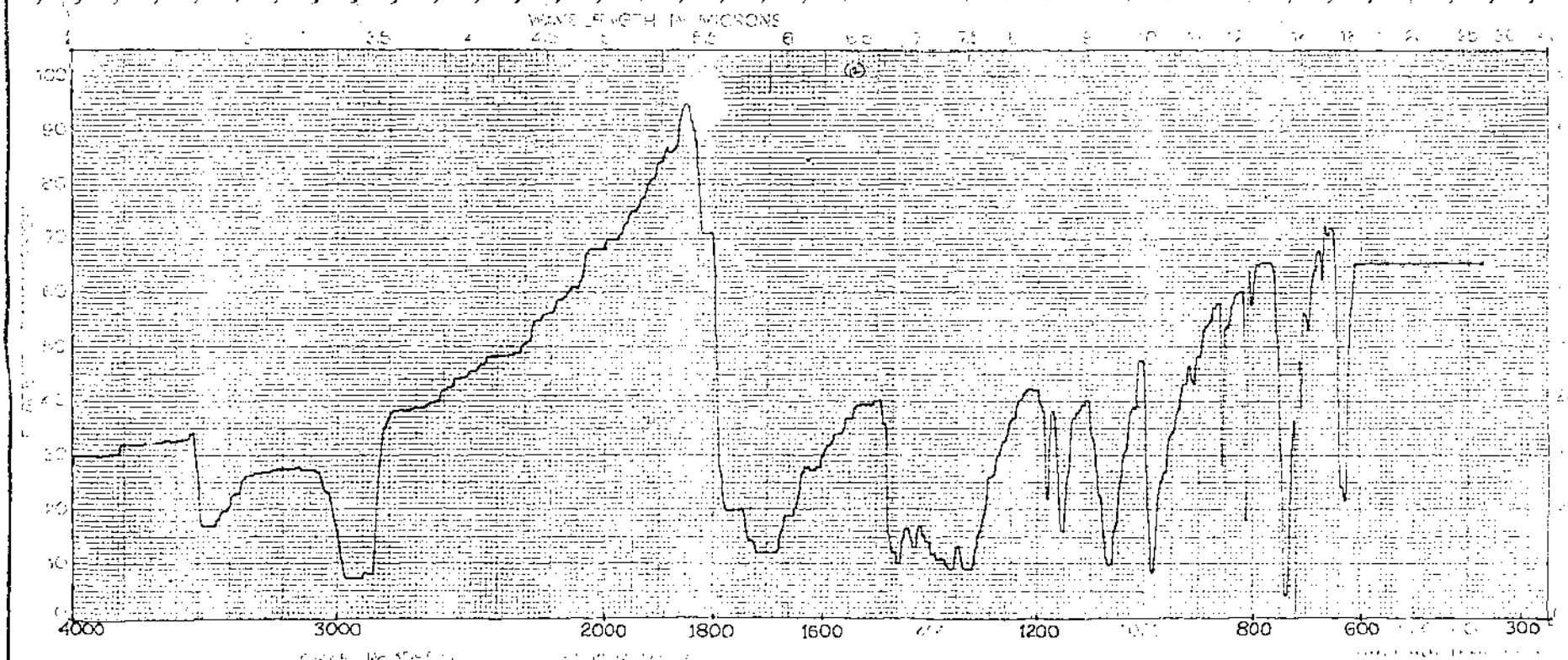
Compound	Molecular weight	
	Found	Calcd (for monomer)
Tributyl tin N-hydroxy phthalimide	446	452
Triphenyl tin N-hydroxy phthalimide	501	512
Tricyclohexyl tin N-hydroxy phthalimide	555	530
Tetrabutyl 1:3 di N-hydroxy phthalimido distannoxane	478	796
Triphenyl tin N-hydroxy succinimide	442	464
Tetrachyclohexyl 1:3 di N-hydroxy succinimido distannoxane	460	814
Tetrabutyl 1:3 di N-hydroxy succinimido distannoxane	452	712

In case of triorganotin derivatives, these values indicated the monomeric nature of the compounds. But in case of di organotin derivatives, the values obtained by Rast method gave abnormally low values. In this connection, it may be referred to some earlier work [Considine et al (137)]. They reported that the $(C_6H_5O)(C_4H_9)_2Sn\text{-}O\text{-}Sn(C_4H_9)_2(OC_6H_5)$ dissociates at higher temperature required for Rast method to give lower values for molecular weight of the compound. It is regretted due to certain difficulties it was not possible to determine the molecular weights of these compounds osmometrically which could give better ideas about the nature of these compounds.

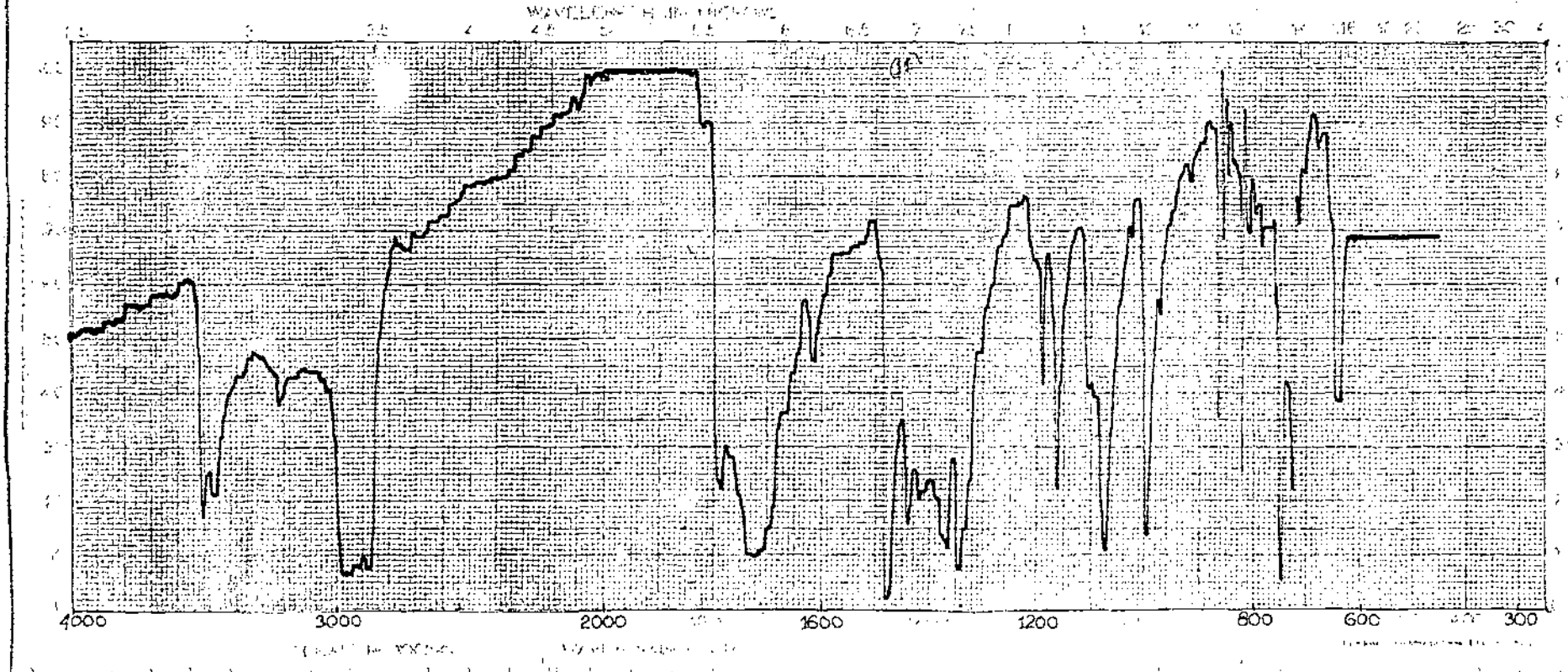
Reactions of N-(hydroxy methyl) phthalimide with diorganotin oxides

1. Dimethyl tin oxide : Reaction of dimethyl tin oxide and N-(hydroxy methyl)phthalimide was carried out in 1:1 molar ratio in benzene and was refluxed for four hours. The product isolated from the reaction mixture was a white crystalline substance (mp 180-81°C). The product was washed several times with chloroform. The elemental analyses gave the following results:

C = 56.51; H = 3.86; N = 3.81 and Sn = 27.08 percent.



IR spectrum of N-(hydroxymethyl)phthalimide (nujol)



IR spectrum of reaction product of Dimethyl tin oxide and N-(hydroxy methyl) phthalimide (nujol)

Important Infrared Spectral Data (cm^{-1})

3500(b), 3200(m), 1710(v.s.b), 1190(m), 1160(s), 1070(s), 995(s), 860(m), 820(s), 750(s), 730(m), 640(m).

The compound was sparingly soluble in common organic solvents. As a result of which ^{1}H, ^{13}C and ^{119}Sn NMR spectra of this compound could not be recorded.

2. Dibutyl tin oxide :

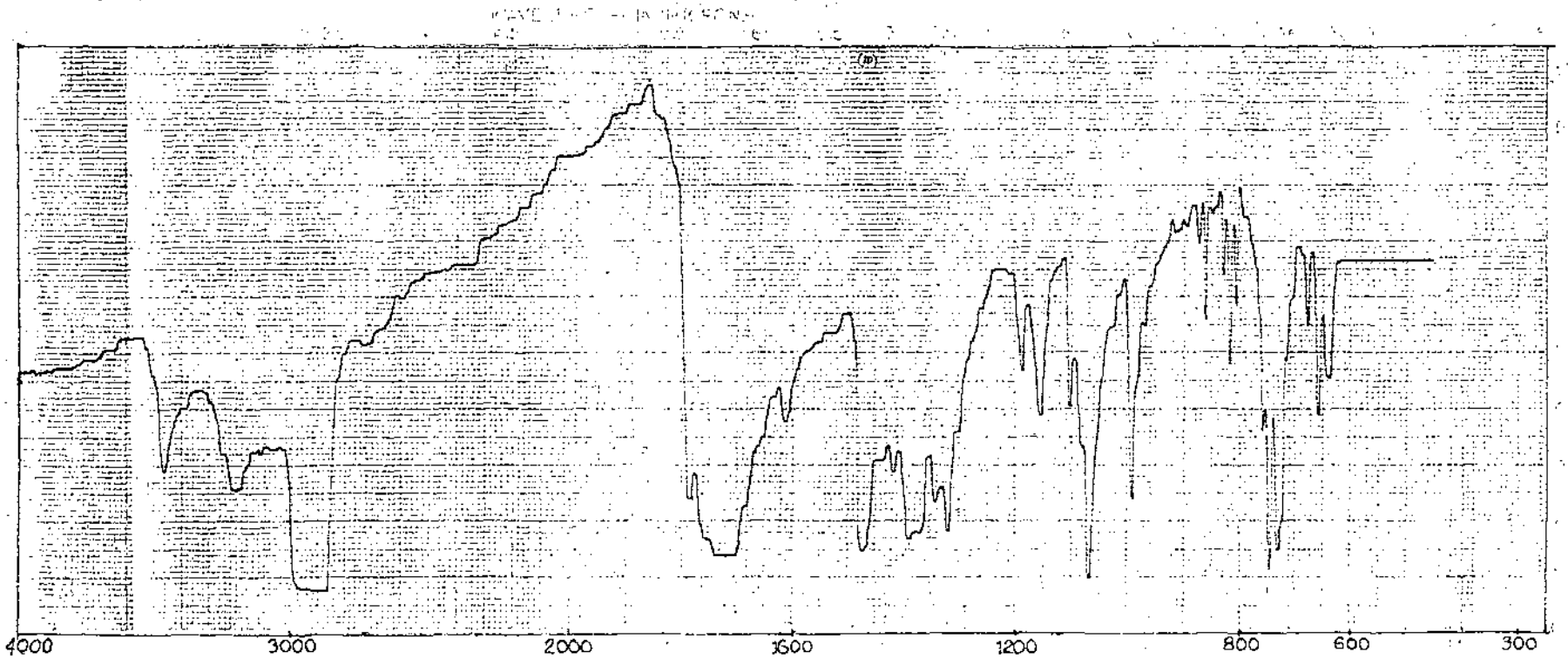
Reaction of dibutyl tin oxide and N-(hydroxy methyl) phthalimide was also carried out in 1:1 molar ratio in refluxing benzene for four hours. A white crystalline product was isolated (mp 190-192°C). The product was washed with chloroform and dried. The elemental analyses gave the following data.

C = 51.02; H = 5.24; N = 1.98 and Sn = 32.83 percent.

The Infrared data (Nujol- cm^{-1}) were as follows:

3490(m), 3200(m), 1720(v.s.b), 1380(s), 1320(s), 1180(w), 1160(m), 1070(s), 990(m), 860(m), 840(m), 750(s), 730(s), 660(m), 640(m).

The compound was also almost insoluble in common organic solvents. Hence ^{1}H, ^{13}C and ^{119}Sn NMR spectra could not be recorded.



IR spectrum of reaction product of Dibutyl tin oxide and N-(hydroxy methyl) phthalimide (nujol)

From the elemental analytical data no reasonal molecular formula for these compounds could be suggested. Moreover, the IR spectra indicated presence of hydroxyl bands. Finally, no NMR spectra could be recorded for these compounds. Hence, it was not possible to suggest the nature of these compounds and therefore, no further organotin derivative was attempted for N-(hydroxy methyl) phthalimide.

D I S C U S S I O N

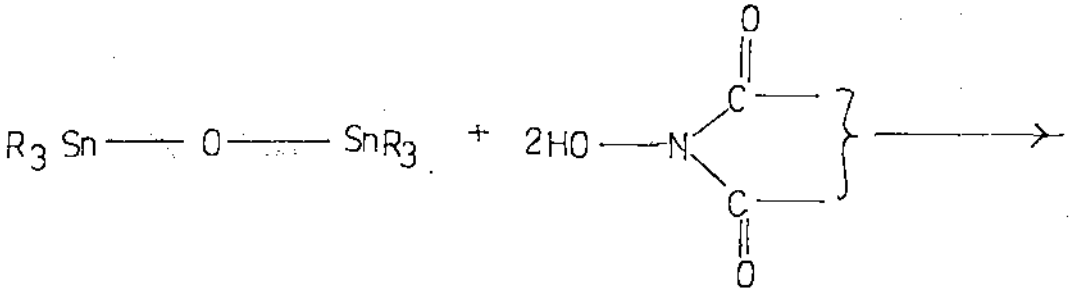
bis (Triorganotin) oxides or polymeric diorganotin oxides generally react with bidentate ligands (H_nL) like β-diketones, 8-hydroxy quinolines, substituted hydroxamic acids, diphenyl carbazones, diphenythiocarbazones etc in the following manners:

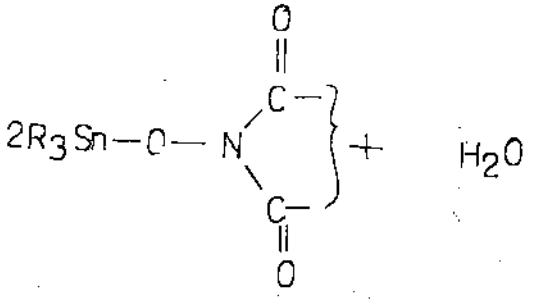
$$R_3Sn - O - SnR_3 + 2\ H_nL \longrightarrow 2R_3SnL + nH_2O$$

$$-R_2Sn - O- + 2H_nL \longrightarrow R_2SnL_2 + nH_2O$$

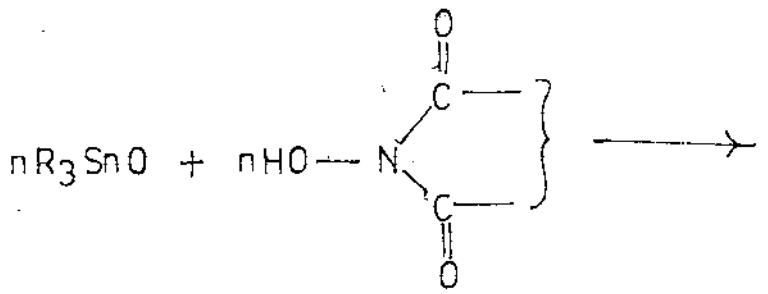
(L = chelate ligands)

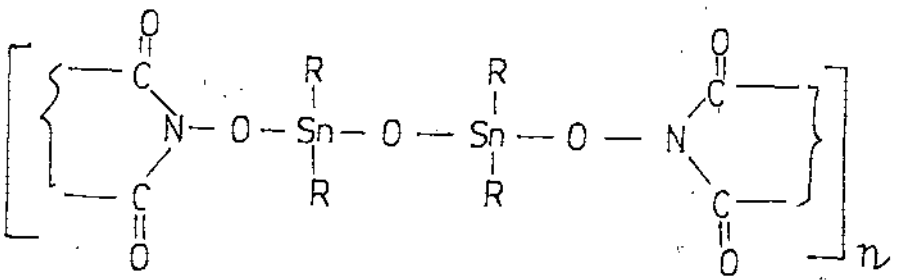
During the reactions between bis (triorganotin) oxides with N-hydroxy succinimide or N-hydroxy phthalimide, it was observed that the triorganotin derivatives of these ligands do not form any chelated species nor these derivatives contain any Sn-O-Sn bonds. These reactions can be illustrated as follows:





But the reactions of diorganotin oxides with N-hydroxy succinimide or N-hydroxy phthalimide proceeded in somewhat different way and the organotin derivatives obtained in these cases always contain Sn-O-Sn bonds and are probably polymeric in nature.

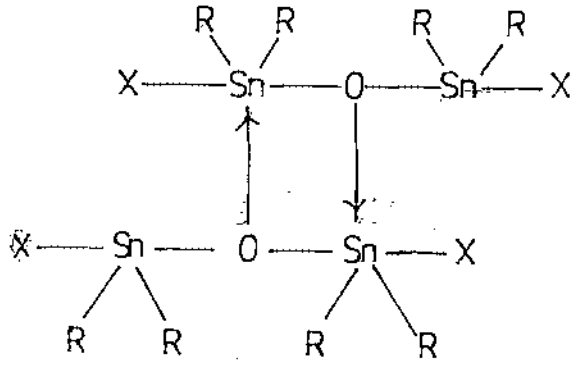




The ^{119}Sn spectra of some of the diorganotin derivatives indicated two types of tin atoms in the compounds.

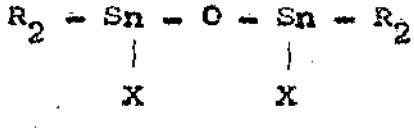
Organo stannoxanes containing Sn-O-Sn bonds are known for last few decades. A number of organo stannoxanes have been reported (138). The characteristic properties due to the Sn-O-Sn bond was discussed by Okawara (139) for tetraalkyl-1,3 di stannoxane $ClR_2SnOSnR_2Cl$ and tetraalkyl 1,3 bis (trimethylsiloxy) distannoxanes $Me_3Si-OR_2Sn-O-SnR_2OSiMe_3$. The above compounds are dimeric in benzene solution and suggested the presence of a four membered ring due to the coordination from the oxygen atom between

two tin atoms of one chain to a tin atom of the other chain.

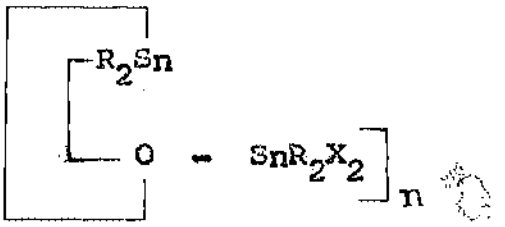


Davies et al (140) reported that the exhaustive hydrolysis of dialkyltin (IV) compounds R_2SnX_2 (X = e.g. halogen or carboxylate) under basic conditions gives the dialkyl tin oxides R_2SnO which are insoluble, amorphous, infusible solids and are usually regarded as high polymers. If however the reaction is carried out with a deficiency of base or with a weak base at least two intermediate hydrolysis products $R_4Sn_2X_2O$ and $R_4Sn_2X(OH)O$ could be isolated. The compounds are usually highly crystalline, soluble and low melting and hence appear not to be highly polymeric.

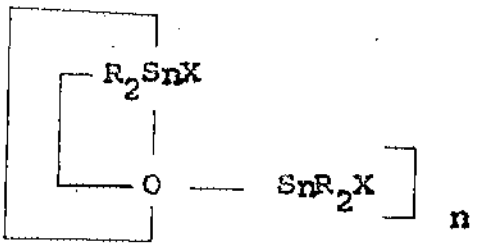
The following structure for $R_4Sn_2X_2O$, was assumed by Pfeiffer & Brach (141).



But Harada in a series of paper (142-146) argued the case for a cyclic oligomeric structure viz.



where the tin has coordination numbers of four and five. There might be a third possibility of structure as shown below



Davies et al (140) confined the presence of non-equivalence of the tin atoms indicating the rejection of the structures suggested by Pfeiffer & Brach. The other two structures contained non-equivalent tin atoms. The ^{119}Sn magnetic resonance spectra of the compounds $Bu_4Sn_2Cl_2O$ and $Bu_4Sn_2Br_2O$ in benzene or carbon tetrachloride at room temperature consisted of two broad overlapping bands of approximately equal intensity indicating the presence of two non equivalent types of tin atoms. The alkyl groups also are equivalent in Pfeiffer structures, whereas those are non-equivalent in the other two structures. Davies et al by PMR spectra, showed the presence of two types of methyl groups in chloroform solution in approximately equal amounts.

Compound of composition $R_4Sn_2XO(OH)$ obtained when the dihalide (R_2SnCl_2) and oxide react in 1:3 mole ratio. These compounds are usually stable, highly crystalline and soluble in organic solvents. The partial hydrolysis of $XR_2Sn-O-SnR_2X$ also yield the corresponding hydroxide $XR_2Sn-O-SnR_2OX$. At the same time the compounds formerly represented as $R_2SnOR_2SnX(OH)$ or $R'(R_2SnO)_3OR.R_2SnX_2$ have been found to be analogous to the distannoxane. There are a wide range of compounds known having compositions of type A($XR_2Sn-O-SnR_2X$) and type B ($XR_2Sn-O-SnR_2OH$) as represented below.

Type A Compounds

($XR_2SnO-SnR_2X$)

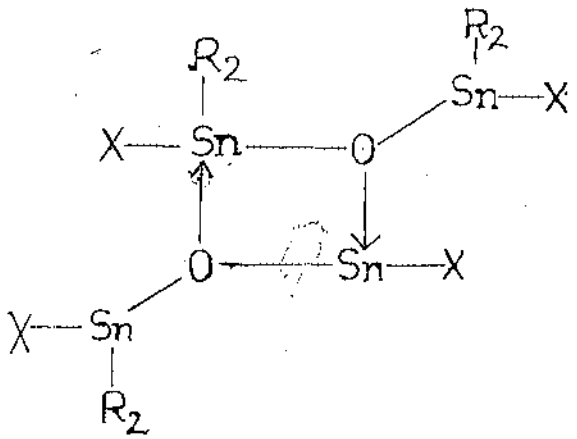
X	R	References
$OSi(CH_3)_3$	$CH_3, C_2H_5, C_3H_7, C_4H_9$	147
F	C_4H_9	148
Cl	$CH_3, C_2H_5, C_3H_7, C_4H_9$	149, 150, 148
Br	C_2H_5, C_3H_7, C_4H_9	150, 148
NCS	C_2H_5, C_3H_7, C_4H_9	148, 151
NCO	CH_3, C_4H_9, C_6H_5	152, 153
OCCR'	CH_3, C_4H_9	149, 150, 154
OC_6H_5	CH_3, C_4H_9	154-156
OC_6H_4Y	CH_3, C_4H_9	154, 156
Camphor sulphoxy	C_2H_5	148
β-Napthoxy	C_4H_9	156
α-Nitroso-β-napthoxy	CH_3, C_2H_5	157
OOR		158

Type B Compounds

($XR_2SnOSnR_2OH$)

X	R	References
Cl	$CH_3, C_2H_5, C_3H_7, C_4H_9$	150,159
Br	$CH_3, C_2H_5, C_3H_7, C_4H_9$	150
I	$CH_3, C_2H_5, C_3H_7, C_4H_9$	150
NCS	C_2H_5, C_3H_7, C_4H_9	151
NCO	C_4H_9, C_6H_5	153
$OOCCH_3$	C_4H_9	148,159

An X-ray crystal study of a type A compound, $(CH_3)_3Si-O-(CH_3)_2Sn-O-Sn(CH_3)_2OSi(CH_3)_3$ showed a dimeric structure containing a four membered ring due to reciprocal coordination of an oxygen atom between two tin atoms of one molecule to a tin atom of the other molecule as is shown by the following structure :



where R and X represent CH_3 and $OSi(CH_3)_3$ groups respectively.

Molecular weight determinations also showed that soluble compounds of both types A and B are dimeric in solution. On the other hand, compounds of the type $R_3SnOSnR_3$ as well as R_2SnX_2 are monomeric in benzene. A sulphide analogous of type A molecules $Cl(C_4H_9)_2Sn-S-Sn(C_4H_9)_2Cl$ is monomeric in benzene. From these observations, Okawara and Wada concluded that the dimerization of A and B type compounds is associated with the Sn-O-Sn linkage and the important factor in the dimerization is the presence of an anionic ligand X, attached to the tin atoms.

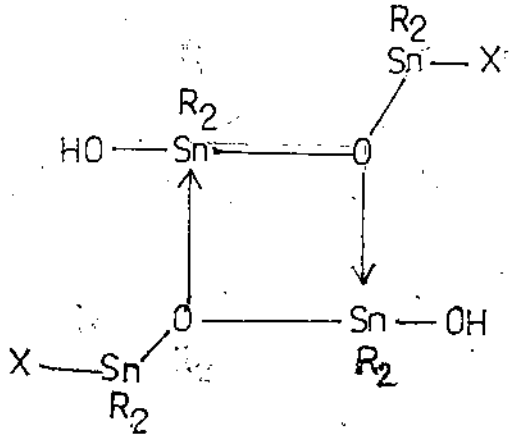
In the dimeric structure of type A distannoxanes there are both tetra coordinated and penta coordinated tin atoms and accordingly, two different kinds of substituents X. This difference is evident in the reaction of $XR_2Sn-O-SnR_2X$ (X = Cl, Br) with an excess of organic base, such as pyridine. One of the two substituents is selectively replaced with formation of a corresponding type B compounds (150).

The molecular weight of the compound in carbon tetra chloride solution at 37.5°C indicated the dimeric nature but at higher temperatures, evidence for dissociation was indicated by the Rast method of molecular weight determination, where a value corresponding to the monomer was obtained for

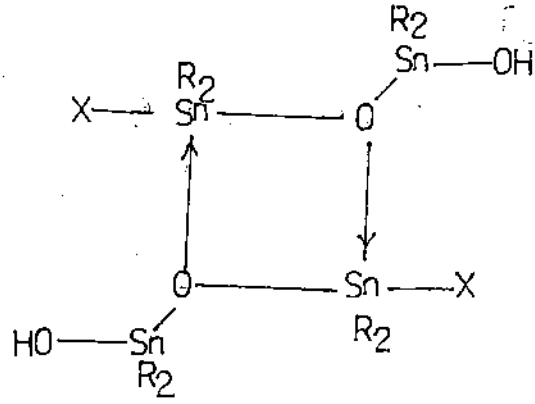
$(C_6H_5O)(C_4H_9)_2Sn-O-Sn(C_4H_9)_2(OC_6H_5)$.

The NMR spectra obtained at various temperatures of the trimethylsiloxy compound revealed that the dimer dissociates in solution at high temperature (160).

From the infrared absorption due to the Sn-O-H stretching vibration of the type B compounds (X = halogens), the presence of hydrogen bonds can not assume in these compounds. These hydroxides are stable against condensation by loss of water even at high temperature below the melting point. There are two probable configurations for the dimeric structure of type B compounds as shown below:



(A)

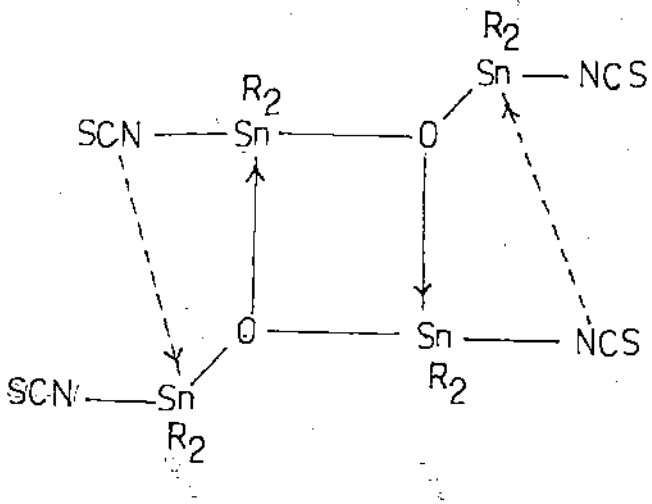


(B)

The configuration A contains the hydroxyl group on the penta coordinated tin atom while the configuration B contains hydroxyl group is on the tetra coordinated tin atom.

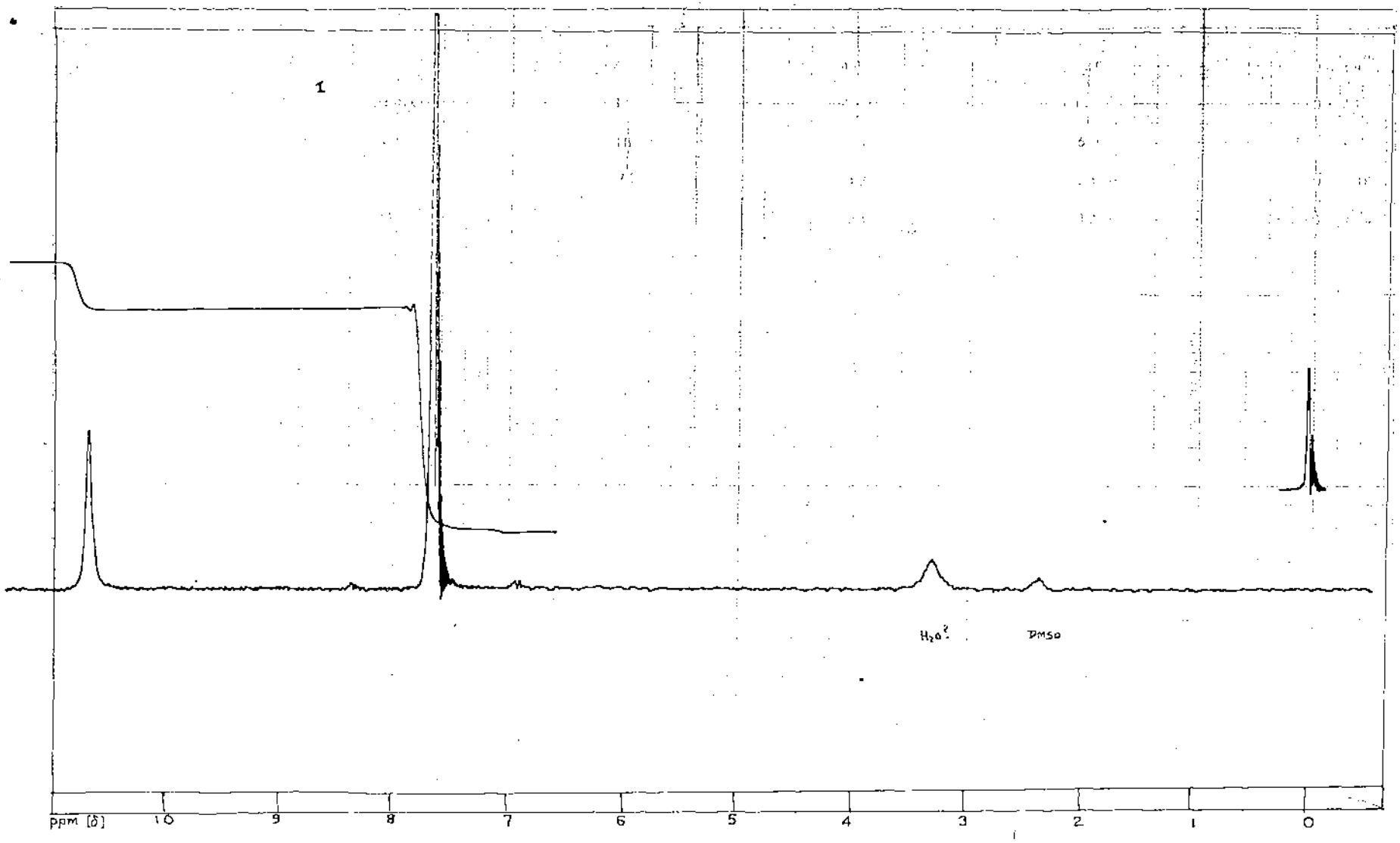
The structure A is favoured upon assumption that, in the partial hydrolysis process from type A compounds, the tin atom which most easily undergoes substitution would be the penta coordinated one (150). Further, the existence of a stable hydroxyl oxygen to the tetra coordinated tin atom similar to that occurring in dimeric $(CH_3)_3SnOH$.

The following, ladder type structure has been used to explain the infrared spectra of $(SCN)R_2SnOSnR_2(NCS)$ and $(SCN)R_2SnOSnR_2OH$ (which have all tin atoms penta coordinated) (161,151).

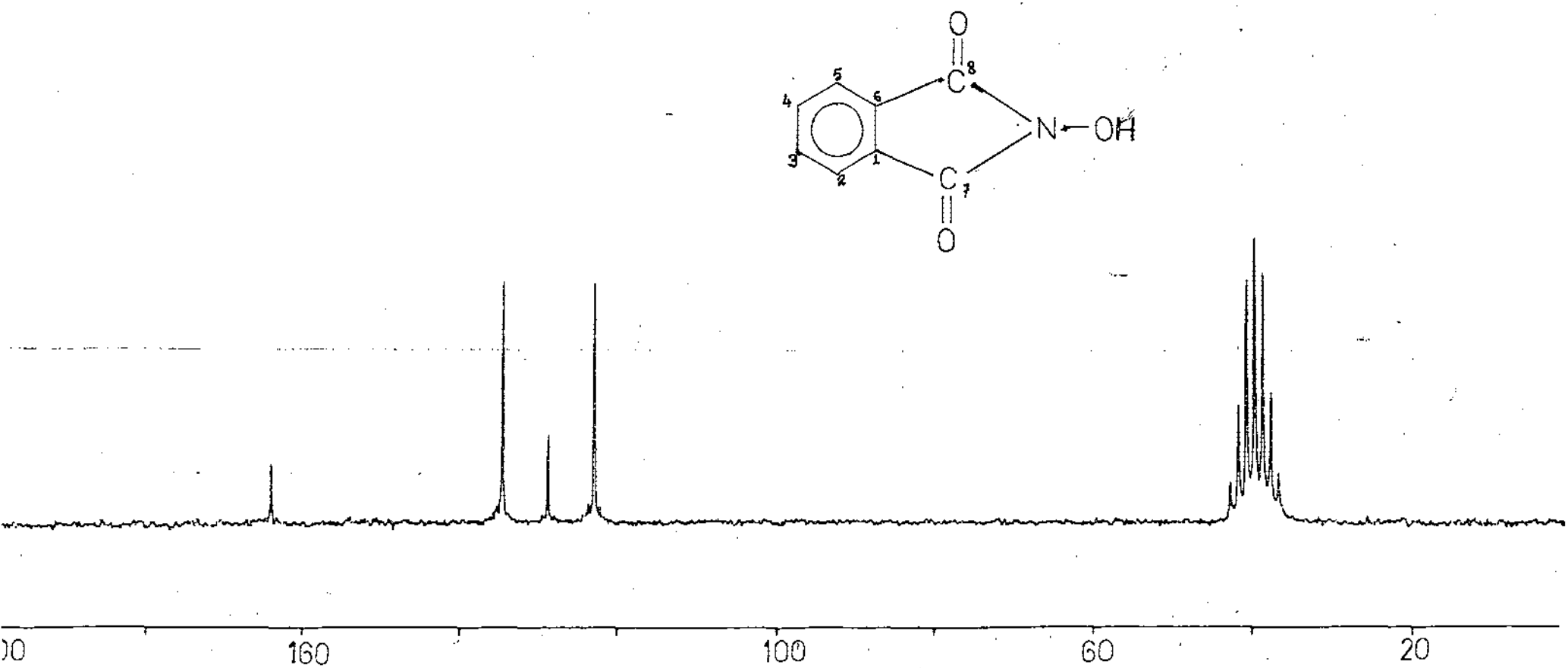


The ladder type structure has been confirmed by an X-ray study of $(CH_3)_3SiO(CH_3)_2Sn\text{-}O\text{-}Sn(CH_3)_2OSi(CH_3)_3$ (162).

In the light of preceeding discussions we would now attempt to discuss some structural aspects of some of the stannoxyl derivatives isolated during the current investigation.



^{1}H NMR spectrum of N-Hydroxy phthalimide



^{13}C NMR spectrum of N-hydroxy phthalimide (in d^6 DMSO)

1. Tributyl tin N-hydroxy phthalimide

The elemental analyses as indicated earlier showed an empirical composition $C_{20}H_{31}O_3NSn$.

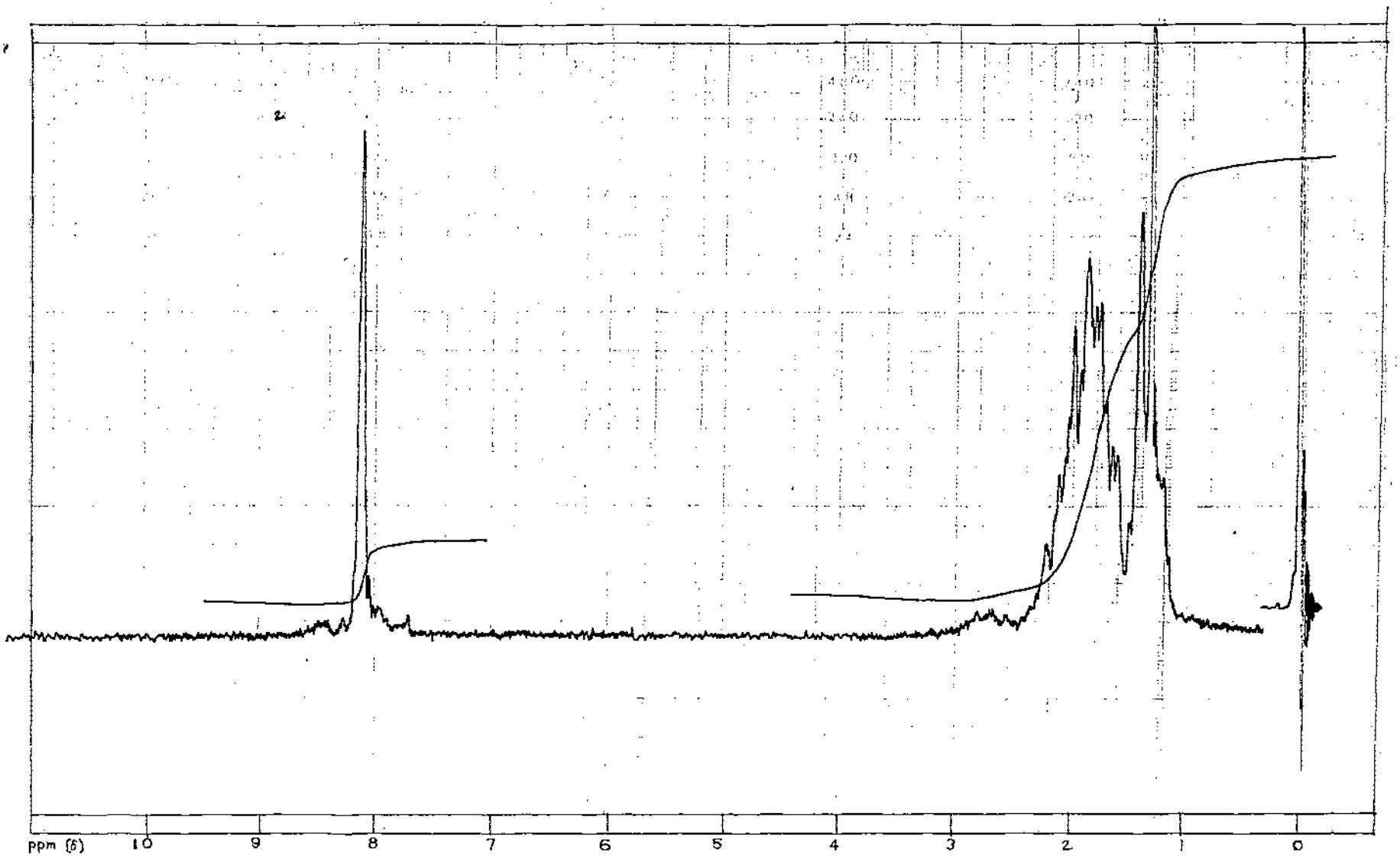
Mol. wt. (Rast Method) Found 446

Calcd (monomer) 452

In N-hydroxy phthalimide, the -OH stretching frequency appeared at 3168 cm^{-1}, but in the tributyl tin N-Hydroxy phthalimide the -OH frequency was totally absent, indicating the substitution of the hydroxyl proton by the tributyl tin moiety.

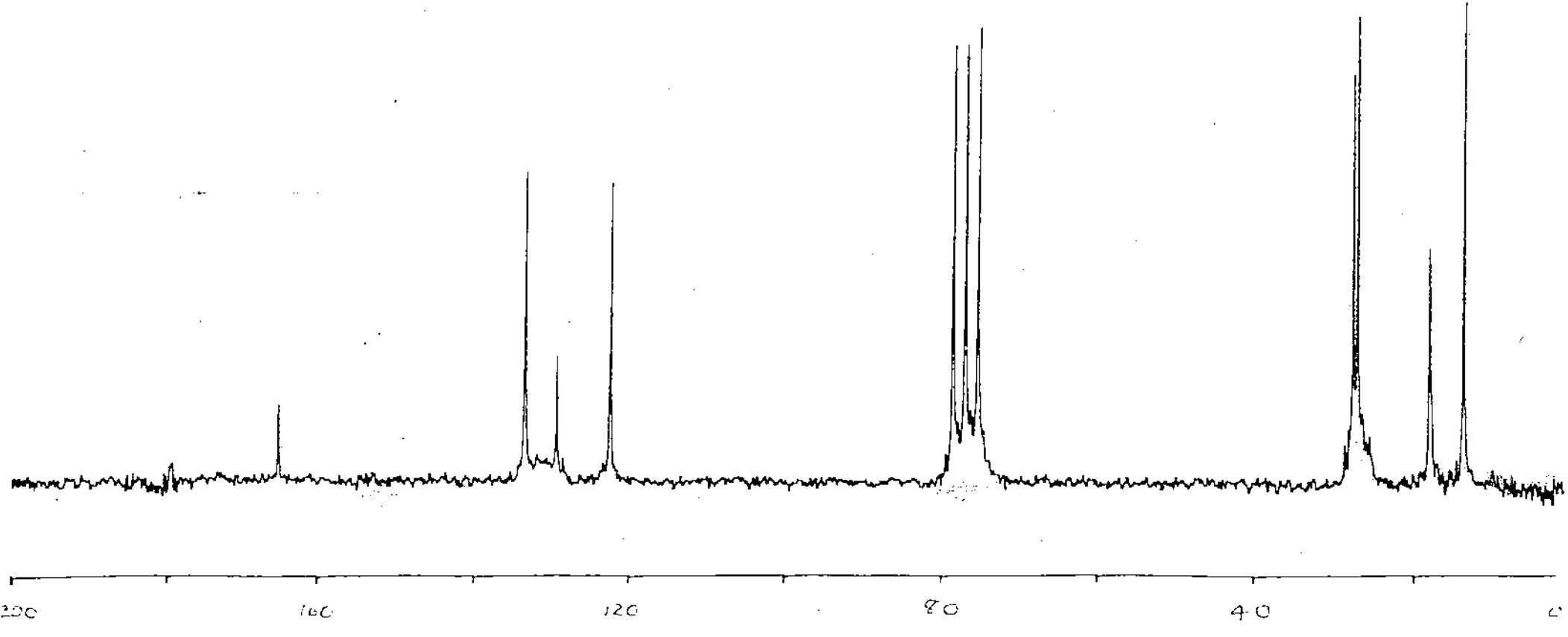
The carbonyl peaks of this compound appeared at 1770 cm^{-1} and 1700 cm^{-1} compared to the carbonyl peaks of N-hydroxy phthalimide, which appeared at 1793 cm^{-1} (s) and 1707 cm^{-1})(v.s.). Though the 1793 cm^{-1} peak of N-hydroxy phthalimide shifted somewhat significantly, the more intense 1707 cm^{-1} peak showed very little shifting indicating the absence of significant coordination of the carbonyl group to the tin atom in the complex. Absorption at 1156 cm^{-1} and 1190 cm^{-1} may be due to NCO coupled vibration.

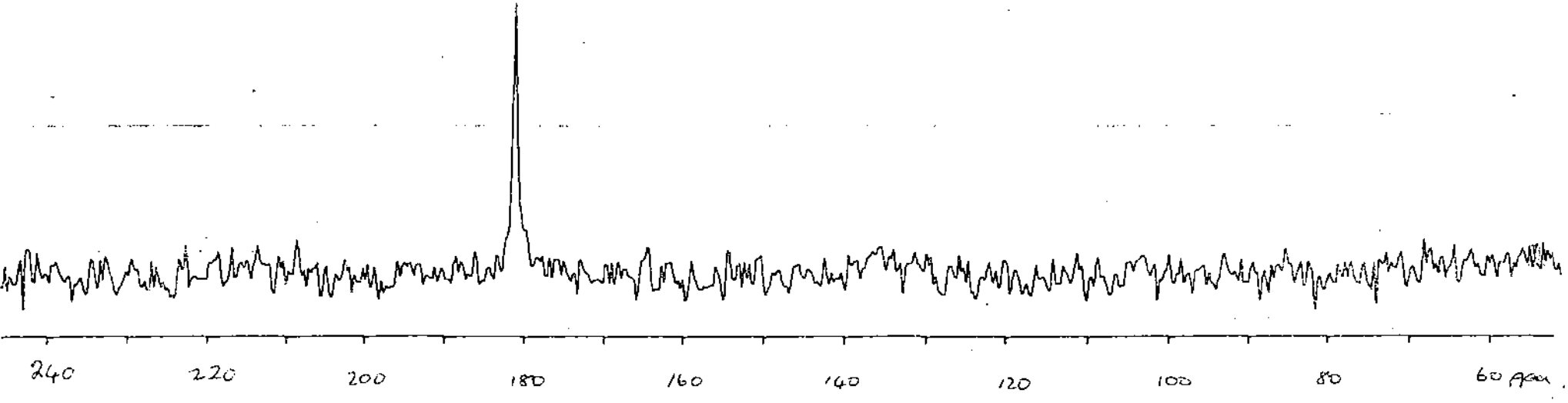
The ^1H NMR spectrum of the compound was recorded at 60 MHz. The methyl protons of the butyl groups appeared at δ 1.38 (9H) while the remaining methylene protons appeared as complex patterns between δ 1.39 - 2.9 (18H). The aromatic protons appeared 7.9 - 8.25 (Ar-4H).



^{1}H NMR spectrum of Tributyl tin N-hydroxy phthalimide

^{13}C NMR spectrum of Tributyl tin N-hydroxy phthalimide (in $CDCl_3$)





^{119}Sn NMR spectrum of Tributyl tin N-hydroxy phthalimide (in $CDCl_3$)

The ^{1}H NMR spectrum of N-hydroxy phthalimide showed aromatic protons at δ 7.64 (Ar-4H) and the hydroxyl proton at δ 10.64 (OH - 1H).

The ^{1}H NMR spectrum of the tributyl tin derivative of N-hydroxy phthalimide showed complete absence of hydroxyl proton as expected.

The ^{13}C NMR spectra was recorded for N-hydroxy phthalimide and also for the tributyltin N-hydroxy phthalimide. The ^{13}C NMR spectrum of the N-hydroxy phthalimide showed peaks at δ 122.86, 128.69 and 134.42 for aromatic carbon atoms (C_3,C_4), (C_2,C_5) and (C_1,C_6) respectively while the carbonyl carbon atoms (C_7,C_8) gave a single peak at δ 164.10. The corresponding ^{13}C NMR spectrum of tributyl tin N-hydroxy phthalimide gave the following peaks:

Aliphatic carbon atoms may be assigned as δ 13.62, 17.88, 27.11 and 27.67 for (C_{12},C'_{12}, C''_{12}), (C_{11},C'_{11} & C''_{11}), (C_{10},C'_{10} & C''_{10}) and (C_9,C'_9 & C''_9) respectively. Aromatic carbon peaks may be assigned as : δ 122.60, 129.52, 133.62 for (C_3,C_4), (C_2,C_5) and (C_1,C_6) respectively.

Carbonyl carbons at δ 165.32 for (C_7,C_8).

The carbonyl carbon atom of tributyl tin derivative appeared at δ 165.32 compared to ligand carbonyl carbon atom appearing at δ 164.10.

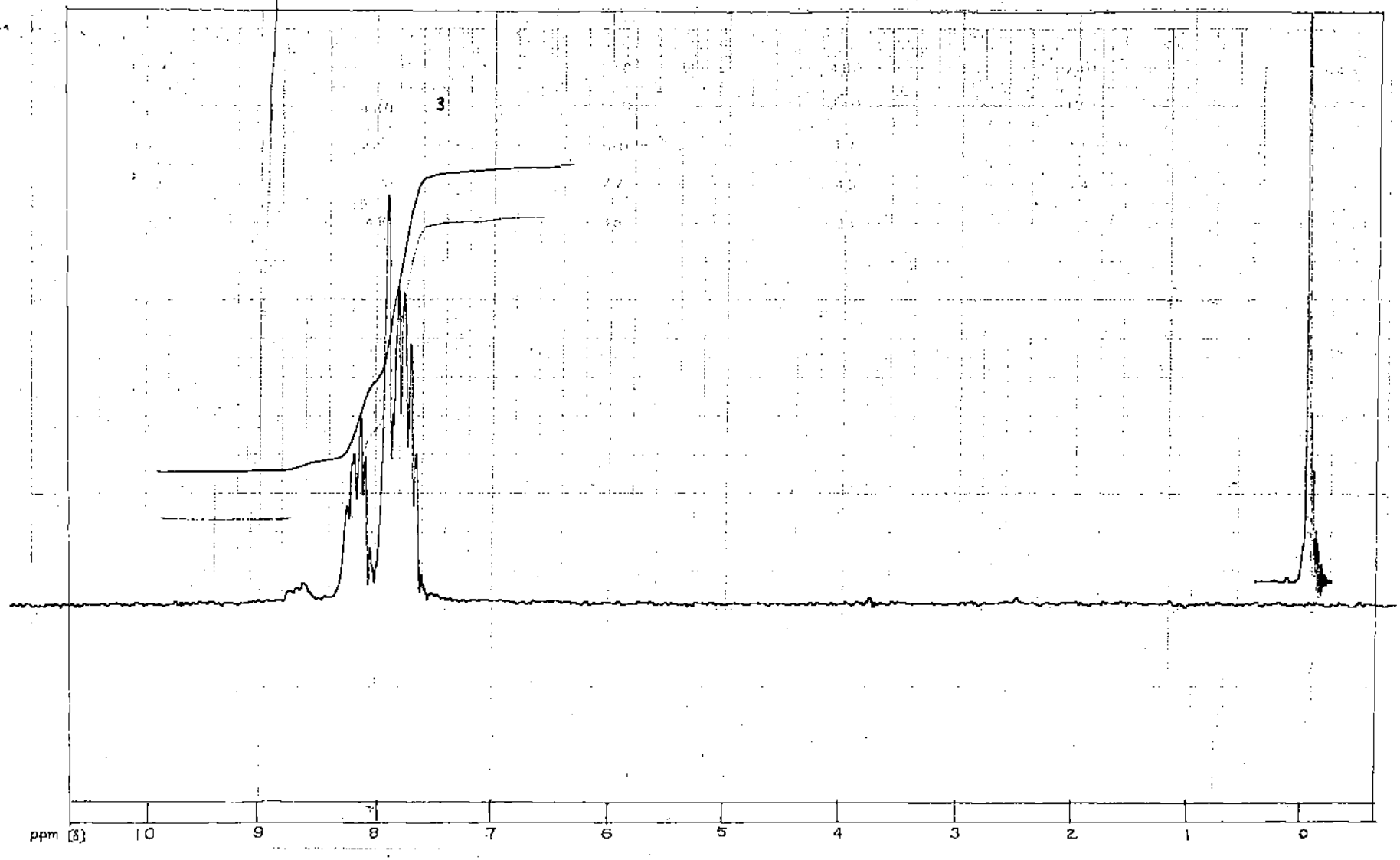
The ^{13}C NMR spectrum and IR spectrum of bis (tricyclohexyl tin) succinyl bis N-phenyl hydroxamate showed strong evidence of chelate formation. In ^{13}C NMR spectrum showed strong shielding effect

of the carbonyl carbon atom peak at δ 153.78 compared to carbonyl carbon atom peak of the ligand, which appeared at δ 172.08. Moreover, in the IR spectrum the $>C=O$ peak appeared at 1585 cm^{-1} in contrast with $>C=O$ peak of succinyl bis N-phenyl hydroxamic acid, which appeared at 1618 cm^{-1}. In case of dibutyl succinyl bis N-p tolyl hydroxamate, the ^{13}C NMR spectrum showed the presence of carbonyl carbon atom peak at δ 164.01 compared to ligand carbonyl peak at δ 171.51. The $>C=O$ stretching frequency of dibutyl derivatives appeared at 1590 cm^{-1} compared to 1615 cm^{-1} of the ligand carbonyl peak in the IR spectra. The IR and ^{13}C NMR spectra indicate strong intramolecular coordination of the carbonyl group to tin atom, where the relevant peaks shifted significantly in IR and ^{13}C NMR spectra.

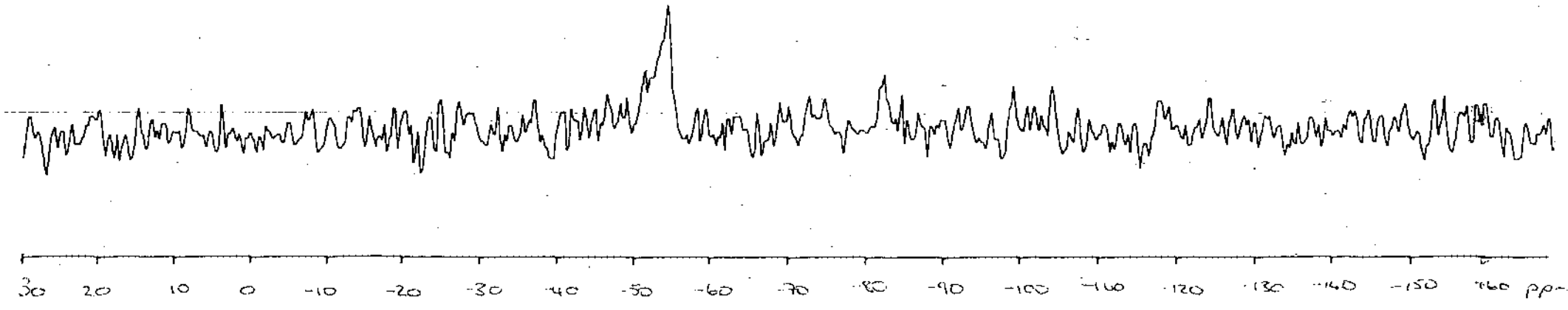
But if we compare the above data with those of the tributyl tin N-hydroxy phthalimide and N-hydroxy phthalimide the question of intramolecular coordination of the carbonyl groups to tin atom probably does not arise. Hence the tributyl tin N-hydroxy phthalimide is not a chelate complex but it is most probably an ester type of compound.

The ^{119}Sn NMR peak for the tributyl tin N-hydroxy phthalimide appeared at δ 181.44. The position of this peak indicated the tetra coordinating nature of tin atom.

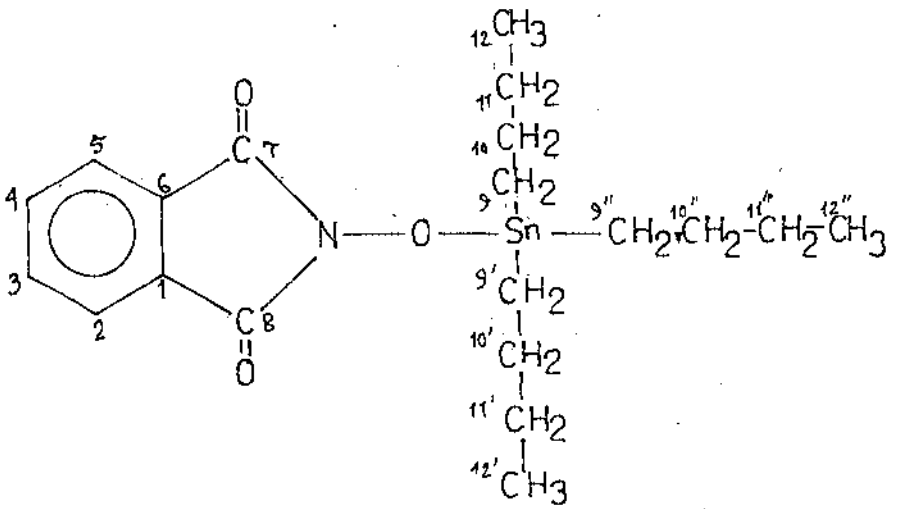
On the basis of the above data the structure of this compound tentatively can be suggested as follows:



^{1}H NMR spectrum of Triphenyl tin N-hydroxy phthalimide



^{119}Sn NMR spectrum of Triphenyl tin N-hydroxy phthalimide (in $CDCl_3$)



2. Triphenyl tin N-hydroxy phthalimide

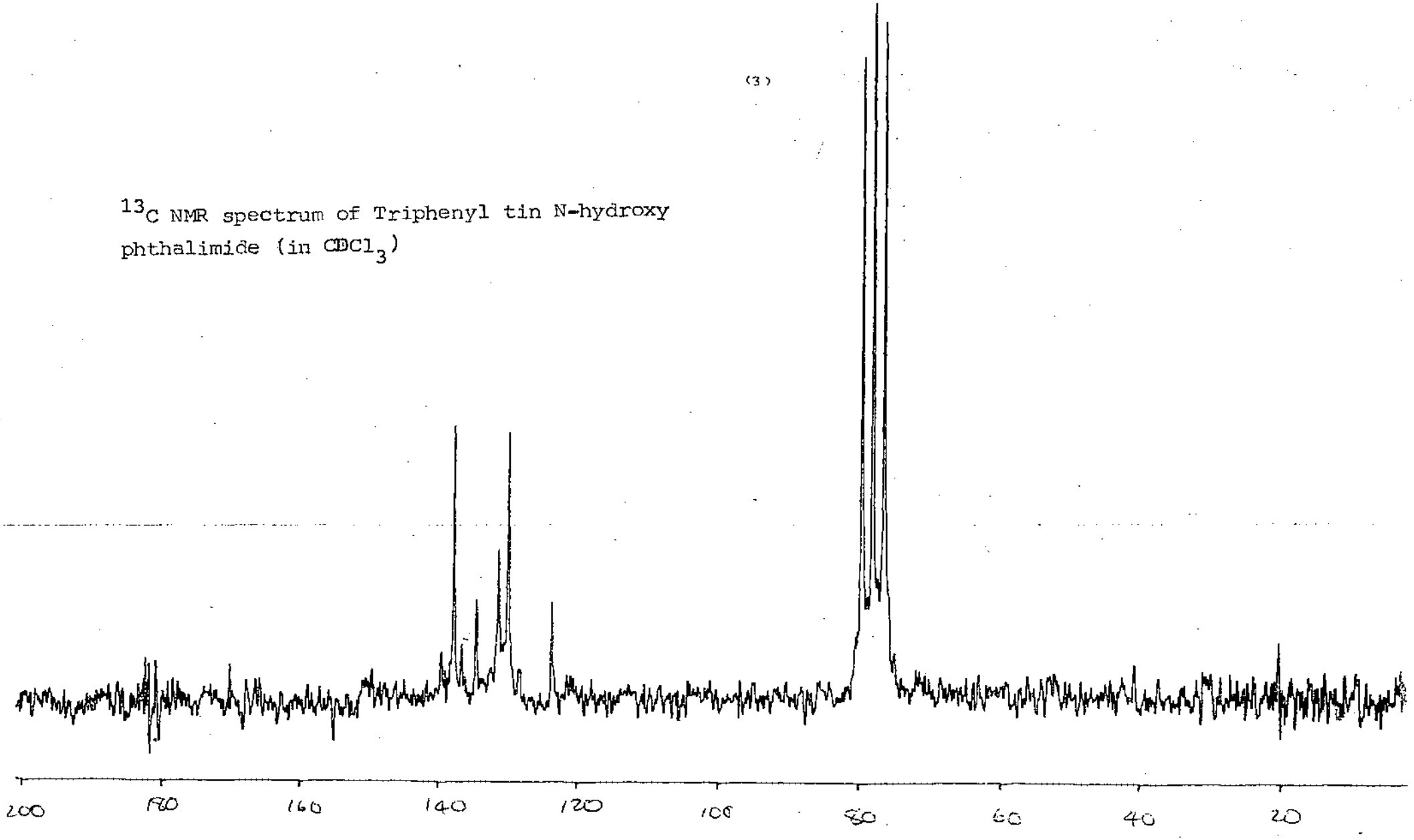
Elemental analyses of this compound showed an empirical formula of $C_{24}H_{19}O_3NSn$.

Mol. wt. (Rast method) Found 501, Calcd (for monomer) 512.

Like the preceeding tributyl tin compound, the IR spectrum indicated the absence of -OH stretching frequency of the ligand, indicated the substitution of the hydroxyl proton by triphenyl tin group.

The carbonyl peaks appeared at $\sim$1770 cm^{-1} and $\sim$1690(s). Here also a marginal shifting of carboxy peaks occurred, though significant coordination of carbonyl group to the tin atom might be absent. The peaks due to phenyl groups appeared at appropriate positions. The peaks at 1160 cm^{-1} and 1190 cm^{-1} may be due to NCO coupled vibration.

^{13}C NMR spectrum of Triphenyl tin N-hydroxy phthalimide (in $CDCl_3$)



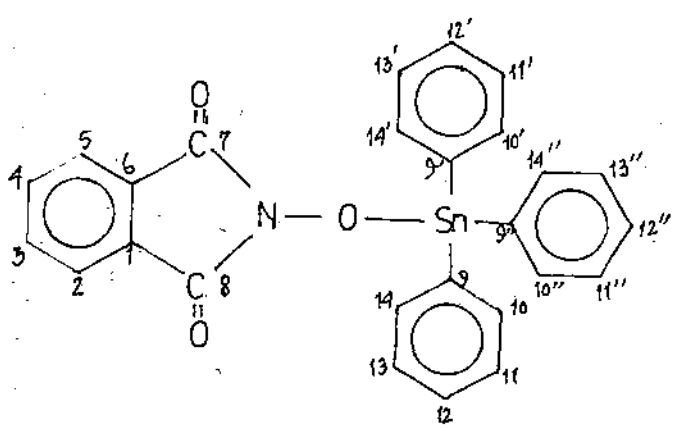
The ^{1}H NMR spectrum showed a group of peaks at δ 7.6 - 8.0; 8.04 - 8.16 and 8.45 - 8.80. It was not possible to assign ligand aromatic protons and tin aromatic protons in a conclusive manner from the spectrum obtained. However, the spectrum showed absence of hydroxyl proton of the ligand in the triphenyl tin derivative.

The ^{13}C NMR spectrum obtained was not desired quality. It did not record any peak for carbonyl carbon atom, probably due to weak intensity of that peak. It however, showed seven peaks for aromatic carbon atoms at δ 122.74, 129.12, 129.61, 129.89, 130.51, 133.66, 136.95. Assignment (164) may be made as follows (C_{11},C_{13} & etc), (C_1,C_6 & etc), (C_2,C_5 & etc), (C_{12} & etc), (C_3,C_4 & etc), (C_{10},C_{14} & etc) and (C_9 & etc).

In absence of the carbonyl carbon atom peak it is not possible to comment on the coordination of carbonyl group to tin atom.

The ^{119}Sn NMR peak appeared at δ -54.33 due to the tetra coordinating nature of the tin atom in this derivative.

Hence the suggested structure of Triphenyl tin N-hydroxy phthalimide may be indicated as follows:



3. Tricyclohexyl tin N-hydroxy phthalimide

The elemental analyses suggested the empirical composition of the compound $C_{26}H_{37}O_3NSn$.

Mol. wt. (Rast method) Found 555

Calcd (monomer) 530.

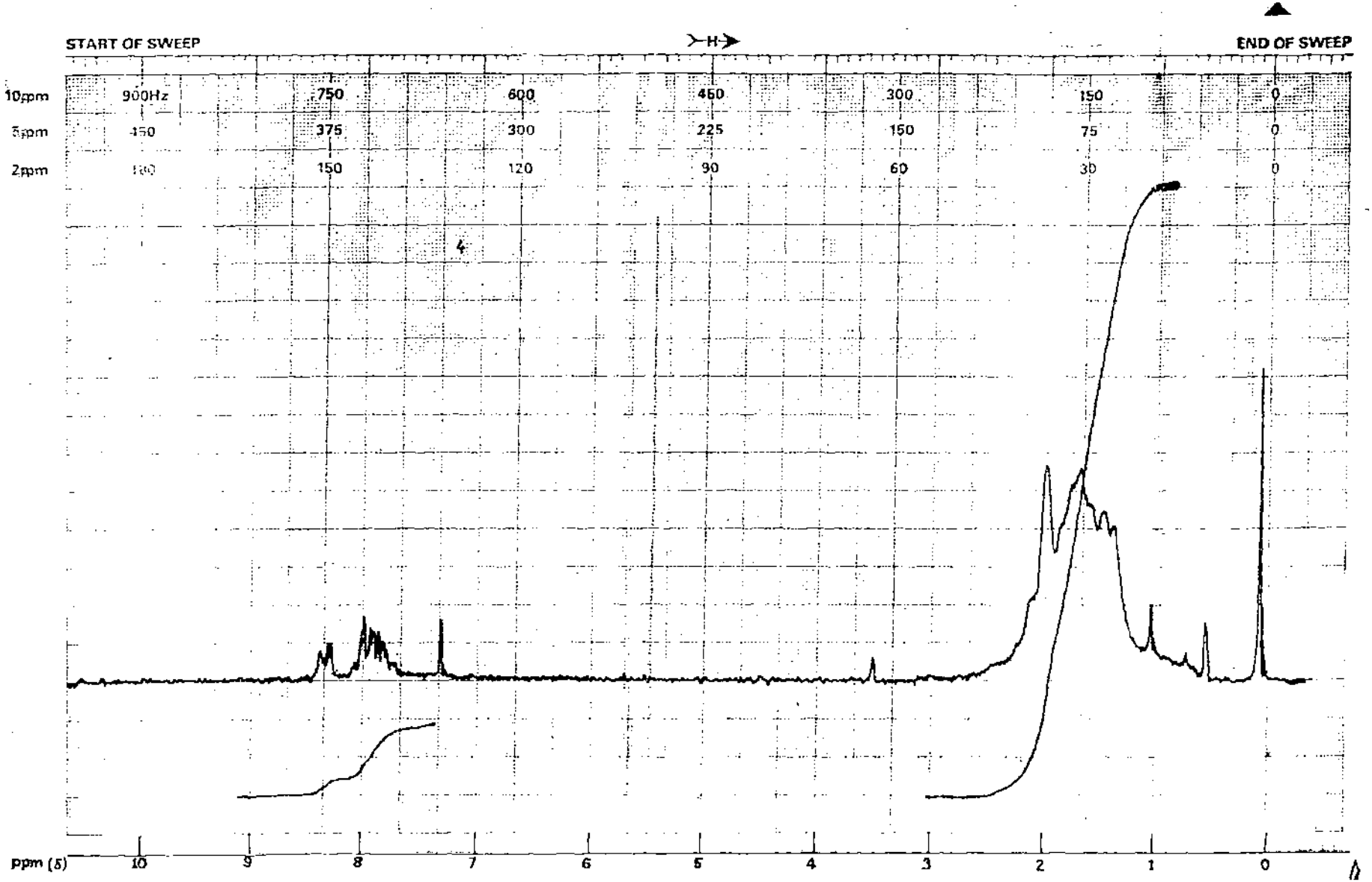
The IR spectrum showed the absence of -OH stretching frequency of the ligand indicating the substitution of the hydroxyl proton by tricyclohexyl tin group.

The carbonyl peak appeared at $\sim$ 1700 cm^{-1}(s). The shifting was negligibly small in comparison with the ligand major carbonyl peak which was found at 1707 cm^{-1}. Here also most probably there was no coordination from the carbonyl group to the tin atom. The peaks at 1165 and 1180 cm^{-1} may be assigned as NCO coupled vibration.

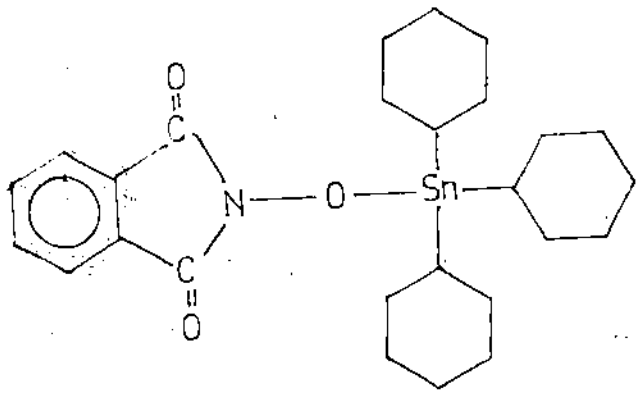
The ^1H NMR spectrum showed a group of complex peaks in the region δ 1.0 to 2.4 (for 33H). The aromatic protons appeared in the region of δ 7.6-8.3 (for 4H) as complex pattern.

It was not possible to obtain ^{13}C and ^{119}Sn spectra for this compound.

Hence comparing the other triorganotin derivatives the following structure can be suggested.



^{1}H NMR spectrum of Tricyclohexyl tin N-hydroxy phthalimide



4. Tetramethyl 1:3 di N-hydroxy phthalimido distannoxane (Polymeric)

The elemental analyses indicated an empirical formula for the compound $C_{20}H_{20}O_7N_2Sn_2$.

Absence of the -OH stretching frequency supported the removal of hydroxyl proton by the dimethyl tin moiety. The carbonyl peaks appeared at 1763 cm^{-1} and 1677 (v.s.). There was some shifting in the carbonyl peaks. So there may be some kind of carbonyl coordination, intramolecular or intermolecular.

At 1181 cm^{-1} and 1158 cm^{-1} the bands appeared may be due to N-CO coupled vibration. An additional band appeared at 594 cm^{-1} due to Sn-O-Sn bond. Sn-C stretching frequency obtained at 500 cm^{-1}.

^{1}H, ^{13}C and ^{119}Sn NMR could not be recorded due to very poor solubility of the compound in organic solvents.

5. Tetrabutyl 1:3 di N-hydroxy phthalimido distannoxane (Polymeric)

From the elemental analyses the suggestive empirical composition of the compound was $C_{32}H_{44}O_7N_2Sn_2$.

Apparent molecular weight obtained (Rast method)

478, Calcd 796.

Like earlier cases, there was no OH stretching frequency in the IR spectrum of the compound which was present in the ligand. So the proton of the hydroxyl group was replaced by dibutyl tin group.

The carbonyl stretching frequency bands appeared at 1761 cm^{-1} and 1697 cm^{-1}. In comparison with the ligand carbonyl peaks there was only a small shift.

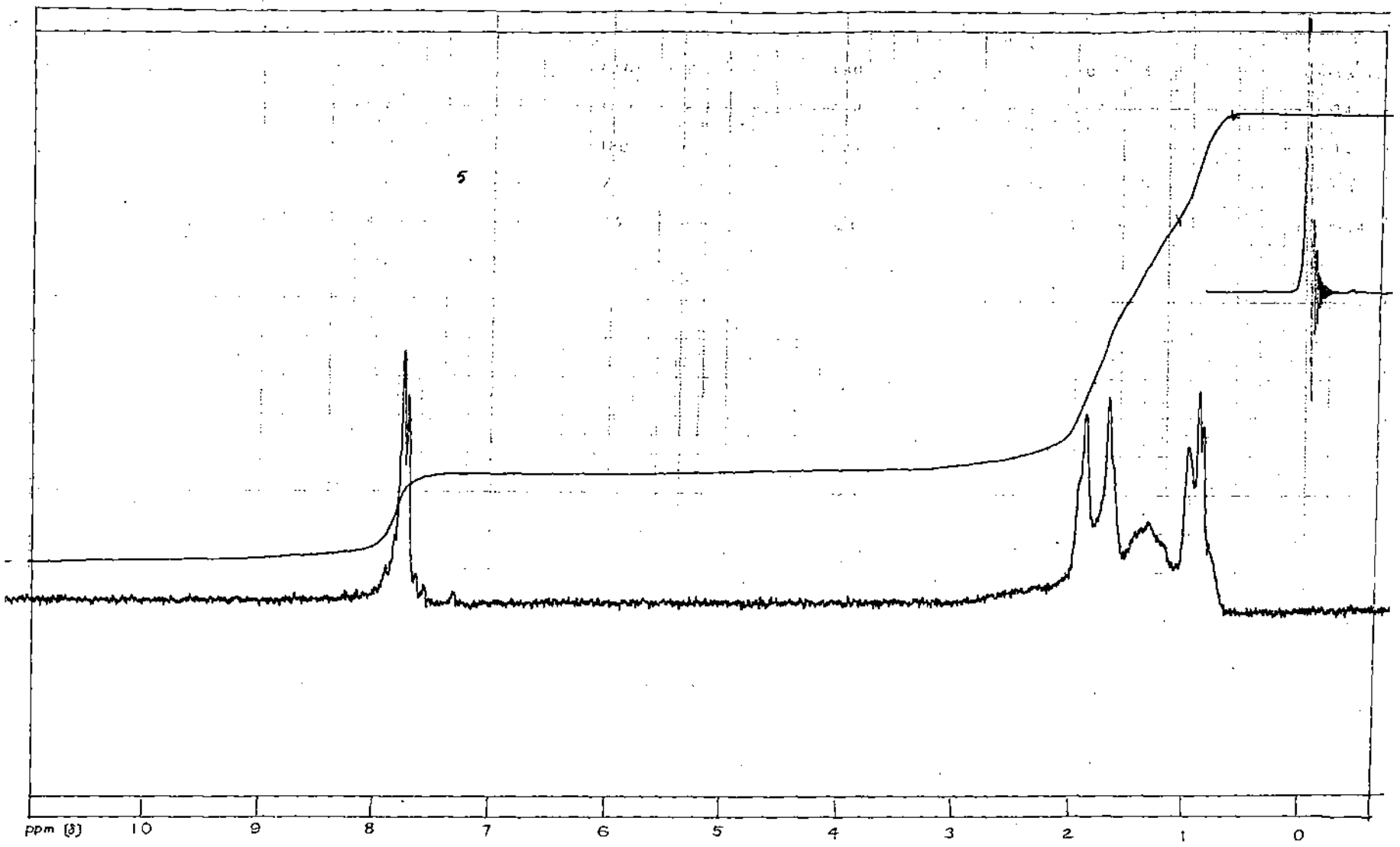
The N-C-O coupled vibration may be at 1182 cm^{-1} and 1156 cm^{-1}.

The peak at 576 cm^{-1} is due to Sn-O-Sn bond.

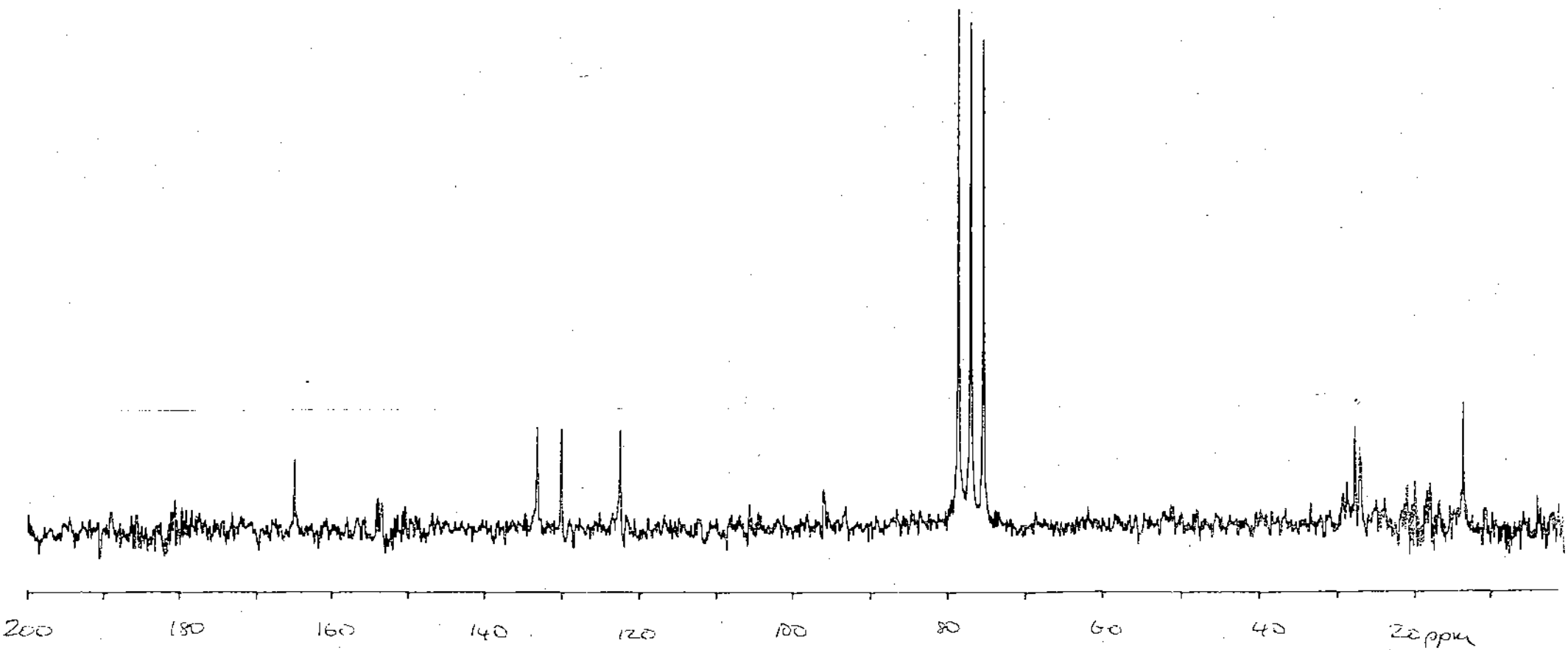
Sn-C stretching frequency appeared at 497 cm^{-1}.

^1H NMR spectrum showed peaks at δ 0.90(t) (for 12H) and from δ 1.10-2.05 (for 24 methyl protons). Aromatic protons appeared in the region δ 7.58-7.80 (for 8H). The spectrum showed that the hydroxyl protons is totally absent here in the compound.

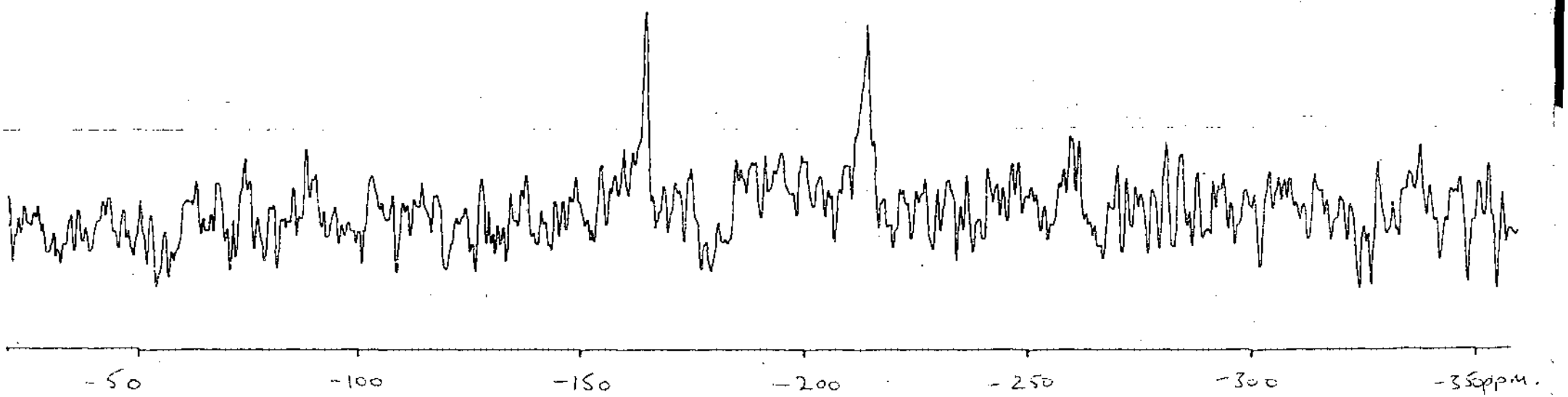
In the ^{13}C NMR spectrum methyl carbons (C_{12}, etc) appeared at δ 13.54, other methylene carbon peaks may be assigned (163) as δ 26.76, 26.89 and 27.52 for (C_9 & etc), (C_{11} & etc) and (C_{10} & etc)



^{1}H NMR spectrum of Tetrabutyl 1 : 3 di N-hydroxy phthalimido distannoxane



^{13}C NMR spectrum of Tetrabutyl, 1:3 di N-hydroxy phthalimido di stannoxane (in $CDCl_3$)



^{119}Sn NMR spectrum of Tetrabutyl 1:3 di-N-hydroxy phthalimido di stannoxane (in $CDCl_3$)

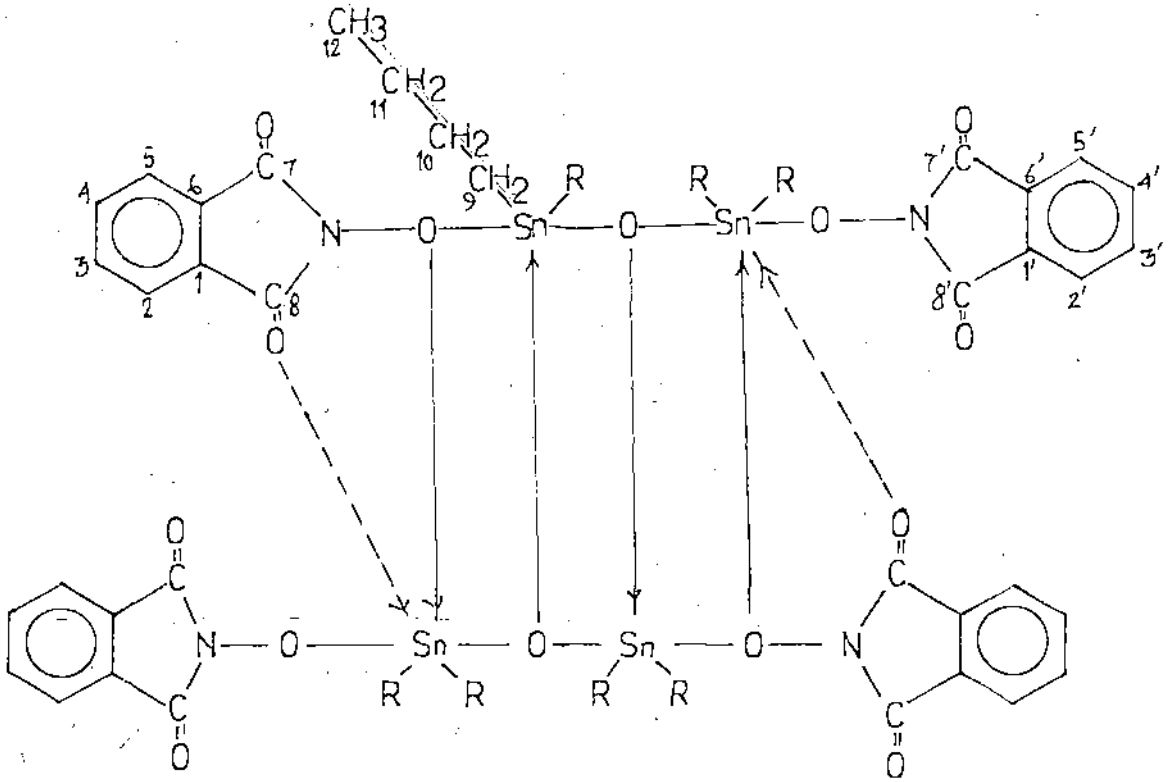
respectively. The aromatic carbons showed signals at δ 122.48, 130.05 and 133.18 which may be assigned (164) as (C_1,C_6 & etc), (C_2,C_5) and (C_3,C_4 & etc) respectively. The carbonyl carbons (C_7,C_8) appeared at δ 164.84.

The ^{119}Sn NMR spectrum showed two peaks at δ -164.46 and -218.87 showing that there were two kind of tin atoms having different environments. The values indicated that most probably one corresponded to penta coordinated tin and another hexa coordinated tin.

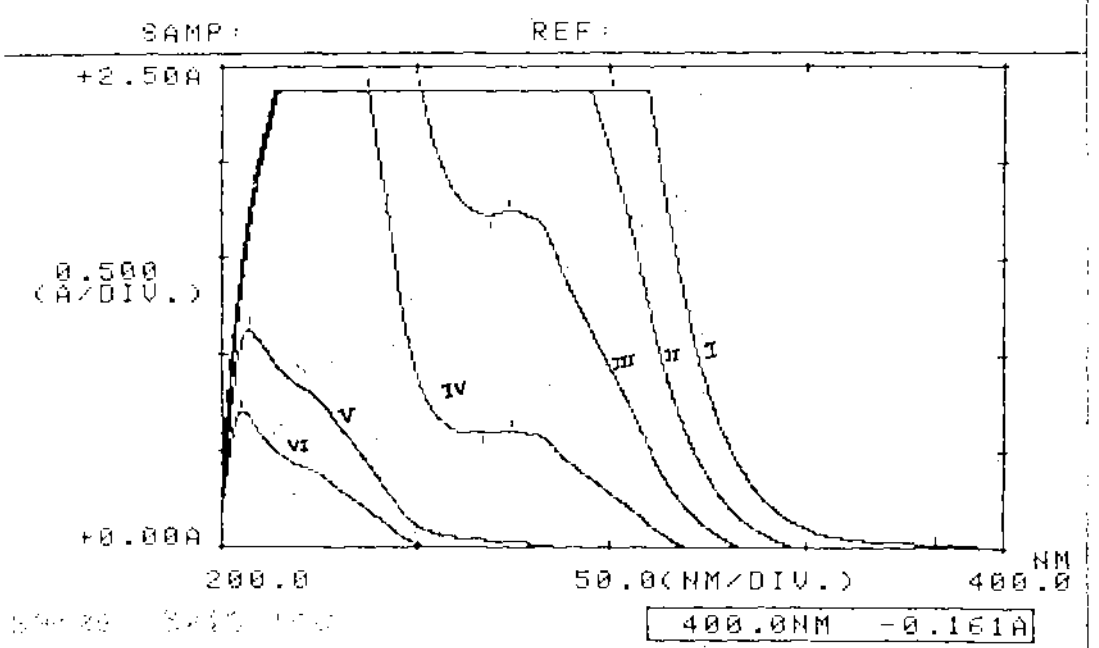
With N-hydroxy phthalimide, diorganotin oxides, yield organotin compounds which contained Sn-O-Sn linkages, as indicated by the presence of an additional peak at ~575 cm^{-1}. Diorganotin oxides in many cases form hexa coordinated monomeric R_2SnL_2 (LH_n = 8 hydroxy quinoline, substituted hydroxamic acids, diphenyl carbazones, β-diketones, dithizones etc). But with a trihydroxamic acid like N-hydroxy phthalimide, no such chelate compound could be obtained. The present investigation clearly showed stannoxane derivatives are formed. Due to some experimental difficulties, the molecular weight of these complexes could not be determined osmometrically and molecular weight determination by Rast's method gave rather abnormal values in some cases. The stannoxane derivatives obtained during the current investigation were ester types, not discrete chelate complexes. This conclusion was arrived at on the basis of the following observations. The carbonyl frequencies of the dimethyltin derivative and dibutyl tin derivative appeared at 1677 cm^{-1} and 1697 cm^{-1} respectively for more intense

carbonyl peak, in comparison 1707 cm^{-1} for the ligand. For chelate formation in case of substituted mono or di hydroxamic acids, the shifting of carbonyl peak of the ligand to chelate derivatives were of the order of $\sim$ 45-85 cm^{-1}. Again the ^{13}C NMR carbonyl carbon atom signal shifted about δ 6.0-7.0 for organotin derivatives in the high field but in the dibutyl tin derivative of N-hydroxy phthalimide the carbonyl carbon atom appeared at δ 164.84 compared to that of N-hydroxy phthalimide at δ 164.01.

The above data, along with appearance of Sn-O-Sn peaks at $\sim$576 cm^{-1} in the IR spectra, lead us to suggest the structure of tetraorgano 1:3 di N-hydroxy phthalimido distannoxane in the following way.



(R = n-butyl)



UV spectral of Tetrabutyl 1:3 di N-hydroxy phthalimido distannoxane [I-5.0 x 10^{-4}(M)] diluted subsequently 10 times in each step (II, III, IV, V and VI).

In such structure some of tin atoms with penta coordinated, while the other will be hexa coordinated in nature. There might be intermolecular carbonyl coordination to the tin atom, as a result of which there might be some shifting of carbonyl frequency in the organotin derivatives but these shifting may not be significant enough to suggest the intramolecular carbonyl coordination to the tin atom. The ^{119}Sn peaks suggest the presence of penta and hexa coordination of tin atoms (δ -164.46 and -218.87) for Tetrabutyl 1:3 di N-hydroxy phthalimido distannoxane.

The UV spectra of this compound in MeOH solution at different dilution support this suggestion. One would expect some hypsochromic shift of the peak with the decrease of intermolecular carbonyl coordination resulting from the decreasing concentration of the compound in MeOH.

In absence of precise molecular weight data and X-ray evidence, the above suggested structures may be considered somewhat tentative in nature.

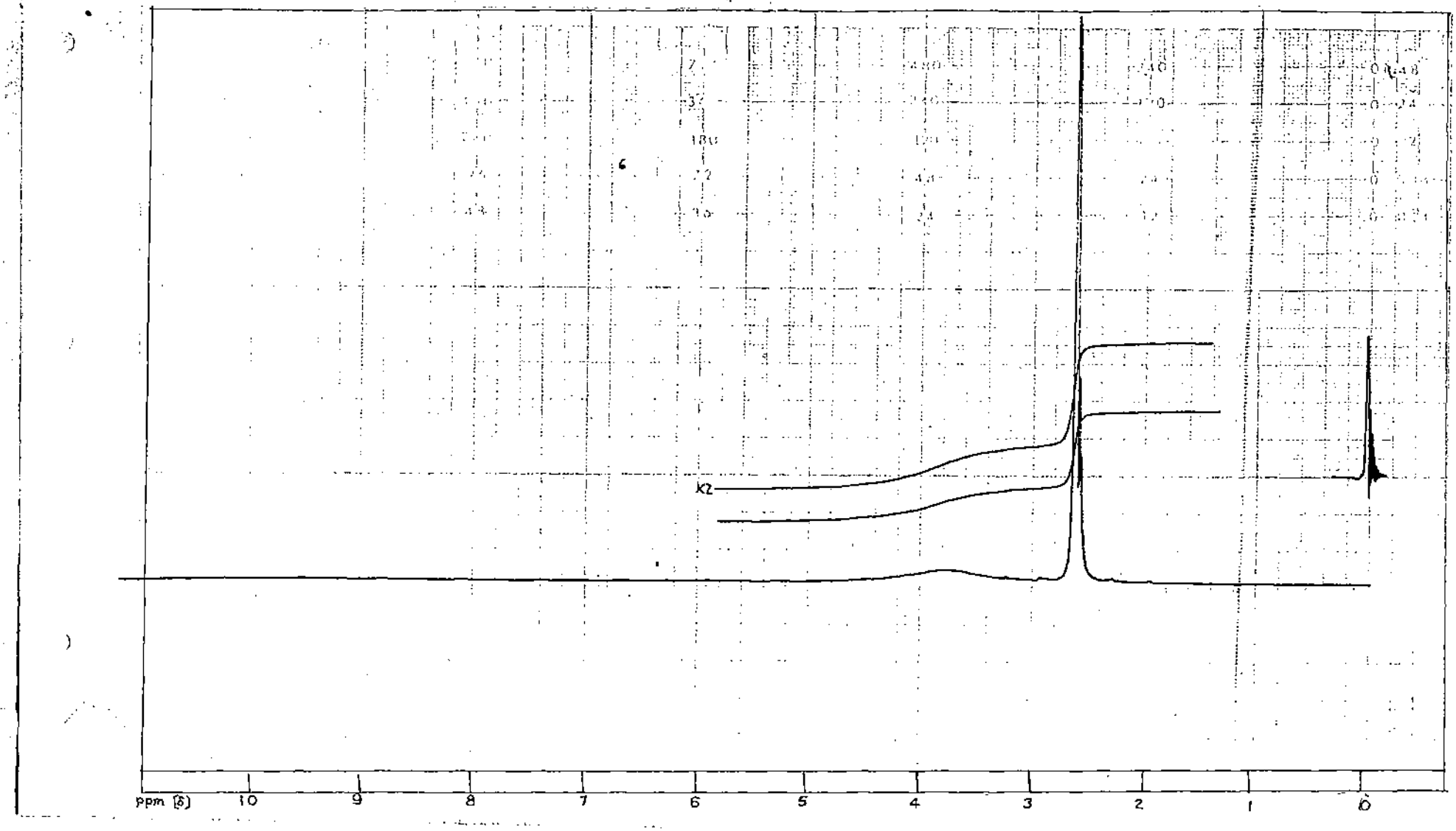
6. Triphenyl tin N-hydroxy succinimide

Empirical composition of the compound obtained from elemental analyses was $C_{22}H_{19}O_3NSn$.

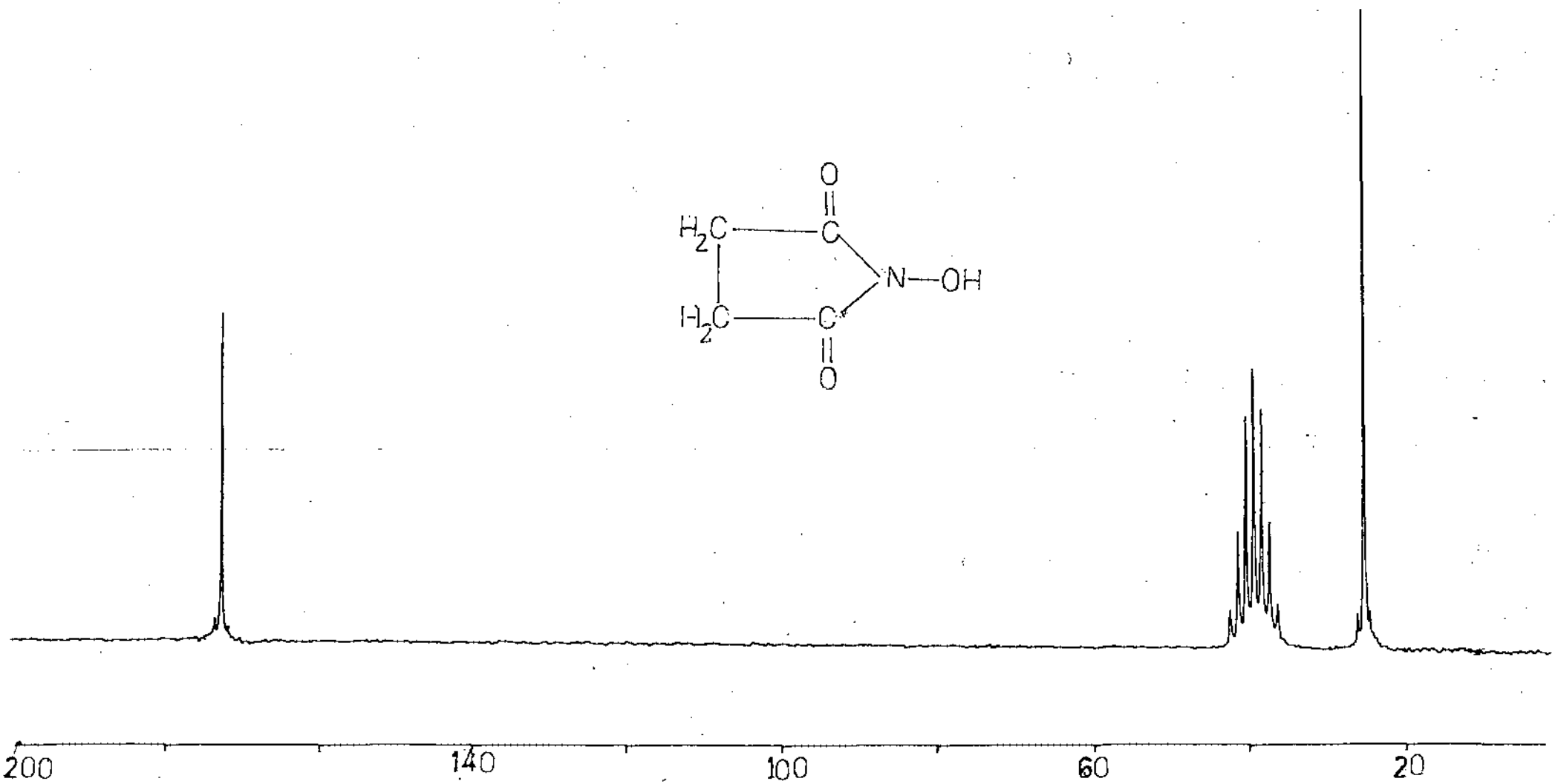
Apparent molecular weight (Rast method)

Found 442, Calcd (monomer) 464.

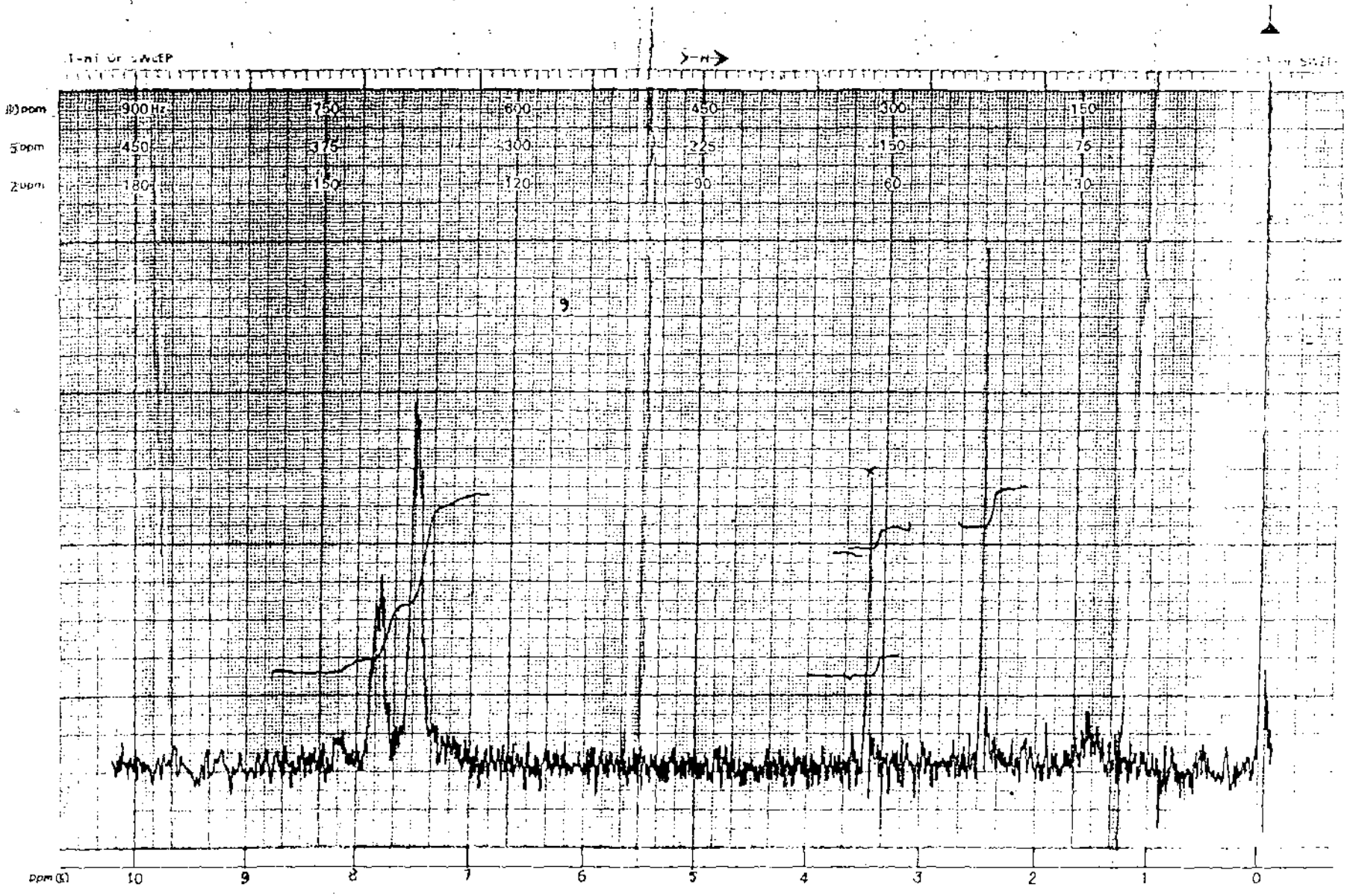
In the IR spectrum of N-hydroxy succinimide-OH stretching frequency absorption occurred at 3000 cm^{-1}. But in the triphenyl



^{1}H NMR spectrum of N-Hydroxy succinimide

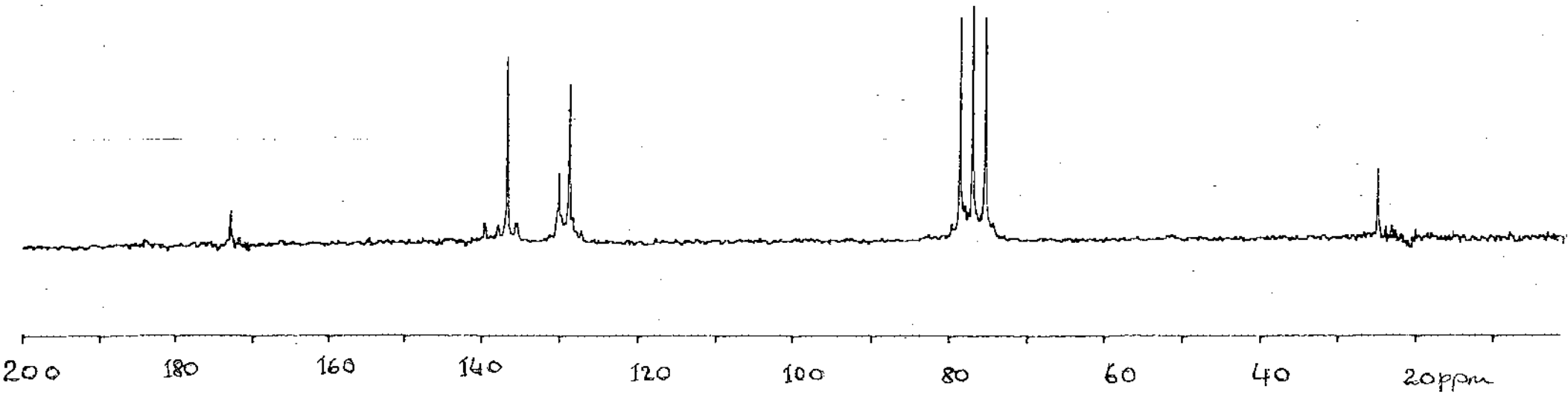


^{13}C NMR spectrum of N-hydroxysuccinimide (in d6 DMSO)



^{1}H NMR spectrum of Triphenyltin N-hydroxy succinimide

^{13}C NMR spectrum of Triphenyl tin N-hydroxy succinimide (in $CDCl_3$)



^{13}C S 73

tin derivative there was no absorption in this region indicating the complete removal of the hydroxyl proton.

Carbonyl absorption bands of N-hydroxy succinimide found at 1775 cm^{-1} and 1700 cm^{-1} (broad) [due to symmetric and anti symmetric mode of stretching vibration]. In case of the triphenyl tin derivative carbonyl absorption bands appeared at ~1785 cm^{-1} and ~1705 cm^{-1}(s), almost the same position as in the ligand. The peaks due to phenyl groups appeared at appropriate positions.

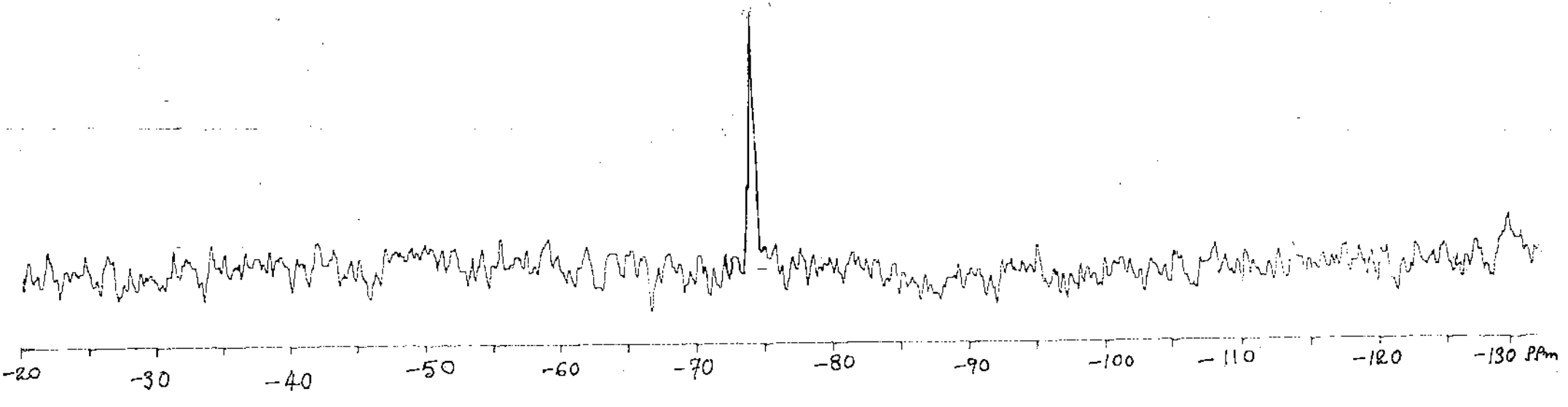
The band at 1240 cm^{-1} may be due to NCO coupled vibration.

^{1}H NMR spectrum of the compound showed that the hydroxyl proton was totally absent. Methylene protons appeared at δ 2.47(t) [for 4H]. Aromatic protons as two group of protons in the region δ 7.3-7.65 (for 10 Ar.H) and δ 7.7-7.9 (for 5 Ar.H).

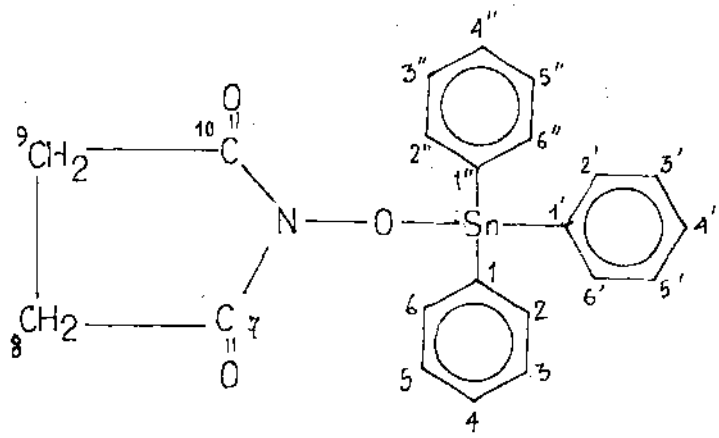
In the ^{13}C NMR spectrum of the ligand N-hydroxy succinimide, carbonyl carbons appeared at δ 172.74 and a single signal for the methylene carbons appeared at δ 25.12. In case of the triphenyl tin N-hydroxy succinimide, methylene carbons (C_8,C_9) appeared at δ 24.25. The signals for aromatic carbons may be assigned (164) as δ 136.75, 130.36, 130.10 and 128.79 for (C_1 & etc), (C_2,C_6 & etc) (C_4 & etc) and (C_3,C_5 & etc) respectively. The carbonyl carbons (C_7,C_{10}) appeared at δ 172.90. In comparison with ligand carbonyl carbon, there was no significant shifting.

^{119}Sn NMR spectrum showed a single peak at δ -74.44 indicating tetra coordinated tin atom.

^{119}Sn NMR spectrum of Triphenyl tin N-hydroxy succinimide (in $CDCl_3$)



The above results are similar to triphenyl tin N-hydroxy phthalimide and like the earlier, we can suggest the structure of triphenyl tin N-hydroxy succinimide as follows:



7. Tetra cyclohexyl 1:3 di N-hydroxy succinimido distannoxane (Polymeric)

On the basis of elemental analyses, the empirical formula of the compound can be written as $C_{32}H_{52}O_7N_2Sn_2$.

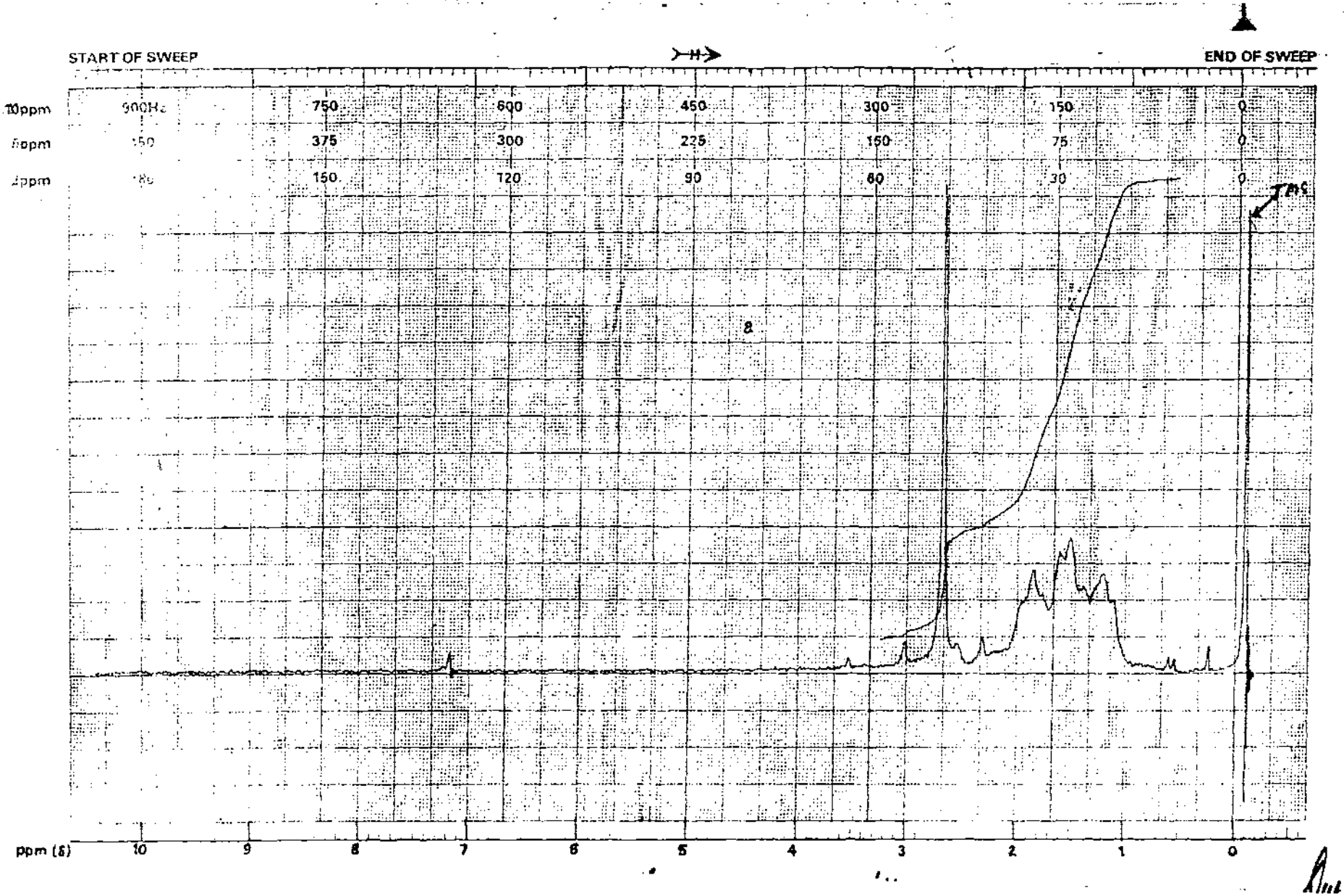
Apparent molecular weight (Rast method)

Found 460; Calcd 814.

In the IR spectrum, once again there was no band due to -OH stretching frequency.

Carbonyl absorption bands appeared at 1780 cm^{-1} and 1660 cm^{-1}. Compared to the ligand IR spectrum, there was shifting in the case of antisymmetric more intense band.

The band at 1250 cm^{-1} appeared most probably due to N-C-O coupled vibration.

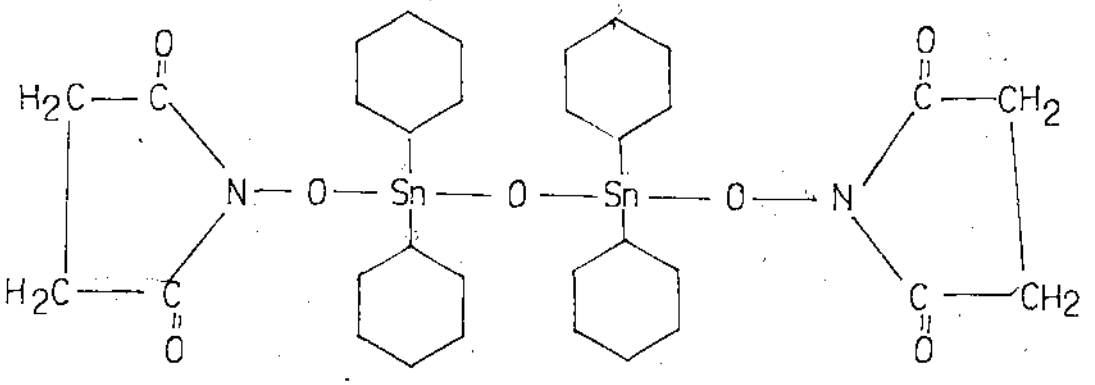


^{1}H NMR spectrum of Tetracyclohexyl 1:3$_{di}$N-hydroxy succinimido distannoxane

At 580 cm^{-1}, absorption due to Sn-O-Sn bond appeared.

Sn-C stretching frequency appeared at 490 cm^{-1}.

In the ^1H NMR spectrum, as expected there was no signal for hydroxyl proton, for methylene protons signal was obtained at δ 2.8 (for 8H). A group of signals appeared in the region δ 1.3-1.8 for the cyclohexyl protons (for 44H). Though tricyclohexyl tin hydroxide was reacted with N-hydroxy succinimide, the ^1H NMR spectra indicated a dicyclohexyl tin derivative could only be obtained. Comparing the previous compounds, we may suggest the formation of the following type of compound.



8. Tetramethyl 1:3 di N-hydroxy succinimido distannoxane (Polymeric)

The analytical data suggested the empirical formula for the compound as $C_{12}H_{20}O_7N_2Sn_2$.

Molecular weight could not be done applying Rast's method as the compound was insoluble in camphor.

IR spectrum of the compound showed no hydroxyl stretching frequency, a similar observation as have been made in earlier cases.

The carbonyl absorption bands found at 1776 cm^{-1} and 1700 cm^{-1} no carbonyl shifting occurred compared to ligand carbonyl absorptions.

An additional band appeared at 576 cm^{-1} which was due to Sn-O-Sn bond.

Sn-C stretching frequency found at 535 cm^{-1}.

The peak at 1245 cm^{-1} most probably due to N-C-O coupled vibration.

^{1}H, ^{13}C and ^{119}Sn NMR for this compound could not be recorded, because the compound had very poor solubility in common organic solvents.

In the absence of adequate data, it was not possible to suggest any reasonable structure of this compound, though it may have a composition like the earlier diorganotin derivatives.

9. Tetrabutyl 1:3 di N-hydroxy succinimido distannoxane (Polymeric)

From the elemental analyses the empirical formula of the compound can be written as $C_{24}H_{44}O_7N_2Sn_2$.

Apparent molecular weight have been found 442 (Rast's method), Calcd 712.

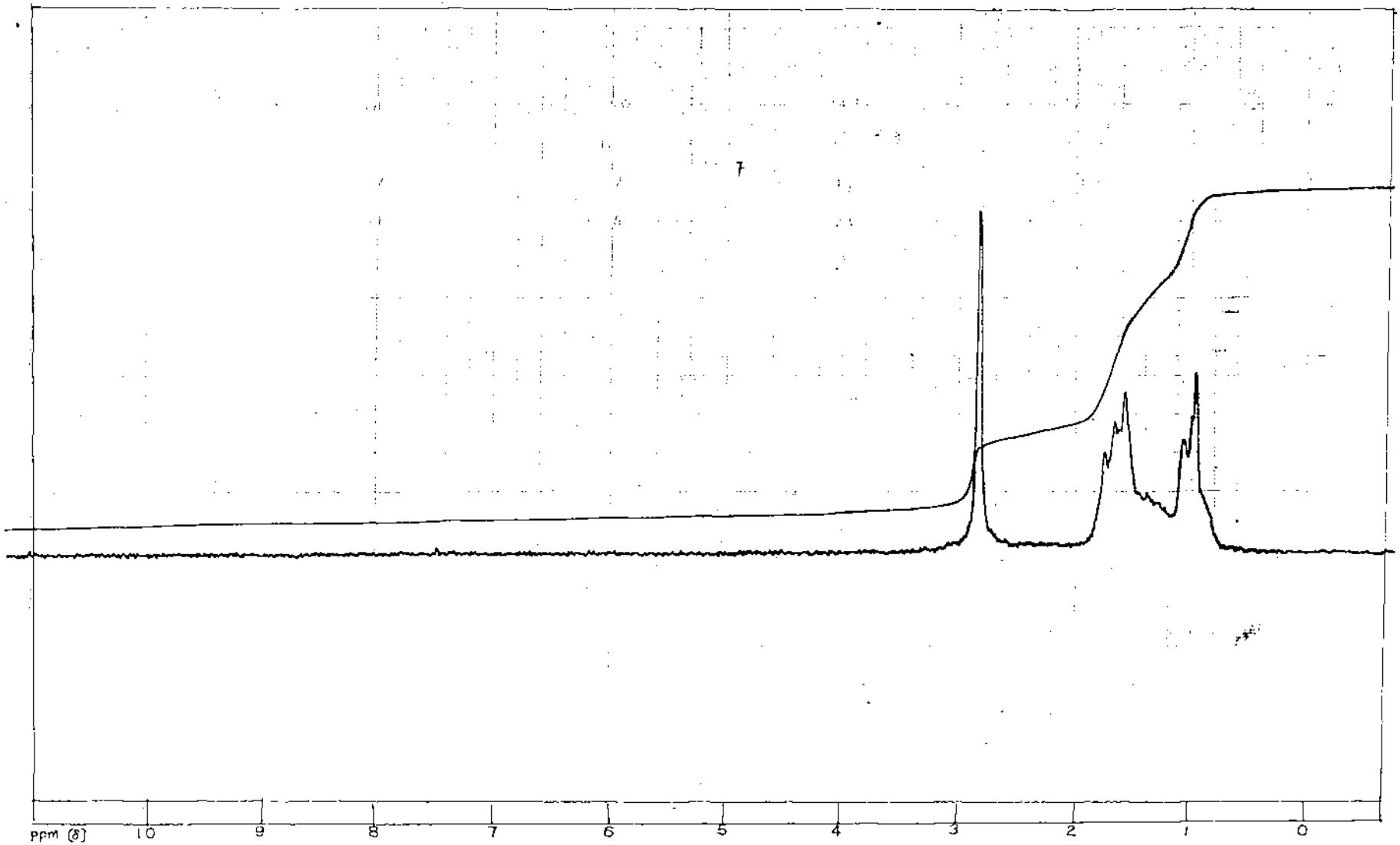
In the IR spectrum of the compound carbonyl absorption bands appeared at 1780 cm^{-1} and 1690 cm^{-1}. Carbonyl absorption did not shift significantly compared to the ligand carbonyl absorption bands.

The band at 1240 cm^{-1} may be due to N-C-O coupled vibration.

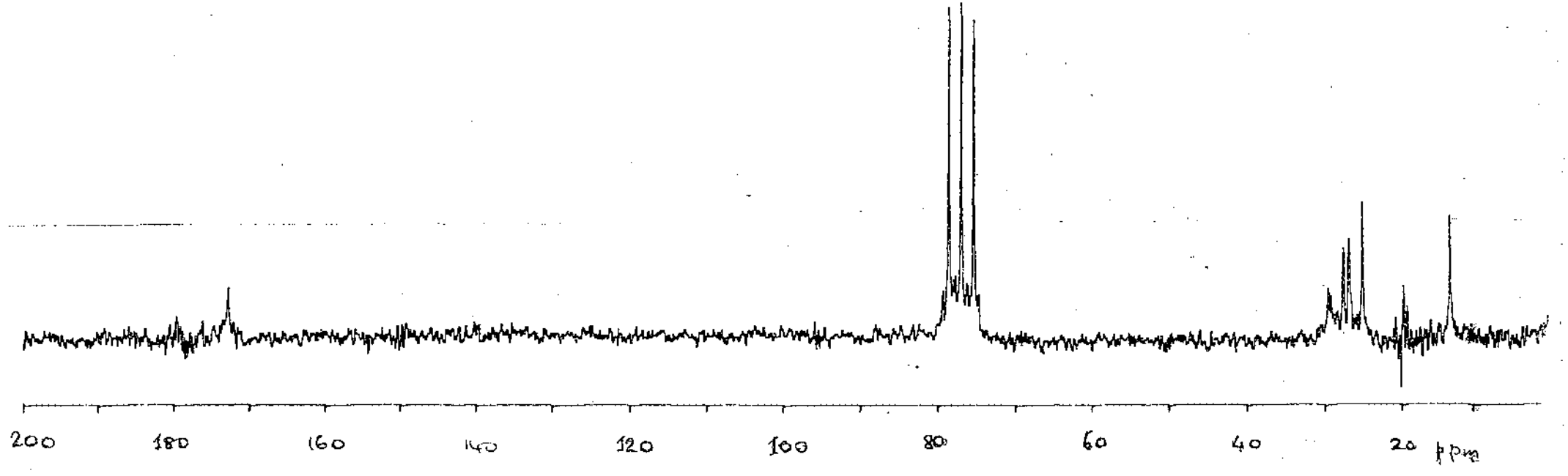
Absorption due to Sn-O-Sn bond found at 580 cm^{-1} and Sn-C stretching band appeared at 560 cm^{-1}.

The ^1H NMR spectrum of tetrabutyl 1:3 di N-hydroxy succinimido distannoxane showed no hydroxyl proton signal. The methylene protons due to succinyl group gave a single signal at δ 2.82 (for 8 protons) while the methylene protons of the butyl group found in the region δ 1.2-1.8 (for 24 protons) and methyl protons appeared in the region δ 0.9-1.1 (for 12 protons).

In the ^{13}C spectrum of tetra butyl 1:3 di N-hydroxy succinimido distannoxane, the methyl carbons (C_4,C_4, etc) found at δ 13.61 and the methylene carbons of butyl groups may be assigned (163) as δ 26.75, 26.86 and 27.53 for (C_1 & etc), (C_3 & etc) and (C_2 & etc) respectively. The succinyl methylene carbons (C_6,C_6,, C_7 & C_7,)

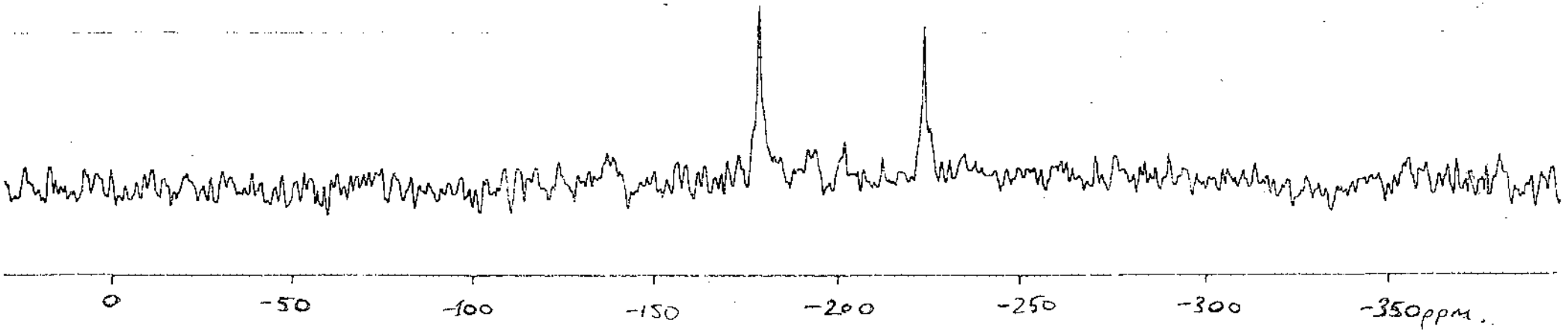


$^{1}_{H}$ NMR spectrum of Tetrabutyl 1 : 3 di N-hydroxy succinimido distannoxane



^{13}C NMR spectrum of Tetrabutyl 1:3 di N-hydroxy succinimido distannoxane (in $CDCl_3$)

$^{13}C\{^1H\}$



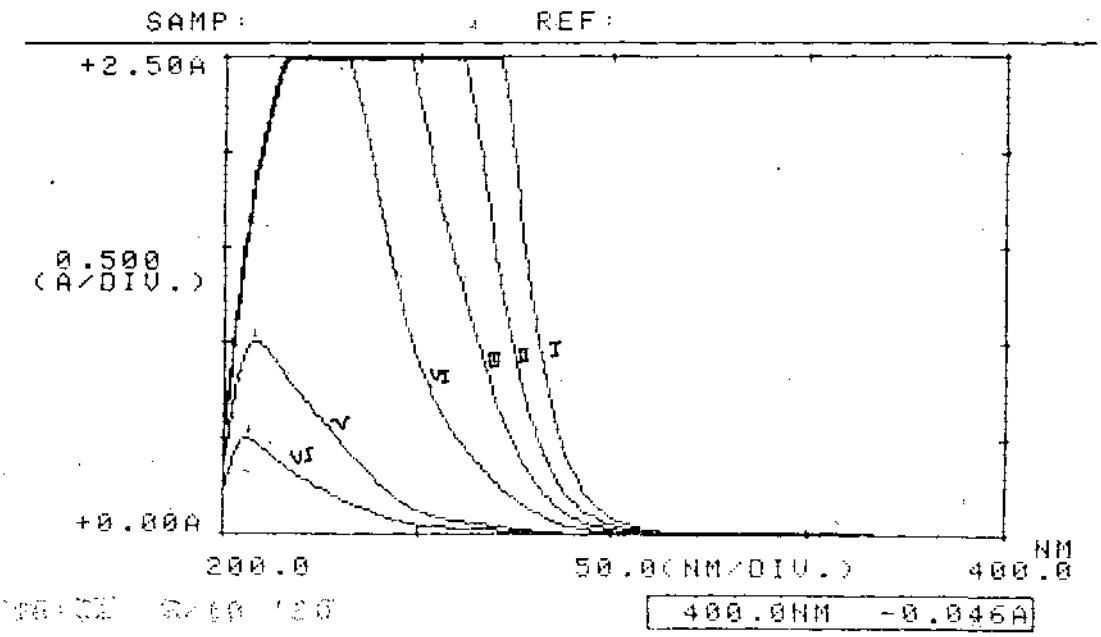
^{119}Sn NMR spectrum of Tetrabutyl 1 : 3 di N-hydroxy succinimido distannoxane (in $CDCl_3$)

appeared at δ 25.02. The carbonyl carbons (C_5,$C_{5'}$, C_8 & $C_{8'}$) found at δ 172.77.

The ^{119}Sn NMR spectrum of this compound showed two tin signals at δ -178.85 and -223.50.

So far we have discussed the available data for the diorganotin derivatives of N-hydroxy succinimide, it has been found that these type of compounds showed similar behaviour as have been shown by the diorganotin derivatives of N-hydroxy phthalimide. Here again the distinct Sn-C-Sn bond appeared in the range of 570-580 cm^{-1} in IR spectrum, showing that stannoxane derivatives are formed. Carbonyl absorption bands for the diorganotin derivatives of N-hydroxy succinimide showed no significant shifting. Only in the case of dicyclohexyl tin derivative the -CO absorption shifted 40 cm^{-1} in case of the major peak. But in case of dibutyl tin derivative $\Delta\nu$ is only 10 cm^{-1} and in the case of dimethyl tin derivative it was not shifted at all. The observations indicate that significant intramolecular coordination did not occur from carbonyl group to tin atoms.

Evidence also came from the ^{13}C spectral data. Here again it is found that significant shifting did not occur for the carbonyl carbon, which have been found in case of definite chelate compound (carbonyl carbon shifted about δ 6.0-7.0). But in case of tetra butyl 1:3 di N-hydroxy succinimido distannoxane the signal for carbonyl carbon appeared at δ 172.77 whereas this was obtained for the ligand at δ 172.74.



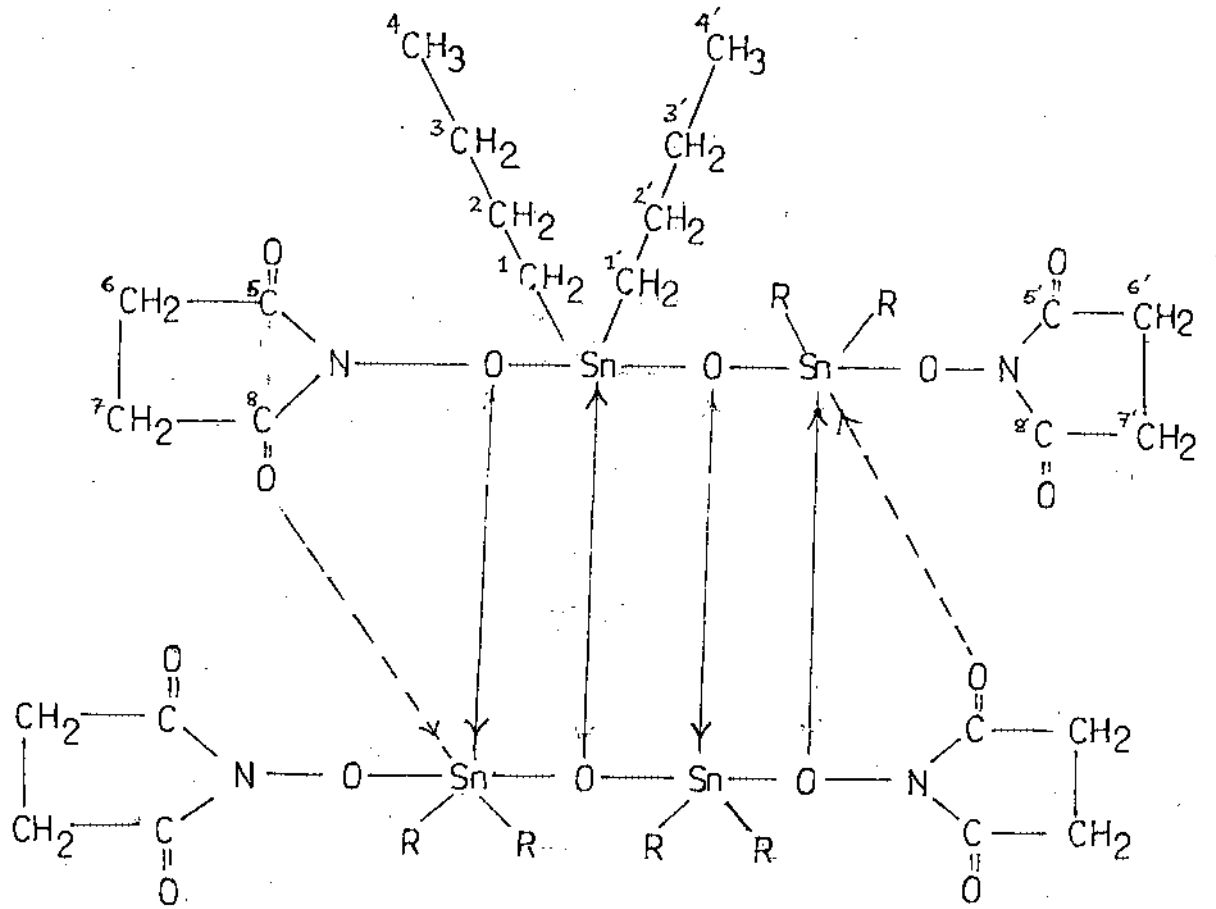
UV spectra of Tetrabutyl 1:3 di N-hydroxy succinimido distannoxane [I-5.6 x 10^{-4}(M)] diluted subsequently 10 times in each step (II, III, IV, V and IV).

So from the above discussions, it may be stated that diorganotin derivatives of N-hydroxy succinimide were not discrete chelate compounds having intramolecular coordination to tin. But they are ester type compounds, like the diorganotin derivatives of N-hydroxy phthalimide. But they are possibly not monomer. The apparent molecular weights obtained by Rast's method were not satisfactory, that may be due to high temperature dissociation. The molecular weight data in solution phase for different concentration and using different polar solvents (osmometric determination) could have given better information, but unfortunately could not be successfully explored.

The tin signal obtained in the ^{119}Sn NMR for tetrabutyl 1:3 di N-hydroxy succinimido distannoxane indicated that the compound is not a simple monomeric ester. There were two tin signals (δ -178.85 & -223.50), the values nearly matches to two kind of tin atoms having penta coordination and hexa coordination environments. This characteristic of the compound may be explained from the polymeric nature of tetra organo 1:3 di N-hydroxy succinimido distannoxane. Most probably intermolecular coordination bond formed from CO group to tin atom, which was responsible for changing the coordination sphere of tin atoms.

This phenomenon also gains support from the UV spectrum. It would be expected that with dilution the weak intermolecular coordination bonds disappear. So in the UV spectrum a hypsochromic shift is expected with lowering of concentration. The series of UV spectra (shown in fig.) with decreasing concentration supports this contentions.

Hence on the basis of available data the compound can be reported as follows:



(R = n-Butyl)

R E F E R E N C E S

1. S.J. Blunden, P.A. Cusak and R. Hill, Industrial Uses of Tin Chemicals, Royal Society of Chemistry, 7, 1985

2. C.E. Moore, Atomic Energy Levels, Circular 467, National Bureau of Standards, Vol. 1, Government Printing Office, Washington D.C., 1949.

3. E. Krause and V. Grosse, Die Chemicals dermetallogaischen Verbindurgen Berntraeger, Berlin, 311-372, 1937.

4. R.K. Ingham, S.D. Rosenberg and H. Gilman, Chem. Rev., 60, 459, 1960.

5. R.W. Weiss (Ed.), Organometallic Compounds, Vol. II, 2nd Ed., Springer Verlay, New York, 158-518, 1967.

6. D. Seyferth and R.B. King, Annual Surveys of Organometallic Chemistry, Vol. 2, Elsevier, New York, 161-183, 1966.

7. D. Seyferth and R.B. King, Annual Surveys of Organometallic Chemistry, Vol. 2, Elsevier, New York, 176-80, 1966.

8. D. Seyferth and R.B. King, Annual Surveys of Organometallic Chemistry, Vol. 3, Elsevier, New York, 236-258, 1967.

9. J.G.A. Luijten, Organomet. Chem. Rev. B, 4, 359, 1968.

10. J.G.A. Luijten, Organomet. Chem. Rev. B, 5, 687, 1969.

11. J.G.A. Luijten, Organomet. Chem. Rev. B, 6, 486, 1970.

12. E.J. Bulten, Organomet. Chem. Rev. B, 9, 248, 1972.

13. E.J. Bulten, J. Organomet. Chem. 53, 1-96, 1973.

14. P.G. Harrison, J. Organomet. Chem. 58, 49-152, 1973.

15. P.G. Harrison, J. Organomet. Chem., 79, 17-174, 1974.

16. P.G. Harrison, J. Organomet. Chem. 109, 241-362, 1976.

17. P.G. Harrison, N.T.P. Inf. Rev. Sci, Inorganic Chem. Ser. Two 1, 81-118, 1975 Ed. by Aglett. B.I. Butterworth, London.

18. P.G. Harrison, J. Organomet. Chem. 58, 49, 1973.

19. R.C. Poller, The Chemistry of Organotin Compounds, Logos Press Ltd., London, 1970.

20. A.K. Sawyer (Ed.), Organotin Compounds, Vol. 1, Marcel Dekker INC, New York, 1971.

21. A.K. Sawyer (Ed.), Organotin Compounds, Vol. 2, Marcel Dekker INC, New York, 1971.

22. A.K. Sawyer, Organotin Compounds, Vol. 3, Marcel Dekker INC, New York, 1972.

23. Stephen J. Lippard (Ed), Progress in Inorganic Chemistry, Vol. 24, John Wiley & Sons INC, New York, 1978.

24. Gmelin (Ed), Hand Book of Inorganic Chemistry, Vol. 29, Part 2, Springer Verlag Berlin, Heidelberg, New York, 1975.

25. V.S. Petrosyan, N.S. Yashina and O.A. Rentov, Advances in Organometallic Chemistry, Academic Press, Vol. 14, 63-92, 1976.

26. Alwyn G. Davies and P.J. Smith, Advances in Inorganic Chemistry, 23, 1-77, 1980.

27. John W. Connolly and Carl Hoff, Advances in Organometallic Chemistry, Academic Press, 19, 123-153, 1981.

28. R.C. Poller, J. Organomet. Chem., 3, 321, 1965.

29. M. Gielen and N. Sprecher, Organomet. Chem. Rev. 1, 455, 1966.

30. I.P. Beletskaya, K.P. Butin, A.N. Ryabtsev and O.A. Rŭntov, J. Organometal. 59, 1-44, 1973.

31. E. Frankland, Liebigs Ann. Chem., 171, esp. 71, 212, 1849.

32. E. Frankland, J. Chem. Soc. 2, 267, 1850.

33. C. Lowig, Liebigs Ann. Chem. 84, 308, 1852.

34. I.R. Beattie, Quart. Rev. 17, 382, 1963.

35. R. Ueede, Y. Kawasaki, T. Tanaka and R. Okawara, J. Organomet. Chem., 5, 194, 1966.

36. W.H. Nelson, D.F. Martin, J. Inorg. Nucl. Chem., 27, 89, 1965.

37. G.C. Ghosh and A.K. Ghosh, Ind. J. Chem. Soc., 21, 524-526, 1982.

38. G.C. Ghosh, Ph.D. Thesis, North Bengal University, India, 1978.

39. A.K. Mallick, Ph.D. Thesis, North Bengal University, India, 1982.

40. D. Pal Choudhuri, Ph.D. Thesis, North Bengal University, India, 1983.

41. W.H. Nelson and D.F. Martin, J. Inorg. Nucl. Chem., 27, 89, 1965.

42. K. Kawakami and R. Okawara, J. Organomet. Chem., 6, 249, 1966.

43. W. Gerrad, E.F. Mooney and R.G. Rees, J. Chem. Soc., 740, 1964.

44. W.H. Nelson and D.F. Martin, J. Organomet. Chem., 4, 67, 1965.

45. R.C. Poller and J.N.R. Ruddick, J. Chem. Soc (A), 2273, 1969.

46. T. Tanaka, M. Komura, Y. Kawasaki and R. Okawara, J. Organomet. Chem., 1, 484, 1964.

47. H.G. Langer, U.S. 3, 120, 550, Feb. 4, 1964.

48. I. Foldesi and G. Straner, Acta,Chim, Acad, Sci. Hung, 45, 313, 1965 [Chem. Abs., 64, 3591h, 1966]

49. K. Kawakami and R. Okawara, J. Organomet. Chem., 6, 249, 1964.

50. J.M. Holmes, R.D. Peacock and J.C. Tatlow, J. Chem. Soc. (A), 6, 2012, 1967.

51. E.O. Schlemper, Inorg. Chem., 6, 2012, 1967.

52. G. Faraglia, L. Roncucci and R. Barbieri, Ric. Sci. Rend, Sez. A. 8(2), 205, 1965.

53. D. Dutta, Ph.D. Thesis, North Bengal University, India, 1970.

54. M. Komura and R. Okawara, Inorg. Nucl. Chem. Letters, 2, 93, 1966.

55. D.P. Gaur, G. Srivastava and R.C. Mehrotra, Ind. J. Chem., 12, 399, 1974.

56. T.N. Srivastava, M.P. Agarwal and K.L. Saxena, J. Inorg. Nucl. Chem., 35, 306, 1973.

57. C.D. Barsode, P. Umapathy and D.N. Sen, J. Ind. Chem. Soc., 52, 942, 1975.

58. C.D. Barsode, P. Umapathy and D.N. Sen, J. Ind. Chem. Soc. L 111(8), 761, 1976.

59. C.D. Barsode, P. Umapathy and D.N. Sen, J. Ind. Chem. Soc. 54(12), 1172-77, 1977.

60. V.G. Kumar Das, Ng Seik, Weng J. Singh, P.J. Smith and R. Hill, J. Organomet. Chem., 214(2), 183-90, 1981.

61. B.K. Deb and A.K. Ghosh, Canad. J. Chem., 65, 1241, 1987.

62. B.K. Deb and A.K. Ghosh, Polyhedron, 5, No. 3, 863-870, 1986.

63. J. Otera, Y. Kawasaki and T. Tanaka, Inorg. Chim. Acta, 1, 294, 1967.

64. B.S. Saraswat, G. Srivastava and R.C. Mehrotra, Symposium on metal-organic and organometallic compound, Deptt. of Chemistry, University of Rajasthan, India, 1978.

65. Katsuhike, Kawakami and Toschio Tanaka, J. Organomet. Chem., 49, 409-15, 1973.

66. H. Prent, F. Huber, H.J. Haupt, R. Cefalu and R. Barlien, Z. Anorg. Chem., 410, 88, 1974.

67. S.S. Sandhu, G.K. Sandhu and S.K. Puskarna, J. Organomet. Chem., 70, 67, 1974.

68. B.N. Ghosh, C.A. Vol. 98, 658, 1983 (Issue 15).

69. A. Saxena, J.P. Tandon and A.J. Crowe, Polyhedron, 4(6), 1085-9, 1985 [Eng]

70. F. Bonati and R. Ugo, J. Organomet. Chem., 10, 257, 1967.

71. E.J. Kupchik and P.J. Calabretla, Inorg. Chem., 4, 973, 1965.

72. F. Bonati and R. Ugo, J. Organomet. Chem., 10, 257, 1967.

73. E.J. Kupchik and P.J. Calabretla, Inorg. Chem., 4, 973, 1965.

74. P.G. Harrison and A. Mangia, J. Organomet. Chem., 120, 211, 1976.

75. T.N. Srivastava, V. Kumar and A. Bhargova, Ind. Chem. Soc., 54 (6), 591-5, 1977.

76. T.N. Srivastava and R.B. Rastogi, Ind. J. Chem., Sect A, 16A (3), 221-3, 1978.

77. T.N. Srivastava, V. Kumar and O.P. Srivastava, Natl. Acad. Sci. Lett. (India), 1 (3), 97-100, 1975.

78. T.N. Srivastava and R.B. Rastogi, J. Ind. Chem. Soc., 55(5), 521-2, 1978.

79. T.N. Srivastava and R.B. Rastogi, J. Ind. Chem. Soc., 56 (6), 634-6, 1979.

80. K. Chandra, A.K. Garg, A.C. Jain, N. Kumar and B.S. Gard, J. Ind. Chem. Soc., 57(4), 378-81, 1980.

81. C.P. Sharma, N. Kumar, M.C. Khandapal, S. Chandra and V.G. Bhide, Ind. J. Chem. Sect. A, 19A(11), 1092-4, 1980.

82. T.N. Srivastava and R.B. Rastogi, J. Ind. Chem. Soc., 58(1), 66-9, 1981.

83. R.J. Magee and M.J.O. Connor, Inorg. Chim. Acta, 34(1), 107-12, 1979.

84. M. Komura, T. Tanaka and R. Okawara, Inorg. Chim. Acta., 2, 321, 1968.

85. W.H. Nelson and M.J. Aroney, Inorg. Chem., 12, 132, 1973.

86. E.L. Muetterties and C.M. Wright, J. Am. Chem. Soc., 86, 5132, 1964.

87. P.G. Harrison, J. Organomet. Chem., 38, 5, 1972.

88. P.G. Harrison, Inorg. Chem., 12, 1545, 1973.

89. B. Pradhan, Ph.D. Thesis, North Bengal University, India, 1977.

90. P.G. Harrison and J.A. Richards, J. Organomet. Chem., 185, 9, 1980.

91. M.K. Das and M. Nath, Proc. 68th Session, Indian Science Congress, 1961, Chem. Sec. abs. Inorg. 86.

92. B. Pradhan and A.K. Ghosh, J. Organomet. Chem., 131, 23, 1977.

93. W. Lossen, Ann. Chem. 150, 314, 1869.

94. F.A. Kuehl, Jr., F.J. Wolf, N.R. Trenner, R.L. Peek, R.P. Buhs, E. Howe, I. Pulter, B.D. Munnewell, R. Ormonol, G. Downing, J.B. Lyons, E. Newstead, L. Chariet and K. Folkers, J. Am. Chem. Soc., 77, 2344, 2345, 1955.

95. T. Emergy and J.B. Neilands, J. Am. Chem. Soc., 3658, 1960.

96. B.E. Hackley, Jr., R. Plapinger, M. Stolberg and T. Wagner-Jauvegg, J. Am. Chem. Soc., 77, 3651, 1955.

97. S.R. Sandler and W. Karo, Organic Functional group Preparations, Academic Press (London), Vol. III, 407, 1972.

98. S.R. Sandler, W. Karo, Organic Functional Group Preparations, Academic Press INC (London) Ltd. Vol. III, 410-32, 1972.

99. W. Werner, Chem. Ber., 25, 27, 1892.

100. R.T. Coutts, Canad. J. Pharm. Sci., 2, 1, 1967.

101. R.T. Coutts, Canad. J. Pharm. Sci., 2, 27, 1967.

102. E. Shaw, J. Am. Chem. Soc., 71, 67, 1949.

103. H.L. Yale, Chem. Rev. 33, 209, 1943.

104. R.J.W. Cremlyn and R.H. Still, Named and Miscellaneous Reactions in Practical Organic Chemistry, Heineman, London, p. 128, 1967.

105. E. Bamberger, Chem. Ber., 52, 1111, 1919.

106. S.G. Tandon and S.C. Bhattacharya, J. Chem. Eng. Data, 7, 553, 1962.

107. D.E. Ryan, Canad. J. Chem., 38, 2488, 1960.

108. U. Priyadarshini and S.G. Tandon, Canad. J. Chem., 12, 143, 1967.

109. D.C. Bhura and S.G. Tandon, Canad. J. Chem., 14, 278, 1969.

110. V.D. Gupta and S.G. Tandon, J. Ind. Chem. Soc., 45, 9, 1969.

111. V.D. Gupta and S.G. Tandon, J. Ind. Chem. Soc., 47, 973, 1970.

112. Y.K. Agarwal and S.G. Tandon, Ind. Chem. Soc., 48, 397, 1971.

113. N.N. Ghosh and D.K. Sarkar, J. Ind. Chem. Soc., 45, 550, 1968.

114. N.N. Ghosh and D.K. Sarkar, J. Ind. Chem. Soc., 628, 1969.

115. W.P. Jencks, J. Am. Chem. Soc., 80, 4581, 1958.

116. A. Miolati, Chem. Ber., 25, 699, 1892.

117. C. Hoffmann, Chem. Ber., 22, 2854, 1889.

118. F. Elay and R. Lenaers, Chem. Rev. 62, 155, 1962.

119. H. Wieland, Ann. Chem., 353, 65, 1907.

120. F. Schouteden, Markomol. Chem., 27, 246, 1958.

121. C.A. Fetscher and S.A. Lipowski, U.S. Pat. 3, 345, 344, Oct. 3, 1967.

122. A.K. Majumdar, N. Benzoylphenyl hydroxylamine and its analogues, Pergamon Press, Oxford, 1972.

123. B. Pradhan and A.K. Ghosh, Current Science (India), 55, 555, 1982.

124. C.K. Narula and V.D. Gupta, J. Ind. Chem. Soc., LVII, 230, 1980.

125. P.G. Harrison and J.K. Richards, J. Organomet. Chem., 185, 9, 1980.

126. S.K. Choudhuri, P.S. Roy and A.K. Ghosh, Ind. J. Chem., 23A, 917, 1984.

127. S.K. Choudhuri, P.S. Roy and A.K. Ghosh, Ind. J. Chem., 22A, 996, 1983.

128. S.K. Choudhuri, P.S. Roy and A.K. Ghosh, Ind. J. Chem., 23A, 533, 1984.

129. S. Datta, Ph.D. Thesis, North Bengal University, India, 1989.

130. J.G.A. Luijten and G.J.M. Vander Kerk, Investigation in the field of Organotin Chemistry, Tin Research Institute, Greenfor, 84, 1966.

131. A.I. Vogel, A Text Book of Practical Organic Chemistry, Longman, London, 1961.

132. K. Sisido, Y. Takeda and Z. Kingawa, J. Am. Chem. Soc., 83, 538, 1961.

133. H. Gilman and S.D. Rosenberg, J. Am. Chem. Soc., 74, 5580, 1952.

134. K.A. Elegbede and R. McLean, J. Organomet. Chem., 20, 387, 1955.

135. S.R. Sandler and W. Karo, Organic Functional Group Preparation, Academic Press, New York, Vol. III, p. 100.

136. Kung-Tsung Wang, Donald N. Brattesani and Borris Weinstein, J. Heterocyl. Chem., 3, 98, 1966.

137. W.J. Considine, J.J. Ventara, A.J. Gibbons Jr. and A. Ross, Canad. J. Chem., 41, 1239, 1963.

138. R.K. Ingham, S.D. Rosenberg and H. Gilman, Chem. Revs., 60, 459, 1960.

139. R. Okawara, Proc. Chem. Soc., 383, 1961.

140. D.L. Alleston, A.G. Davies, M. Hancock and R.F.M. White, J. Chem. Soc., 5469, 1963.

141. P. Pfeiffer and O. Brach, Z. Anorg. Chem., 87, 229, 1914.

142. Harada, Bull. Chem. Soc. Japan, (a) 2, 105, 1927; (b) 4, 266, 1929; (c) 6, 240, 1931.

143. Harada, Sci. Papers Inst. Phys. Chem. Res., Tokyo, (a) 35, 290, 1939; (b) 36, 497, 1939; (c) ibid, p. 501; (d) ibid, p. 504; (e) 38, 115, 1940; (f) ibid, p. 146.

144. Harada, Bull. Chem. Soc. Japan, 15, 455, 1940.

145. Harada, Sci. Papers Inst. Phys. Chem. Res., Tokyo, (a) 39, 419, 1942; (b) 42, 57, 1947; (c) ibid, p. 62; (d) ibid, p. 64.

146. Harada, Report Sci. Res. Inst. (Japan), 24, 177, 1948.

147. R. Okawara, D.G. White, K. Fujitani and H. Sato, J. Am. Chem. Soc., 83, 1342, 1961.

148. D.L. Alleston, A.G. Davies, M. Hancock and M.F.R. White, J. Chem. Soc. 5470, 1963.

149. R. Okawara and E.G. Rochow, J. Am. Chem. Soc., 82, 3285, 1960.

150. R. Okawara and M. Wada, J. Organomet. Chem. (Amsterdam) 1, 81, 1963.

151. M. Wada, M. Nishino and R. Okawara, J. Organomet. Chem. (Amsterdam) 3, 70, 1965.

152. E.G. Rochow, D. Seyferth and A.C. Smith, J. Am. Chem. Soc., 75, 3099, 1953.

153. A.S. Mufti, R.C. Poller, J. Chem. Soc., 5055, 1965.

154. M. Ohara, R. Okawara and Y. Nakamura, Bull. Chem. Soc., Japan, 38, 1379, 1965.

155. W.J. Considine and J.J. Ventura, J. Org. Chem., 28, 221, 1963.

156. W.J. Considine, J.J. Ventura, A.J. Gibbons Jr. and A. Ross, Canad. J. Chem., 41, 1240, 1963.

157. T. Tanaka, R. Ueeda, M. Wada and R. Okawara, Bull. Chem. Soc., Japan, 37, 1554, 1964.

158. A.G. Davies and I.F. Graham, Chem. & Ind. (London), 1622, 1963.

159. D.L. Allesten, A.G. Davies and M. Hancock, J. Chem. Soc., 5477, 1964.

160. W.J. Considine and A.G. Baum, Organomet. Chem. 3, 308, 1965.

161. M. Wada and R. Okawara, J. Organomet. Chem., 1966.

162. R. Okawara et al, 2nd Intern. Symp. Organomet. Chem. Wisconsin, 1965, p. 128, 1965.

163. M. Nadvornik, J. Holecek, K. Handlir and A. Lycka, J. Organomet. Chem., 275, 43-51, 1984.

164. J. Holecek, K. Handlir, M. Nadvornik and A. Lycka, J. Organomet. Chem. 258, 147-153, 1983.

P A R T - II

I N T R O D U C T I O N

Organotin carboxylates comprise one of the most important class of compounds in the ever expanding field of organotin chemistry. Apart from the theoretical and structural interests, organotin carboxylates are finding importance in industry and agriculture, many of these groups of compound have already find 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 discussion with varying degree of details are available on these compounds (1-4) and as such only some important aspects will be presented here.

Preparative Methods of Organotin Carboxylates

The organotin carboxylates are readily prepared by a number of methods. One of the most important being reaction between organotin oxides (or hydroxides) and carboxylic acids or anhydrides (5-12).

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

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

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

The water produced in these reactions was usually removed azeotropically, for example a number of carboxylates containing oxime residues (C=N) have been made for biological testing by distilling a benzene solution of the reactions (13,10).

$$(Bu_3Sn)_2O + RR'C{=}NOCH_2COOH \longrightarrow$$

$$2Bu_3SnOCOCH_2ON = CRR' + H_2O$$

Alternatively the reactants are heated in suitable solvent until there is no further liberation of water (14).

$$(Bu_3Sn)_2O + 2HOC_6H_4COOH \xrightarrow{100\text{-}110^{\circ}C}$$

$$2\ Bu_3SnOCOC_6H_4OH\text{-}O + H_2O$$

Another major preparative method is reaction between organotin halides and alkali metal or, less commonly, silver salts of carboxylic acids (15).

$$R_3SnCl + R'COOM \longrightarrow R_3SnOCOR' + MCl$$

(M = Na, K, Ag)

By heating organosilicon carboxylates with diphenyltin oxide, carboxylate groups are readily transferred from silicon to tin (16,17).

$$Et_2Si(OCOR)_2 + Ph_2SnO \longrightarrow Ph_2Sn(OCOR)_2 + Et_2SiO$$

(R = Me, Et)

Organotin hydrides react with carboxylic acids with the evolution of hydrogen.

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

when dihydrides react with carboxylic acids the initially formed dicarboxylate equilibriates with unreacted dihydride as follows (18).

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

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

I

Dibutyltindihydride in the presence of excess acid, given the dicarboxylate, $Bu_2Sn(OCOR')_2$ but, with a deficiency of acid, the hydride carboxylates (I, R = Bu) are formed which then slowly decompose to give hydrogen and the distannane dicarboxylates (II, R = Bu). When diphenyltin dihydride reacts with carboxylic acids the distannane dicarboxylates (II, R = Ph) are, effectively the only

$$2R_2Sn(H)OCOR' \longrightarrow R_2Sn(OCOR')Sn(OCOR')R_2 + H_2$$

II

products irrespective of the conditions used (55).

Organotin halocarboxylates, $R_2Sn(X)OCOR'$, are most conveniently made by heating together, in an inert solvent, equimolar proportions of a dihalide and dicarboxylate (2,7).

$$Bu_2SnBr_2 + Bu_2Sn(OCOMe)_2 \longrightarrow 2Bu_2Sn(Br)OCOMe.$$

Other methods include reaction between a dihalide and a metal carboxylate (19,20):

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

or from a dihalodistanoxane and a carboxylic acid or anhydride (21).

$$ClR_2SnOSnR_2Cl + 2R'COOH \longrightarrow 2R_2Sn(Cl)OCOR' + H_2O$$

Dibutyltin derivative of maleic acid was prepared by reaction between dibutyltin oxide and an alkyl hydrogen maleate (19,22). Dibutyl tin maleate was isolated as a monohydrate and also in anhydrous trimeric and tetrameric forms (19) by the reaction of dibutyltin oxide with maleic acid or maleic anhydride (19,23). From the method of manufacture and its physical properties it appears that the dibutyltin maleate made commercially for the stabilisation of poly vinyl chloride, is a mixture of oligomeric and probably polymeric forms.

Though it is rarely used as a preparative method, esters can be made by the cleavage of organic groups (usually vinyl or phenyl) from tin by carboxylic acids (24).

Roy and Ghosh (28) gave another reaction pathway for the symthesis of organotin carboxylate by demetallation reactions of triorganotin carboxylates with mercury salts.

Organotin carboxylates have been reviewed by Okawara and Wada (25). The series of triorganotin carboxylates investigated were of the following types, $R_3SnOOCR'$, where R = CH_3, C_2H_5, $n\text{-}C_3H_7$, $n\text{-}C_4H_9$, R' = H, CH_3, CH_2Cl, $CHCl_2$ and CCl_3.

From the different features of the infrared spectra of various trialkyltin carboxylates in the solid state and in carbon tetrachloride solution as shown in table, and from the result of the temperature dependence of the absorption intensities, Jansen et al (26) and Cummins and Dunn (27) have concluded that trialkyltin carboxylates are polymeric in the solid state with planar trialkyltin group and bridging acyloxy groups and are ester-like monomers in dilute solution.

Table

Compounds	CO_2 frequencies cm^{-1}		SnC_3 frequencies cm^{-1}	
	Solid state	Solution	Solid state	Solution
$(CH_3)_3SnO_2CCH_3$	1565,1412	-	547	
$(C_2H_5)_3SnO_2CH_3$	1572,1412	1655,1302		
$(n\text{-}C_4H_9)_3SnO_2CCH_3$	1572,1410	1647,1300		
$(C_6H_{13})_3SnO_2CCH_3$	1570,1408	1650,1304		
$(CH_3)_3SnO_2C_{11}H_{23}$	1567,1410	1642,1302	548	548,516

The diorganotin dicarboxylates of the type $R_2Sn(OCOR')_2$ are known for many years. The structure of diorganotin dicarboxylates was first suggested for dimethyl tin diformate by Okawara et al (25), which included a linear dimethyltin cation and a formate anion. Details of IR spectral analysis of diorganotin carboxylates have been discussed.

Organotin tri carboxylates e.g. $C_2H_5Sn(O_2CC_6H_5)_3$ was prepared and characterised by Razuvaev and et al (29). However these compounds have only been reported with ambiguities or discretely n-Butyltin and phenyl tin tri carboxylates have been prepared from their trichlorides. Of which n-butyltin triacetate and tripropionate are monomeric in camphor solution. A number of compounds of tricarboxylates which have been studied, e.g. $n\text{-}C_4H_9Sn(O_2CCH_3)_3$, $n\text{-}C_4H_9Sn(O_2CC_2H_5)_3$, $n\text{-}C_4H_9Sn(O_2C\text{-}n\text{-}C_3H_7)_3$, $n\text{-}C_4H_9Sn(O_2C\text{-}i\text{-}C_3H_7)_3$, $n\text{-}C_4H_9Sn(O_2C\text{-}n\text{-}C_4H_9)_3$, $C_6H_5Sn(O_2CCH_3)_3$, $C_6H_5Sn(O_2CC_2H_5)_3$, $C_6H_5Sn(O_2C\text{-}n\text{-}C_3H_7)_3$ and $C_6H_5Sn(O_2C\text{-}i\text{-}C_3H_7)_3$.

Diorganotin mono carboxylates of the general formula $R_2SnX(O_2CR')$ are known. The compound of this type was first reported by Okawara and Rochow (30). The compounds of this series having general formula R_2SnXY already being prepared are given in the table.

Table

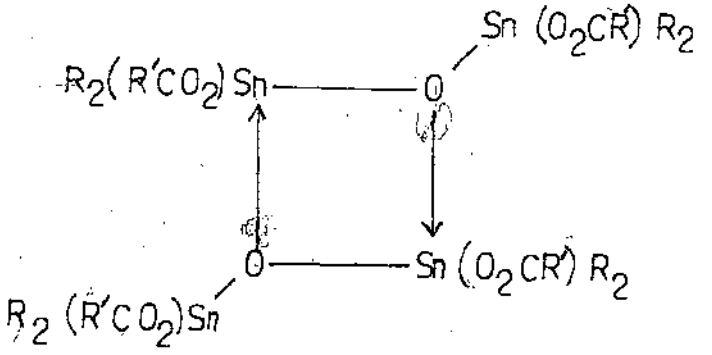
R_2SnXY compounds

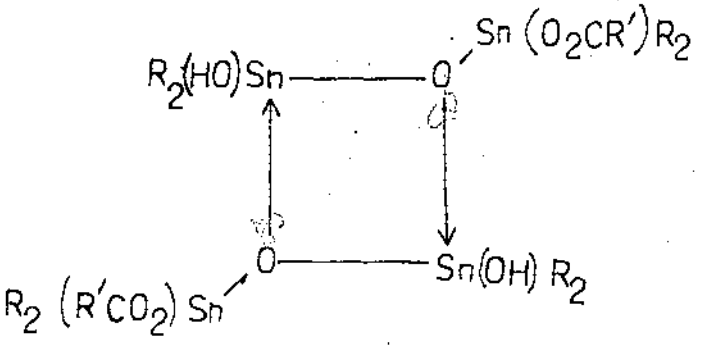
R	X	Y	Ref.
$n\text{-}C_4H_9$	H	O_2CCH_3	31,32
CH_3	Cl	O_2CH	33
CH_3	Cl	O_2CCH_3	33,34
CH_3	Cl	$O_2CC_2H_5$	35
CH_3	Br	O_2CCH_3	35
CH_3	I	O_2CCH_3	35
C_2H_5	Cl	O_2CH[a]	36
C_2H_5	Cl	O_2CCH_3	36
$n\text{-}C_3H_7$	Cl	O_2CH[a]	36
$n\text{-}C_3H_7$	Cl	O_2CCH_3	36
$n\text{-}C_4H_9$	Cl	O_2CH[a]	36
$n\text{-}C_4H_9$	Cl	O_2CCH_3	36,37,38
$n\text{-}C_4H_9$	Br	O_2CCH_3	39,40
$n\text{-}C_4H_9$	I	O_2CCH_3	37
$n\text{-}C_4H_9$	Cl	methyl maleyloxy	41
$n\text{-}C_4H_9$	OCH_3	O_2CCH_2Cl[b]	42
$n\text{-}C_4H_9$	OCH_3	O_2CCH_3	37
$n\text{-}C_4H_9$	OCH_3	$O_2CC_{11}H_{23}$	37

[a] Each compound has one molecule of water

[b] Denoted as $(n\text{-}C_4H_9)_2Sn(OCH_3)_2 \cdot (n\text{-}C_4H_9)_2Sn(O_2CCH_2Cl)_2$ in the original paper.

Carboxylate derivatives of organotin distannoxane compounds are also known (33,34,37,39,43-47). The following dimeric structures for these compounds have been suggested.





Another organotin carboxylates, hexaacetoxy ditin $Sn_2(O_2CCH_3)_6$ (48) has been prepared as white fine crystals by heating hexaphenylditin with glacial acetic acid at 120°C.

Khoo and Smith (49) have been prepared some carboxylate derivatives of amino substituted benzoic acid. These are (O-aminobenzoato) triphenyl tin, $Ph_3Sn[O-(H_2N)C_6H_4CO_2]$ and

(p-aminobenzoato) triphenyltin, $Ph_3Sn[p\text{-}(NH_2)C_6H_4CO_2]$.
Reaction of bis (triphenyltin)oxide with o-amino benzoic acid in refluxing benzene solution gave (o-amino benzoato) triphenyl tin. Similarly when p-amino benzoic acid was used as a reactant the (p-amino benzoato) triphenyl tin derivative obtained. Following the above method another compound [o-(dimethylamino)benzoato] triphenyl tin has been obtainted (50). The triphenyl tin esters of hydroxy substituted benzoic acid have been reported (51) (o-Hydroxy benzoato) triphenyl tin, $Ph_3Sn[o\text{-}(OH)C_6H_4CO_2]$ has been prepared in refluxing benzene. In a similar fashion (o-methoxy benzoato) triphenyl tin, $Ph_3Sn[o\text{-}(CH_3O)C_6H_4CO_2]$; [p-(methylthio)benzoato] triphenyltin, $Ph_3Sn[p\text{-}(CH_3S)C_6H_4CO_2]$; (o-thiobenzoato) diphenyltin, $Ph_2Sn[o\text{-}(S)C_6H_4CO_2]$ have been prepared. The nuclear magnetic resonance spectral studies and X-ray crystallographic studies have been made thoroughly on these compounds.

Physical properties of Organotin Carboxylates

In organotin carboxylates the Sn-C 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. The solubility of triorganotin carboxylates is low in common organic solvents because of their polymeric associated structure. Many of the carboxylates have low melting points indicating covalent nature of the compounds.

The polymeric stanoic acids are colourless and infusible but a few of them are soluble in $CHCl_3$ and CCl_4 and are reasonably stable towards hydrolysis.

Structural aspects

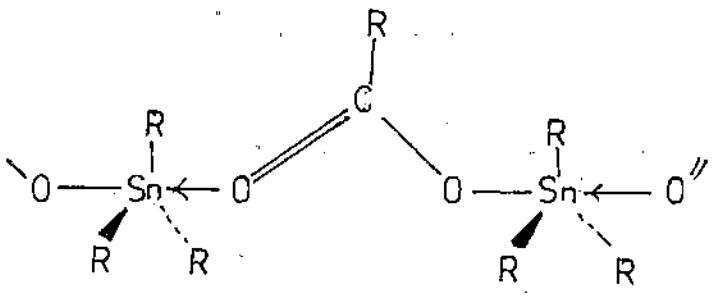
Freeman (52) suggested the ionic nature of bonding for organotin carboxylate, which was also supported by Okawara et al from the investigation of infrared spectra of some methyl tin acetates and formates (30). However, Beattie and Gilson pointed out that the spectroscopic evidence might be interpreted in terms of either bridging carboxylate groups or simple acetate ion (53). From viscosity measurements, Jansen et al supported the bridging structure (54). More refined infrared and molecular weight studies (54-56) indicate that in general, compounds of the formula $R_3SnOOCR'$ exist as linear polymers in the solid and even in concentrated solutions of non poler solvents but are monomeric in dilute solutions.

Infrared Spectroscopy

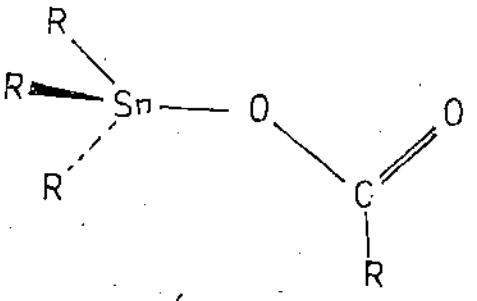
Carbonyl group absorption:

A comparison of the IR spectra $Me_3SnOOCCH_3$ with that of $Me_3SiOOCCH_3$ points to the essential difference of structures between these two class of compounds. The trimethyl silyl derivative possess normal ester structure as evidenced by the appearance of assymmetric stretching frequency of the carbonyl group ($\nu_{as}CCO$) at 1725 cm^{-1} (57,58). The trimethyl stannyl acetate, on the other hand, show $\nu_{as}(OCO)$ at 1576 cm^{-1}, the absorption frequency being similar to $\nu_{as}(OCO)$ of 1578 cm^{-1} in $NaOOCCH_3$. Presence of a symmetrical carbonyl

group of the ionised $RCOO^-$ type [$\nu_{as}(OCO)$ 1550-1610 cm^{-1} and $\nu_s(OCO)$ 1300-1400 cm^{-1}] is, therefore indicated. All carboxylates of the type $R_3SnOCOR'$ and $R_2Sn(OCOR')_2$ (R = alkyl/aryl group) show such symmetric and assymmetric carbonyl absorption in solid state. On dissolving the compounds in non polar non-coordinating solvents, the assymmetric 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 $\Delta\nu(\nu_{as}\ OCO - \nu_s OCO)$ is generally found to be less than 200 cm^{-1} in solid state and greater than 250 cm^{-1} in solution (58,59). This has been interpreted in terms of bidentate and an almost symmetrical carbonyl 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) (60-65) having a monodentate carboxyl group. Molecular weights of the carboxylates also supports monomeric structure (VB) in solution with the exception of trimethyl tin formate which exists as an equilibrium of associated and unassociated forms in $CHCl_3$ (61). 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. triphenyl tin 2-ethyl hexoate) the compounds assume monomeric ester like structures in solid state as a result of steric hindrance exerted by the bulky organic groups (57,66-70). Thus, tricyclohexyl,



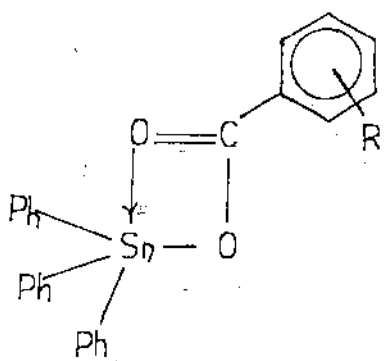
(VA)



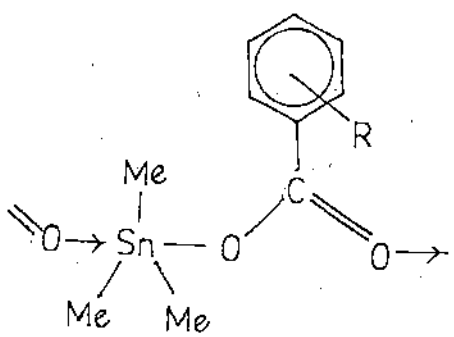
(VB)

triisopropyl, trineopentyl 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 polymerisation. For Ph_3Sn derivatives while $Ph_3SnOOCCHMe_2$ and $Ph_3SnOOCH = CH_2$ are penta coordinated polymers. $Ph_3SnOOCCMe_3$. $Ph_3SnOOCCMe = CH_2$ and $Ph_3SnOOCCl_3$ are tetra coordinate monomers in the solid state (71). Recently it has also been claimed that triphenyl tin derivatives of chlorobenzoic acid, salicyclic acid and o-anisic acid are discrete five coordinated form in the solid state (64,65,72). In contrast, trimethyl tin derivatives of these

carboxylic acids are in the intermolecular chain structures (72). Intramolecular carbonyl coordination takes place in case of triphenyl tin derivatives (Fig. A) whereas intermolecular carbonyl coordination occurs in case of trimethyl tin derivatives (Fig. B). An analogous



(A)



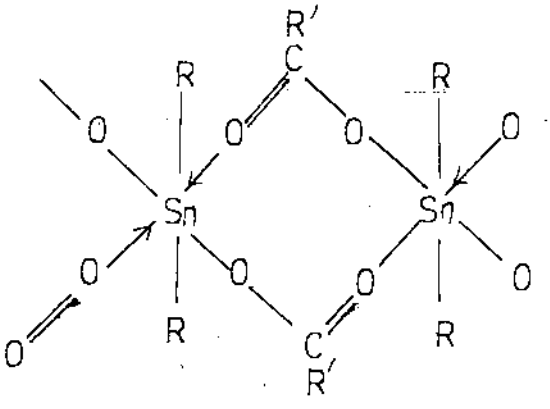
(B)

R = Cl, OH, NH_2

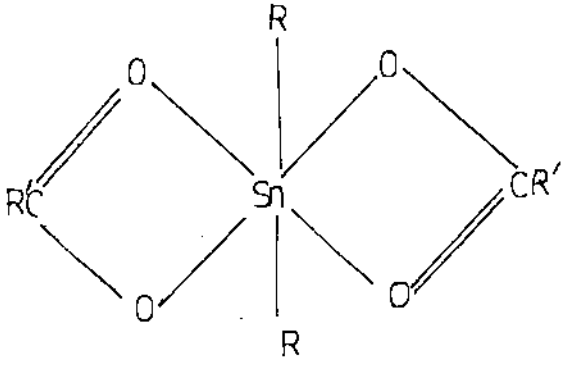
situation is also observed in the oxinate carboxylates e.g. $RSn(Ox)_2OOCR'$ which also have monomeric structures in solid state (73). Trimethyl tin glycinate also has a polymeric chain structure in solid state ($\nu_{as}OCO$ and $\nu_{s}OCO$ are 1630 and 1398 cm^{-1} respectively). but bridging occurs via the NH_2 groups (74).

The structure of dialkyltin dicarboxylate was first suggested for dimethyl tin diformate by Okawara (33) which included a linear Me_2Sn cation and a formate anion. Further studies have been carried out on dialkyltin diacetates (75,35) which suggest that in the neat liquid or solid state, those adopt a polymeric structure (VIA) with intermolecularly bridging carboxylate groups and an octahedral <u>trans</u> R_2SnX_4 tin atom geometry. In solution, these compounds are

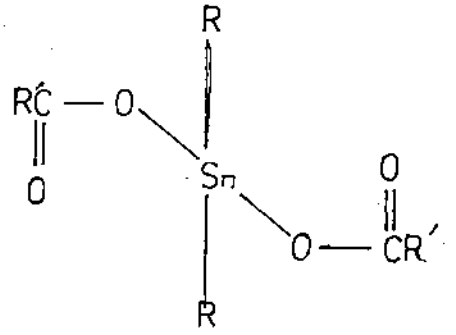
monomeric on evidenced by raising of $\nu_{as}(OCO)$ frequencies. The molecules have been suggested to be octahedral with intramolecularly chelated carbonyl groups (VIB)(2). It is, however, equally likely that these compounds assume a non-chelated ester like structure in solution (VIC). The dialkyl chlorotin 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 atom occupying a trigonal bipyramidal <u>cis</u> R_2SnX_3 geometry (76).



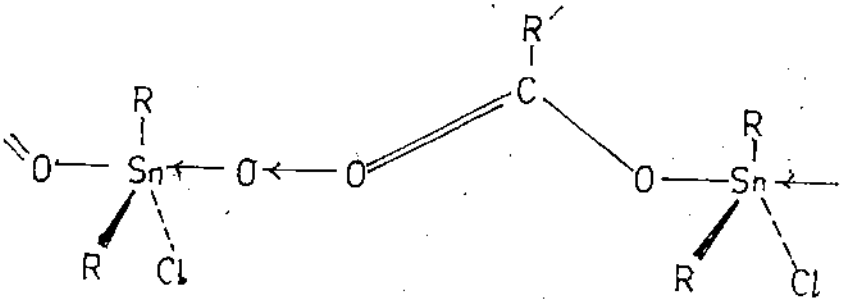
(VI A)



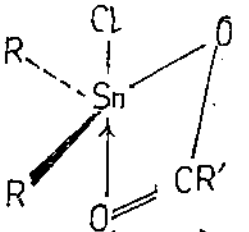
(VI B)



(VIC)



(VII A)

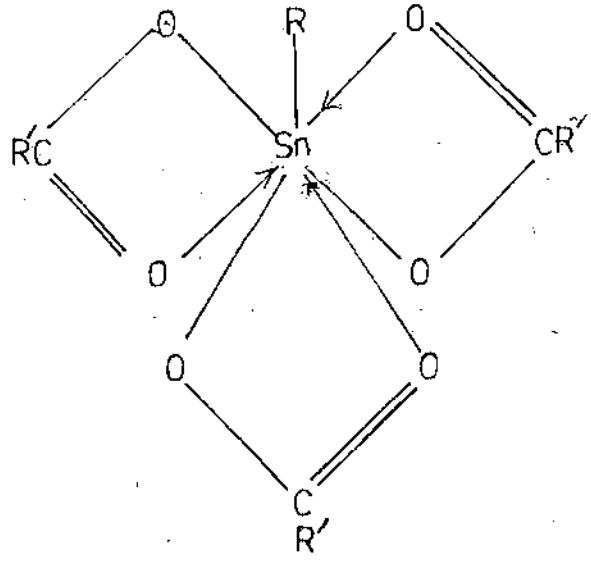


(VII B)

The structure of bis (trimethyl stannyl) ester of a dicarboxylic acid (malonic acid) has been determined and shows that in $Me_3SnOCCCH_2COOSnMe_3$, each carbonyl group links planar Me_3Sn moieties intermolecularly to form a three dimensional polymeric net work (77).

The IR spectra of a number of mono organotin tricarboxylates 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 (78). 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).

The infrared spectrum of $(CH_3)_2Sn(OOCH)_2$ shows bands associated with the COO group at 1588 cm^{-1} (antisym. str) and 1390 cm^{-1} (sym. str.). The frequencies are quite similar to those observed for NaOOCH. Further, the spectrum reveals only one band in the KBr region, indicating a linear arrangement of SnC_2 moiety. The spectra of $(n\text{-}C_3H_7)_2Sn(OOCCH_3)_2$ and $(n\text{-}C_4H_9)_2Sn(OOCCH_3)_2$ show bands due to the COO stretching vibration at 1610 cm^{-1} and 1380 cm^{-1} (79). These bands are observed at the same frequencies even in cyclohexane solution, in which the diacetate exist as monomers. These observations suggest a trans-bis (chelate) configuration for this type of compound.

The infrared spectrum of $ClR_2SnOOCCH_3$ in the solid state shows one of the characteristic bands associated with the anti-symmetric stretching vibration of the COO group at 1540-1565 cm^{-1}. In carbon tetrachloride or benzene solution the band shifts to near 1600 cm^{-1}. This indicates that some structural changes have occurred on solution, but still suggest a non ester type of acetoxy group. Molecular weight determinations show that these compounds are monomeric in benzene. With these observations, a chelate structure has been proposed for the compounds in solution (36).

The infrared spectra of $ClR_2SnOCCH.H_2O$ in the solid state indicates the existence of formoxy groups of the ionic type, and it may be assumed that a hexa coordinated tin atom is involved in these monohydrates.

In eluciding the structure of organotin carboxylates, the role of ^{119}Sn and ^{13}C NMR spectroscopy, tin 119m Mossbauer spectroscopy alone with the single crystal X-ray analysis have significantly contributed towards some definite conclusions. The ^{119}Sn chemical shift indicates the coordination number around tin atom in an organotin compound. It particularly produces a large upfield shift of (^{119}Sn) with the change of coordination number from four to five or six or even higher.

Examination of the tin 119m Mossbauer quadruple splitting parameters can help in identifying the nature of bridging carboxylate groups and also from discrete intramolecular monomeric structures.

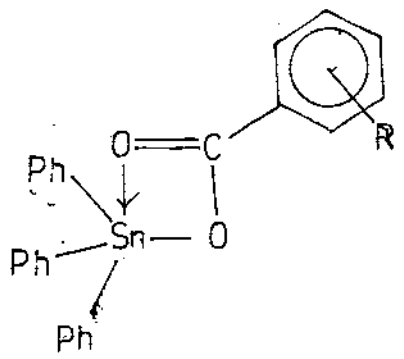
The role of ^{13}C NMR spectra was exploited by Lycka et al (65,80) for elucidation of structures of some triorganotin carboxylates.

Finally the single crystal X-ray analysis has settled the structures of some organotin carboxylates conclusively.

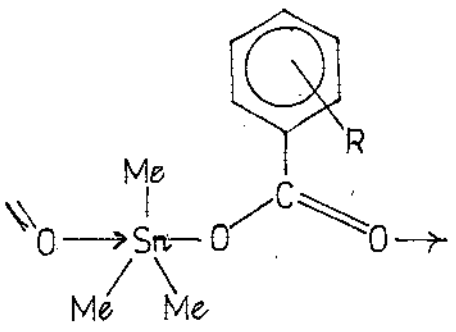
Utilising the above tools, Holmes et al (50,51,72,82), has established the structures of a number of organotin carboxylates. They studied the structures of the following compounds:

1. [o-(Dimethyl amino)benzoato] triphenyltin
2. (o-Amino benzoato)triphenyl tin
3. (p-Amino benzoato)triphenyl tin
4. (o-Hydroxybenzoato)triphenyl tin
5. (o-Methoxy benzoato)triphenyltin
6. [p-(Methylthio)benzoato] triphenyltin
7. (o-thiobenzoato)diphenyltin
8. (o-chlorobenzoato)triphenyltin
9. (p-chlorobenzoato)triphenyltin
10. (o-Methoxy benzoato)trimethyl tin
11. (o-Hydroxy benzoato) trimethyl tin.

Two structural types have been found in these compounds. Penta coordinated discrete molecules (A) in which intramolecular coordination occurs and penta coordinated polymeric chain structures (B) in which intermolecular coordination occurs. We will discuss here one of each type of compounds as examples.



(A)

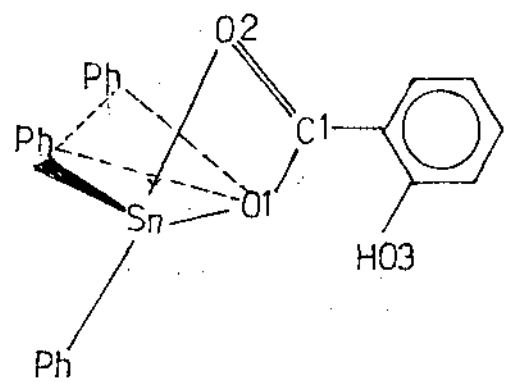


(B)

Let us discuss first one of the (A) type compound; (o-hydroxy benzoato)triphenyl tin. Examination of the infrared spectra of this compound in Nujol mull and in carbon tetra chloride revealed very similar carbonyl stretching frequency, at 1625-1630 cm^{-1}, relative to those of the uncomplexed acids (1660-1670 cm^{-1}). The latter shift is related to the carbonyl group coordination. As indicated earlier the carbonyl band exhibits same frequency both in solid and in solution phase. So their structures are same in both solid and solution phase.

The basic structure of ($_o$-hydroxy benzoato) triphenyl tin ester, results from a distortion from tetrahedral geometry induced by the approach of an oxygen atom, 02 or of the carboxylate group at a tetrahedral face opposite one of the tin phenyl groups. The distortion is toward trigonal bipyramid that contains 02 and the latter phenyl group at axial sites. The axial Sn - 02 lengths are considerably longer than the equitorial Sn - 01 bond length . Tin

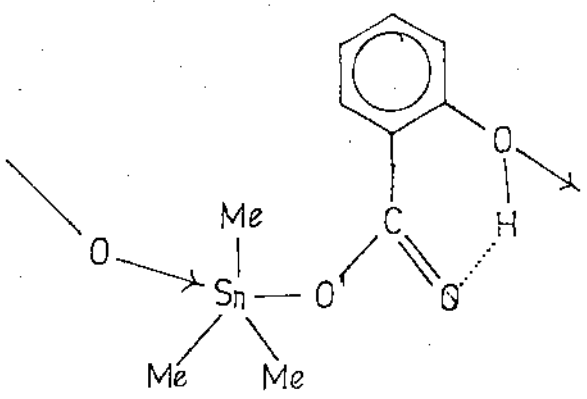
119m Mossbauer data give quadrupler splittings with and additional weak bonding interaction to the tin atom involving 03 from a C-glide related molecule, Sn-03' = 3.05 A°, in which 03 approaches the tetrahedral face opposite that approached by 02, Sn-02 = 3.07A° and having the edge defined by CA 1 and CC 1 in common



The intramolecular hydrogen bond formed from the orthohydroxy group of salicyclic acid [02.....H_3 = 1.93 A°] contributes in causing the longer Sn - 02 bond length.

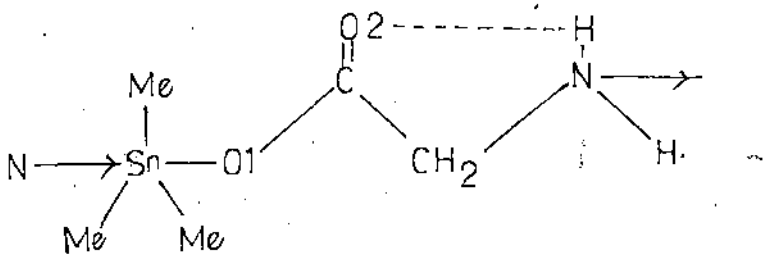
.Now we will discuss with the case of (B) type of compounds. As with other trimethyl tin esters of carboxylic acids, both the anisic acid derivative and the salicylate reside in a chain polymeric form in the solid state. However, unlike anisic acid derivative , which has a form (B) with the carboxyl oxygen atom responsible for intermolecular bridging, the salicylate shows the carboxyl oxygen involved in hydrogen bonding with the o-hydroxyl group. Here the oxygen atom of the ortho hydroxy group serves as the intermolecular

bridging ligand (C).



(C)

This coordination difference is reminiscent of that which occurs in the trimethyl tin glycinate (74) i.e. intermolecular coordination takes place via the amine



nitrogen atom rather than the acyl oxygen atom of the carboxyl group. Again hydrogen bonding is present.

The infrared data are most instructive in comparing solid and solution state structures. For the anisic acid derivative, changes in the carbonyl group stretch ν_{COO}, and an increase in

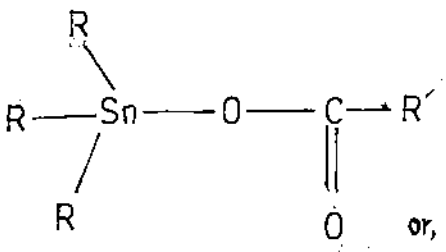
the number of tin methyl group stretches, ν_{SnC_3}, on going from the solid to a chloroform solution imply a greater structural change compared to that occurring with the salicylate derivative, which shows relative invariance in these quantities. The asymmetric stretch ν_{COO} appearing at 1630 cm^{-1} is in the range associated with the discrete form (A) structure and represent a lowering from that found in the free acids (81) . The implication is that the polymer form (B) found for the solid state of o-anisic acid derivative is disrupted in solution. In the case of salicylate derivative which is represented in terms of hydrogen bonded chain in solid state (B), solution apparently causes little structural change. Molecular weight data in solution for both the compounds imply the presence of a monomer while ν_{OH} for second is insensitive to dilution and is extremely broad, suggesting retention of the intramolecular hydrogen bonding found for the solid. The principal occurrence on solution of salicylate compound is the rupture of the weak intermolecular Sn-O "bond".

The single absorption for (1) in the solid corresponding to the ν_{Sn-C} stretch at 545 cm^{-1} and the two absorptions in solution, at 540 cm^{-1} and 510 cm^{-1}, are consistent with a planar Me_3Sn arrangement, as found for the solid, which becomes non planar, i.e. more tetrahedral in a monomeric form in solution. Solution ^1H NMR of these compounds also supports the monomeric form in solution. Both carbon and tin chemical shifts are very similar to those reported for analogous monomeric tributyl tin carboxylates.

The diorganotin derivatives of carboxylic acids are less in number, there is only one reported compound, (o-thiobenzoato) diphenyltin (51) without any structural details.

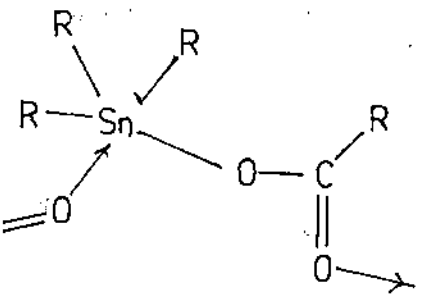
SCOPE AND OBJECTIVE

Organotin carboxylates have been studied quite extensively. These compounds consist of triorganotin mono carboxylate, Diorganotin dicarboxylate and mono organotin tri carboxylates. Detailed structural studies indicate that triorganotin mono carboxylates can exist either as monomer or as polymers e.g.



(A)

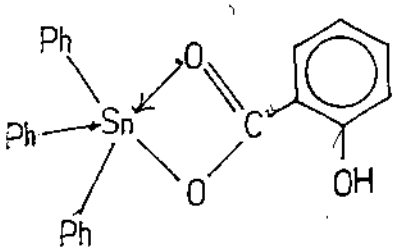
or,



(B)

The former is intramolecularly coordinated while the later is inter molecularly coordinated.

Detailed structural investigations on di organotin carboxylate derivative have not carried out so far, though a some diorganotin dicarboxylates have been reported. Hydroxy carboxylic acid esters also have not been studied extensively so far. The Triphenyl tin-O-hydroxy benzoate have been studied and the following structure have been assigned by Holmes et al (50).



Holmes et al (50) also reported $Ph_2Sn[o\text{-}(S)C_6H_4CO_2]$ though no structural detail was given. In absence of paucity of data on diorganotin mono carboxylates, particularly with hydroxy carboxylic acids, it was considered interesting to investigate the organotin derivative of hydroxy carboxylic acid such as diphenyl glycolic acid in the present investigation. Such an acid contain two replacable protons in near proximities. The intention of the present investigation was to replace both these protons. This was realised during current investigation. Triorganotin compounds are unlikely to replace both these protons possibly due to steric reasons. Therefore, it may lose one organic group to yield diorganotin derivatives. During the present investigation the triorganotin compounds did not yield triorganotin diphenyl glycolate instead they yielded diorganotin diphenyl glycolate. It would be interesting to explore some structural aspects of these diorganotin mono hydroxy carboxylates by IR, ^1H, ^{13}C and ^{119}Sn NMR studies to suggest their structures at least tentatively.

E X P E R I M E N T A L

Tin was estimated gravimetrically as described earlier. Analysis of the compounds for carbon and hydrogen were carried out at Central Drug Research Institute, Lucknow.

Conductance values have been measured in PYE UNICAM conductivity meter (PW 9505) using DMSO as solvent.

The Infrared spectra have been recorded in the range of 4000-600 cm^{-1} for most of the compounds using Beckman IR 20. Few IR spectra also have been taken at RSIC North East Hill University, Shillong.

The following abbreviations have been used for the intensity of the IR absorption bands

v.s. = very strong, s = strong, m = medium, w = weak, b = broad, sh = shoulder, h = hump.

nujol had peaks at 3000-2800 cm^{-1} (vs), 1460 cm^{-1} (s), 1376 cm^{-1} (m).

KBr had characteristic absorption in the range 3600-3400 cm^{-1} (b).

The ^{1}H NMR spectra have been recorded in VA-EM-390, 90 MHz, NMR spectrophotometer at RSIC North East Hill University, Shillong using DMSO d_6 as solvent.

The ^{13}C, ^{119}Sn NMR spectral data for few compounds have been obtained with Bruker WP 80 Sy Multinuclear 90 MHz FT NMR spectrophotometer and JEOL PMX 60 SI CW ^{1}H spectrophotometer at the Department of Chemistry and Biological Chemistry, University of

Essex, Colchester, U.K. d^6 DMSO was used at the solvent and TMS as reference unless otherwise mentioned. For ^{119}Sn NMR spectra tetramethyl tin have been used as reference.

Apparent molecular weight of some of the compounds have been determined following Rast's method. Camphor (mp 178°C) used as solvent, Cryoscopic constant for camphor, K_f = 39.7°C.

Preparation of starting materials

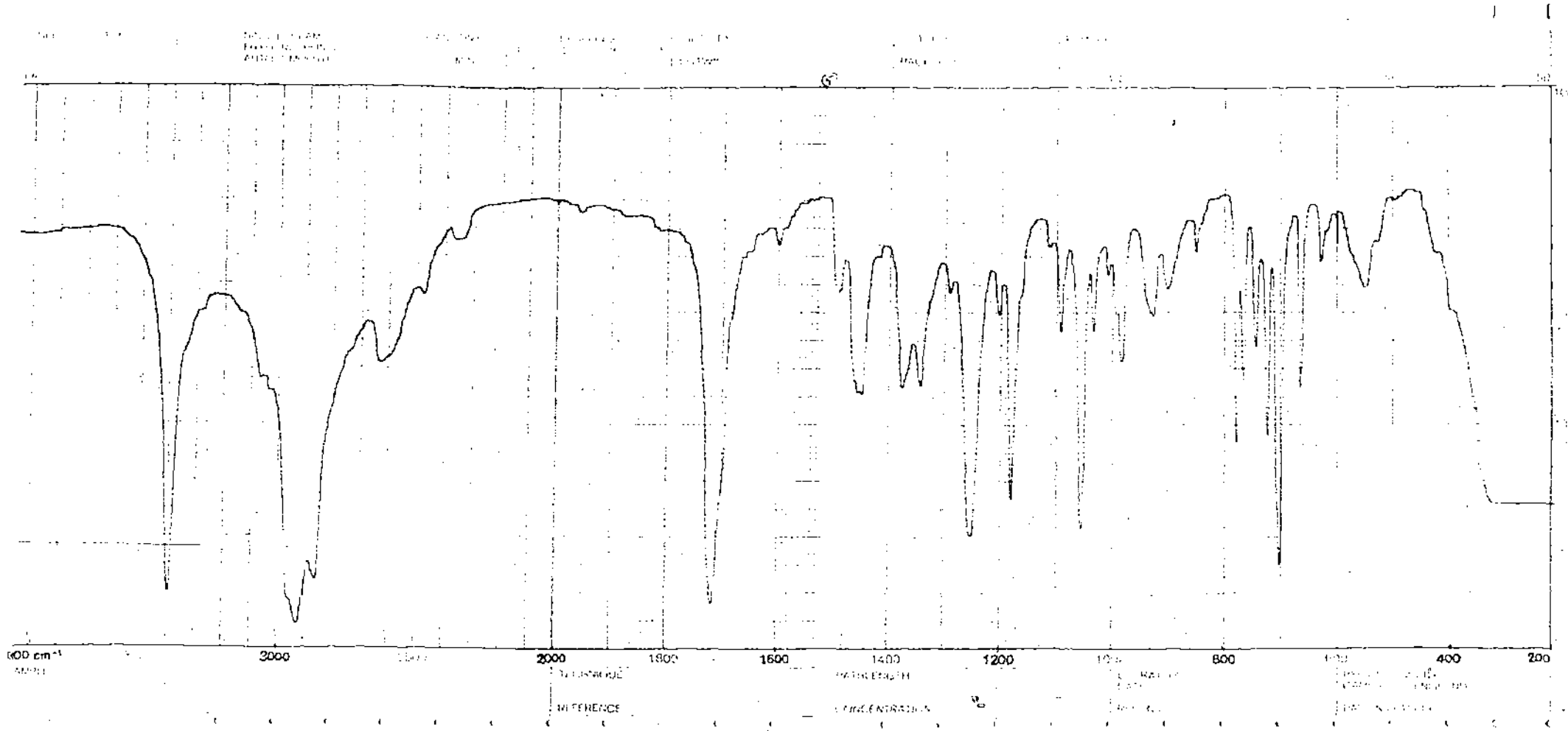
All the solvents required in this experiment have been purified and dried accordingly as described earlier.

1. Diphenyl glycolic Acid

Diphenyl glycolic acid (mp 149-150°C, Merck) was used without further purification.

Important Infrared spectral data (cm^{-1})

3400(s), 2650(w), 1715(s), 1380(m), 1340(m), 1250(s), 1205(w), 1180(s), 1090(w), 1055(s), 1045 (w), 985(m), 950(m), 900(w), 850(w), 780(s), 745(m), 725(m), 700(s), 665(s), 630(h), 600(w), 550(b).



IR spectrum of Diphenyl glycolic acid (nujol)

2. Dibutyl tin diphenyl glycolate

(A) Tributyl tin chloride (1.09 gm, ~ 4m. moles) and diphenyl glycolic acid (913 mg, ~ 4 m. moles) were taken in a round bottom flask. 150 ml chloroform was poured in the flask with constant stirring. The mixture was warmed for 15 minutes on a water bath. The liberated hydrochloric acid was just neutralised with drops of liquor ammonia. The reaction mixture was cooled in refrigerator for 15 minutes, and ammonium chloride was removed from the reaction mixture. The clear filtrate was then refluxed for 3 hours. After reaction it was allowed to cool, filtered and the filtrate was concentrated to about 15 ml. A white product appeared on standing. The compound was washed with methanol and then vacuum dried.

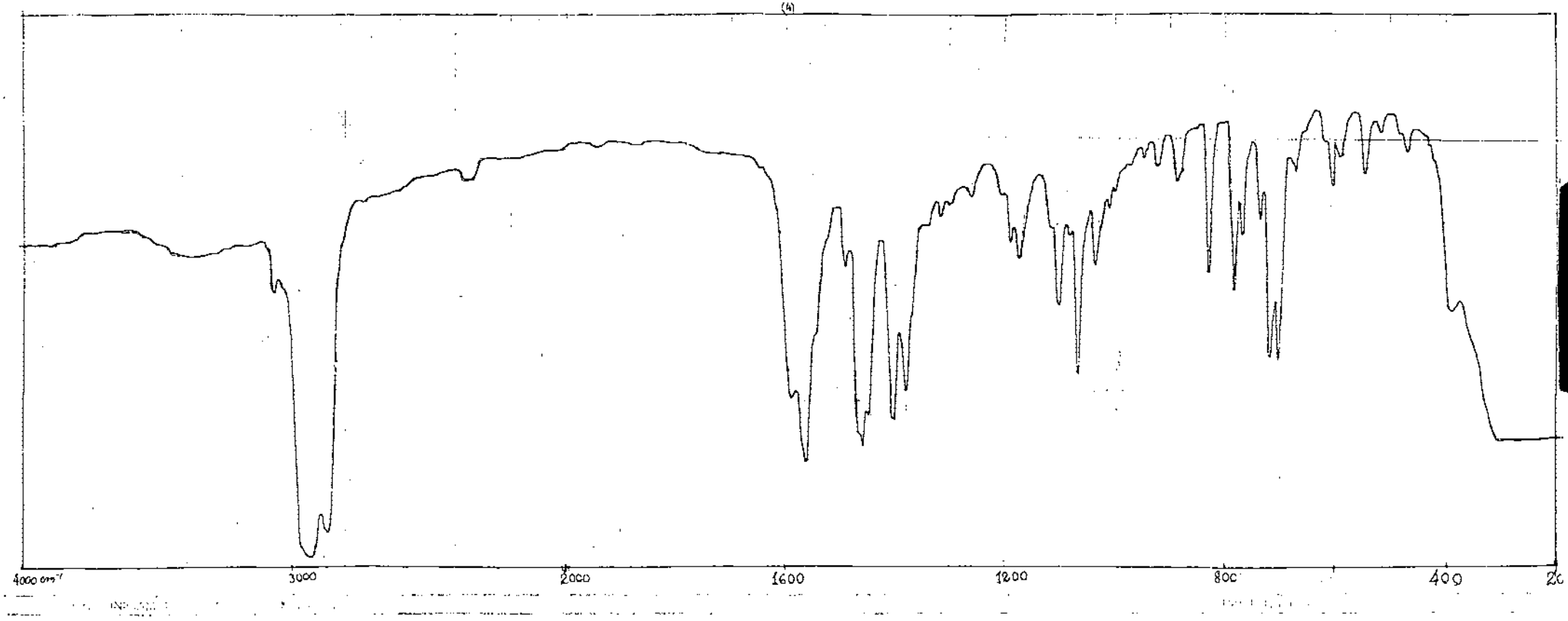
The compound melted at 313°C.

% Analysis for $C_{22}H_{28}O_3Sn$:

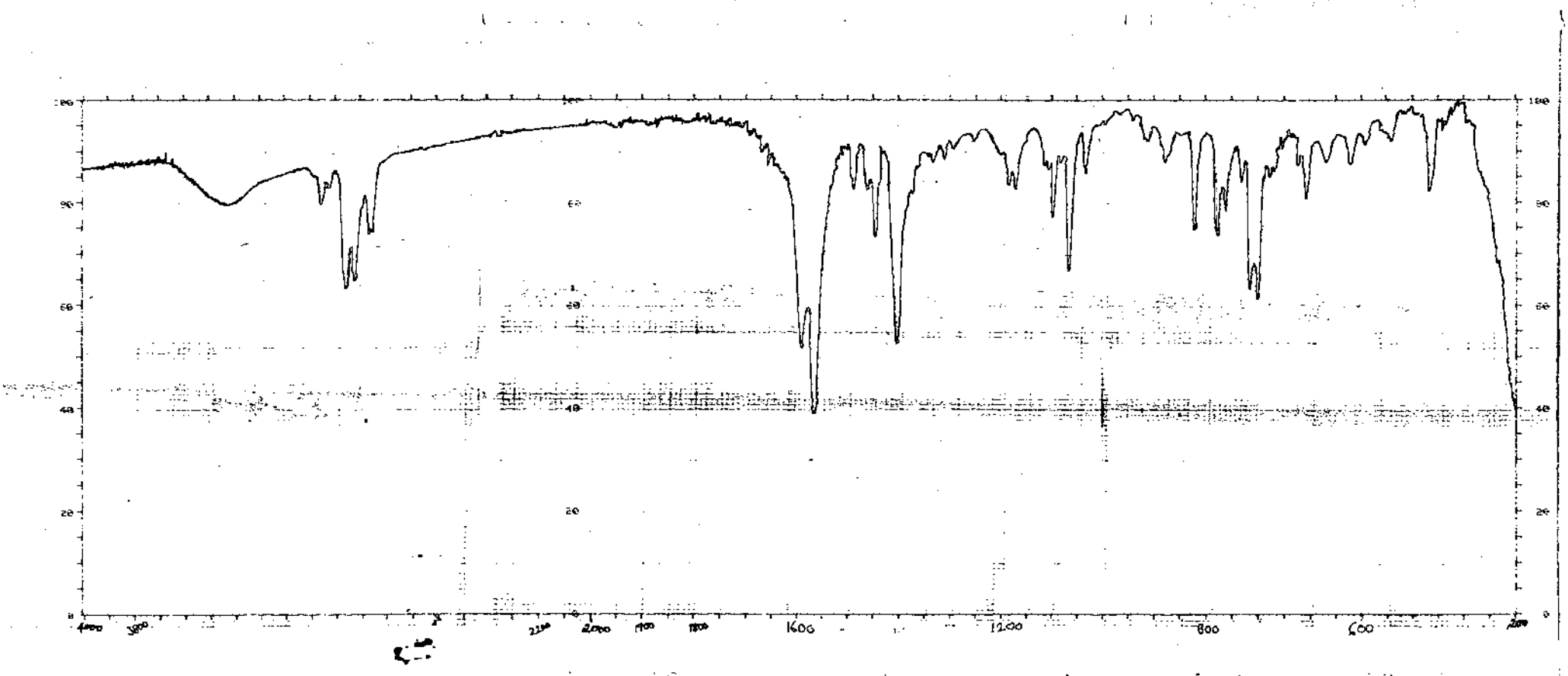
Found	:	C 57.49	H 6.29	Sn 26.02
Calcd	:	C 57.51	H 6.10	Sn 25.92

Important Infrared spectral data (cm^{-1})

1590(s), 1565(s), 1490(w), 1400(s), 1190-1180(m), 1100(m), 1070(s), 1035(w), 920(w), 890(w), 825(m), 780(m), 720(m), 700(m), 600(w), 545(w), 470(w), 380(m).



IR spectrum of Dibutyltin diphenyl glycolate (A) (nujol)



IR spectrum of Dibutyl tin diphenyl glycolate (solution)

(B) Dibutyl tin oxide (996 mg, ~4 m.moles) and diphenyl glycolic acid (913 mg, ~4 m. moles) were taken in a 250 ml round bottom flask. 150 ml of benzene was added to the mixture. This reaction mixture was refluxed for 3 hours fitted with a water separator.

After the completion of reaction, the reaction mixture was allowed to cool and filtered. The filtrate was concentrated to about 10 ml and was allowed to stand for overnight. A white powdery compound appeared. It was washed with warm methanol and dried in vacuum.

(Yield ≈ 62%)

The compound was found to melt at~312°C.

% Analysis for $C_{22}H_{28}O_3Sn$:

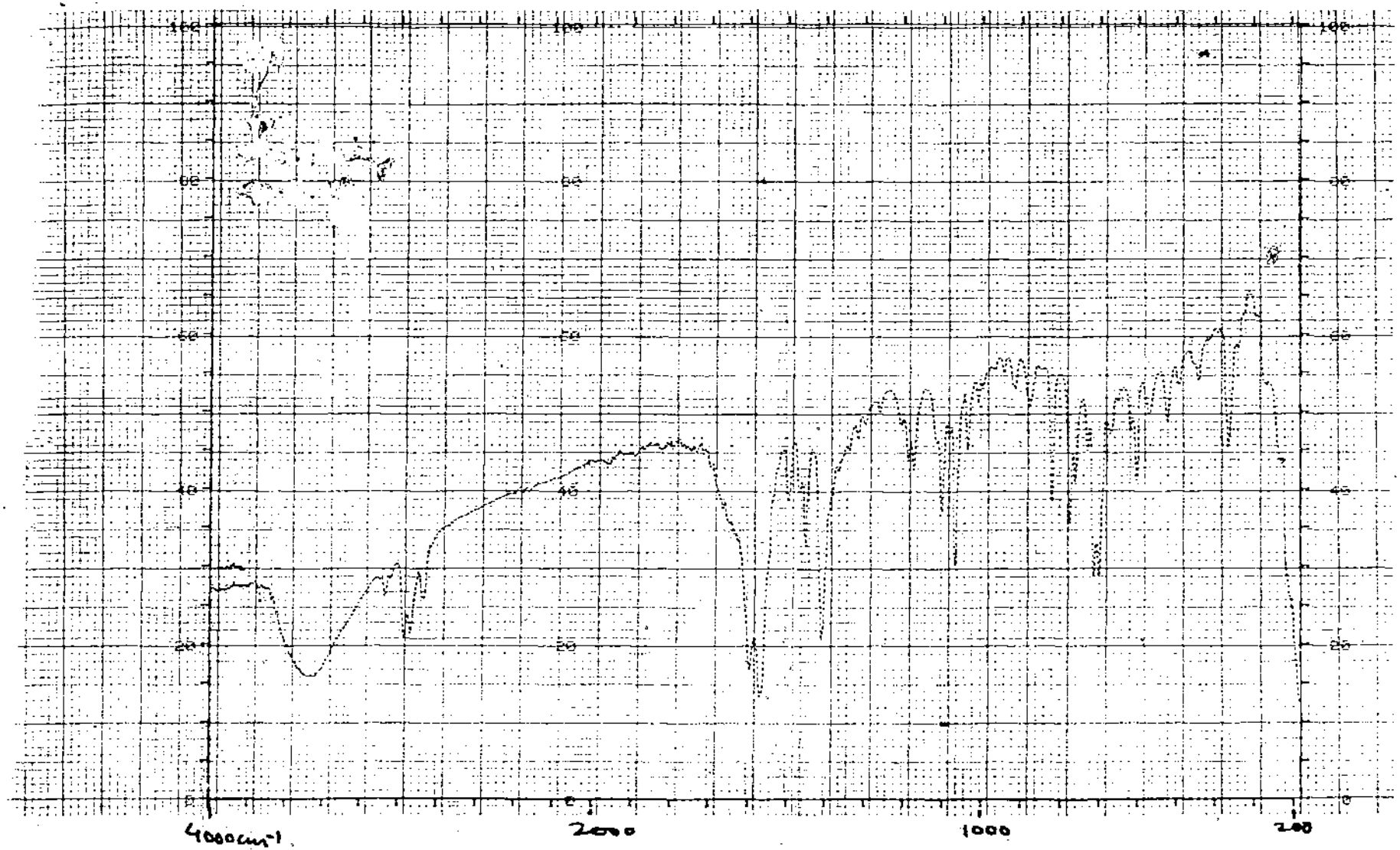
Found :	C 56.86	H 5.92	Sn 24.90
Calcd :	C 57.51	H 6.10	Sn 25.92

Important Infrared spectral data (cm^{-1}):

1590(s), 1570(s), 1500(w), 1400(s), 1180(m), 1100(m), 1080 (s), 1015(w), 910(w), 890(w), 820(m), 790(m), 720(m), 700(m), 600(m), 540(w), 510(w), 500(w), 450(w), 380(m), 280(h).

Mixed melting point of the compounds of reaction (A) and (B) was found to be 311-12°C.

So these two compounds are same.



IR spectrum of Dibutyl tin diphenyl glycolate (KBr)

3. Diphenyl tin diphenyl glycolate

(A) Triphenyl tin chloride (1.54 gm, ~4 m. moles) was dissolved in 200 ml chloroform in a round bottom flask. Diphenyl glycolic acid (913 mg, ~4 m. moles) was added with shaking. The mixture was warmed for 15 minutes on a steam bath. The hydrochloric acid liberated in the reaction mixture was just neutralised with drops of liquor ammonia. The reaction mixture was then refrigerated for another 15 minutes. The deposited ammonium chloride was separated by filtration. The reaction was then carried out by refluxing for 3 hours. It was then cooled and then concentrated to about 15 ml- white powdery product appeared on standing for few hours.

The compound was recrystallised from methanol and dried in vacuum desiccator.

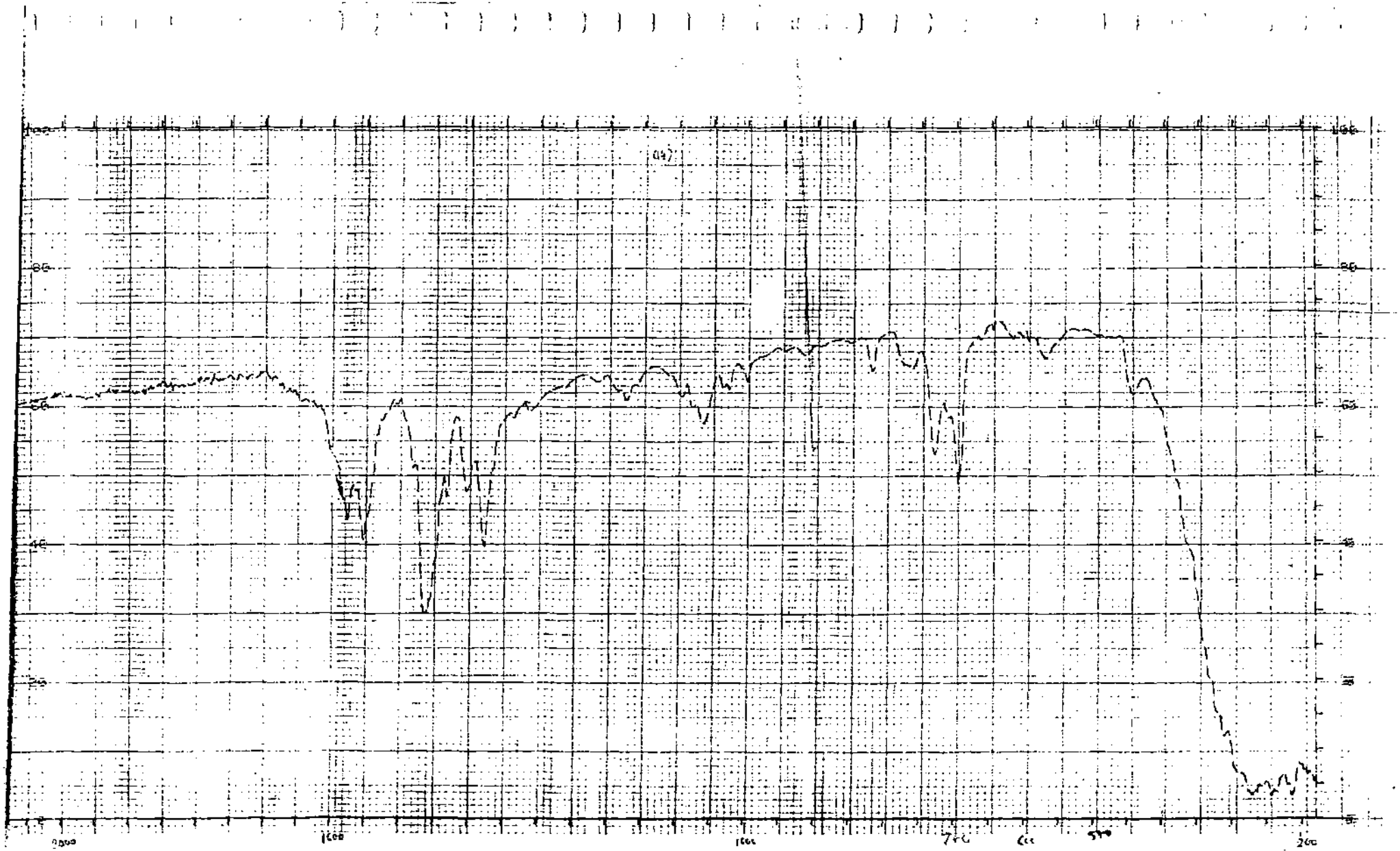
The compound decomposed after 282°C.

% Analysis for $C_{26}H_{20}O_3Sn$:

Found :	C 61.69	H 3.72	Sn 23.22
Calcd :	C 62.52	H 4.00	Sn 23.84

Important Infrared spectral data (cm^{-1})

1578(s), 1555(s), 1390(s), 1180(m), 1100(m), 1040(m), 950(w), 940(w), 840(m), 760(m), 740(s), 700(s), 680(m), 655(s), 570(w), 450(w).



IR spectrum of Diphenyl tin diphenyl glycolate (A)
(nujol)

(B) Diphenyl tin dichloride (1.38 gm, ~4 m. moles) and diphenyl glycolic acid (913 mg, ~4 m.moles) were taken in a round bottom flask. 200 ml chloroform was added to it. The mixture was shaken and warmed for half an hour. The liberated hydrochloric acid was neutralised by drops of liquor ammonia. It was cooled in refrigerator for 15 minutes and filtered off. The clear solution was refluxed for 3 hours.

The mixture was allowed to cool and then filtered. The filtrate was concentrated to about 10 ml. Kept overnight, white crystalline product appeared.

(Yield = ~55%).

The compound was purified by repeated crystallisation from methanol and dried in vacuum.

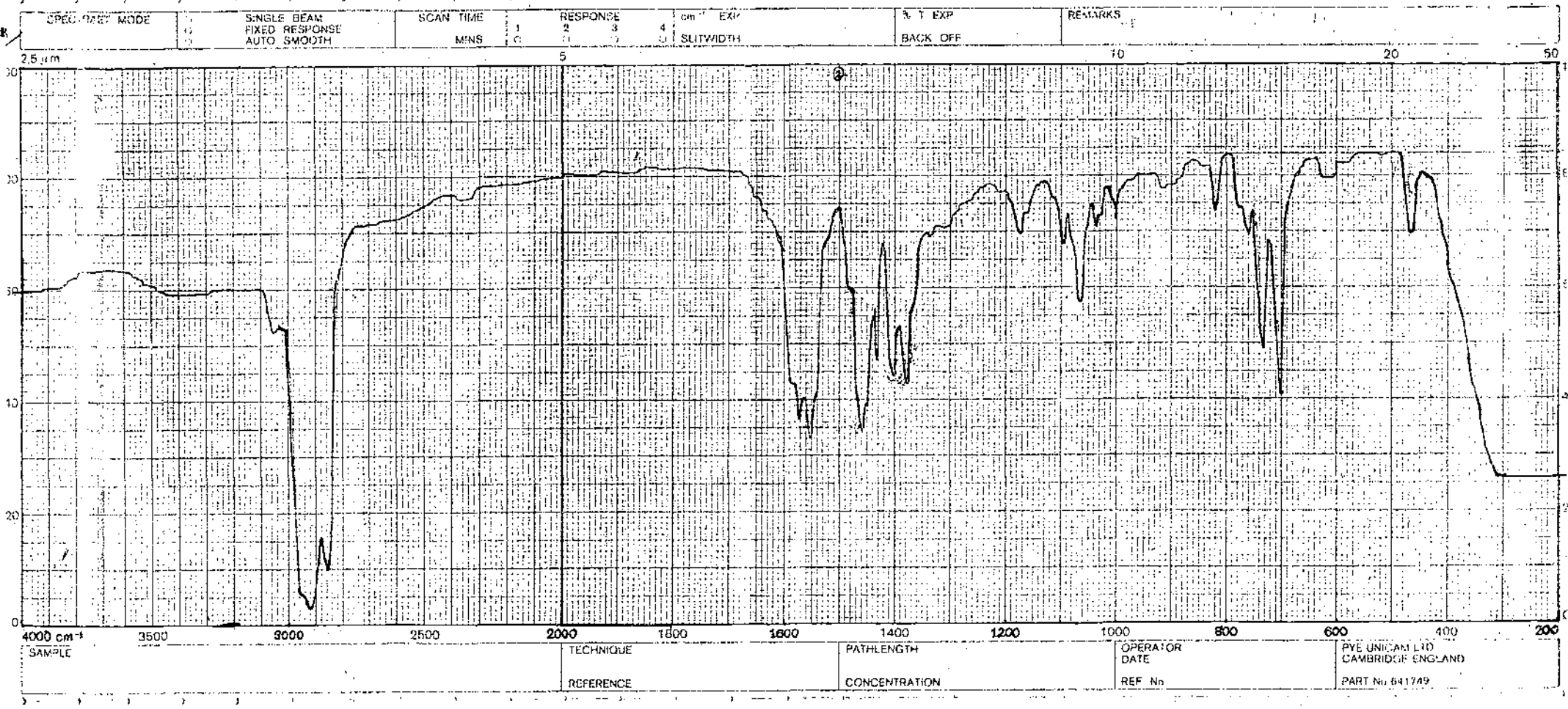
The compound decomposed at 280-282°C.

% Analysis for $C_{26}H_{20}O_3Sn$:

Found :	C 61.71	H 3.80	Sn 23.64
Calcd :	C 62.52	H 4.00	Sn 23.84

Important Infrared spectral data (cm^{-1})

1575(s), 1550(s), 1380(m), 1175(w), 1100(w), 1060(m), 1040(w), 1000(w), 900(w), 820(w), 760(w), 725(m),700(s), 610(w), 470(m).



IR spectrum of Diphenyl tin diphenyl glycolate (B) (nujol)

The mixed melting point of products of reaction (A) and (B) was found ~280°C (decomposed). So, diphenyl tin diphenyl glycolate was obtained in both the cases.

4. Dibenzyl tin diphenyl glycolate

A mixture of 1.27 gm (~4 m. moles) of dibenzyl tin oxide and 913 mg (~4 m. moles) of diphenyl glycolic acid was taken in a round bottom flask. 150 ml benzene was poured in the mixture with stirring. The mixture was refluxed for 4 hours with a water separator. After refluxing, the reaction mixture was cooled and filtered. The filtrate was concentrated to about 15 ml. White crystaline product appeared on standing for overnight.

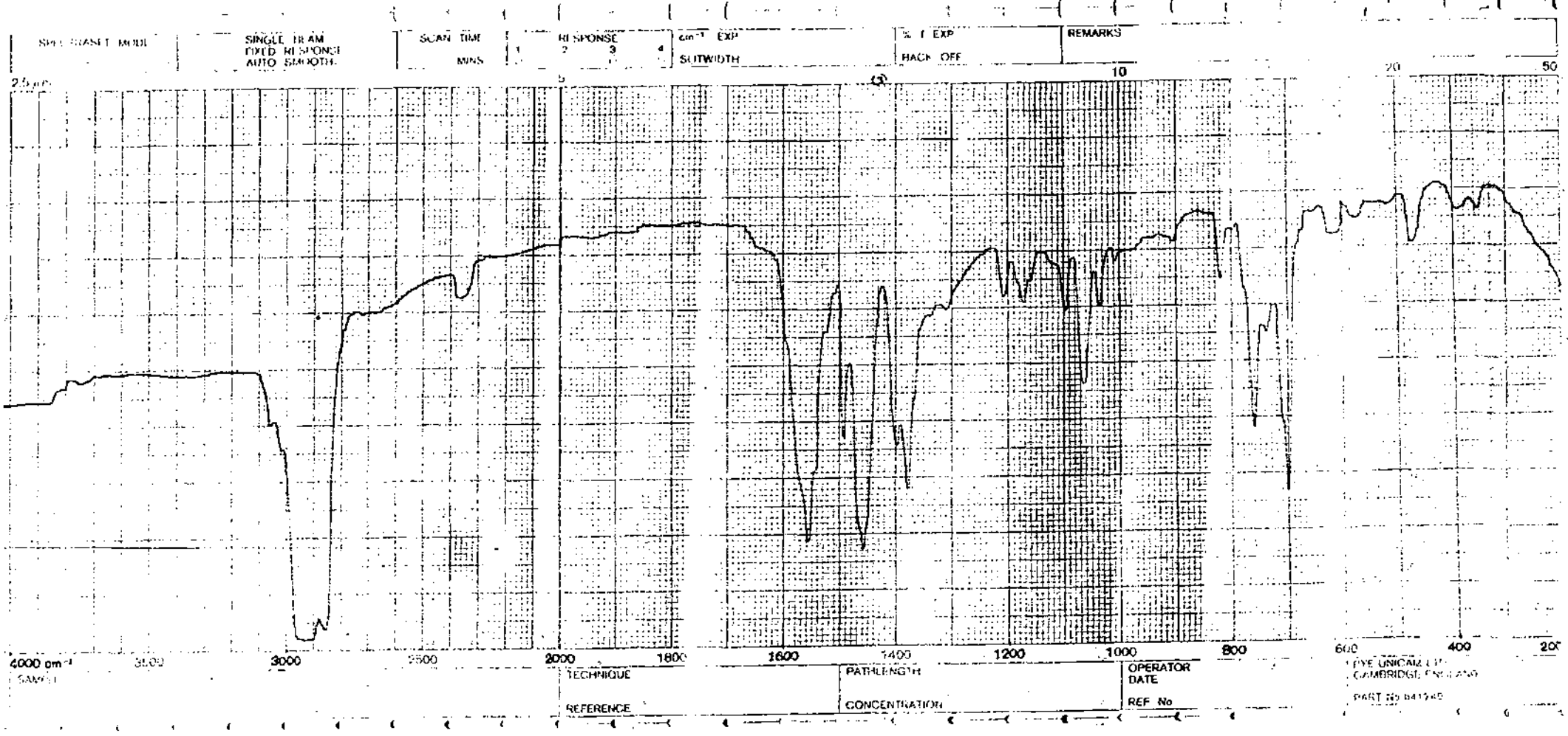
Purification have been done by washing several times with warm chloroform.

(Yield = ~50%).

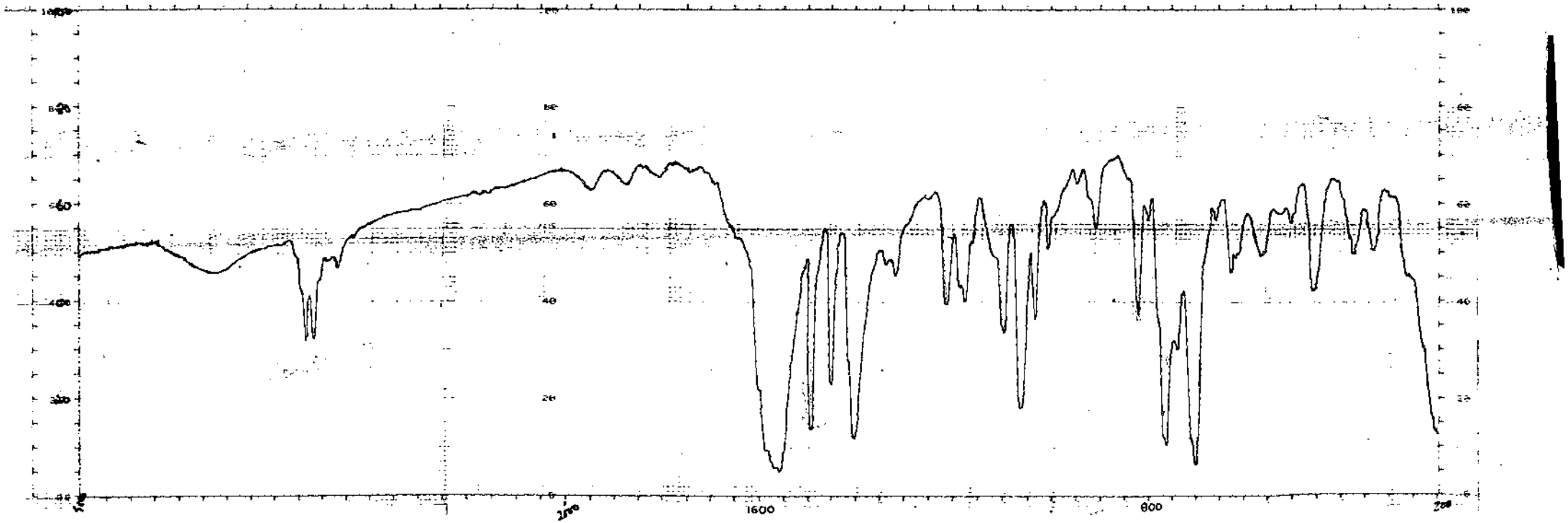
The compound melted at 226°C and decomposed after this temperature.

%Analysis for $C_{28}H_{24}O_3Sn$:

Found	:	C 63.82	H, 3.41	Sn 22.42
Calcd	:	C 64.24	H 3.82	Sn 22.75



IR spectrum of Dibenyl tin diphenyl glycolate (nujol)



IR spectrum of Dibenzyl tin diphenyl glycolate (Solution)

Important Infrared spectral Data (cm^{-1}):

1558(s), 1400(m), 1380(s), 1210(m), 1175(w), 1100(m), 1070(m), 1040(w), 1010(w), 910(w), 820(m), 760(s), 740(w), 700(s), 620(w), 570(vw), 470(w), 400(h), 350(h).

5. Dimethyl tin bis (diphenyl glycolate)

A mixture of dimethyl tin oxide (660 mg, ~ 4 m. moles) and diphenyl glycolic acid (1.83 gm ~ 8 m. moles) was taken in a round bottom flask. 200 ml benzene was added to the mixture with stirring. The reaction mixture was refluxed for 4 hours fitted with a water separator.

The reaction mixture was cooled and filtered out the suspended unreacted mass. The clear solution was concentrated to about 20 ml and kept overnight. A white powdery product appeared.

(Yield = ~55%).

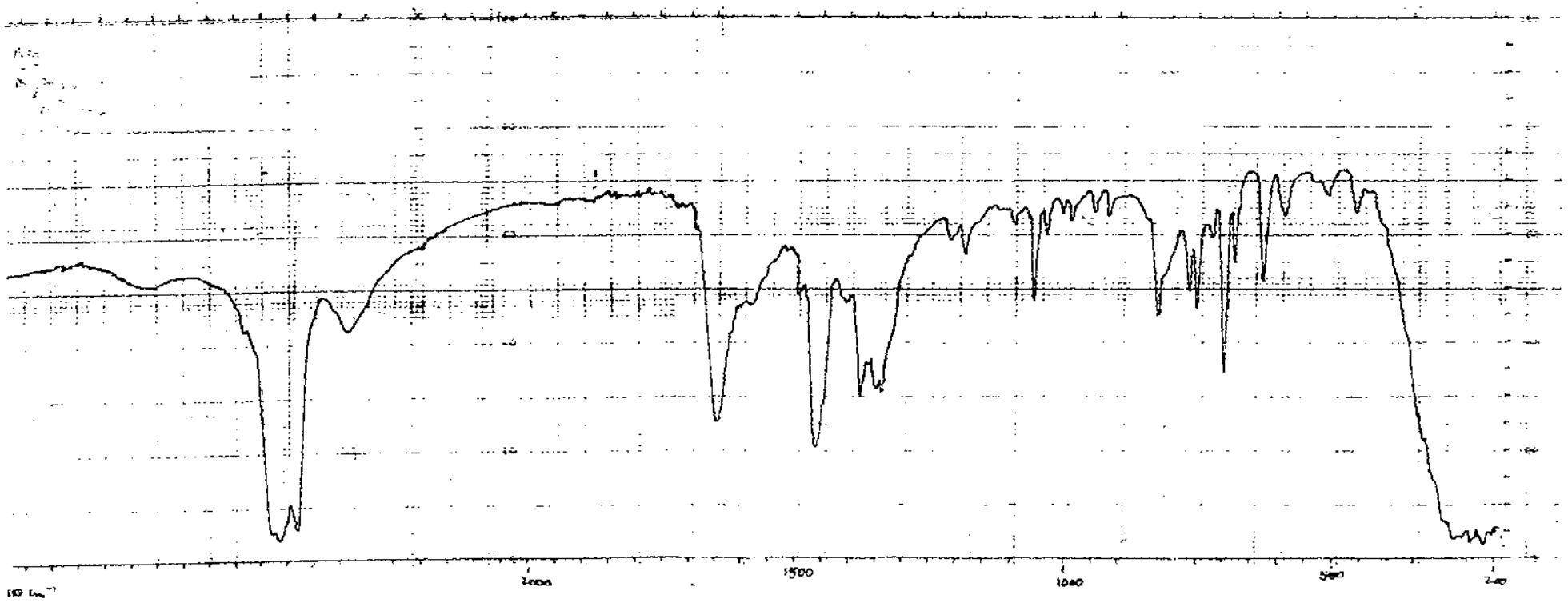
The compound was purified by repeated crystallisation from chloroform and finally dried in vacuum.

The compound was found to melt at 197-98°C.

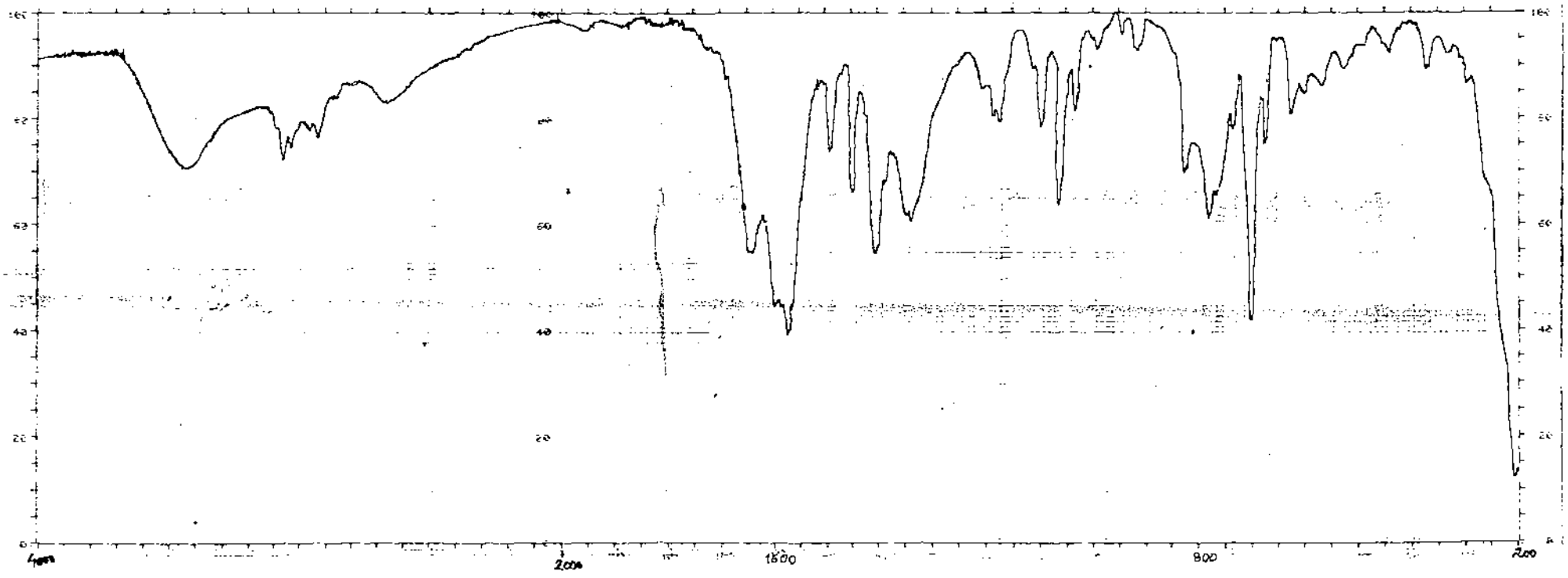
The same compound was found, when the reactants were used in 1:1 molar proportion, though the yield was rather poor.

% Analysis for $C_{30}H_{26}O_6Sn$:

Found :	C 59.26	H 4.14	Sn 20.19
Calcd :	C 59.90	H 4.32	Sn 19.80



IR spectrum of Dimethyl tin bis (diphenyl glycolate) (Nujol)



IR spectrum of Dimethyl tin bis(diphenyl glycolate) (Solution)

Important Infrared Spectral Data (cm^{-1})

1650(s), 1340(m), 1190(w), 1055(m), 1000(w), 950(w), 910(w), 830(m), 760(m), 750(m), 700(s), 680(w), 615(m), 580(w), 510(w), 460(w), 250(w).

6. Dicyclohexyl tin diphenyl glycolate

A mixture of tricyclohexyl tin hydroxide 1.54 gm (~4 m. moles) and 913 mg (~4 m. moles) of diphenyl glycolic acid was taken in a round bottom flask. 200 ml benzene was poured in it. The reaction mixture was refluxed for three hours with water separator.

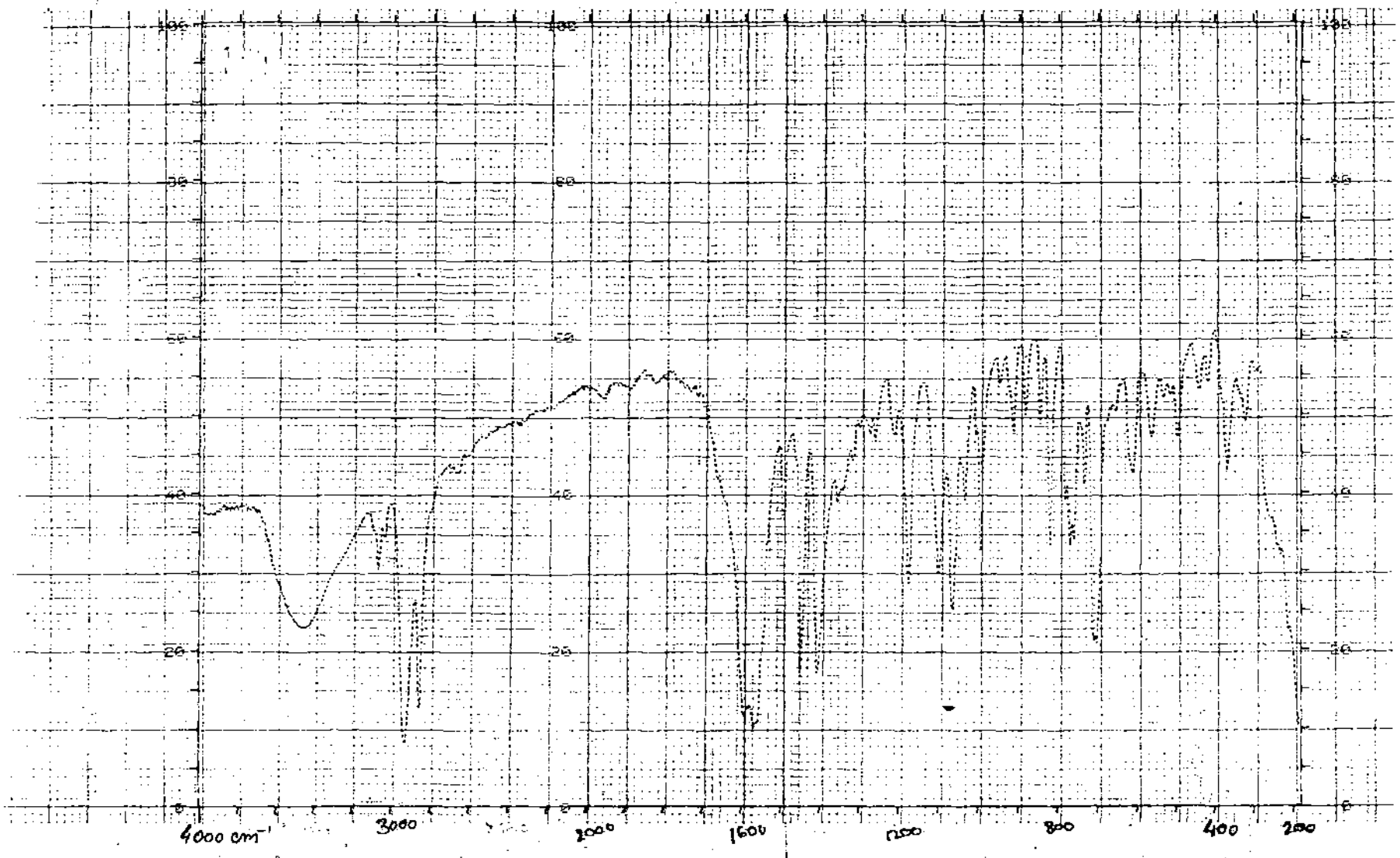
After reaction the mixture was cooled and filtered off the unreacted suspensions. The clean solution was concentrated to about 15 ml and kept overnight. A white crystalline product appeared. Purified by washing with hot chloroform and then dried in vacuum.

(Yield = ~52%).

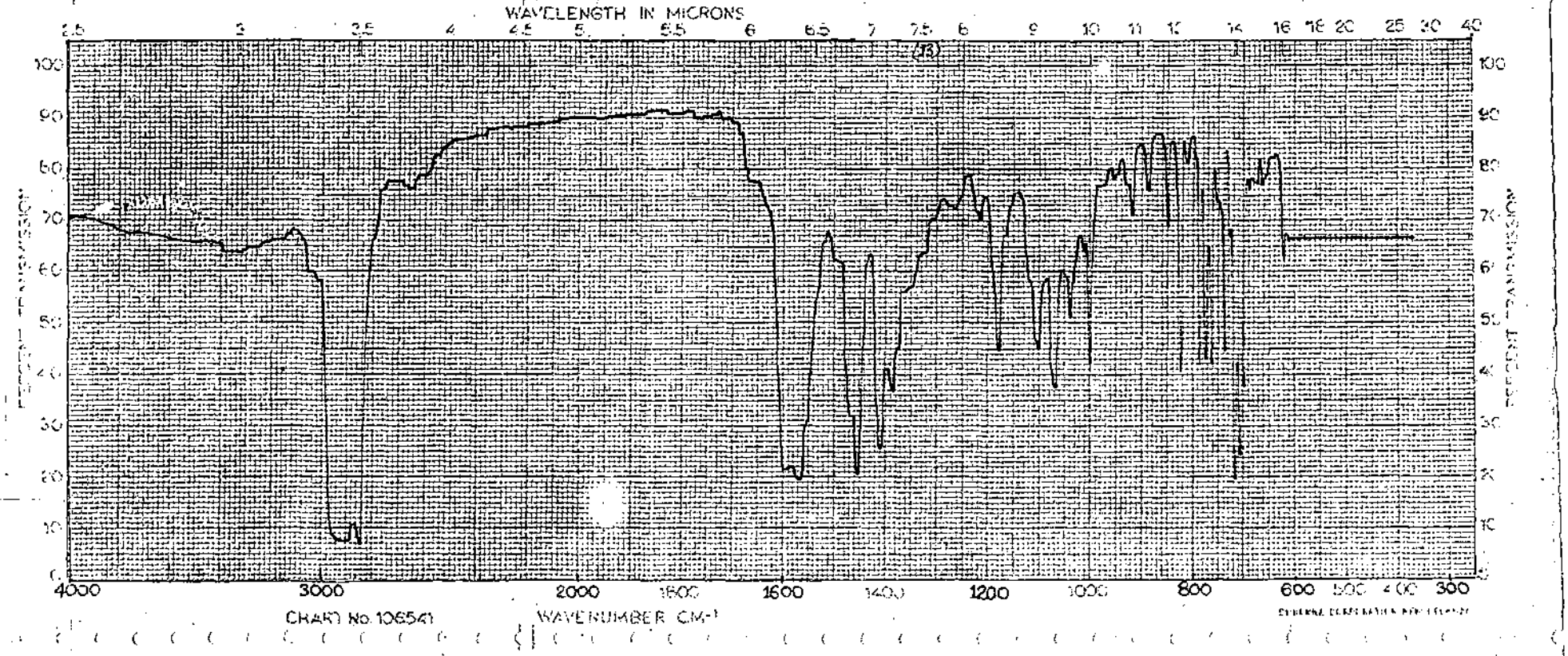
Melting point was found at 320°C.

% Analysis for $C_{26}H_{32}O_3Sn$:

Found	:	C 60.84	H 6.06	Sn 23.10
Calcd	:	C 61.05	H 6.26	Sn 23.28



IR spectrum of Dicyclohexyl tin diphenyl glycolate (KBr)



IR spectrum of Dicyclohexyl tin diphenyl glycolate (nujol)

Important Infrared Spectral Data (cm^{-1})

1600(s), 1570(s), 1500(w), 1420(s), 1400(s), 1220(w), 1200(w), 1190(m), 1100(m), 1090(m), 1010(w), 1000(m), 910(w), 890(w), 810(m), 780(m), 700(m), 610(m), 590(w), 500(w), 440(w), 390(m), 330(w).

7. Dipropyl tin diphenyl glycolate

Tri n-propyl tin chloride (1.13 gm, ~4 m. moles) and diphenyl glycolic acid (913 mg, ~ 4 m. moles) were taken in 200 ml chloroform. Warmed it on a water bath for 15 minutes. The liberated hydrochloric acid was neutralised with the dropwise addition of liquor ammonia. The mixture was refrigerated for another 15 minutes and then deposited ammonium chloride was separated by filtration. The clear filtrate was refluxed for four hours. After reaction, the solution was concentrated to about 15 ml and kept overnight in refrigerator. A white powdery product appeared.

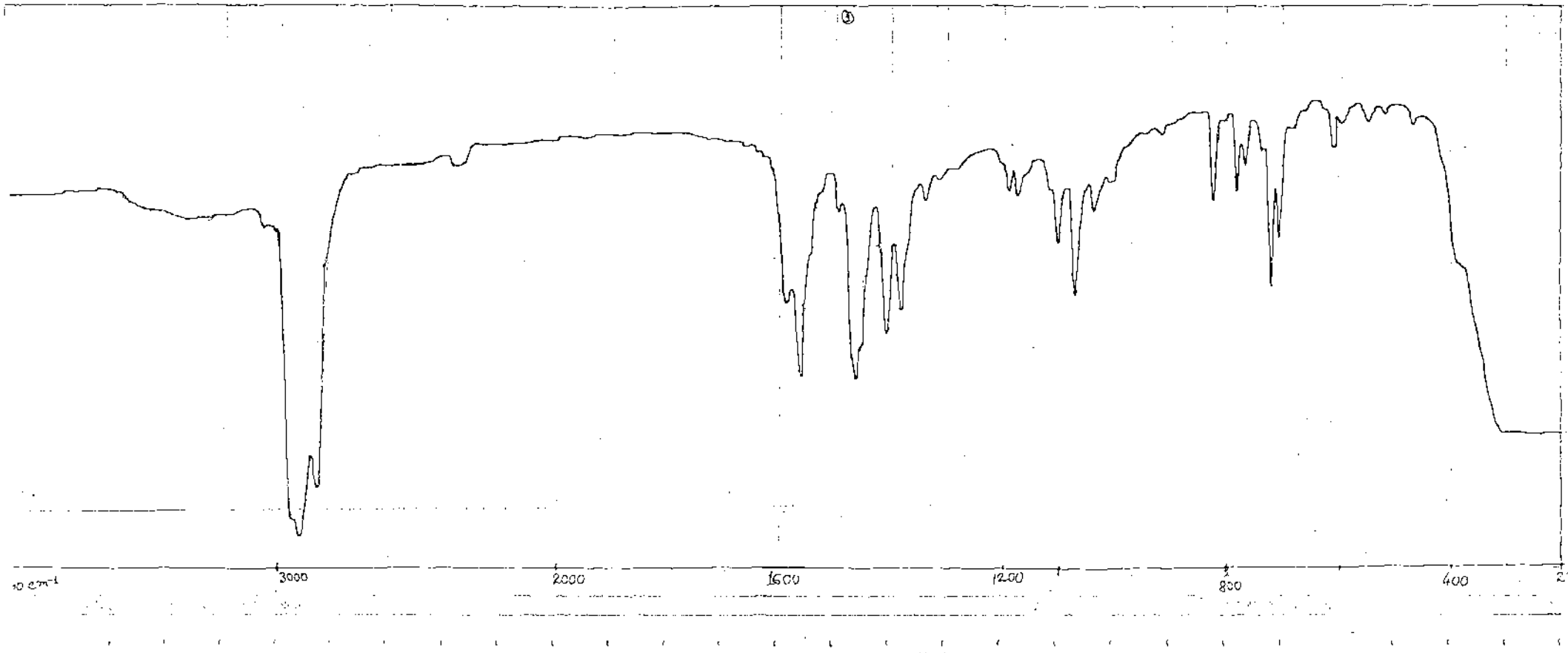
The compound was purified by repeated washing with hot chloroform.

(Yield = ~ 50%)

The compound decomposed after 230°C.

% Analysis for $C_{20}H_{24}O_3Sn$

Found :	C 56.83	H 6.06	Sn 26.28
Calcd :	C 55.68	H 5.56	Sn 27.60



IR spectrum of Dipropyl tin diphenyl glycolate (nujol)

Important Infrared spectral data (cm^{-1})

1590(m), 1565(s), 1500(w), 1380(m), 1340(w), 1190(w), 1180(w), 1100(w), 1070(m), 1040(w), 825(w), 780-760(w), 720(m), 710(m), 610(m), 550(w), 470(w).

Some Attempted Reactions

Reactions of diphenyl glycolic acid have also been carried out with tribenzyl tin chloride, $(MeOCOCH_2CH_2)_2SnCl_2$ and $C_6H_5CH(SnCl_3)CH_2COC_6H_5$. But a gummy product was obtained in each case, from which pure compound could not be isolated.

TABLE I

MOLAR CONDUCTANCE OF SOME OF THE COMPOUNDS

Temp. 25°c Solvent : DMSO

Compound	Molar Conductance (Λ) Mho cm^2
Dibutyl tin diphenyl glycolate	27.24
Dibenzyl tin diphenyl glycolate	26.27
Diphenyl tin diphenyl glycolate	29.00
Dicyclohexyl tin diphenyl glycolate	26.32
Dimethyl tin bis (diphenyl glycolate)	31.27

TABLE II

^{1}H NUCLEAR MAGNETIC RESONANCE SPECTRAL DATA

Compound	Chemical shift (δ)		
	Aromatic protons	Alkyl protons	Others
Diphenyl glycolic acid	7.26-7.68(m)	5.65(comp)	
Dibutyl tin diphenyl glycolate	7.2-7.72(comp)	0.62-1.00(t) 1.02-1.9(comp)	
Diphenyl tin diphenyl glycolate	7.25-7.80 (comp)		
Dimethyl tin bis(diphenyl glycolate)	7.02-7.5 (comp)	0.42(s)	
Dibenzyl tin diphenyl glycolate	6.9-7.4(comp)	2.90(d) 2.85(d)	

s = singlet, d = doublet, t = triplet, q = quartet, comp = complex, m = multiplet.

TABLE III

^{13}C NUCLEAR MAGNETIC RESONANCE SPECTRAL DATA

Compound	Chemical shift (δ)		
	Aromatic carbons	Alkyl carbons	Other carbons
Diphenyl glycolic acid	128.41 128.30 127.87 127.35		152.37 141.72
Dibutyl tin diphenyl glycolate	127.05 126.87 126.08	26.38 25.26 21.78 13.29	147.40
Dimethyl tin bis (diphenyl glycolate)	126.58 126.34 125.53	16.9	145.74 134.74
Dicyclohexyl tin diphenyl glycolate	127.10 126.94 126.40 126.17		147.52 30.90 29.50 28.58 27.95

TABLE IV

^{119}Sn NUCLEAR MAGNETIC RESONANCE SPECTRAL DATA

Compound	Chemical shift (δ)
Dibutyl tin diphenyl glycolate	-142.12
Dicyclohexyl tin diphenyl glycolate	-199.37
Dimethyl tin bis (diphenyl glycolate)	-123.02

An attempt have been made to determine the apparent molecular weight of the compounds by Rast method. But in some cases Rast method could not be followed because these compounds were insoluble in camphor.

In the experiment camphor (mp 178°C) having cryoscopic constant 39.7°C have been used.

TABLE V

APPARENT MOLECULAR WEIGHT DATA

Compound	Molecular weight	
	Found	Calcd (for monomer)
Dibutyl tin diphenyl glycolate	423	459
Dibenzyl tin diphenyl glycolate	488	523
Dicyclohexyl tin diphenyl glycolate	547	511
Dipropyl tin diphenyl glycolate	453	431
Dimethyl tin bis (diphenyl glycolate)	590	601

TABLE VI

SOME INFRARED SPECTRAL DATA IN SOLUTION

Compound	Solvent	Major IR absorption frequency (cm^{-1})
Dibutyl tin diphenyl glycolate	THF	2980(m), 1600(s), 1560(vs), 1450(m), 1410(s), 1180(w), 1110(w), 1020(m), 1040(w), 815(m), 770(m), 705(m), 710(m), 605(h), 580(w) 520(w), 320(m)
Dibenzyl tin diphenyl glycolate	THF	3080(m), 3060(m), 1585(sh), 1560(vs), 1490(s), 1420(s), 1410(s), 1320(w), 1220(m), 1180(m), 1100(m), 1065(s), 1140(m), 1010(w), 915(m), 820(m), 760(s), 740(w), 760(s), 630(w), 555(w), 505(v.w), 460(m), 360(w), 320(w).
Dimethyl tin bis (diphenyl glycolate)	THF	3080(m), 1650(s), 1585(v.s.), 1500(m), 1430(m), 1410(s), 1340(s), 1180(m), 1160(m), 1070(s), 1040(w), 820(w), 770(s), 700(s), 680(w), 615(w), 570(w), 515(w), 370(w)

A broad peak or a hump was obtained ~ 3500 cm^{-1} perhaps due to the solvent used.

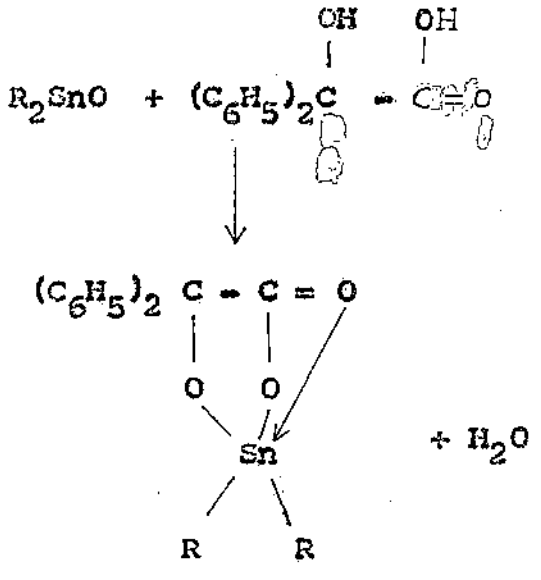
TABLE VII

COMPARATIVE INFRARED CO_2 FREQUENCIES OF SOME COMPOUNDS IN SOLID STATE & IN SOLUTION

Compound	CO_2 frequencies (cm^{-1})	
	Solid state	Solution state
Dibutyl tin diphenyl glycolate	1570	1565
Dibenzyl tin diphenyl glycolate	1650	1643
Dimethyl tin bis (diphenyl glycolate)	1558	1553

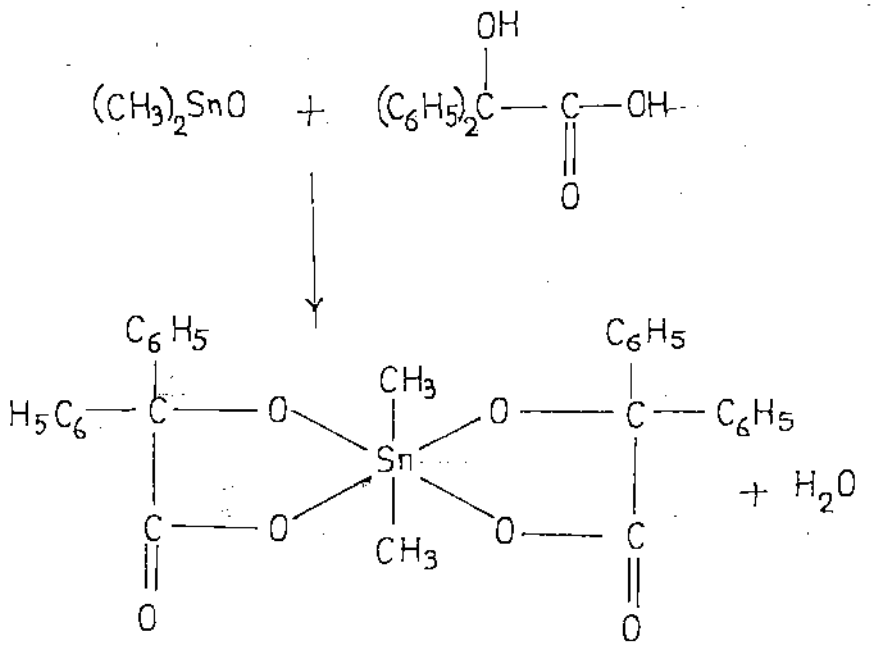
D I S C U S S I O N

During the current investigation, some organotin diphenyl glycolates have been prepared. The triorganotin derivatives however, could not be isolated, though reactions were carried out with triorganotin compounds with diphenyl glycolic acid. Tri organotin compounds on reaction with diphenyl glycolic acid yielded corresponding diorganotin derivatives. However, few more diorganotin diphenyl glycolates were isolated and characterised. The diorganotin derivatives could be obtained from the following type of reactions



(R = Bu, Ph, Bz, Cy, Pr)

with $(CH_3)_2SnO$, however the reaction proceeded as follows:



All these reactions liberated water molecules, which was separated by Dean Stark water separator. On working up the reaction mixture, the organotin derivatives were obtained in crystalline state or as powdery solids.

The elemental analyses gave satisfactory data for the suggested molecular composition of these compounds. The infrared spectra of the compounds were recorded.

Infrared spectra

The ν —OH peak of diphenyl glycolic acid was found absent in all these organotin derivatives, suggesting replacement of both of the hydroxyl and carboxyl protons of the ligand. Several IR spectra of the derivatives have been recorded upto 200 cm^{-1} in Nujol, KBr and in T.H.F. There are number of peaks in the region

of 300-600 cm^{-1}, some of which could possibly due to ν_{Sn-C} and ν_{Sn-O} frequencies but due to some confusing nature of these peaks, we refrain from unambiguous assignments of ν_{Sn-C} and ν_{Sn-O} peaks in these organotin derivatives. These spectra certainly indicate characteristic peaks from some ligand and organotin moieties but we would like to concentrate on the peaks due to carbonyl groups of the ligand and organotin derivatives.

ν_{CO} peaks of the ligand and organotin derivatives (cm^{-1})

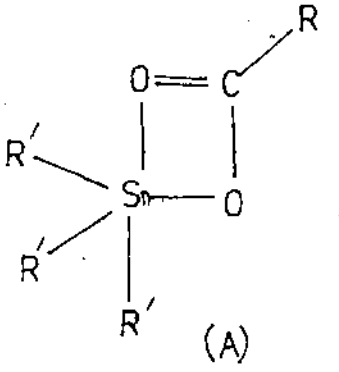
Diphenyl glycolic acid	1715
Dibutyl tin diphenyl glycolate	1595, 1570 (nujol) 1595, 1570 (KBr) 1600, 1560 (T.H.F. solution)
Dibenzyl tin diphenyl glycolate	1558 (nujol) 1585(sh), 1560(T.H.F. solution)
Diphenyl tin diphenyl glycolate	1575, 1550 (nujol)
Dicyclohexyl tin diphenyl glycolate	1600, 1570 (KBr)
Di-n-propyl tin diphenyl glycolate	1590, 1560(nujol)
Dimethyl tin bis (diphenyl glycolate)	1650 (nujol) 1650, 1585 (T.H.F. solution) (mid point of three peak)

Compared to carbonyl peak of Diphenyl glycolic acid, the carbonyl peaks of the organotin derivatives were shifted considerably indicating the formation of the esters. However in most cases, two peaks appeared, one in the range of 1585-1600 cm^{-1} while the other band appeared $\sim$ 1560-1570 cm^{-1}. The latter bands are more intense than the former ones. In case of Dimethyl tin bis (diphenyl glycolate), only one band appeared at 1650 cm^{-1} in nujol, but in T.H.F. solution the same compound gave a peak at 1650 cm^{-1} and a group of three bands around 1570 cm^{-1}. The shifting of carbonyl bands from 1715 cm^{-1} to around 1570 cm^{-1} for most of the compounds may be due to coordination of C = O group to tin atom, in addition to the replacement of the proton of $-\overset{\overset{O}{\|}}{C}-OH$ group. The ^{119}Sn spectra which will be discussed later, support such suggestion for most of the organotin derivatives except for the dimethyltin derivative. The infrared spectra do not show any significant spectral changes between the solid and solution state for most of diorganotin derivatives.

Before proceeding on further discussions of the diorganotin diphenyl glycolates, it may be relevant to discuss some structural aspects of some known organotin carboxylates.

In 1960 Okawara et al (30) investigated the infrared spectra of some methyltin acetates and formates. They interpreted the spectra of trimethyl tin carboxylates e.g. $(CH_3)_3SnOOCR'$ ($R' = H, CH_3$) in terms of ionic structures, since the spectra showed the existence

of a planar trimethyl tin group and indicated an ionic type carboxylate group. However Beattie and Gilson pointed out that the spectroscopic evidence might also be interpreted in terms of either bridging carboxylate groups or simple acetate ions (53). Viscosity measurements by Jansen et al (54) supported the bridging structure. The X-ray diffraction of trimethyltin formate indicated that the structure consisted a planar trimethyl tin and a formoxy group arranged alternately along a helix chain. The tin atoms are penta coordinated by three carbon atoms and two oxygen atoms (25). Recently, a number of workers have studied different types of organotin carboxylates by IR, ^{13}C and ^{119}Sn NMR and X-ray diffraction studies. From their results, it may be concluded that organotin carboxylates can be classified into two major groups. These may be monomeric discrete intramolecular chelated carboxylates (82)

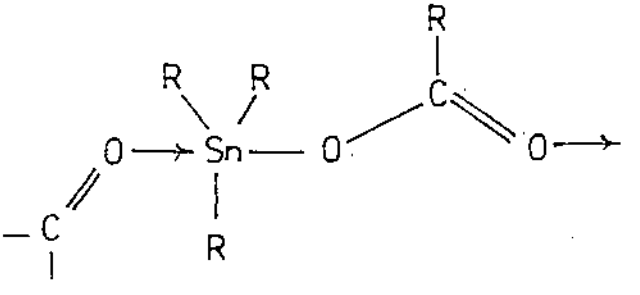


(A)

R = alkyl or aryl

R' = aryl

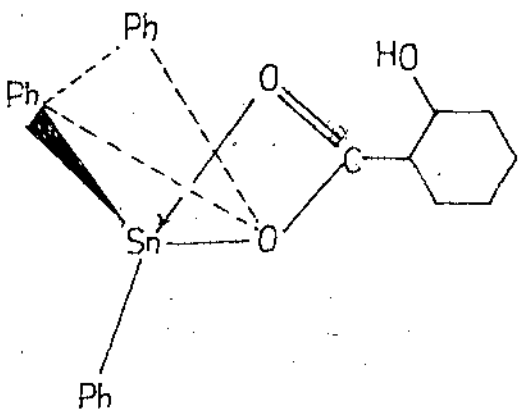
associated arrangements containing five coordinated tin atoms.



(B)

The interplay among various factors are responsible for the preferential appearance of one of the five coordinated representations A and B.

Holmes and his co-workers (51) also studied the triphenyl tin esters of salicyclic acid and suggested the following schematic[a] representation of the structural form

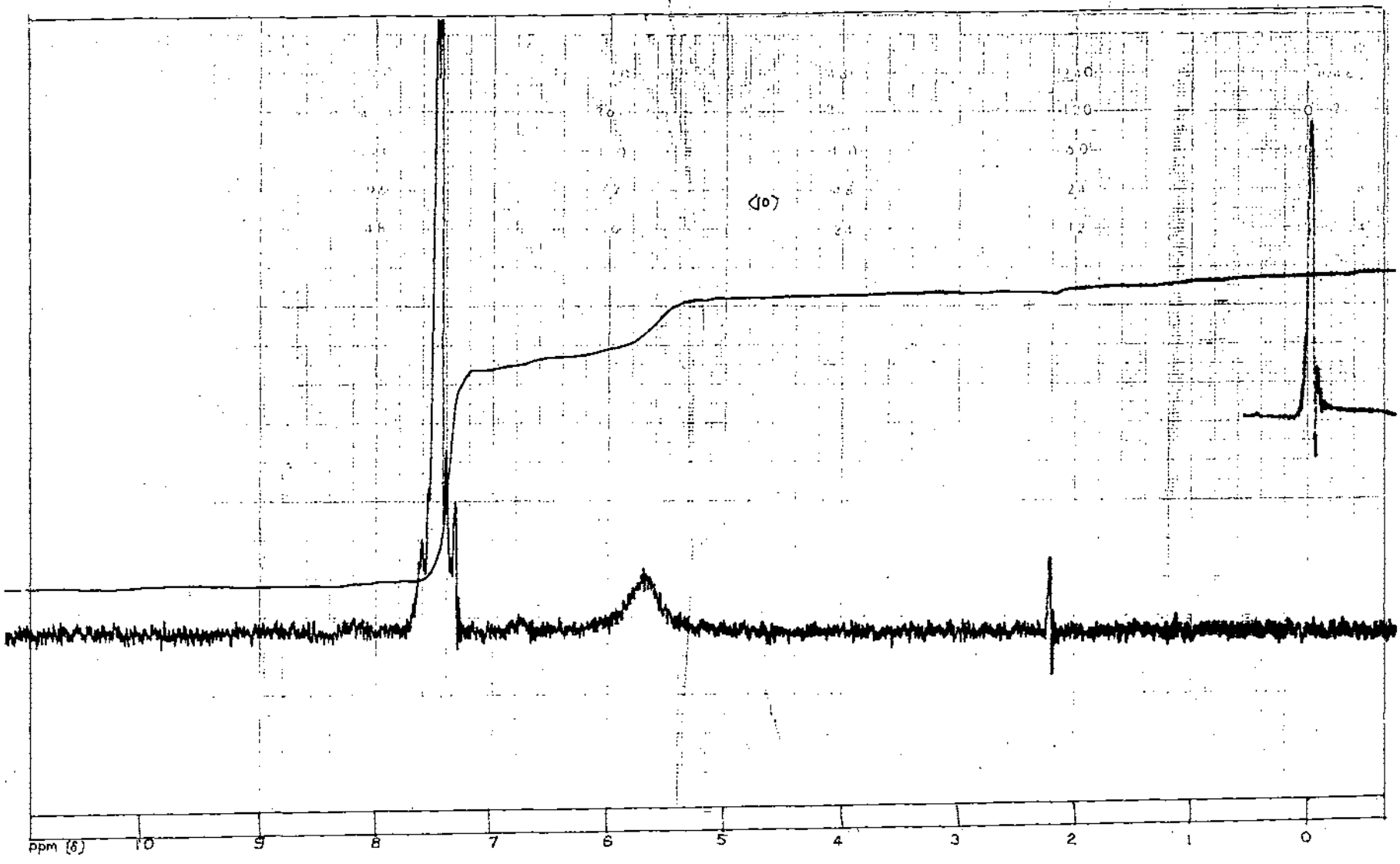


Similar type of intramolecular chelated structures are present with a number of organotin carboxylates.

Under the above context, the physicochemical data obtained for Diorganotin diphenyl glycolates may be discussed.

^{1}H NMR spectra

The ^{1}H NMR spectrum of free diphenyl glycolic acid in $CDCl_3$ gave a complex peak centered at δ 5.65 (carboxyl and hydroxyl protons 2H) and another complex pattern δ 7.26-7.68 (ArH = 10H).



^{1}H NMR spectrum of Diphenyl glycolic acid

Dibutyl tin diphenyl glycolate (in d^6 DMSO)

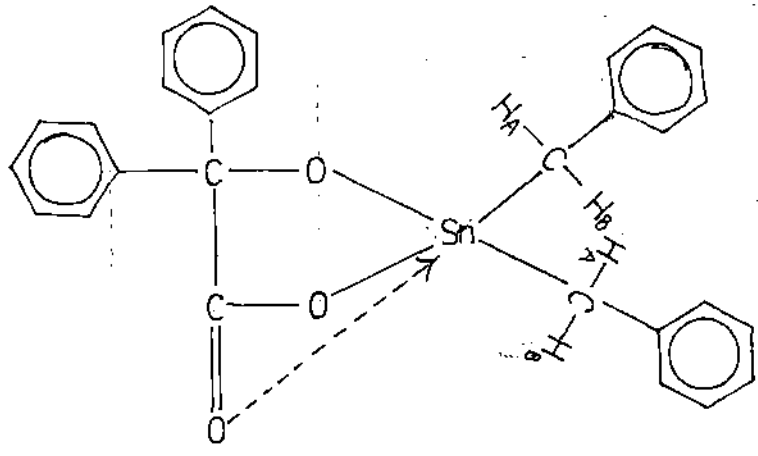
Carboxyl and hydroxyl protons were found to be completely absent and the alkyl protons appeared as triplet at δ 0.62-1.00 (butyl methyl -6H) and methelene protons appeared as complex pattern in between δ 1.02-1.9 (butyl methylene protons 12H). The aromatic protons appeared as complex pattern in between δ 7.2-7.72 (ArH = 10H).

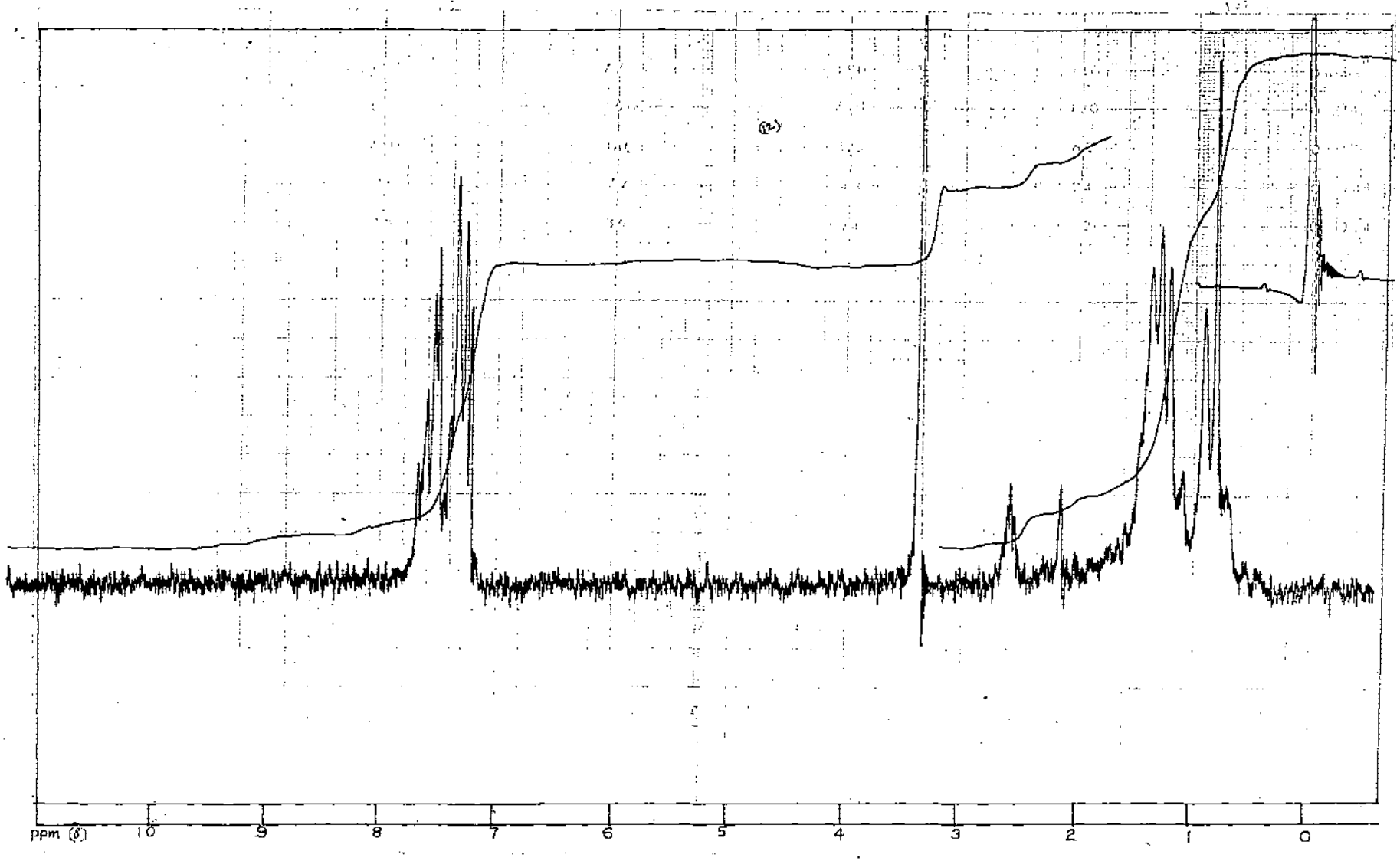
Diphenyl tin diphenyl glycolate

Like the butyl derivative, the carboxyl and hydroxyl protons were totally absent, the aromatic protons gave three groups of complex pattern peaks in between δ 7.15-7.80 in d^6 DMSO. It was not possible to assign unambiguously for different types of aromatic protons of this compounds.

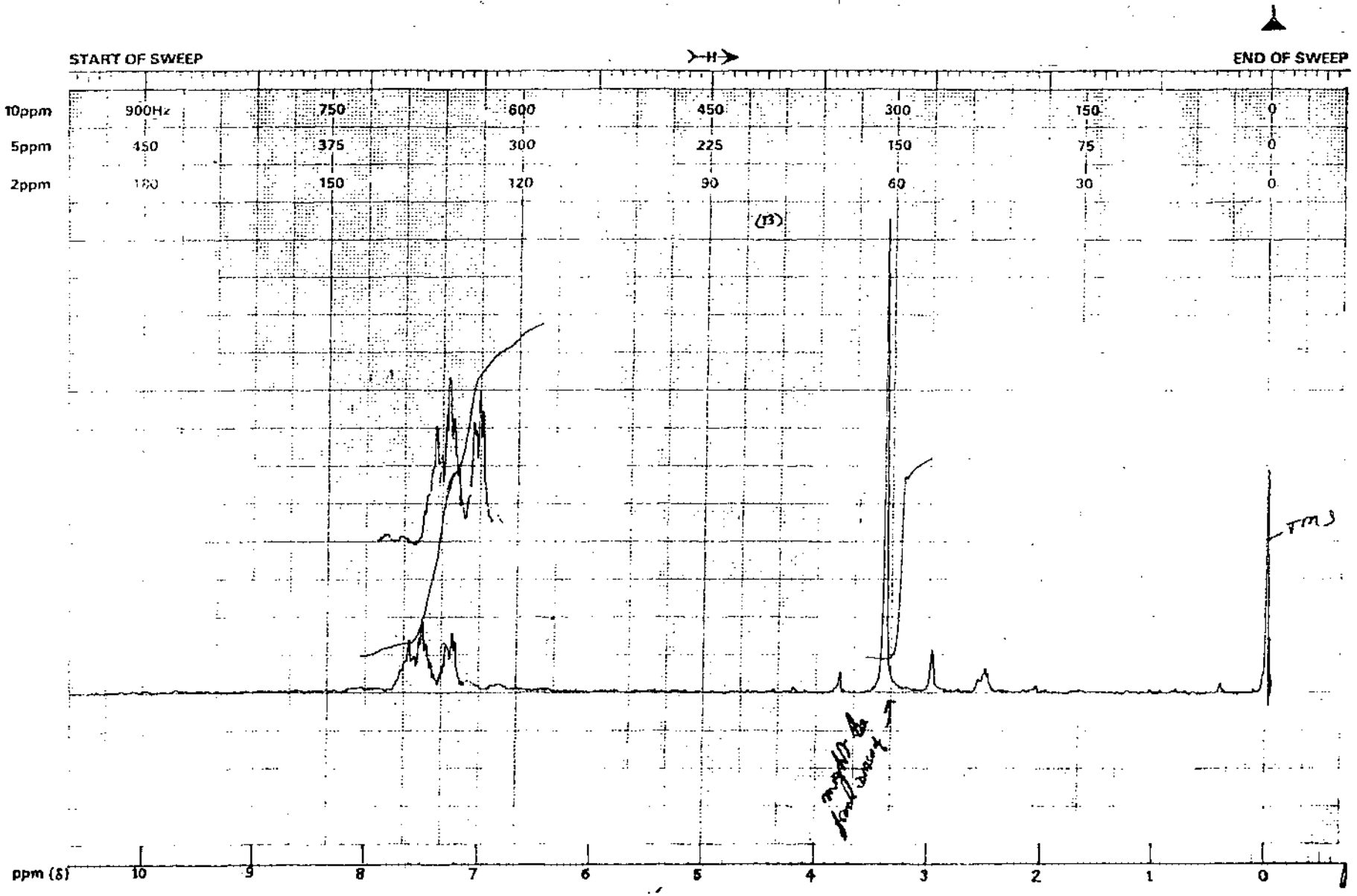
Dibenzyl tin diphenyl glycolate

Carboxyl and hydroxyl protons were found to be absent. The benzylic methylene protons appeared at δ 2.9 (2H) as doublet ($H_{BB'}$, J = 27 Hz) and δ 3.85 (2H) ($H_{AA'}$) as doublets (J = 27 Hz). The benzylic methylene protons splitted (82).

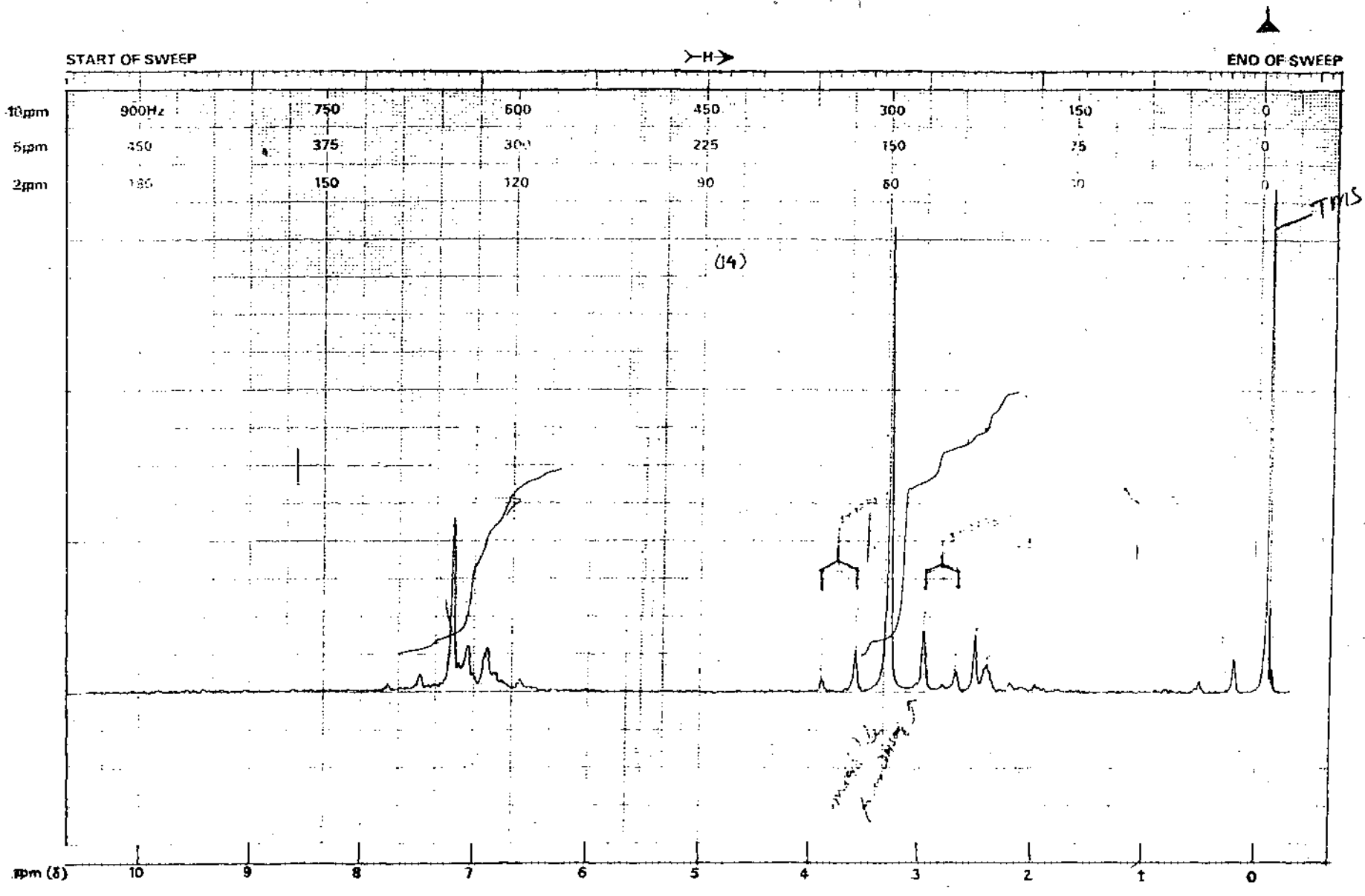




^{1}H NMR spectrum of Dibutyl tin diphenyl glycolate



^{1}H NMR spectrum of Diphenyl tin diphenyl glycolate



^{1}H NMR spectrum of Dibenzyl tin diphenyl **glycolate**

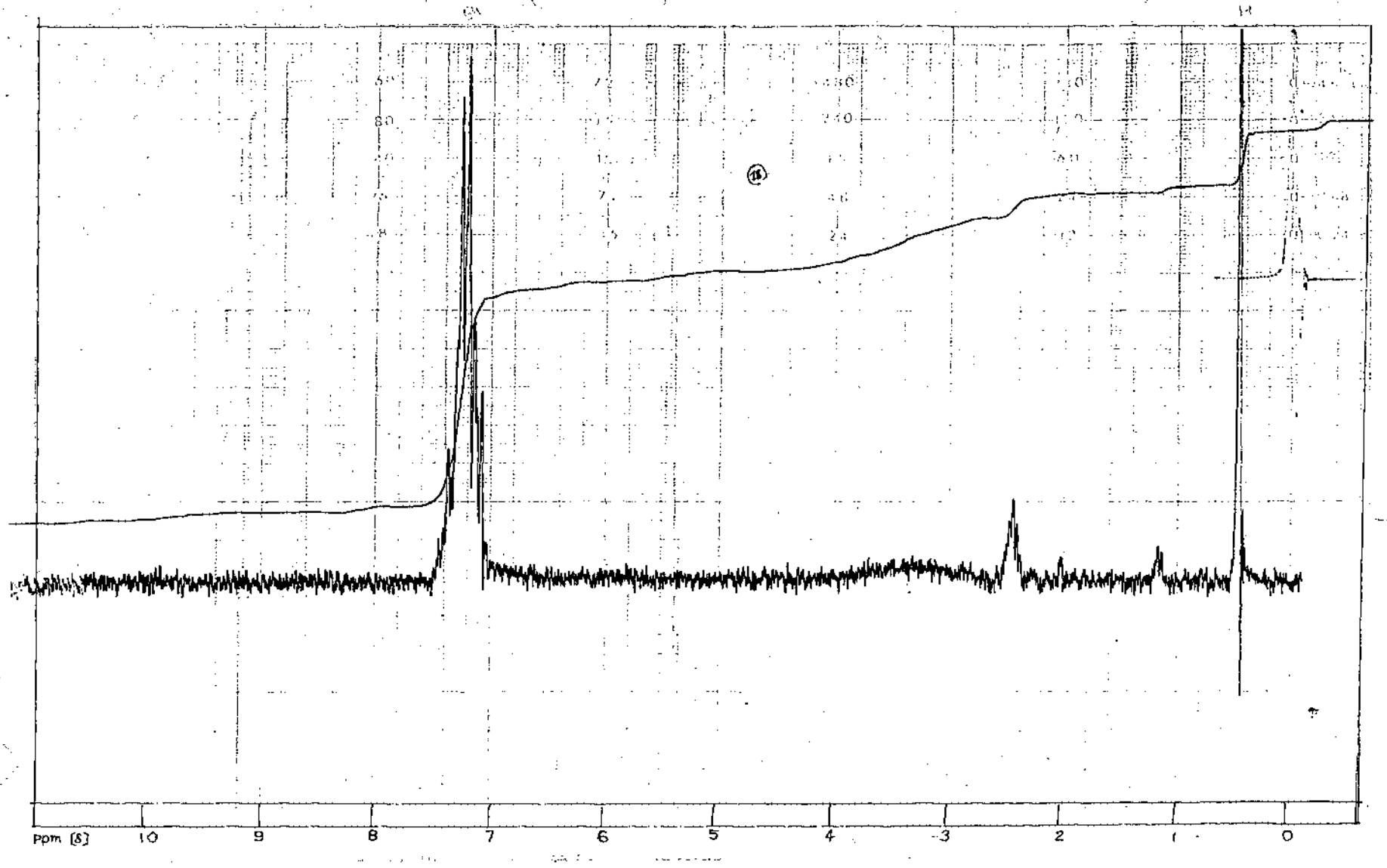
The aromatic protons appeared at δ 6.9-7.4 (ArH = 20H) as complex pattern. Here also it was not possible to assign individual type of aromatic protons.

Dimethyl tin bis (diphenyl glycolate)

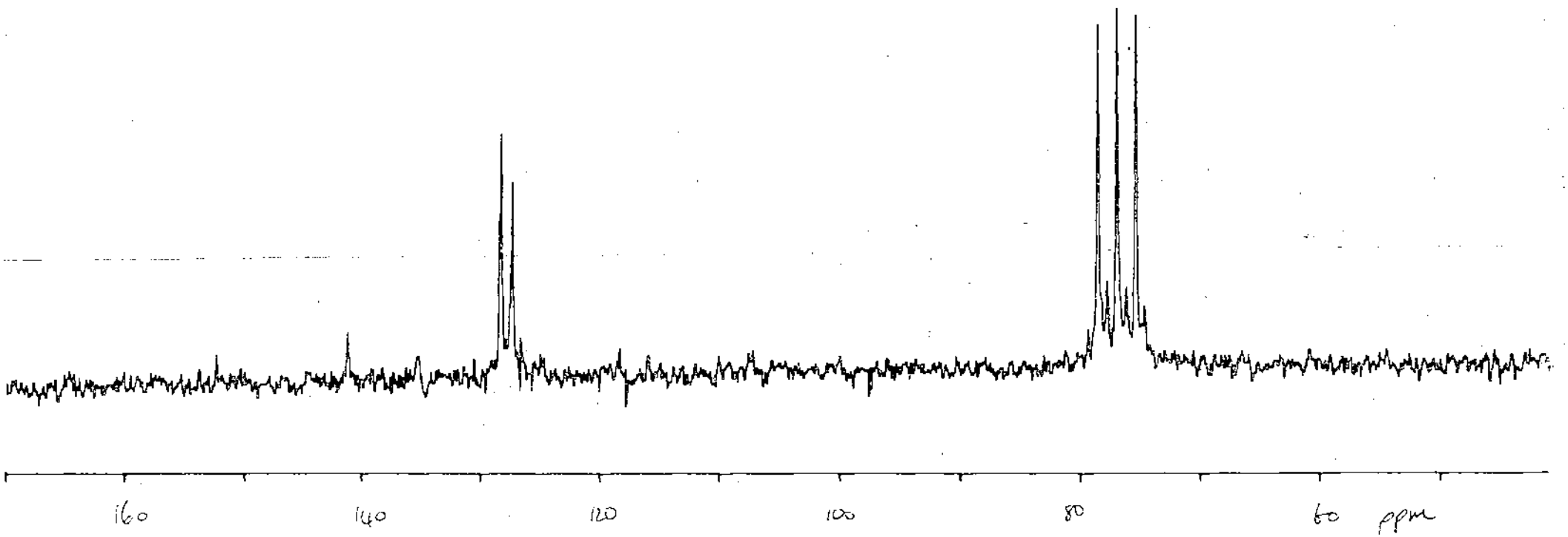
Here also carbonyl and hydroxyl protons were absent. The dimethyl tin protons appeared as singlet at δ 0.42 (methylene protons -6H), suggesting trans disposition of the methyl groups. The aromatic protons appeared as complex pattern in between δ 7.02-7.5 (ArH = 20H). The ratio of aromatic and aliphatic protons in this compound indicate bis ester type compound, unlike the earlier compounds.

^{13}C NMR spectra

The ^{13}C NMR spectra were recorded for only three organotin derivatives. The ^{13}C NMR spectrum for Diphenyl glycolic acid gave

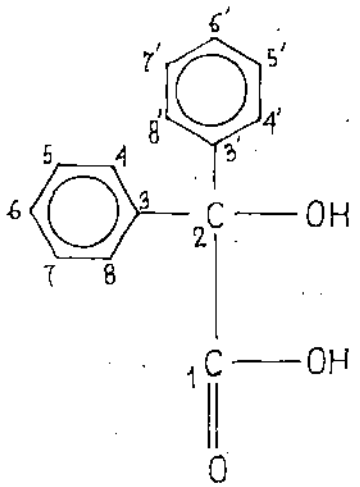


^{1}H NMR spectrum of Dimethyl tin bis (diphenyl glycolate)



^{13}C NMR spectrum of Diphenyl glycolic acid (in $CDCl_3$)

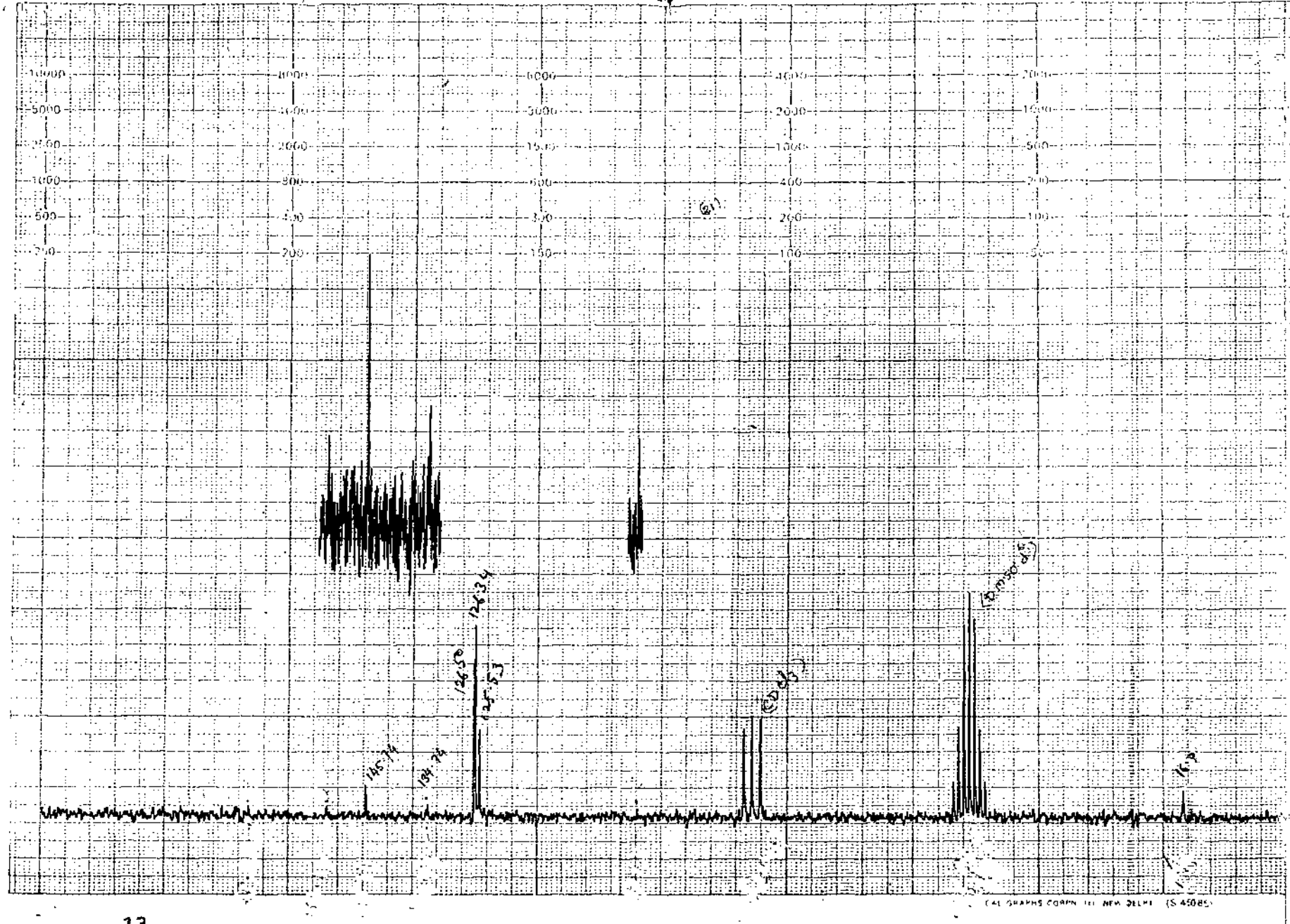
four peaks at δ 127.35 (C_5, $C_{5'}$, C_7 & $C_{7'}$), 127.87 (C_4, $C_{4'}$, C_8 & $C_{8'}$), 128.30 (C_3 & $C_{3'}$) and 128.41 (C_6 & $C_{6'}$) aromatic carbon atoms.



The C_1 carbon atom appeared at δ 152.37, while C_2 carbon atom appeared at δ 141.22.

Dimethyl tin bis (diphenyl glycolate)

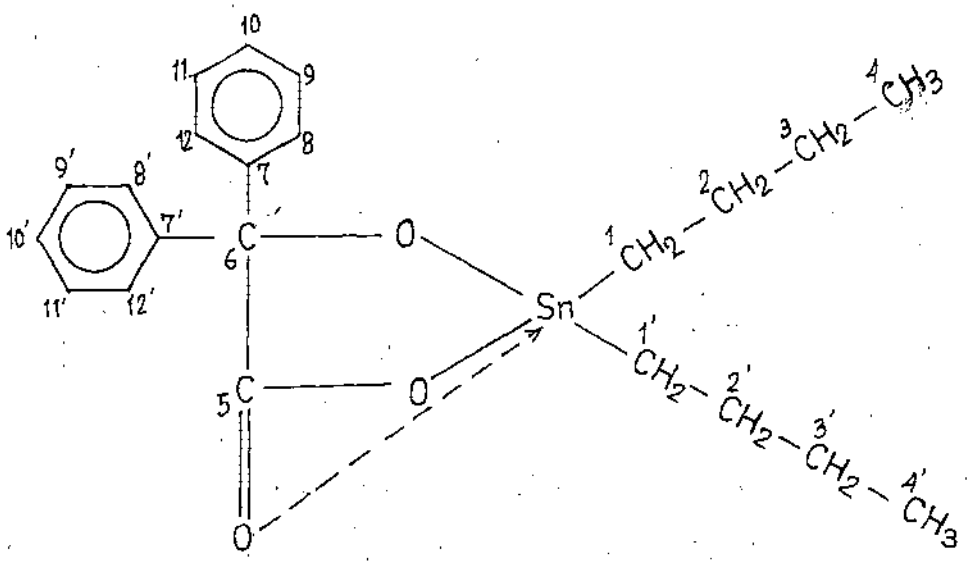
The ^{13}C NMR spectrum gave a number of characteristic peaks. The methyl carbon atoms appeared as a single peak at δ 16.9 while $-\overset{|}{C}-OH$ carbon atom appeared at δ 134.74 and $O=\overset{|}{C}-OH$ carbon atom appeared at δ 145.74. The shielding of $=\overset{|}{C}-OH$ and $O=\overset{|}{C}-OH$ carbon peaks, strongly suggest the formation of an ester type organotin derivative. The aromatic carbon atoms gave only three peaks at δ125.53, 126.34 and 126.58 instead of four peaks exhibited by the free ligand. The fourth peak may be merged on any of these above three peaks.



^{13}C NMR spectrum of Dimethyl tin bis (diphenyl glycolate)

Dibutyltin diphenyl glycolate

The aliphatic peaks appeared in between δ 13.29-26.38 and may be assigned (80) as follows:



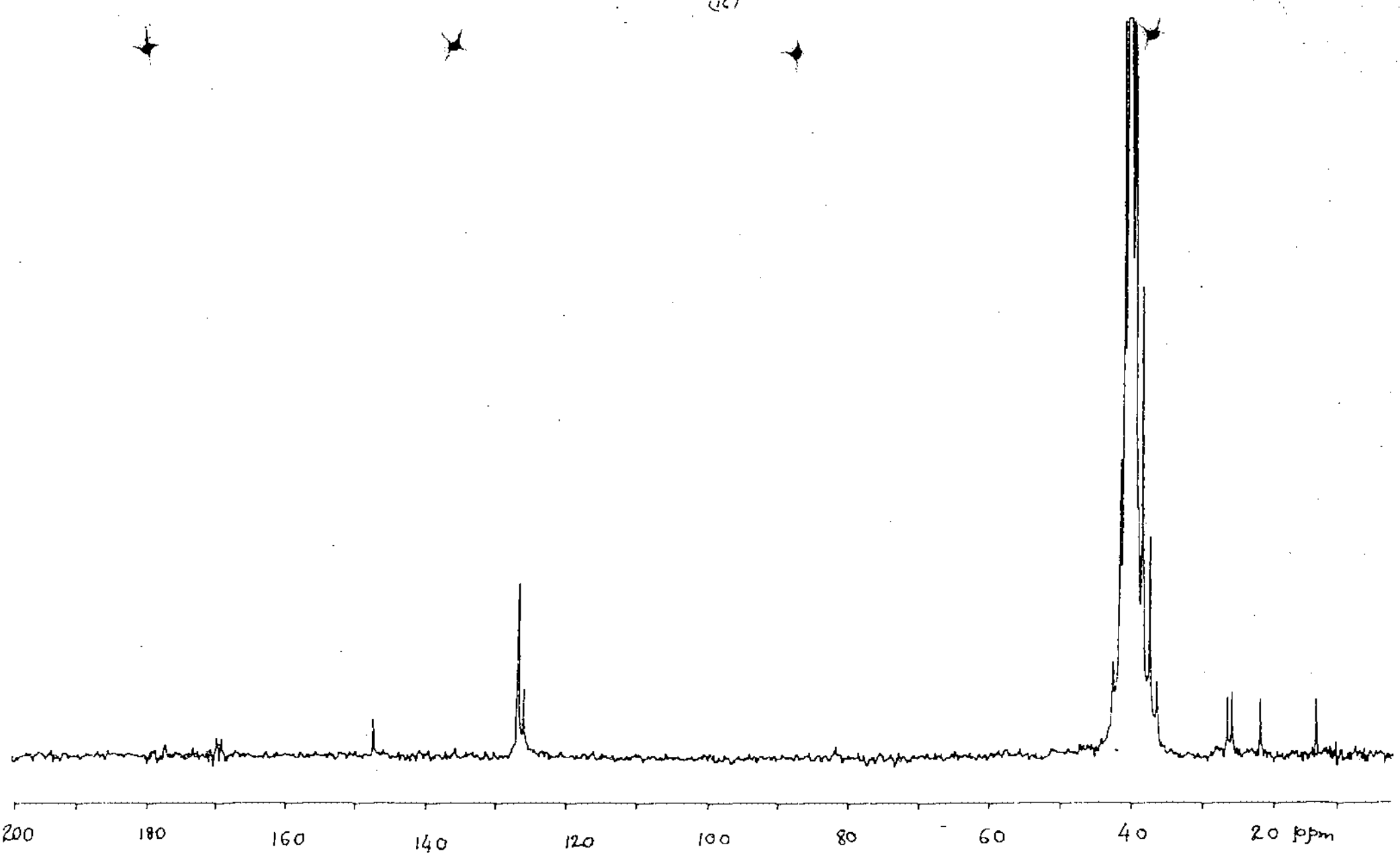
δ 13.29 $C_4, C_{4'}$

δ 21.78 $C_1, C_{1'}$

δ 25.26 $C_3, C_{3'}$

δ 26.38 $C_2, C_{2'}$

The C_5 carbon atom appeared at δ 147.40 while due to poor intensity of the spectrum the C_6 carbon atom peak could not be



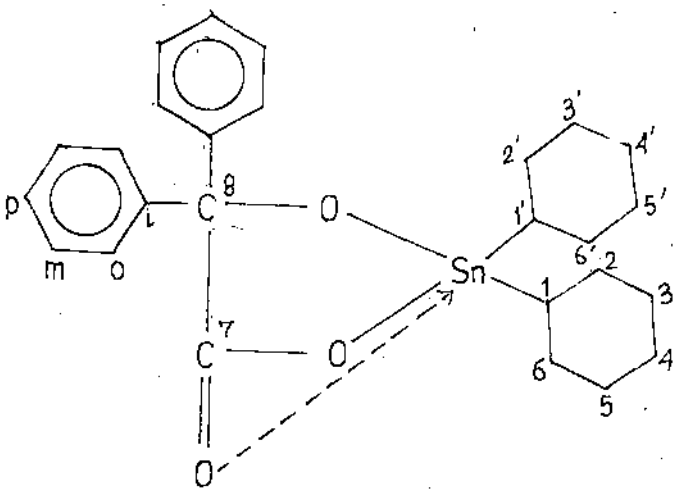
^{13}C NMR spectrum of dibutyl tin diphenyl glycolate (in d^6 DMSO)

unambiguously assigned. Compared to ligand, the C_5 carbon atom peak showed considerable shielding.

The aromatic carbon atoms gave three peaks like the dimethyl tin derivative at δ 126.08, 126.87, 127.05.

Dicyclohexyltin diphenyl glycolate

The ^{13}C NMR spectrum gave four peaks at δ 27.95, 28.58, 29.50 and 30.90 for cyclohexyl ring carbon atoms. For them assignment may be made as follows:

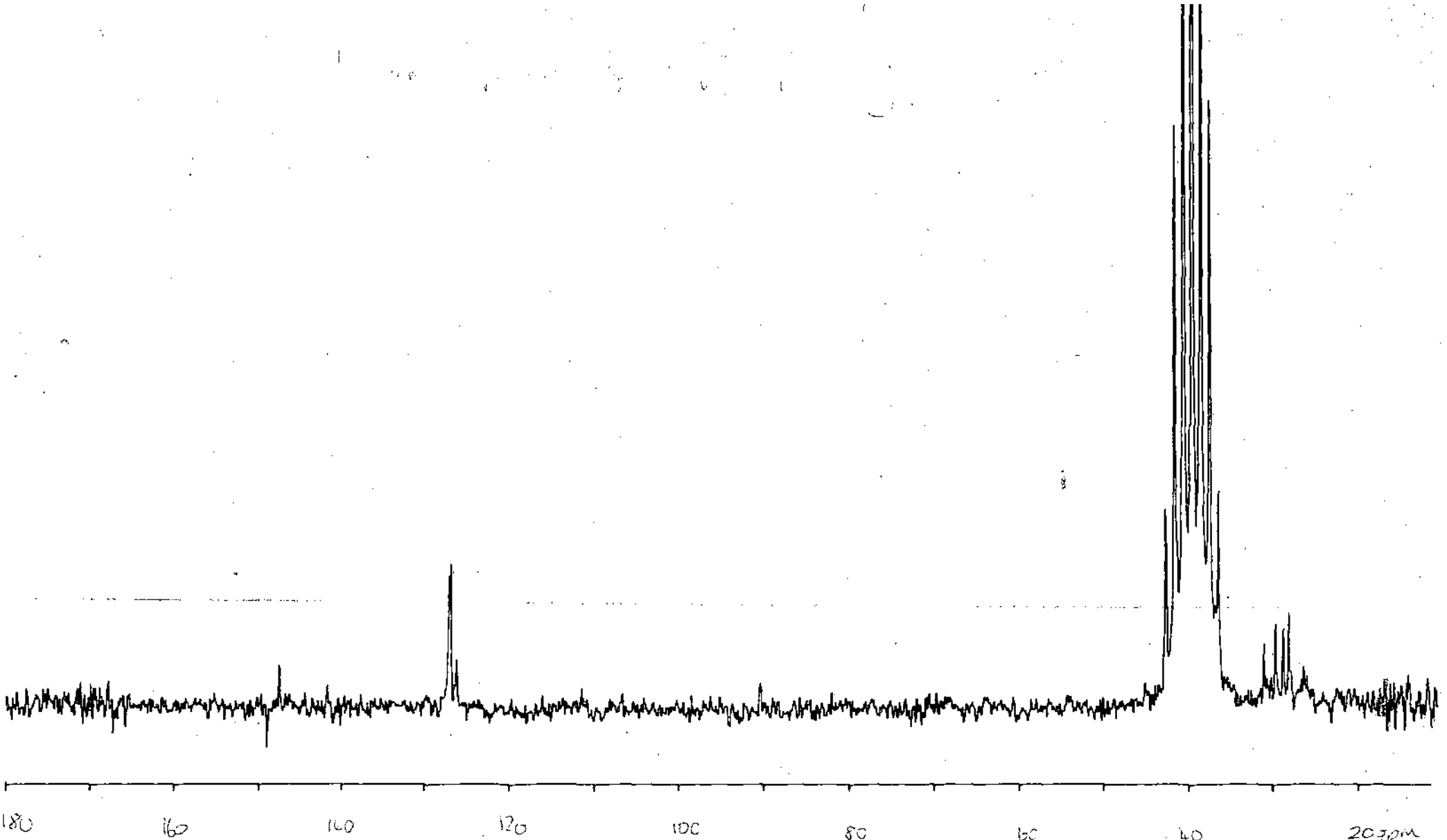


δ 27.95 - C_4, C_4,

δ 28.58 - C_1, C_1,

δ 29.50 - C_3, C_3,, C_5, C_5,

δ 30.90 - C_2, C_2,, C_6, C_6,



^{13}C NMR spectrum of Dicyclohexyl tin diphenyl glycolate (in d^6 DMSO)

The C_8 carbon signal could not be detected due to poor intensity of the spectrum, while C_7 carbon gave a signal at δ 147.52. The spectrum recorded signals for aromatic carbon atoms which may be assigned (84) as follows:

δ 126.17 (m)

δ 126.40 (p)

δ 126.94 (o)

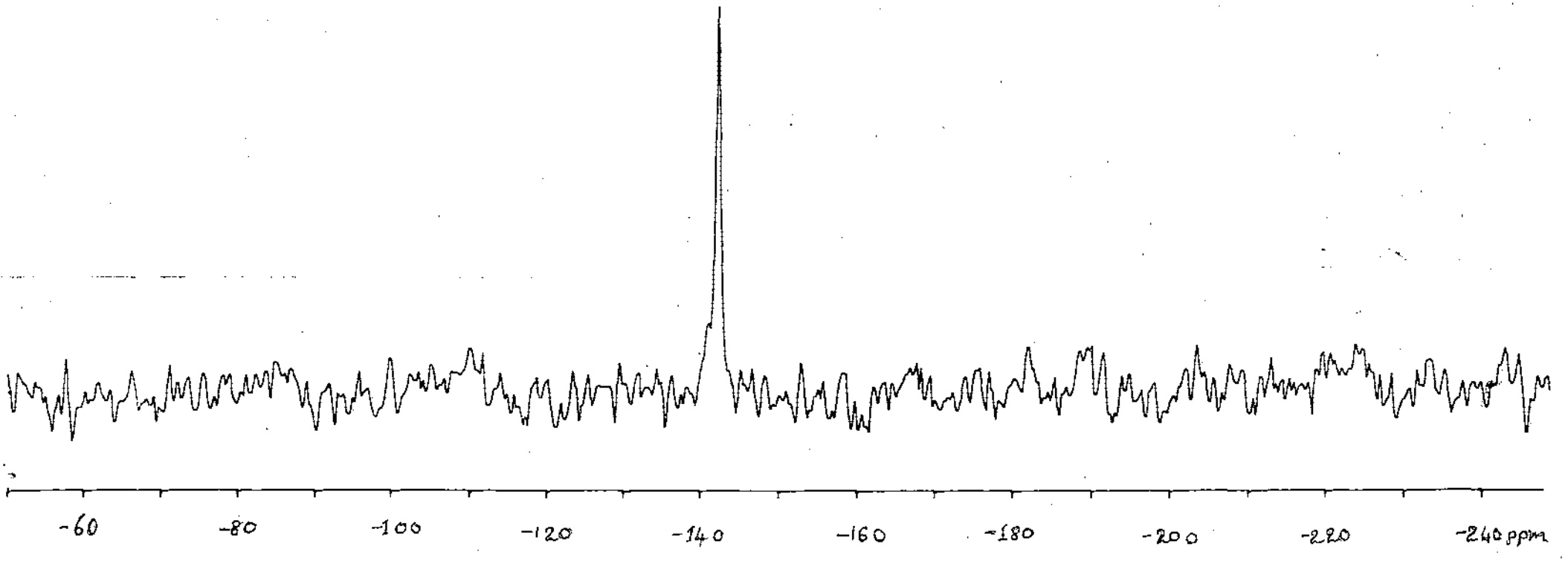
δ 127.10 (i)

^{119}Sn NMR spectra

Due to certain limitations, it was possible to record ^{119}Sn spectra only for three compounds. Even these three spectra along with IR and ^{13}C spectra gave some indications about the nature of some diorganotin diphenyl glycolates.

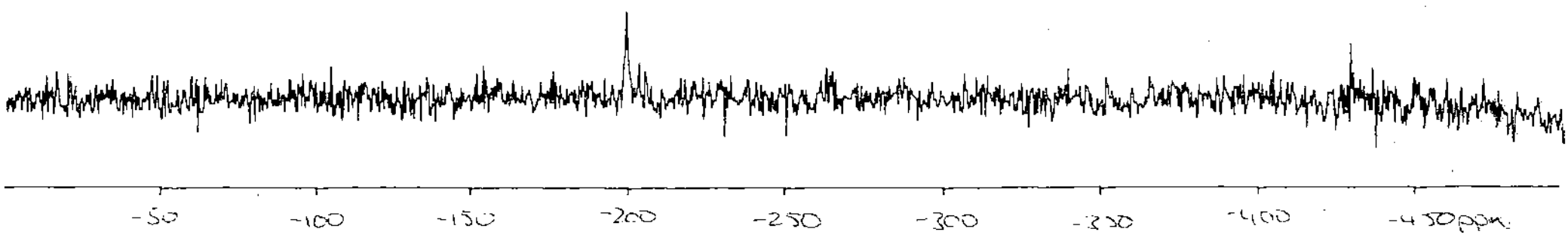
^{119}Sn NMR spectral data

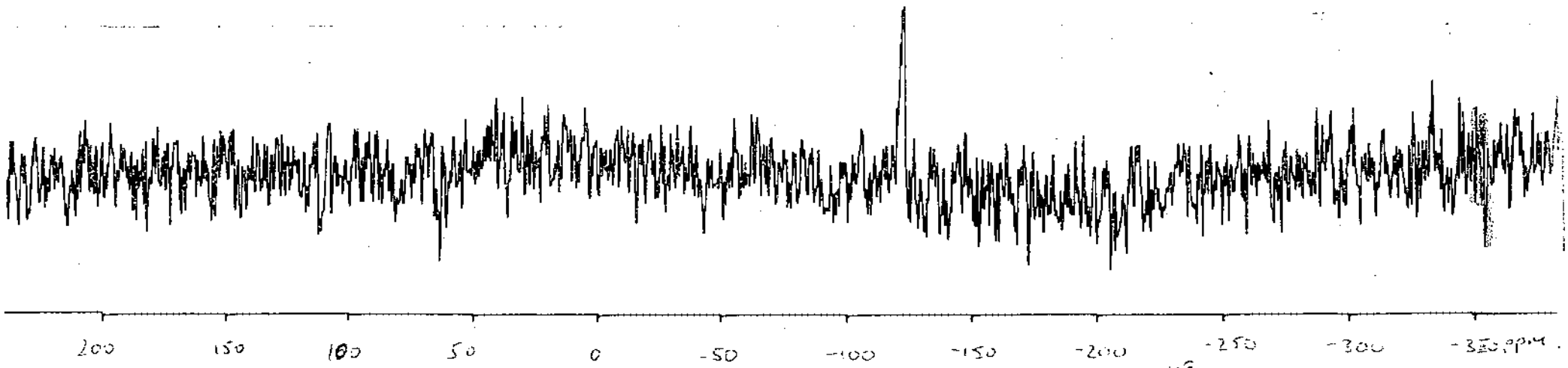
Compound	Chemical shift (δ)
Dibutyl tin diphenyl glycolate	-142.12
Dicyclohexyl tin diphenyl glycolate	-199.37
Dimethyl tin bis (diphenyl glycolate)	-123.02



^{119}Sn NMR spectrum of Dibutyl tin diphenyl glycolate (in DMSO)

^{119}Sn NMR spectrum of Dicyclohexyl tin diphenyl glycolate (in DMSO)

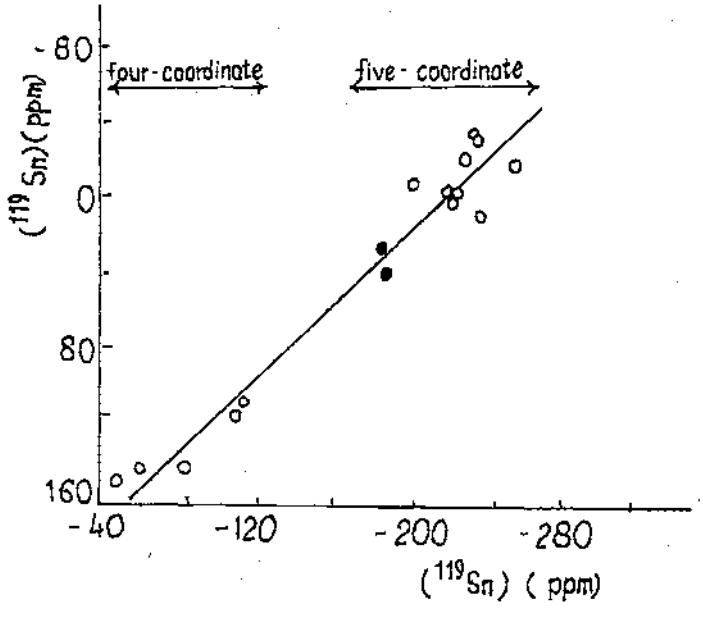




^{119}Sn NMRspectrum of Dimethyl tin bis (diphenyl glycolate)
(in d^6 DMSO)

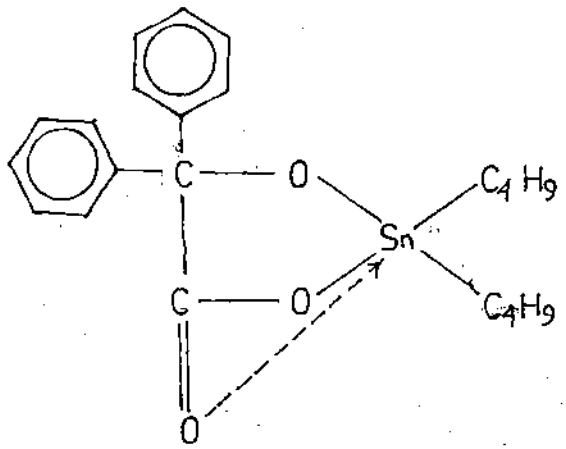
The dibutyl tin diphenyl glycolate had ^{119}Sn signal at δ -142.12 indicating penta coordinating nature.

Nadvornik, Handlir and Lycka (80) reported that the chemical shift δ 99.4 to 152.8 ppm are typical of a quasi tetrahedral arrangement of a simple trialkyltin compound with a tetra coordinate tin atom. On changing from tetra coordinate tin to penta coordinate tin, an upfield shift of δ (^{119}Sn) by 100-190 ppm usually takes place. The expected range δ (^{119}Sn)Bu ppm may be given by following figure



Correlation of ^{119}Sn chemical shifts in tri n-butyl tin (IV) compounds with ^{119}Sn chemical shifts in triphenyltin (IV) analogues.

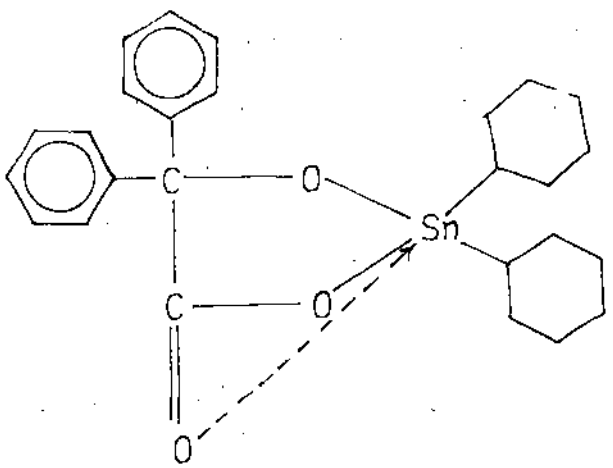
On comparing, the Dibutyl tin diphenyl glycolate has a value $\delta^{119}Sn$ peak value of -142.12 ppm, which may also indicate hexa coordinating tin atom. But it should be borne in mind, the spectra was recorded in coordinating solvent d^6 DMSO, hence it is quite expected that Dibutyl tin diphenyl glycolate can register more upfield shift for ^{119}Sn peak, than expected for a penta coordinated tin atom. The compound was sparingly soluble in $CDCl_3$, hence the spectrum was recorded in d^6 DMSO. On the basis of molecular formula and molecular weight (Rast method) we may suggest the following composition for Dibutyl tin diphenyl glycolate.



The CO_2 absorption frequency in IR spectra showed an unusually strong shift from 1715 cm^{-1} to ~ 1570 cm^{-1} indicating strong coordination from >C = O group of the carboxylate ion, which supports $\delta(^{119}Sn)$ value.

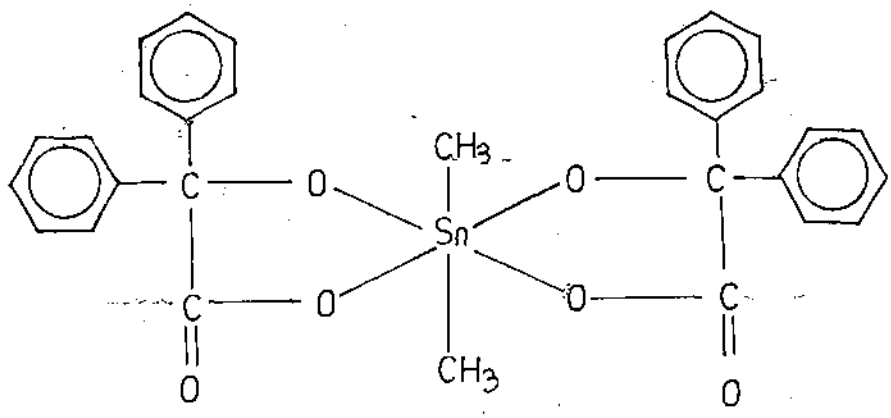
The ^{119}Sn spectra of dicyclohexyl tin diphenyl glycolate was also recorded in d^6 DMSO solvent. The ^{119}Sn peak appeared at δ -199.37 indicating a similar structure like the above dibutyl

derivatives. The IR shift is also similar here for CO_2 group. Hence we may tentatively suggest the structure of Dicyclohexyl tin diphenyl glycolate as follows



Though detailed data are lacking for other diorganotin diphenyl glycolates. These may have similar structures like dibutyl or dicyclohexyl tin derivatives.

The Dimethyl tin derivative is somewhat different from the other diorganotin derivatives, having two diphenyl glycolic acid residues. Elemental analyses, molecular weight and ^{1}H NMR spectra strongly support the formation of Dimethyl tin bis (diphenyl glycolate). The ^{119}Sn peak for this compound appeared at δ -123.02. This may be due to hexa coordinated tin atom of the following type:



In this compound, coordination from the carbonyl oxygen of acid groups may be absent, otherwise it would render the tin atom either hepta or octa coordinating. In that case, we would expect much higher upfield shift of ^{119}Sn signal. Moreover, the CO_2 shift is much smaller, compared to other diorganotin derivatives. It shifts from 1715 cm^{-1} to 1650 cm^{-1} only compared to $\sim$1570 cm^{-1} as in other diorganotin derivatives.

In absence of X-ray data (for which we had no access) all these structures may be considered somewhat tentative in nature.

R E F E R E N C E S

1. R.C. Poller, The Chemistry of Organotin Compounds, Lagos, London, Chapter 10, 1970.

2. R. Okawara and M. Wada, 'Organotin Compounds', Ed. A.K. Sawyer, Marcel Dekkar, New York, Vol. II, 253, 1971.

3. R. Okawara and M. Wada, Adv. Organomet. Chem. 5, 137, 1967.

4. W.P. Neumann, The Organic Chemistry of Tin, Willey, Cahp. 17.

5. T.F. Boller and R.S. Drago, J. Am. Chem. Soc., 87, 5015, 1965.

6. A. Cassol, L. Magon and R. Barbieri, J. Chromatog, 19, 57, 1965.

7. E.L. Muettertin and C.M. Wright, J. Am. Chem. Soc., 86, 5132, 1964; 87, 4706, 1965.

8. R.G. Peanson, J. Am. Chem. Soc. 85, 3553, 1963.

9. R.C. Poller, J. Organomet. Chem., 3, 321, 1965.

10. R.C. Poller and D.L.B. Toley, J. Chem. Soc. (A), 2035, 1967.

11. M. Shindo, Y. Matsumura and R. Okawara, J. Organomet. Chem. 11, 299, 1968.

12. G. Tagliavini and P. Zanella, Anal. Chim. Acta., 40, 33, 1968.

13. R.C. Poller and D.L.B. Toley, J. Chem. Soc. (A), 2035, 1967.

14. J. Otera, Y. Kawasaki and T. Tanaka, Inorg. Chim. Acta., 1, 294, 1967.

15. R.D. Chambers and T. Chivers, Organomet. Chem. Rev., 1, 279, 1966.

16. J. Efer, D. Quaas and W. Spichale, Z. Chem., 5, 390, 1965.

17. N.A. Matwiyoff and R.S. Drago, Inorg. Chem., 3, 337 (1964).

18. W. Gerrard, E.F. Mooney and G.R. Rees, J. Chem. Soc., 740, 1964.

19. I.P. Gol'dshtein, E.N. Gur'yanova and K.A. Kocheshkov, Dokl. Akad. Nauk, S.S.S.R. 138, 1099, 1961.

20. D. Helberg, Pent. Lebeusm. Rundsch, 63, 69, 1967.

21. A.S. Mufti and R.C. Poller, J. Chem. Soc. , 5055, 1965.

22. W.H. Nelson, W.R. Randall and D.F. Martin, Inorg. Synth., 9, 52, 1967.

23. D.N. Sen and P. Umapathy, Indian J. Chem., 5, 209, 1967.

24. A. Henderson and A.K. Holliday, J. Organomet. Chem., 4, 377, 1965.

25. R. Okawara and M. Wada, Advances in Organometallic Chemistry, Vol. 5, Academic, New York, 137-167, 1967.

26. M.J. Jansen, J.G.A. Luijten and G.J.M. Vander Kerk, Rec. Trav. Chim., 82, 90, 1963.

27. R.A. Cummins and P. Dunn, Austrelian J. Chem., 17, 185, 1964.

28. A. Roy and A.K. Ghosh, Inorg. Chim. Acta., 29, L275-L277, 1978.

29. G.A. Razuvaev, N.S. Vyazankin and O.A. Shchepetkava, Tetrahedron, 18, 667, 1962.

30. R. Okawara and E.G. Rochow, J. Am. Chem. Soc., 82, 3285, 1960.

31. A.K. Sawyer and H.G. Kuivila, J. Am. Chem. Soc., 82, 5958, 1960.

32. A.K. Sawyer and H.G. Kuivila, J. Org. Chem., 27, 837, 1962.

33. R. Okawara and E.G. Rochow, J. Am. Chem. Soc., 82, 3285, 1960.

34. G.A. Razuvaev, O.A. Shchepetkova and N.S. Vyazankin, Zhur. Obshchei. Khim., 32, 2152, 1962.

35. Y. Maeda and R. Okawara, J. Organomet. Chem., 10, 247, 1967.

36. M. Wada, M. Shindo and R. Okawara, J. Organomet. Chem., 1, 95, 1963.

37. A.G. Davies and P.G. Harrison, J. Chem. Soc. C, 298, 1967.

38. A.K. Sawyer and H.G. Kuivila, Chem. Ind., 260, 1961.

39. D.L. Alleston and A.G. Davies, J. Chem. Soc., 2050, 1962.

40. A.K. Sawyer and H.G. Kuivila, J. Org. Chem., 27, 610, 1962.

41. A.S. Mufti and R.C. Poller, J. Chem. Soc. C, 1362, 1967.

42. N.N. Zemlyanskii, I.P. Gol'dstein, E.N. Gur'yanova, O.P. Syutkina, E.M. Panov, N.A. Slovokhotova and K.A. Kocheshkov, Izvest. Akad. Nauk S.S.S.R., Ser Khim., 728, 1967.

43. D.L. Alleston, A.G. Davies, M. Hancock and R.F.M. White, J. Chem. Soc. 5469, 1963.

44. T. Harada, Sci Papers, Inst. Phys. Chem. Research, 57, 25, 1963.

45. K.A. Kocheshkov, E.M. Panov and N.N. Zemlyanskii, Izvest. Akad. Nauk S.S.S.R. Otdel. Khim. Nauk, 2255, 1961.

46. M. Chara, R. Okawara and Y. Nakamura, Bull. Chem. Soc. Japan, 38, 1379, 1965.

47. N.S. Vyazankin, G.A. Razuvaev, O.S. D'yachkovskaya and O.A. Shchepetkova, Dokl. Akad. Nauk, S.S.S.R. 143, 1348, 1962.

48. E. Wiberg and H. Behringer, Z. Anorg. Allgem. Chem., 329, 290, 1964.

49. L.E. Khoo and F.E. Smith, Inorg. Chim. Acta., 53, L83, 1981.

50. R.G. Swisher, J.F. Vollano, V. Chandrasekhar, R.O. Day and R.T. Holmes, Inorg. Chem. 23, 3147-3152, 1984.

51. J.F. Vollano, R.O. Day, D.N. Roy, V. Chandrasekhar and R.R. Holmes, Inorg. Chem., 23, 3153-3160, 1984.

52. J.P. Freeman, J. Am. Chem. Soc., 80, 5994, 1958.

53. I.R. Beattie and T. Gilson, J. Chem. Soc., 2585, 1961.

54. M.J. Jansen, J.G.A. Luijten and G.J.M Van der Kerk, Rec. Tran. Chim., 82, 90, 1963.

55. R. Okawara and M. Chara, Bull. Chem. Soc., Japan, 36, 623, 1963.

56. R. Okawara and M. Ohara, J. Organomet. Chem., 1, 360, 1964.

57. B.F.E. Ford, B.V. Liengme and J.R. Sams, J. Organomet. Chem., 19, 53, 1969.

58. B.Y.K. Ho and J.J. Zuckerman, J. Organomet. Chem., 49, 1, 1973.

59. G. Roge, F. Huber, H. Prent, A. Silvesti and R. Barbieri, J. Chem. Soc., 595, 1983.

60. R.E. Hester, J. Organomet. Chem., 23, 123, 1970.

61. V. Peruzzo, G. Plazzogna and G. Tigliavini, J. Organomet. Chem., 18, 89, 1969.

62. P.B. Simons and W.A.G. Graham, J. Organomet. Chem., 8, 479, 1967.

63. E.V. Van Der Berghe and G.P. Van Der Kelem, Inorg. Chim. Acta., 2, 89, 1968.

64. M.A. Meshbi, Spectrochimica Acta, 32A, 1327, 1976.

65. J. Holeck, K. Handlir, M. Nadvornik and A. Lycka, J. Organomet. Chem., 258, 147, 1983.

66. W.T. Reichle, Inorg. Chem., 5, 87, 1966.

67. H. Zinnmer, O.A. Homberg and M. Jayawant, J. Org. Chem., 31, 3857, 1966.

68. N.W. Alleck and R.E. Timms, J. Chem. Soc. (A), 1876, 1968.

69. R. Barbieri, L. Pellerito, N. Bertazzi and G.C. Stocco, Inorg. Chim. Acta, 11, 173, 1974.

70. J.J. Bruke and P.C. Lauterbur, J. Chem. Soc., 83, 326, 1961.

71. B.F.E. Ford and J.R. Sams, J. Organomet. Chem., 31, 47, 1971.

72. P.J. Smith, R.O. Day, V. Chandrasekhar, J.M. Holmes and R.R. Holmes, Inorg. Chem., 25, 2495, 2499, 1986.

73. B. Majee, A. Roy and S. Banerjee, Ind. J. Chem., 16A, 6, 542, 1978.

74. B.Y.K. Ho, K.C. Molley, F. Reidinger, J.J. Zuckerman and J.A. Zubieta, J. Organomet. Chem., 187, 213, 1980.

75. Y. Maeda, C.R. Dilland and R. Okawara, Inorg. Nucl. Chem. Letters, 2, 197, 1966.

76. W.D. Honnick and J.J. Zuckerman, J. Organomet. Chem., 178, 133-155, 1979.

77. U. Schubert, J. Organomet. Chem., 10, 247, 1967.

78. H.H. Anderson, Inorg. Chem., 3, 912, 1964.

79. H. Sato and R. Okawara, Intern. Symp. Mol. Struct. Spectr. (Amsterdam), 4, 67, 1965.

80. M. Nadvornik, J. Holeck, K. Handlir and A. Lycka, J. Organomet. Chem., 275, 43-51, 1984.

81. R.C. Agarwal and P. Singh, Inorg. Nucl. Chem., 27, 2593, 1965.

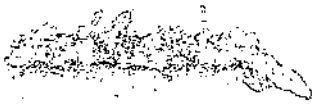
82. R.R. Holmes, R.O. Day, V. Chandrasekhar, J.F. Vollano and J.M. Holmes, Inorg. Chem., 25, 2490-2494, 1986.

83. G. Van Koten and J.G. Noltes, Organotin Compounds : New Chemistry and Applications, Ed. J.J. Zuckerman, New York, 1976, p. 277, 278.

84. J. Holecek, K. Handlir, M. Nadvornik and A. Lycka, J. Organomet. Chem., 258, 147-153, 1983.

P A R T III

I N T R O D U C T I O N



In the earlier parts, the preparation and characterisation of some new organotin compounds have been reported. Since, triorganotin compounds exhibit a wide range of biological properties, some attempts will be described in the subsequent pages of the biological properties of some selected compounds, described in preceding pages. A brief review of some important biological properties (antifungal and acaricidal) may be given here.

Search for new pesticides is essential as even successful pesticides can loose their effectiveness due to growth of resistence of pests towards those pesticides. Moreover, consideration of environmental pollution may lead to discontinuance of some successful pesticides. In the search of new pesticides, organometallic compounds are increasingly gaining importance. Organomercurials have played an important role until recently as successful biocidal agents. But due to high mammalian toxicities and possibilities of biomethylation of mercury compounds, the use of organomercury compounds are now a days severely restricted and may ultimately be totally discontinued. Organotin compounds may replace organomercury compounds in some of their biocidal applications.

The principal advantages of the organotin agrochemicals which mainly possess prophylactic action (1) are their relatively low phytotoxicity, their generally low toxicity to non-target organisms and the lack of resistance by croppests to these chemicals.

Furthermore, triorganotin compounds undergo degradation in the environment eventually, to form harmless inorganic tin residues.

A. Antifungal Activity

As pointed out earlier, the first investigation in the field of antifungal activity of organotin compounds were carried out by van der Kerk and Luijten in 1954 (2). It was found by them that only triorganotin (R_3SnX) derivatives are the powerful fungicides. A number of tetra-, di-, and monosubstituted organotin compounds were tested and all showed very little or practically no activity, compared to triorganotin derivatives.

Zedler and Beiter (3), Hartel (4), Kubo (5) and Kaars Sijpestijn (6) have also studied the antifungal activity of triorganotin derivatives against a number of plant pathogenic fungi.

Although many phytopathogenic fungi prove to be highly sensitive to organotin compounds in vitro, some parasitic fungi e.g. Phytophthora in festans on potato, Corcospora beticola on sugar beet and Septoria apii on celeriac etc are at present successfully controlled by organotins under field conditions.

Experiments with a series of organotin compounds on obligate parasitic fungi have been carried out by Hartel (4) and by Tempel (7). The former found that Peronospora on grape is more effectively suppressed by tributyl tin than by trimethyl tin or triethyl tin compounds. Against powdery mildew on cucumber the triethyl tin

derivative appeared to be optimally active whereas the tributyl and triphenyl tin derivatives were the most effective compounds against powdery-mildew on barley and the tripentyl and trihexyl tin derivatives against apple mildew.

In the symmetrical trialkyltin series the propyl and butyl compounds generally are the most active derivatives, the presence of these particular groups are not the necessary condition for high activity. This becomes manifest when unsymmetrical trialkyl tin acetates were tested (8). From these investigations of van der Kerk and Luijten, it was concluded that among the trialkyl tin acetates, maximum activity is associated with a total number of 9 to 12 carbon atoms in the alkyl group regardless of the nature of the individual group.

Regarding the triaryl tin compounds, tri-m-tolyltin acetate and tri-p-tolyltin acetate appeared to equal triphenyltin acetate in activity, whereas tribenzyl and tris (2-phenyl-ethyl)tin acetate were also considerably active (9).

Interesting independent work by Hartel (10) with trialkyl and triaryl tin compounds showed that in the laboratory, trialkyl and particularly tributyl tins are better fungicides than triaryl tin compounds but that the reverse is true in the field. This has been ascribed to the lower stability and the higher volatility of the former. Moreover, triaryl tin compounds are less phytotoxic than trialkyl tin compounds.

In the early 1960's the first organotin compound, triphenyltin acetate was introduced under the trade name, 'Brestan' commercially by Farbwerke Hoechst A.G. and shortly later Philips Duphar N.V. introduced triphenyl tin hydroxide under the trade name 'Du-Ter' (11). In 'Brestan Super', triphenyl tin acetate is combined with manganese ethylene bis dithiocarbamate (maneb). A similar preparation of Fisons Pest Control, called 'Fennite', combines triphenyl tin hydroxide with maneb . A number of commercial preparations based on these active ingradients are at present marketed under different trade name. The organotin fungicides have almost completely ousted the formerly dominating inorganic copper fungicides for the control of certain diseases of potato, sugar beet and celeriac. Later on, it was also found that a number of important tropical plant diseases viz. those in coffee, rice, groundnut, banana and onion can be controlled successfully (12) by organotins.

The problem of toxic residues from sprays with organotin compounds has been thoroughly investigated. An important feature is the relatively short half life of the compounds on plant leaves in the field. In potato tubers, less than 0.1 mg of tin per Kg was found after the foliage had been repeatedly sprayed with triphenyl tin acetate, after ... days

In Kenya, for controlling the leaf rust disease of coffee, copper based fungicides are used extensively at present. But many farmers are concerned that a build up of copper may occur in the soil after many years of repeated spraying with copper fungicides,

resulting the growth inhibition of cultivated plants. Hence, alternatively, 'Du-Ter Extra' [47.5% W.P. (Wettable powder) active ingredient triphenyl tin hydroxide] has been recommended by the Kenyan Coffee Research Foundation for the treatment of leaf rust and also as an anti-feedant for the giant looper caterpillars that attack the foliage of Coffee plants (13).

Recently Smith et al (14) reported organotin pyridine-2-carboxylates and substituted triazine derivatives (100 ppm) can control coffee leaf rust and coffee bacterial blight disease in vitro.

From the available literature it seems that much work has not been done for controlling the plant pathogenic fungi by using organotin compounds. Srivastava (15) reported that diphenyltin dichloride is the most active fungi toxic agent against Collototrichum falcatum , among diaryltin dichlorides and their activities on complexation, formation with 2,2'-bipyridyl and 1, 10-phenanthroline are slightly increased. Mehrotra (16,17) reported the fungicidal and bactericidal properties of some new organotin compounds. Ram Kishun et al (18) tried to control the bacterial leaf spot of sunnhemp by using the organotin preparation 'Brestan-60' and 'Du-Ter', and found that the compounds failed to inhibit the growth of the causal organism Xanthomonas Patelii in vitro. Mohanty and Mohapatra (19) found the high effectiveness of 'Brestanol' (triphenyl tin chloride) for controlling the blast disease of fingermillet. 'Brestan-60' with high effectiveness for controlling the tikka disease of ground nut and early blight of potato have

been reported by Addy (20). In the present investigation, some organotin compounds were used for determining their antifungal activity against some fungal species *in vitro*.

B. Miticidal Activity

Mites like insects are another important and significant type of pest of crops and plantation, causing serious losses both in terms of quality and quantity of product. The insect pests have received sufficient attention while mites have long remained rather neglected probably due to their microscopic size and obscure nature, even though they have the potentiality of causing extensive damages in agriculture. Majority of mites feed on plants causing various types of direct damages like loss of chlorophyll, appearance of stipplings of bronzing of foliage, stunting of growth producing plant deformities and reduction of yield. Many of these are known as vector of plant viral diseases causing heavy loss to growers.

The plant mites have drawn attention to the workers since the time of Homer who first referred to them as early as 850 B.C. Linnaeus in 1758 listed nearly thirty species in his book "Systema Naturae". The importance was further realised in 19th and 20th centuries through the outstanding works of Kramer Megnin Canestrine, Berlese, Oudemans, Evans (1957), Evans et al (1961), Krantz (1970), Hughes (1976), Gupta (1985). Jeppson et al (1975) brought out a comprehensive book on mites injurious to economic plants (25).

Mites have a high reproductive potential, may have several generation during a season, regarded as genetically plastic organism and new races are formed continually, it undergoes continuous chemical selection. It was found at after the repeated use of a pesticide group resistance occurs quite rapidly. When resistance develops to currently used acaricides, new compounds presumably with different modes of action are required which will last for sometime to protect crops from mite nuisances.

The principle of mite control and the different chemicals used for this purpose have been discussed elaborately by Jeppson (1965) (26).

Sulphur vapour had been used as an acaricide for quite sometime successfully. However, under certain conditions it shows phytotoxicity to the host plant, same in the case with petroleum oil and dinitrophenol. The use of synthetic organic pesticide started during 1940's. The first to be used was "Neotran". Later several others, as 'Ovex', 'Aramite', 'Deneton', 'Chlorobenzilate', 'Dicofol', 'Fenson', 'Dioxathion ', 'Tetradifon', 'Carbophenothion', 'Ethion', 'Binapacryl', 'Movestan', 'Galecron', etc appeared.

The principles involved in the chemical control of the mites are basically the same as applicable in case of insects. Use of improved agricultural practices application of DDT and reduction of predator population due to random use of broad spectrum pesticides are some of the reasons which necessitated to the adaptation of more improved chemical control of the mites.

Acaricides are some what specific in their action. A certain pesticide may be effective for a certain group of mites but may be quite ineffective against a related group. The acaricides not only kill by direct contact and penetration through its integument but also as stomach poison and as fumigant. Therefore, before a pesticide is spread some factors such as its mode of action, its translocation property if any, its residual property, the plant on which it is to be sprayed, the stage of the mite to be sprayed, climatic condition prevailing before and after spraying, population migration in relation to rainfestation etc. should be considered to assess the efficacy of the acaricide.

At present there has been much criticism of the use of some groups of acaricides because of adverse ecological effects. The organo chlorines have been found to be most hazardous and several countries have either banned or restricted their uses. The use of less persistent organophosphorous compounds is also under hard scrutiny. In this connection the search for an alternate class of acaricides with different mode of action, specific and less harmful to the environment is being carried out in different countries for a long time. In the year 1968 a major break through in the field of agriculture was obtained with the development of a completely new type of miticide - 'Plictran'. The product based on trycyclohexyltin hydroxide was introduced into the U.S. market as a result of the joint research effort by Dow and M & T Chemicals (27,28).

As it has been discussed earlier organotin compounds were already known for their biocidal uses and the commercial success of 'Plictran' encouraged other research workers in this area. Species specificity of organotin derivatives suggests that when R = C_6H_{11} (cyclo) or $PhMe_2CH_2$ of a R_3SnX compound, the compound would be a powerful selective miticide. This led to the introduction of the few other organotin miticides. These are 1-tricyclohexyl stannyl 1,2,4-triazole ('Peropal') (29) and bis (2-methyl 2-phenyl propyl tin) oxide (30) commonly referred to as bis (neophyltin) oxide ('Vendex' or 'Torque').

'Plictran' is a specific contact acaricide with a moderate initial toxicity and with repellent anti feeding properties. The duration of protective action lasts for 20 days or more. It was first registered for the control of mites in apples and pears etc. Now it is registered in many European and in other third world countries as an acaricide on citrus, stone fruits and hops as well as apples and pears. The commercial formulation consists of wettable powders which are readily dispersed in water. The active ingredients are applied at a very low concentration e.g. at rates of 2-3 ounce per 100 gallon of spray (15 to 22.5 gm/100 litre water) registered in the U.S. market (31,32,33). 'Plictran' was found to be very effective in controlling red spider mite in lady's finger compared to "Monocroptophos" 36 WSC, 'Carbendenzim' 50 WP and urea. It's efficacy was not diminished when mixed with other agro chemicals. The safety of 'Plictran' to the Coccinillid mite predator, Stethorus sp. was also confirmed during the investigation (34). 'Plictran'

was tested (35) for its effectiveness in comparison to Malathion, oxydemeton methyl and wettable sulphur against Tetranychus cucurbital. A significant reduction of mite population was observed in plots treated with 'Plictran' 50 WP after 1,3,7,10 days of spraying while others did not give any control of the pest; no phytotoxicity of the treated plants was observed. Prevention of Panonychus ulmi and apple-rust mite with 'Plictran' along with 'Vendex' was very significant (36). Evaluation of 'Plictran' against the pink tea-mite (Acaphylla theae) was as effective as standard 'Dicofol' and 'Ethion' (37). 'Plictran' had toxicological parameter to those of chlorine and sulphur containing preparations and had a high ovicidal activity and was highly toxic to mobile phases of the spider mite (38). Periodic application of 'Plictran' caused no resistance development even after ninety consecutive generation and was effective against spider mite population resistant to others especially phosphorous-containing acaricides. The use of 'Plictran' was recommended in rotation with 'Dicofol' and 'Arex', where a resistance to phosphorous-containing and chlorine containing acaricides had developed. Spraying Cotton plants (39) with Zool, 03% Plictran per hectare controlled spider mite by 96% to 96.3% and prevented oviposition, and also showed low toxicity to beneficial entomo-acariphages. This phenomenon was also observed (40) on Strawberries in Southern California when 'Plictran' at 0.25 and 0.75 lb/acre was applied to Tetranychus urticae. Significantly fewer T. urticae occurred in plots receiving 'Plictran' at 0.75 lb/acre than at 0.25 lb/acre. The yields were greater than that of untreated control.

Similar result was obtained (41) when 'Murfite' (Cyhexatin + Murfite mixture; 300 + 160 g/ha) and Cyhexatin (250 g/ha) was applied in the strawberry crop yield with cyhexatin. Residue bioassays with 'Plictran' (42) along with 'Propargite', 'Dicofol', 'Carbophenothion', 'Hexakis' and 'Abamectin' were conducted against three populations of two spoted spider-mites. Behavioural responses (Wulf-off and spin-down) was significantly greater than that of control with 'Plictran', 'Hexakis' and 'Carbophenothion'. Cyhexatin was compared for its toxicity (43) to 'Chloropropylate', 'Azinophosmethyl', 'Methidathion', 'Fervalerate' and 'Benomyl' against 'Panonychus ulmi Tetranychus urticae, Aculus fockeri, Aculus finlandicus. For all above Plictran was highly toxic at the level of their LC_{95} values and the application concentrations used in orchards. Studies on the efficacy of three acaricides (44) on lady's finger revealed that the best result was obtained with 'Plictran' (350, 400 g/ha) and its effect lasted even after 14 days of spraying. One week after spraying all other treatments 'Plictran' (200, 250, 300 g/ha) were found to be on per with others and may even superior to 'Dicofol' 18.5 E.C. and 'Ethion' 50% E.C.

"Peropal" is most effective against the members of Tetranychidae. At 0.004, 0.02 and 0.1% concentration it caused 160% mortality of Tetranychus urticae sprayed once at 0.025% and 0.0025% it persisted long enough to kill 100% of T. urtical population. It mainly acts as contact poison with a merked repellent effect (45). Green house experiments were performed (46) to establish a comparison

of the effectiveness of 'Peropal' against three 'Tetranychus urticae' strains of varying sensitivity to conventional acaricides. Results showed that 'Peropal' was effective against a number of mite species (46).

'Vendex' applied (47) at 2-3 lb/acre to citrus orchards controlled citrus rust mites upto four months. It is also effective against organophosphorous and organochlorine resistant mites showing low toxicity to beneficial mites and honey bees.

As a consequence of wide application of organotin acaricides it is a evident that some resistance might be developed by the mite towards these acaricides. It has been found that (48) Tetranychus urticae failed to develop resistance against 'Plictran' and 'Peropal' over 100 generations even after treated for 40 times whereas over after 18-23 generations resistance to 'Actellic' and 'Etaphos' increased 360 and 1000 fold respectively.

Acaricides show variations in effectiveness against eggs and adults. The egg is generally highly resistant to usual contact acaricides as the eggs have a complex protective membrane surrounding the embryo, which possess difficulty in the penetration of the acaricides, thus it becomes difficult to destroy the eggs along with the adults. But if the eggs are not destroyed completely there remain the chance of rainfestation. So it is important to assess the effectiveness of acaricides as an ovicides i.e. they should possess lethal action on the eggs, as indicated by the cessation of embryonic development.

E X P E R I M E N T A L

Materials and Methods:

A. Fungicidal Activities

(i) Compounds:

Triphenyltin N-hydroxy succinimide, triphenyltin N-hydroxy phthalimide and tributyltin N-hydroxy phthalimide reported in earlier section, have been tested for fungi toxicities.

(ii) Organisms:

(a) *Helminthosporium oryzae*

Breeda de Haan — causal organism of brown leaf spot disease of rice.

(b) *Alternaria solani* (E II and Mart) Jones and Grout — causal organism of early blight disease of potato.

(iii) Culture Media:

Solid media [malt extract agar (21)]:

20 g malt extract (Difco) was boiled in water till dissolved. 20g agar agar (Kobe-Japan) was added and boiled until agar agar was well dissolved. 0.05g chloramphenicol was suspended in 5 ml of 95% alcohol and added to the medium as anti bacterial agent. The volume of the medium was then made upto 1 litre by addition of water. pH of the medium was adjusted with sodium hydroxide to 6.5. Medium was sterilized at 15 p.s.i. for 20 minutes.

4. Anti fungal Activities of selected Compounds in vitro.

Anti fungal activities of the compounds were tested following the growth inhibition studies.

Growth inhibitions were studied following the poisoned food technique (22). Acetone solution of suitable quantity of the compounds in sterile distilled water was incorporated into melted malt agar so as to get the desired concentrations of the compound in the media. Media with desired concentrations of compound were poured in petri plates and after solidification were inoculated at the centre with uniform discs (7 mm) of mycelia, punched out with a sterile cork borer from the advancing zone of a culture test fungus. Three replications on each test with appropriate control under same conditions were maintained. The petri plates were then incubated at 30 ± 1°C in dark. Linear growth of the fungal discs were measured after regular intervals and the percentage of inhibition over control was calculated following the equation

$$\frac{C-T}{C} \times 100$$

[where C = control, T = treated] given by Vincent (23).

5. Determination of ED_{50} and ED_{95}

The ED_{50} [effective dose for 50% inhibition] and ED_{95} [effective dose for 95% inhibition] values (μg/ml) were calculated by least-squares regression analysis using computer.

B. Phytotoxicity on Rice

(i) Seed Sample:

Healthy rice seeds of PUSA 2-21 variety collected from Chinsurah Rice Research Farm, Hooghly, West Bengal, were used in the present investigation.

(ii) Compounds:

Triphenyl tin N-hydroxy succinimide, Triphenyl tin N-hydroxyphthalimide and Tributyl tin N-hydroxy phthalimide were used for determining their phytotoxic effect on rice.

(iii) Effect on seed germination :

Healthy rice seeds were dipped in compound suspension of 100, 50 and 25 ppm concentration for 1, 4 and 8 hours. For control, water with requisite amount of acetone was used. The treated seeds were then placed on moist three layered filter paper in closed petriplates. Plates were incubated at 30 ± 1°C. 100 seeds were maintained for each treatment. After 8 days the germinated seeds were counted. Seeds producing a root or a coleoptile were recorded as germinated. Three replications of each test with appropriate control under same conditions were maintained.

C. Miticidal Activities

(1) Compounds:

Tricyclohexyltin N-hydroxy phthalimide, Tetracyclohexyl 1:3 di-N-hydroxy succinimido distannoxane, Dicyclohexyltin diphenyl glycolate and plictan.

(ii) Organism : Green mite

(iii) Determination of acaricidal activity

(a) Collection of specimens

The mite infested leaves or plant parts were brought to the laboratory in polythene bags after tightly closing the mouth of the bag with a rubber band.

(b) Mounting for microscopical examination

Before examining under microscope, high degree of transparency in the mite is needed. This was done by placing the specimen to be examined on a slide and putting a drop of lactic acid over it. The slide was then gently warmed for a few seconds, which reduced the normal opacity of mites, appendages extended. It was then carefully examined under the microscope.

(c) Rearing

Mite was reared in the laboratory in large numbers for experimental purpose. Rearing was one by two methods. These were cultured in bean seedlings, kept in pots. The adult mites were picked up from the infested leaves or plant parts and transferred to the leaves of potted seedlings or the infested plant parts were kept on top of the seedlings. When the detached part dried up the mites migrated to the leaves of the potted seedlings. Petroleum jelly was applied arcund the base of the stem to prevent the escape of the mites.

The other method used were keeping excised leaves of the host plant in petridish (15 cm diameter) over a cotton pad super saturated with water. Leaf was periodically changed and water was added daily to maintain a thin film of water at the margin of leaf to prevent the escape of mites. Mites were transferred on to the leaves by picking up with a fine brush moistered with water.

(d) Slide-dip method for contact toxicity assessment

This method was originated by Voss (56) improved by Dittrich (57). Adult females of known ages were used for the screening. This was done by collecting eggs over 4-5 hours and rearing adults of a new generation which appeared 6-7 days later, at temperature ranging from 27°C to 29°C.

For the test, microscope slide was covered with a strip of double-sided scotch-tape and twenty adult females were stuck on to the tape, on the dorsal side, in two rows of ten. The prepared slides were dipped, for 5 seconds in serial concentrations of the compound being tested. Slides were drained, by placing on edge for 15 minutes, at room temperature. Mortality counts were made after 24, 48 and 72 hours. Mites not showing movement of appendages when touched by a fine brush were recorded as dead. Three tests were conducted at each dosage level. The treated slides were placed on the top of a moist cotton-pad in petri-dishes, which contained water to maintain the humidity. For the control set, slides were dipped in distilled water for the same length of time.

(e) Method of assaying contact plus stomach toxicity

The method followed here was that of Mansour and Plant (58). The mites were released on fresh leaves and sprayed with the different concentration of the compound. Each test was replicated thrice and mortality counts were made after 24, 48 and 72 hours.

(f) Determination of LC_{95} and LC_{50}

The LC_{50} and LC_{95} [lethal concentration for 50% and 95% mortality] (μg/ml) were calculated as earlier using least square regression analysis using a computer.

R E S U L T S

A. FUNGICIDAL ACTIVITY

The triorganotin compounds, particularly triphenyl and tributyltin derivatives, show excellent fungicidal activities. In the fungi toxicities, the anionic part (X) of R_3SnX does not influence the activity considerably. Though more work is necessary, it seems the triorganotin moieties, as expected, retain its fungicidal properties in Triphenyl tin N-hydroxy phthalimide, Triphenyl tin N-hydroxy succinimide and Tributyltin N-hydroxy phthalimide against Alternaria solani and Helminthosporium oryzae.

The results obtained have been tabulated as follows:

TABLE - I

Effect of Triphenyltin N-hydroxy Succinimide on growth of Alternaria solani

Concentration (µg/ml)	Percentage of Growth inhibition over control after		
	24 hrs	48 hrs	72 hrs
1.56	100.00	100.00	100.00
1.25	100.00	100.00	98.92
0.63	97.90	92.50	86.90*
0.31	93.42	78.90*	72.70*
0.13	71.40*	62.50*	55.00*
0.06	56.30*	49.11*	40.00*
0.03	42.20*	35.24*	29.07*
ED_{50}	0.05 µg/ml	0.07 µg/ml	0.09 µg/ml
ED_{95}	0.38 µg/ml	0.71 µg/ml	0.96 µg/ml
Regression constants : $Y = mx + C$			
m	48.66	43.65	44.98
C	115.52	101.62	95.86
r	0.99	0.99	0.99

* Data have been used for regression analysis.

TABLE - II

Effect of Triphenyltin N-hydroxy phthalimide on growth of *Alternaria solani*

Concentration (µg/ml)	Percentage of growth inhibition over control after		
	24 hrs	48 hrs	72 hrs
6.25	100.00	100.00	100.00
3.13	100.00	100.00	96.86
1.56	100.00	99.20	91.11
1.25	100.00	98.16	87.75*
0.63	97.12	87.31*	78.32*
0.31	82.60*	73.35	64.24*
0.13	65.30*	60.21*	52.34*
0.06	50.72*	46.26*	40.12*
0.03	36.28*	32.90*	29.28*
ED_{50}	0.06 µg/ml	0.08 µg/ml	0.11 µg/ml
ED_{95}	0.56 µg/ml	0.94 µg/ml	1.90 µg/ml
Regression Constants : $Y = mx + C$			
m	44.42	41.22	36.69
C	106.77	95.97	84.72
r	0.99	0.99	0.99

* Data have been used for regression analysis.

TABLE - III

Effect of Tributyl tin N-hydroxy phthalimide on growth of Alternaria solani

Concentration µg/ml	Percentage of growth inhibition over control after		
	24 hrs	48 hrs	72 hrs
3.13	100.00	100.00	100.00
1.56	100.00	100.00	99.90
1.25	100.00	99.90	93.61
0.63	98.19	96.20	89.20*
0.31	84.48*	83.12*	82.97*
0.13	67.21*	65.50*	62.11*
0.06	51.50*	49.50*	46.19*
0.03	34.10*	33.71*	33.10*
ED_{50}	0.06 µg/ml	0.06 µg/ml	0.07 µg/ml
ED_{95}	0.47 µg/ml	0.51 µg/ml	0.69 µg/ml
Regression constants : Y = mx + C			
m	50.30	49.59	45.20
C	111.39	109.28	102.04
r	0.99	0.99	0.99

* Data have been used for regression analysis.

TABLE - IV

Effect of Triphenyltin N-hydroxy Succinimide on growth of *Helminthosporium oryzae*

Concentration (µg/ml)	Percentage of growth inhibition over control after		
	24 hrs	48 hrs	72 hrs
15.63	100.00	100.00	100.00
12.50	100.00	100.00	99.34
10.00	100.00	100.00	97.79
6.25	100.00	95.95	95.20
3.13	96.82	87.14*	75.50*
1.56	78.20*	65.21*	58.00*
1.25	73.43*	58.96*	52.22*
0.63	49.31*	38.64*	33.43*
0.31	34.00*	21.29*	15.24*
0.13	11.62*	3.11	1.59
0.06	0.00	0.00	0.00
ED_{50}	0.35 µg/ml	0.88 µg/ml	1.15 µg/ml
ED_{95}	2.98 µg/ml	4.25 µg/ml	6.38 µg/ml
Regression constants Y = mx + C			
m	61.29	65.83	60.50
C	65.86	53.58	46.27
r	0.99	0.99	0.99

* Data have been used for regression analysis.

TABLE - V

Effect of Triphenyltin N-hydroxy phthalimide on growth of *Helminthosporium oryzae*

Concentration (μg/ml)	Percentage of inhibition over control after		
	24 hrs	48 hrs	72 hrs
6.25	100.00	100.00	100.00
3.13	100.00	100.00	98.48
1.56	93.20	86.90*	82.71*
1.25	87.50*	80.90*	76.25*
0.63	74.70*	66.90*	64.90*
0.31	56.25*	53.48*	49.09*
0.13	37.50*	32.12*	30.23*
0.06	24.61	18.20*	14.04*
0.03	8.26	6.11	4.12
.02	0.00	0.00	0.00
ED_{50}	0.21 μg/ml	0.28 μg/ml	0.33 μg/ml
ED_{95}	1.73 μg/ml	2.31 μg/ml	2.79 μg/ml
Regression Constants : $Y = mx + C$			
m	49.36	48.85	48.28
C	83.26	77.26	73.47
r	0.99	0.99	0.99

*Data have been used for regression analysis

TABLE - VI

Effect of Tributyl tin N-hydroxy phthalimide on growth of *Helminthosporium oryzae*

Concentration (µg/ml)	Percentage of growth inhibition over control after		
	24 hrs	48 hrs	72 hrs
6.25	100.00	100.00	100.00
3.13	100.00	100.00	98.22
1.56	100.00	94.02	88.50*
1.25	100.00	87.50*	84.17*
0.63	100.00	84.21*	75.09*
0.31	98.00	72.10*	66.46*
0.13	85.85*	60.00*	50.60*
0.06	77.00*	51.00*	39.49*
0.03	66.00*	40.00*	28.03*
0.02	52.01*	32.03*	15.21*
ED_{50}	0.01 µg/ml	0.06 µg/ml	0.13 µg/ml
ED_{95}	0.18 µg/ml	1.64 µg/ml	2.22 µg/ml
Regression Constants: $Y = mx + C$			
m	40.51	31.73	36.03
C	124.93	88.16	82.46
r	0.99	0.99	0.99

* Data have been used for regression analysis

SUMMARY OF THE RESULTS

TABLE - VII

ED_{95} Values in μg/ml for growth inhibition against *Alternaria solani*

Compound	ED_{95} values μg/ml		
	24 hrs	48 hrs	72 hrs
Triphenyl tin N-hydroxy succinimide	0.35	0.71	0.96
Triphenyl tin N-hydroxy phthalimide	0.56	0.94	1.90
Tributyl tin N-hydroxy phthalimide	0.47	0.51	0.69
Tributyltin (24) acetate	0.77	0.78	0.98

TABLE - VIII

ED_{95} Values (μg/ml) for growth inhibition against *Helminthosporium oryzae*

Compound	ED_{95} values μg/ml (.. hrs)		
	24	48	72
Triphenyl tin N-hydroxy succinimide	2.98	4.25	6.38
Triphenyltin N-hydroxy phthalimide	1.73	2.31	2.79
Tributyltin N-hydroxy phthalimide	0.18	1.64	2.22
Tributyltin (24) acetate	0.38	0.71	0.96

B. PHYTOTOXICITY ON RICE

The *in vitro* tests of fungicidal activity have limited value to the agricultural pesticide chemist because it circumvents the important consideration of phytotoxicity. A fungicide which causes serious phytotoxicity under varied environmental conditions would be a total failure.

TABLE - IX

Effect of triphenyl tin N-hydroxy succinimide, Triphenyltin N-hydroxy phthalimide and Tributyltin N-hydroxy phthalimide on rice seed germination

Compound	Conc. (µg/ml)	Percentage of germinated seed, treated for		
		1 hr	4 hrs	8 hrs
Triphenyl tin N-hydroxy succinimide	100.00	86	84	76
	50.00	88	88	82
	25.00	88	88	86
Triphenyltin N-hydroxy phthalimide	100.00	86	82	78
	50.00	86	82	82
	25.00	88	84	82
Tributyltin N-hydroxy phthalimide	100.00	72	70	64
	50.00	88	84	80
	25.00	88	86	82
Control		91	91	91

C. MITICIDAL ACTIVITIES

It has been pointed out earlier, that Tricyclohexyl tin compounds show excellent miticidal activities. In present investigation, Tricyclohexyl tin N-hydroxy phthalimide, Tetracyclohexyl 1:3 di-N-hydroxy succinimido di stannoxane (obtained from reaction of Tricyclohexyl tin hydroxide and N-hydroxy succinimide) Dicyclohexyl tin diphenyl glycolate (obtained from Tricyclohexyl tin hydroxide and diphenyl glycolic acid) were prepared. Some preliminary experiments were carried out with these compound against one (non identified) green mite, collected from trees of the locality. It may be pointed out here that these results were preliminary in nature, hence no positive conclusion could be made so far about the miticidal activities of these compounds, except that the miticidal activity is substantially reduced compared to 'Plictran' (Tricyclohexyl tin hydroxide) due to the nature of these ligands. It was somewhat surprising that the Tetracyclohexyl 1:3 di-N-hydroxy succinimido distannoxene gave comparable activity to Tricyclohexyl tin N-hydroxy phthalimide. Further investigation are necessary to draw useful conclusions about the miticidal activities of these compounds. However, we present here the results of experiment carried out so far.

TABLE - X

Contact toxicities of Tricyclohexyl tin N-hydroxy phthalimide for Green mite

Concentration (µg/ml)	Percentage of mortality after		
	24 hrs	48 hrs	72 hrs
50	60	65	67.5
20	50	55	55
10	40	42.5	45
5	32.5	32.5	35
2.5	20	27.5	27.5
1.2	17.5	22.5	27.5
0.6	0.5	7.5	7.5
LC_{95} (µg/ml)	672.77	571.42	494.70
LC_{50} (µg/ml)	20.98	15.43	13.36
Regression Constants : Y = mx + C			
m	29.8812	28.6883	28.6935
C	10.4971	15.9076	17.6897
r	0.9912	0.9905	0.9813

TABLE - XI

Contact toxicities of Tetracyclohexyl 1:3 di N-hydroxy succinimido di stanoxane for Green mite

Concentration (µg/ml)	Percentage of mortality after		
	24 hrs	48 hrs	72 hrs
50	57.5	67.5	72.5
20	55	60	62.5
10	55	55	57.5
5	40	45	47.5
2.5	30	35	40
1.2	27.5	30	32.5
0.6	7.5	20	22.5
LC_{95}	738.02 µg/ml	501.21 µg/ml	382.27 µg/ml
LC_{50}	13.50 µg/ml	8.22 µg/ml	6.31 µg/ml
Regression Constants : Y = mx + C			
m	25.8965	25.2143	25.2553
C	20.7270	26.9208	29.7813
r	0.9494	0.9948	0.9957

TABLE - XII

Contact toxicities of Dicylohexyl tin diphenyl glycolate for Green mite

Concentration (µg/ml)	Percentage of mortality after		
	24 hrs	48 hrs	72 hrs
50	50	55	57.5
20	45	47.5	50
10	42.5	45	45
5	30	35	35
2.5	12.5	12.5	1.5
1.2	0.25	7.5	10
LC_{95} (µg/ml)	779.9025	641.1089	420.7501
LC_{50} (µg/ml)	30.3411	23.6638	21.7674
Regression Constants : Y = mx + C			
m	31.9147	31.4060	34.9863
C	2.7014	6.8455	3.1951
r	0.9576	0.9578	0.9218

TABLE - XIII

Contact plus stomach toxicities of 'Plictran' for Green mite

Concentration (µg/ml)	Percentage of mortality after		
	24 hrs	48 hrs	72 hrs
50	83.34	90.00	90.00
20	76.67	83.34	86.67
10	56.67	63.34	66.67
5	46.67	53.34	60.00
2.5	16.67	33.34	36.67
1.2	13.34	23.34	26.67
LC_{95}	65.19 µg/ml	50.31 µg/ml	33.71 µg/ml
LC_{50}	7.57 µg/ml	4.78 µg/ml	3.89 µg/ml
Regression Constant : $Y = mx + C$			
m	48.1501	44.0426	48.0012
C	7.6448	20.0535	21.6632
r	0.9756	0.9885	0.9875

TABLE - XIV

Contact plus stomach toxicities of Tricyclohexyltin N-hydroxy phthalimide for Green mite

Concentration (µg/ml)	Percentage of mortality after		
	24 hrs	48 hrs	72 hrs
50	50	63.34	73.34
20	36.67	46.67	56.67
10	36.67	40.00	53.34
5	26.67	33.34	40.00
2.5	13.34	16.67	23.34
1.2		13.34	20.00
LC_{95}	—	579.29 µg/ml	217.90 µg/ml
LC_{50}	—	20.88 µg/ml	10.45 µg/ml
Regression Constants : Y = mx + C			
m	25.9445	31.1819	34.1194
C	6.3622	8.8475	15.2194
r	0.9682	0.9876	0.9861

TABLE - XV

Contact plus stomach toxicities of Tetracyclohexyl 1:3 di N-hydroxy succinimido distannoxane for Green mite

Concentration (µg/ml)	Percentage of mortality after		
	24 hrs	48 hrs	72 hrs
50	50.00	56.67	63.34
20	43.34	50.00	63.34
10	43.34	46.67	50.00
5	16.67	20.00	33.34
2.5	3.34	06.67	13.34
LC_{95}	639.81 µg/ml	326.84 µg/ml	190.15 µg/ml
LC_{50}	34.08 µg/ml	23.26 µg/ml	14.05 µg/ml
Regression Constants : Y = mx + C			
m	35.3368	39.2104	39.7813
C	4.1569	3.5886	4.3338
r	0.9667	0.9745	0.9762

R E F E R E N C E S

1 B. Sugavanam, Tin Its Uses, 126, 4, 1980.

2. G.J.M. van der Kerk and J.G.A. Luijten, J. Appl. Chem., 4, 314, 1954.

3 R.J. Zedler and C.B. Seiter, Soap Chem., Specialities 38, 101, 1962.

4. K. Hartel, Agr. Vet. Chem. 3, 19, 1962.

5. H. Kubo, Agr. Bio. Chem. (Tokyo), 60, 10706, 1964.

6. A. Kaars Sijpesteijn, F. Rijkens, A.C.J. Luijten and L.C. Willemsens, Antonic Van Leeuvenhoek, J. Microbiol. Scrol., 28, 346, 1962.

7. A. Tempel, Unpublished results, Through Fungicides, Vol. II, Academic Press Inc. New York, 341, 1969.

8. Idem, J. Appl. Chem., 6, 56, 1956.

9. A.G.J. Luijten and G.J.M. van der Kerk, J. Appl. Chem., 11, 35, 1961.

10. K. Hartel, Tin And Its Use, 43, 9, 1958.

11. M.M. Gitlitz, Organotin Compounds: New Chemistry and Applications, American Chemical Society, Washington, 168, 1976.

12. G.J.M. van der Kerk, Organotin Compounds : New Chemistry and Applications, American Chemical Society, Washington, p9, 1978.

13. F.E. Smith, ITRI, Publn. 607

14. F.E. Smith, D. Okiaga and L.E. Khoo, ITRI Publn. 584.

15. T.N. Srivastava, M.P. Agarwal, S.R. Misra and K. Singh, Ind. Phytopathol, 25, 570, 1972.

16. G. Mehrotra and A.N. Dey, J. Ind. Chem. Soc., 52, 197, 1975.

17. Idem , J. Ind. Chem. Soc., 51, 666, 1974.

18. R. Kishun, A.K. Banerjee, L.S. Chauvan and D.V. Singh, Pesticides, 8, 21, 1981.

19. N.N. Mohanty and B.K. Mohapatra, Ind. J. Agr. Sci., 48, 411, 1978.

20. S.K. Addy and B.K. Dash, Proc. of first Int. Symp. on Plant Pathol, I.A.R.I., New Delhi, 1970.

21. G.C. Ainsworth (Director), Plant Pathologist's Pocket Book, Commonwealth Mycological Institute, 238, 1974.

22. Y.L. Nene, Fungicides in plant disease control, Oxford and IBH Publishing Co., New Delhi, India, 286, 1976.

23. J.K. Vincent, Nature, 159, 850, 1927.

24. A.K. Mallick, Ph.D. Thesis, University of North Bengal, Darjeeling, India, 1982.

25. S.K. Gupta, Hand book : Plant mites of India, ZSI, Calcutta, 2, 1985.

26. L.R. Jeppson, Adv. Acarol., 2, 31, 1965.

27. E.E. Kanega, U.S. Pat., No. 3, 264, 177, 1966.

28. C.J. Evans, Tin its Use, 86, 7, 1970.

29. K.H. Buchel and I. Hammann, U.S. Pat., No. 3, 907, 818, 1975.

30. C.A. Horne, U.S. Pat. No. 3, 657, 451, 1972.

31. I. Hammann, K.H. Buchel, K. Bungarz and L. Born, Pflanzenschulz-Nachr, 31, 61, 1978.

32. Anonymus, WHO/Food Add/71 42, 521, 1972.

33. Anonymus, Data Sheet No. ADP 75-111, Shell Chem. Co., San Ramon California, U.S.A.

34. C. Peter, B.V. David and M.K. Zutshi, Pestology, 10 (7), 15, 1986.

35. G.S. Yadav, R.K. Anand, P.R. Yadav, Int. J. Ent., 49, (4) 1987.

36. N.J. Bost, R.O. Paradus and D. Pitre, Phyto protection, 62(1), 1981.

37. N. Maraleedharan and C. Kandaswami, Pesticide, 16(12), 1982.

38. I.V. Zilbermunts and L.M. Zhuravleva, Khim. Selsk. Khos Nos. 3, 1983.

39. A.V. Dzhalivov, Nauchno-Tekl Prog. Med. Biol. Aspekty. Okhr., Okruzhayushchei Sredi. Rutsion, Fspotz. Priv. Resul. 1983 through CA, 102(1), 1944 (1985).

40. G.G. Kennedy, E.R. Oatman and V. Voth, J. Ecoh. Entomol. 69(2), 1976.

41. M.E. Halfor and R.G. McKinlay, Tests Agrochem. Cultiv. No. 6, 1985.

42. D.E. Schiffhaur and R.F. Mizell, J. Econ. Entomol. 81(4), 1988.

43. M. Sestovic, R. Petanovic and K. Vasala, Pesticide, 2(3), 1987.

44. C. Peter, B.V. David and M.K. Zutshi, Pesticide, 21 (6), 1987.

45. I. Hammann, K.H. Buchel and K. Bungarz, Pflanzenschutz-Nachr. 31 (61), 1978.

46. S. King, ITRI Publn. No. 607

47. C.J. Evans, Tin its Uses, 86 (7), 1970.

48. I.V. Zilbermintz and L.M. Zhuravleva, Agrokhimiya No. 5, 1988.

49. S. King, ITRI Publn. No. 607.

50. W.F. King, U.S. Pat. 4, 565, 812, 1986.

51. I.V. Zilbermints and L.M. Zhuravleva, Khim, Sel'sk Khoz, No. 3, 1988 through CA 105(5) , 43091, 1986.

52. Matshhoto Keigo, Fujta Kutsuhiro, Morimusa Masaharu, Yamaguchi Kiyomi and Hirose Toshio, Jp. Pat. 61235, 591, 1983, through CA 108(1), 6185, 1988.

Ibid 62, 39, 590, 1987

53. Idem, through CA 106 (6), 62884, 1987.

54. Idem, Ibid, 62, 39, 592, 1987, through CA 106(25), 198662, 1987.

55. T. Pandit, Ph.D. Thesis, University of North Bengal, Darjeeling, India, 1989.

56. G. Voss, Anz. Schadlinsk, 34, 76, 1961.

57. V. Dittrich, J. Econ. Ent. 55, 644, 1962.

58. F.A. Manscur and H.N. Plant, Phytoparasitica, 7(3), 1979.

APPENDIX

Chemical name of the active ingredients of some commercial pesticides.

	Trade name	Chemical name of the active ingredient
1.	Breston	Triphenyltin acetate
2.	Du-Ter	Triphenyl tin hydroxide
3.	Brestanel	Triphenyl tin chloride
4.	Dicofol	2,2,2-Trichloro-1,1-bis(4-chlorophenyl) ethanol.
5.	Tetradifon	4-chlorophenyl 2, 4, 5-trichlorophenyl sulphone.
6.	Carbophenothion	S-4-Chlorophenyl thiomethyl 0,0-diethylphosphorodithioate.
7.	Ethion	0,0,0,0-Tetraethyl S, S'-methylene bis(phosphorodithioate)
8.	Binapacryl	2-Sec-Butyl-4,6-dinitro phenyl 3-methyl but-2-enoate
9.	Galecron	N-(4-chloro-o-tolyl)-N-N dimethyl formamidine.
10.	Aramite	2-(4-tert-Butyl phenoxy) 1-methyl ethyl 2-chloro ethyl sulphite.
11.	Chlorobenzilate	Ethyl 4,4'-dichlorobenzilate.