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.

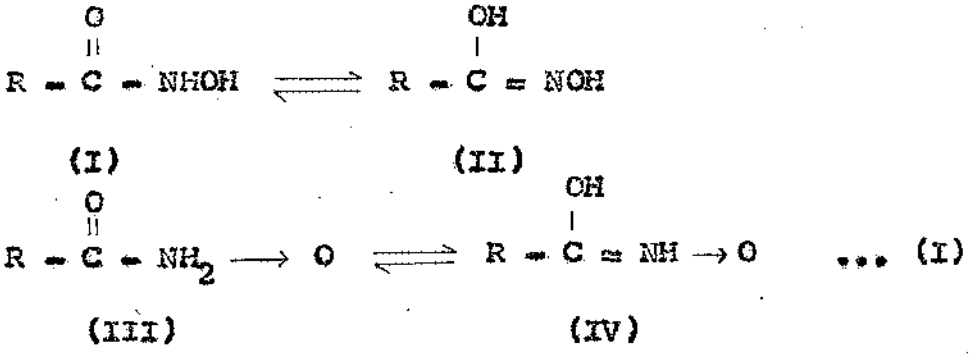
The hydroxamic acids were known for over a century (93) and a considerable body of literature exists on the subject, though the study of their chemistry and practical applications lagged for some years.

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)

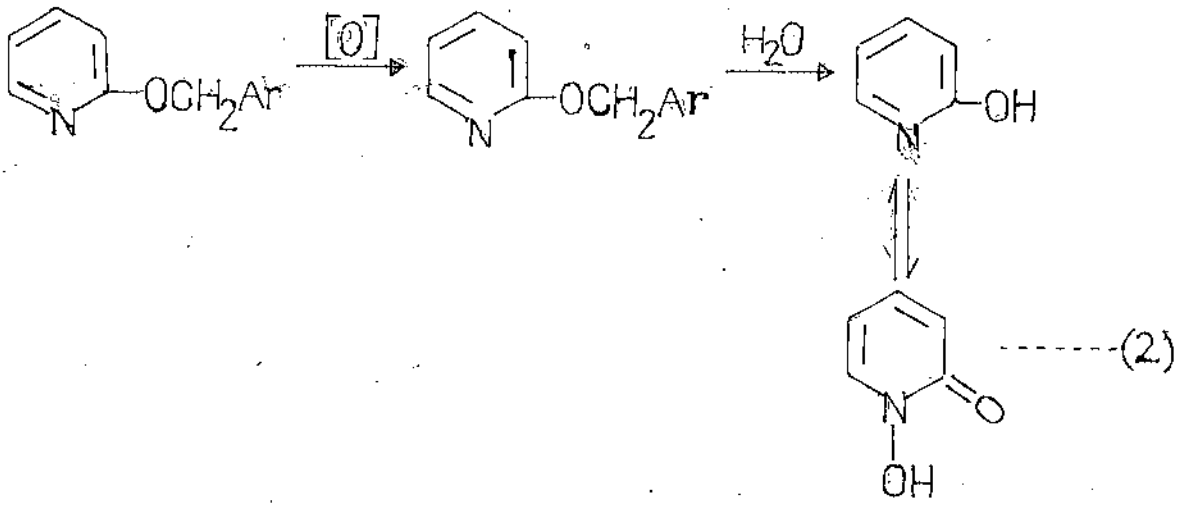
The above structure may be in equilibrium also with other tautomeric forms:



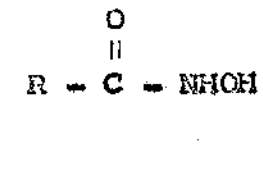
(I) (II)

(III) (IV)

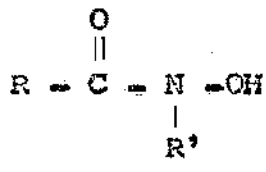
Structure (II) termed as hydroxamic acids constitute only a minor component of the tautomeric equilibrium mixture although derivatives of hydroxamic acids are well known. Structure (III) and (IV) have been added to the list of possible tautomeric forms relatively recently (100,101). Their importance 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):



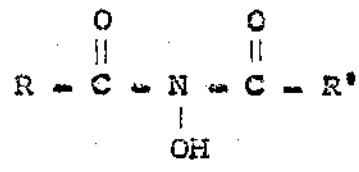
The variety of substituted hydroxamic acid is surprisingly large. If we consider only the structures which may be written upon alkylation and/or acylation of hydroxylamine but ignore the tautomeric derivatives, the following compounds result:

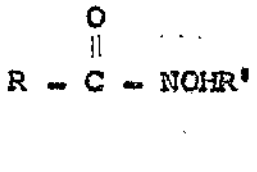


(I)

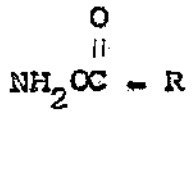


(V)

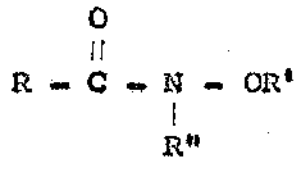




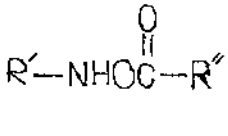
(VII)



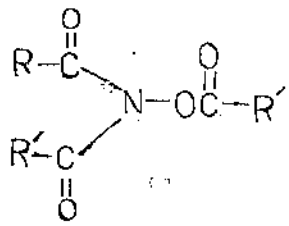
(VIII)



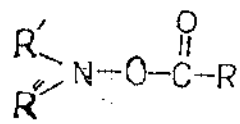
(IX)



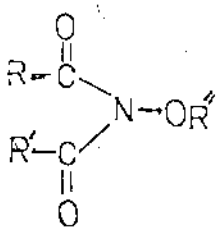
(X)



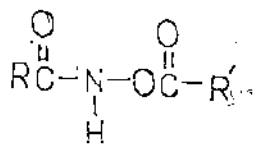
(XI)



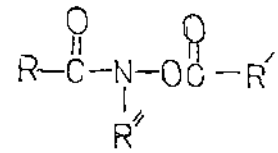
(XII)



(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.

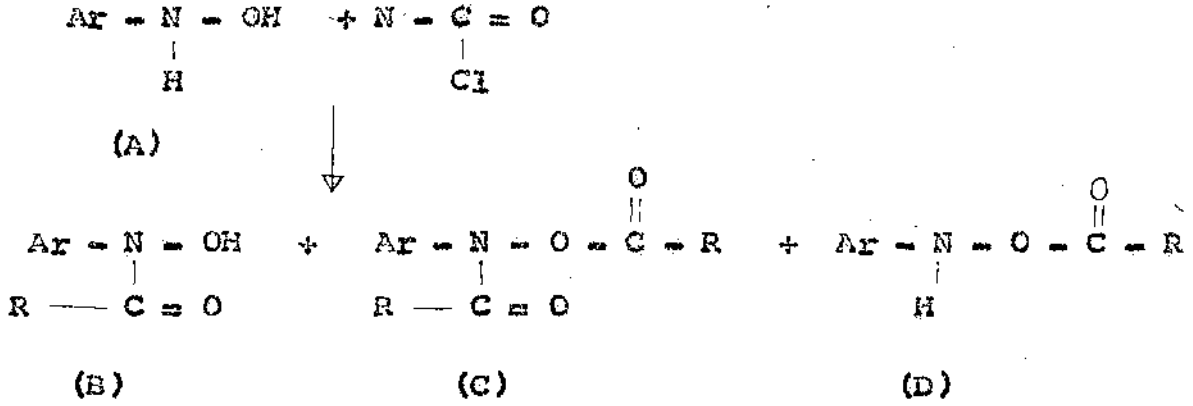
Hydroxamic acids may be prepared by treating esters, acid chlorides or acid anhydrides with hydroxylamine (103) in the presence of alkali and the free acid is obtained by the addition of acid in the appropriate quantity in cold solution.

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

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

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.

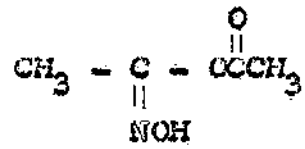
On the basis of Schotten-Baumann reaction, Tandon and co-workers (111, 112) have prepared several N-aryl hydroxamic acids by reacting phenyl hydroxylamine (PhNHOH) with acyl chloride or its derivatives ($R'COCl$) in the presence of dilute alkali.

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

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.

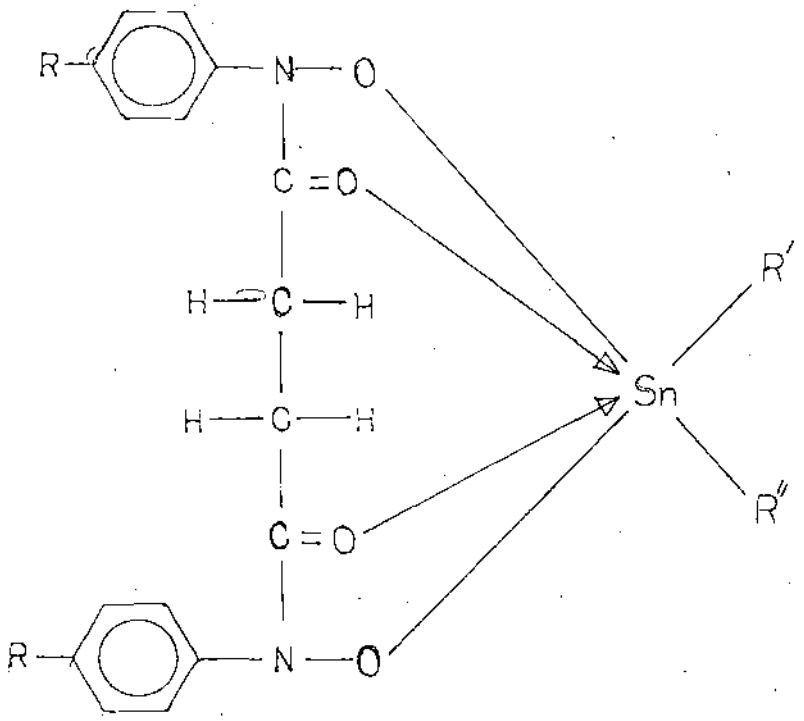
They have also synthesised (128) two new ligands viz. oxalyl bis N-phenyl hydroxamic acid (L) and oxalyl bis N-p-tolyl hydroxamic acid (L'). These have been used to prepare some new types of organotin coordination compounds.

$(R_3Sn)_2L$ (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).

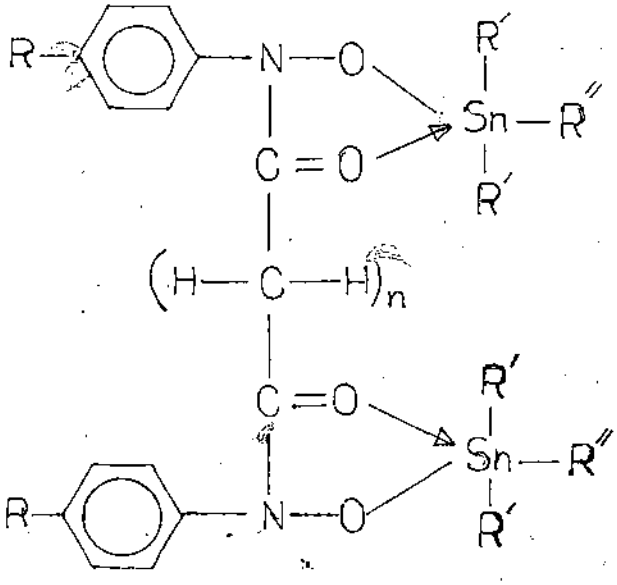
Some of these hydroxamic acids behave as tetradentate ligands



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

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

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



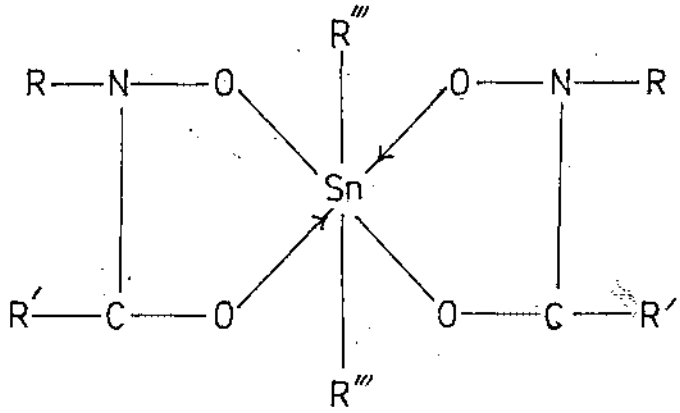
R = H, CH_3 ; R' = Cy, Me; R'' = Cy, Cl

n = 2,3.

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

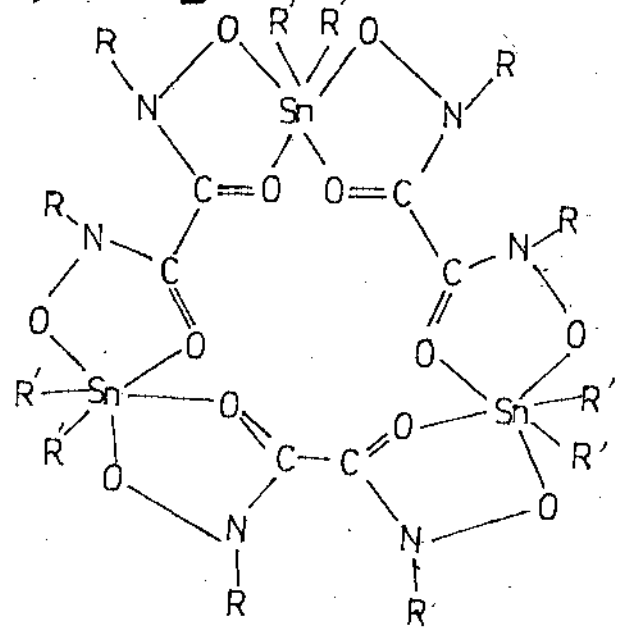
S C O P E A N D O B J E C T I V E

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.

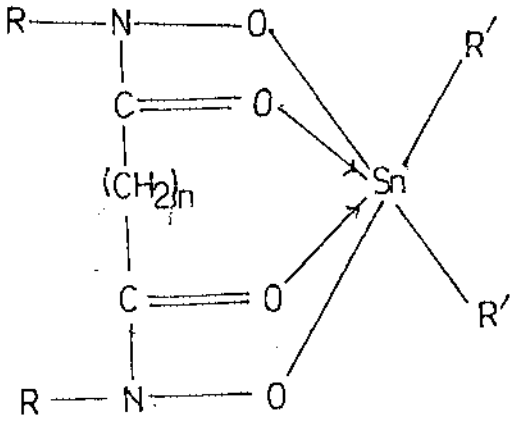


[R = R' = Ph, NO_2-C_6H_4 -, ClC_6H_4 - etc

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



R = Ph pCH_3-C_6H_4 , R' = phenyl

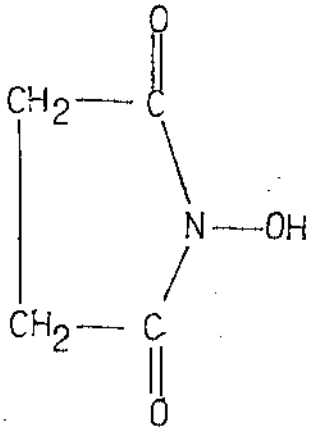


R = Phenyl, p-tolyl

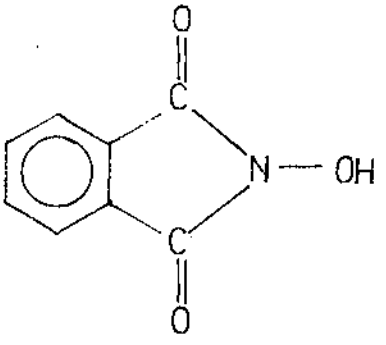
R' = phenyl, benzyl, methyl, butyl, Cl,

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:

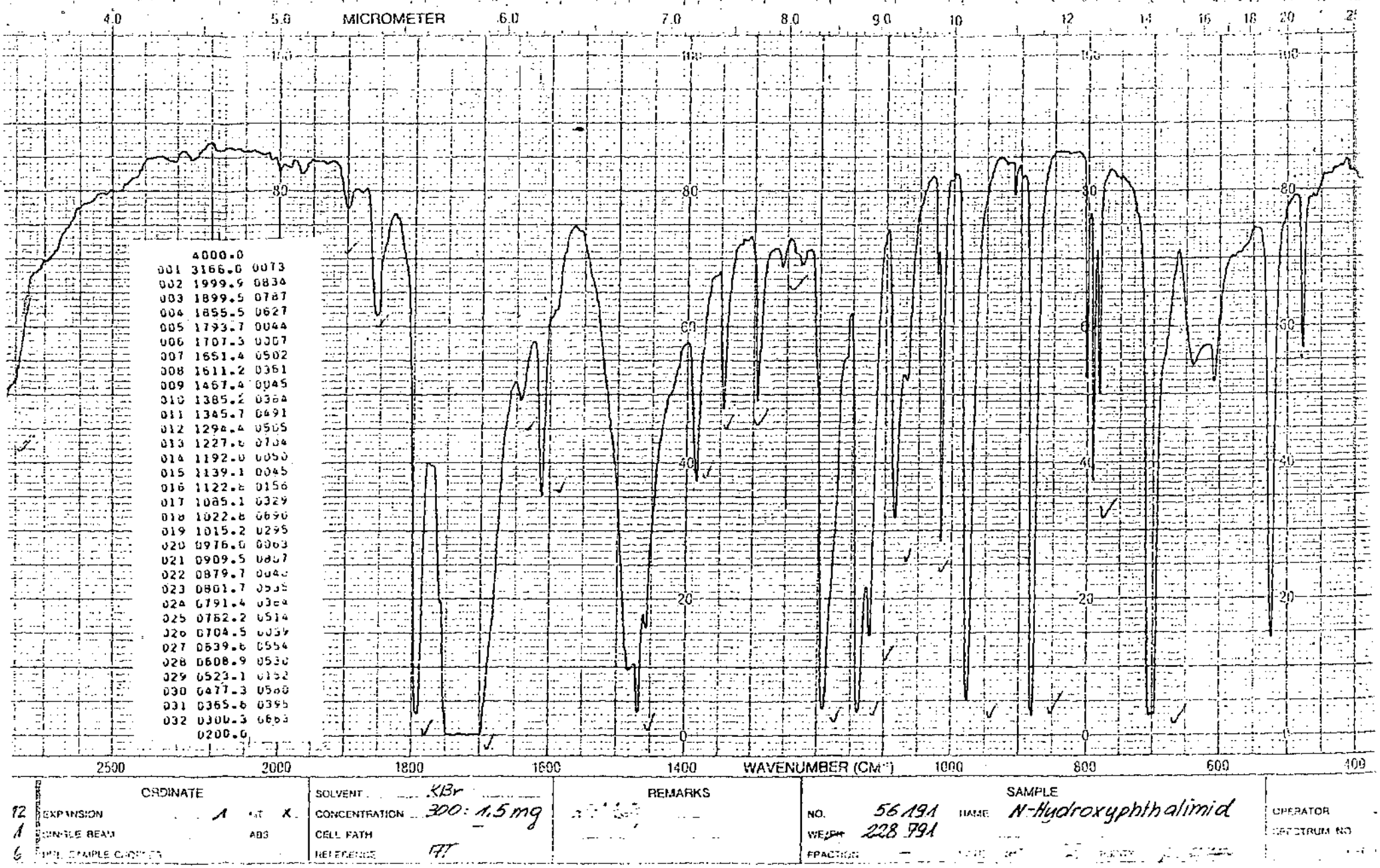
V.S. = very strong, S = strong, m = medium, w = weak, b = broad, sh = shoulder, h = hump, nujol had peaks at 3000-2800 cm^{-1} (V.S.) 1460 cm^{-1} (s), 1376 cm^{-1} (m).

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.

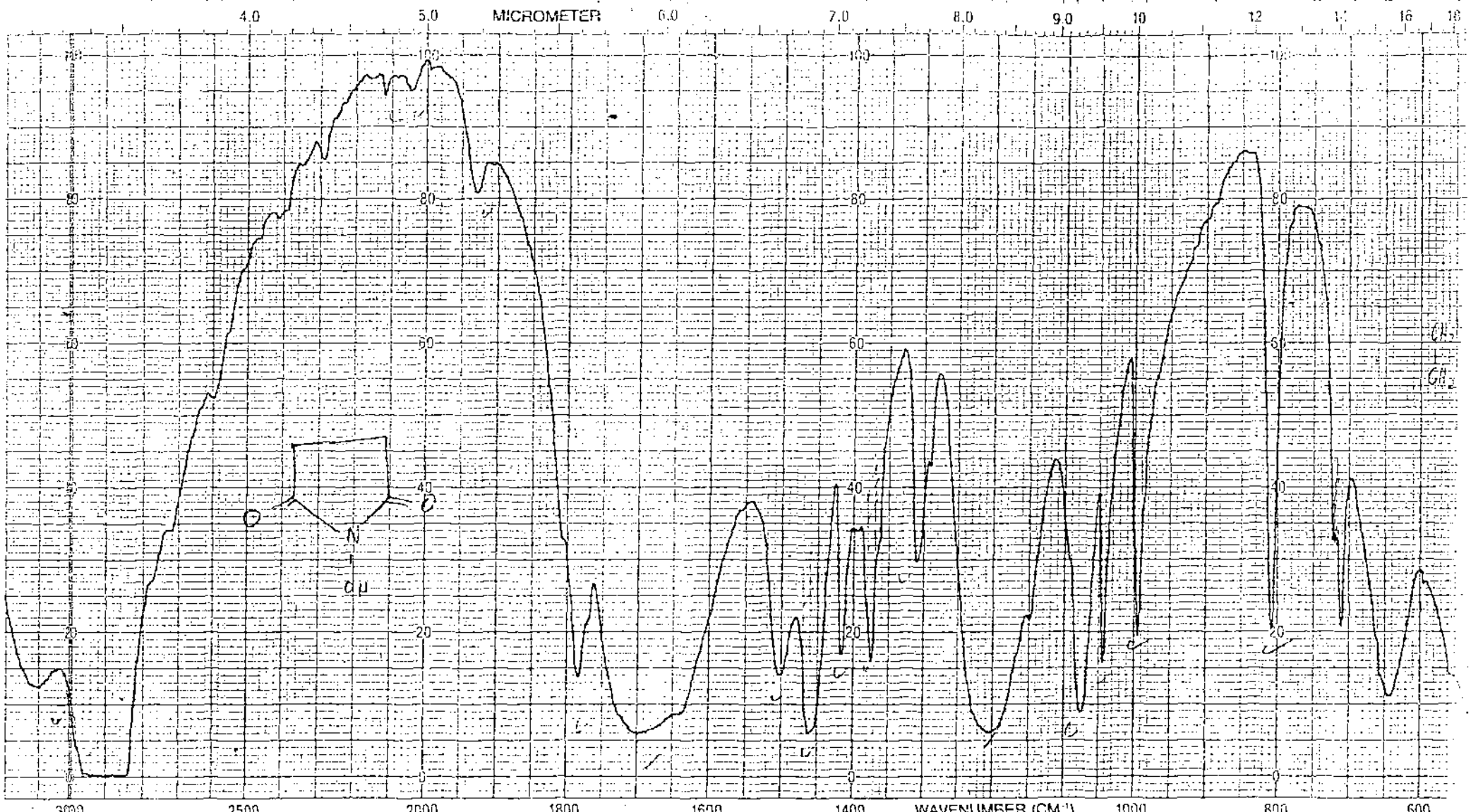
5. Succinic Anhydride

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}):

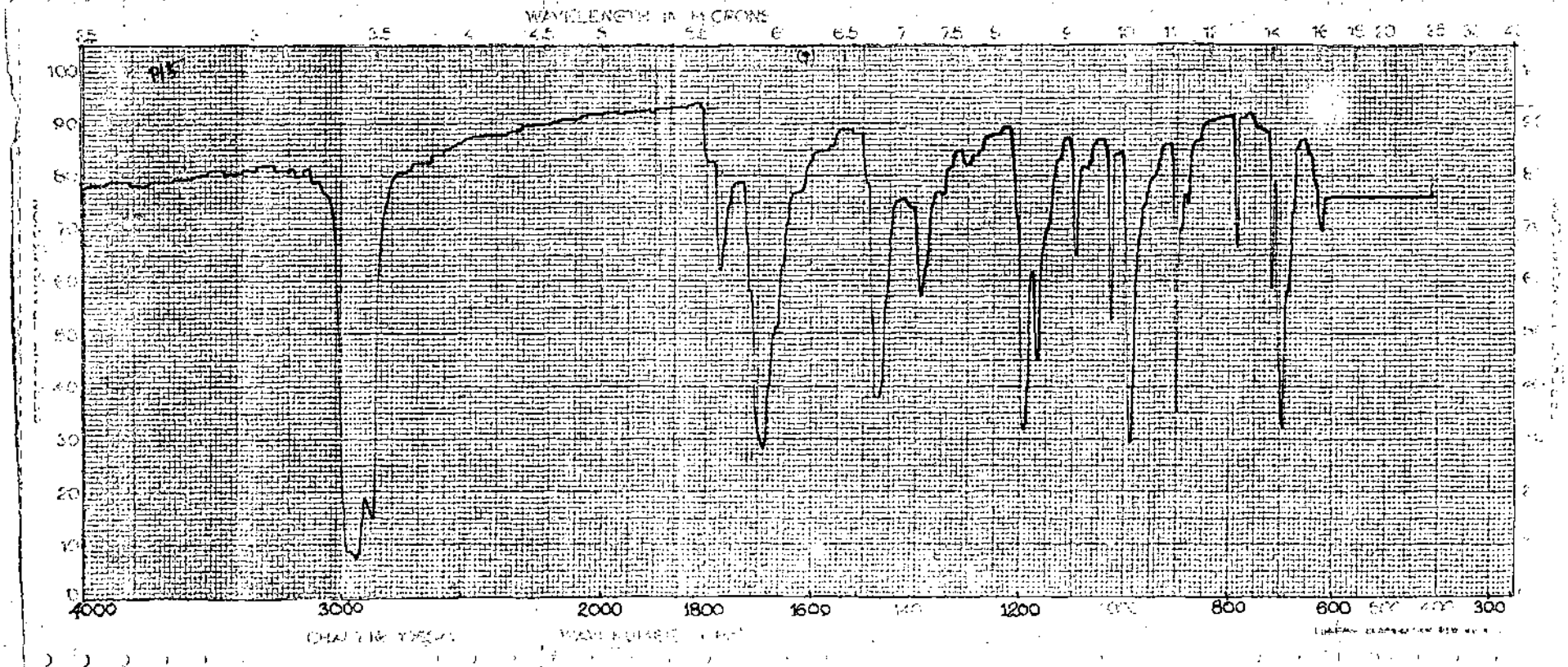
3000(b), 1775(s), 1700(b), 1420(s), 1365(s), 1310(w), 1220(b), 1070(s), 995(s), 810(s), 710(s), 645(s).

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.

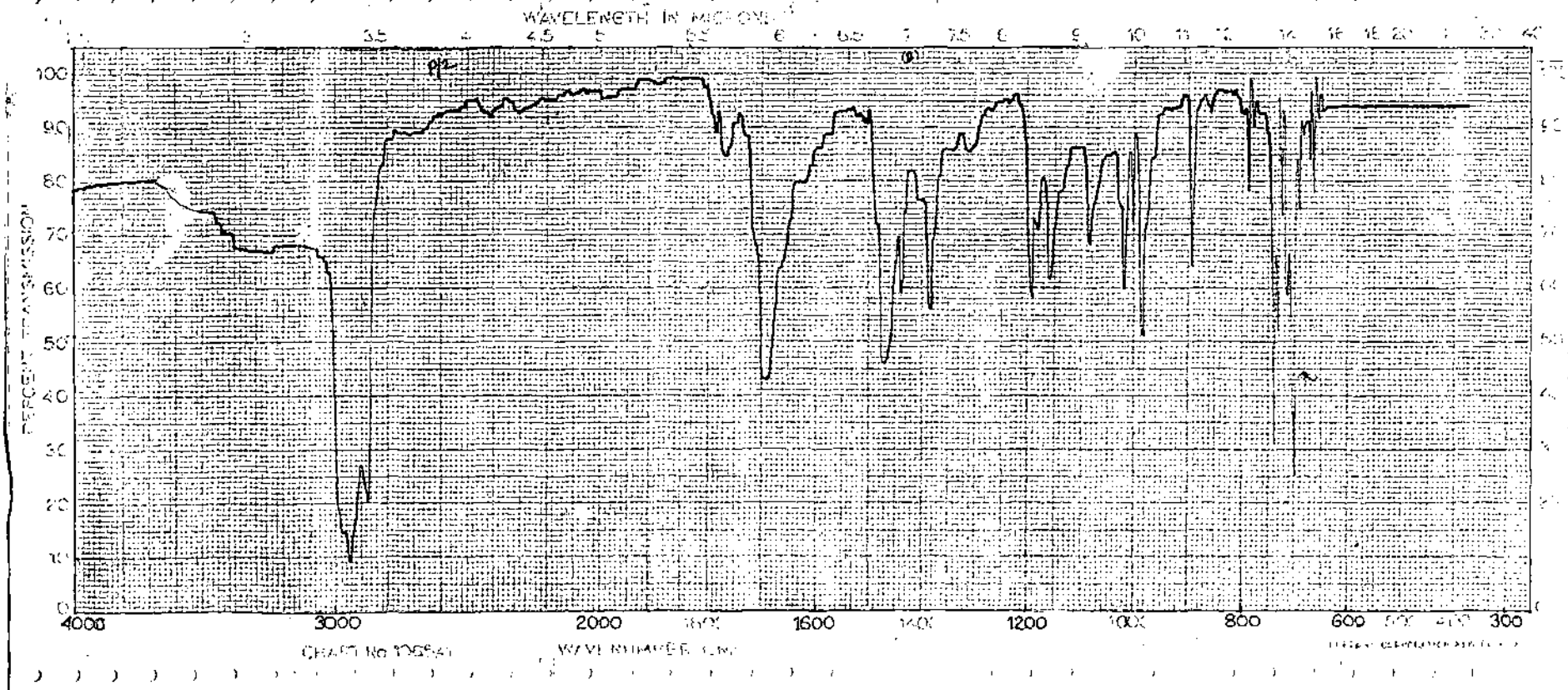
(Yield = ~55%)

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%)

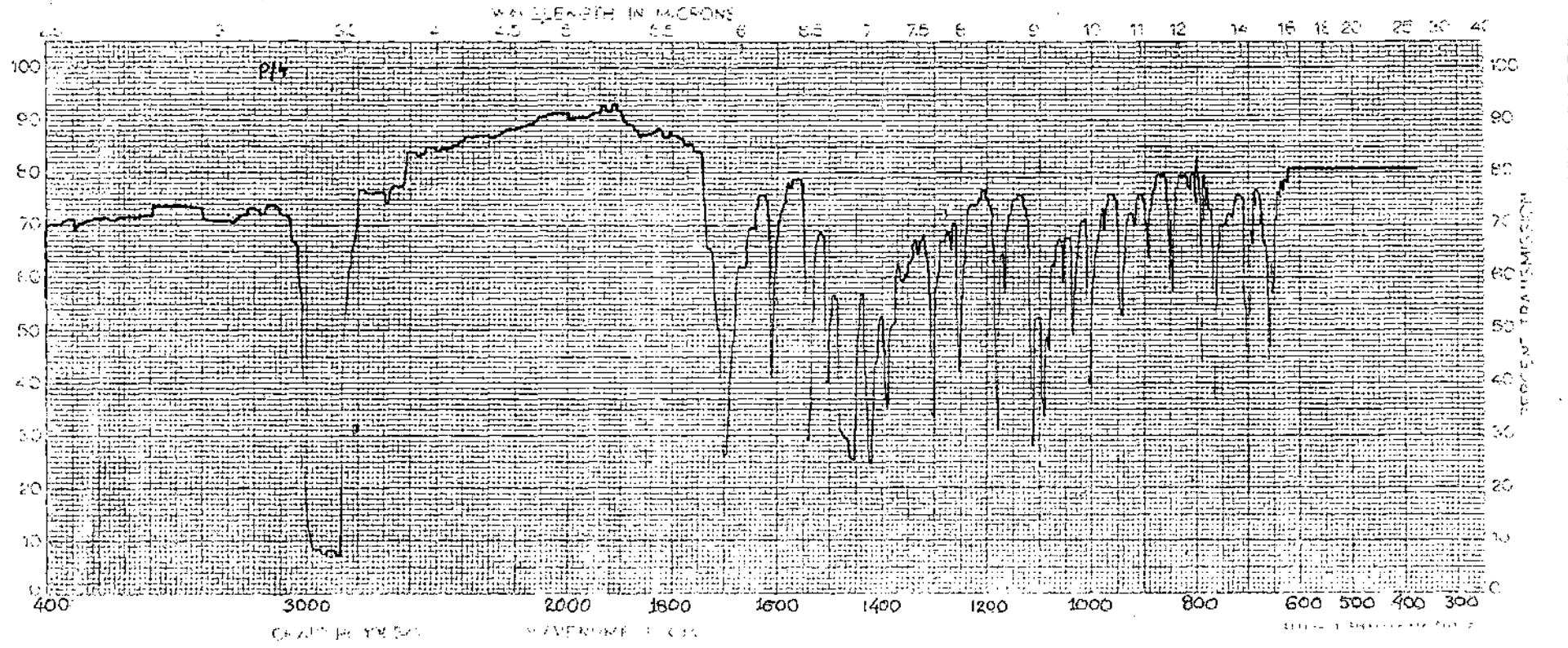
The compound melted at 195-96°C.

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

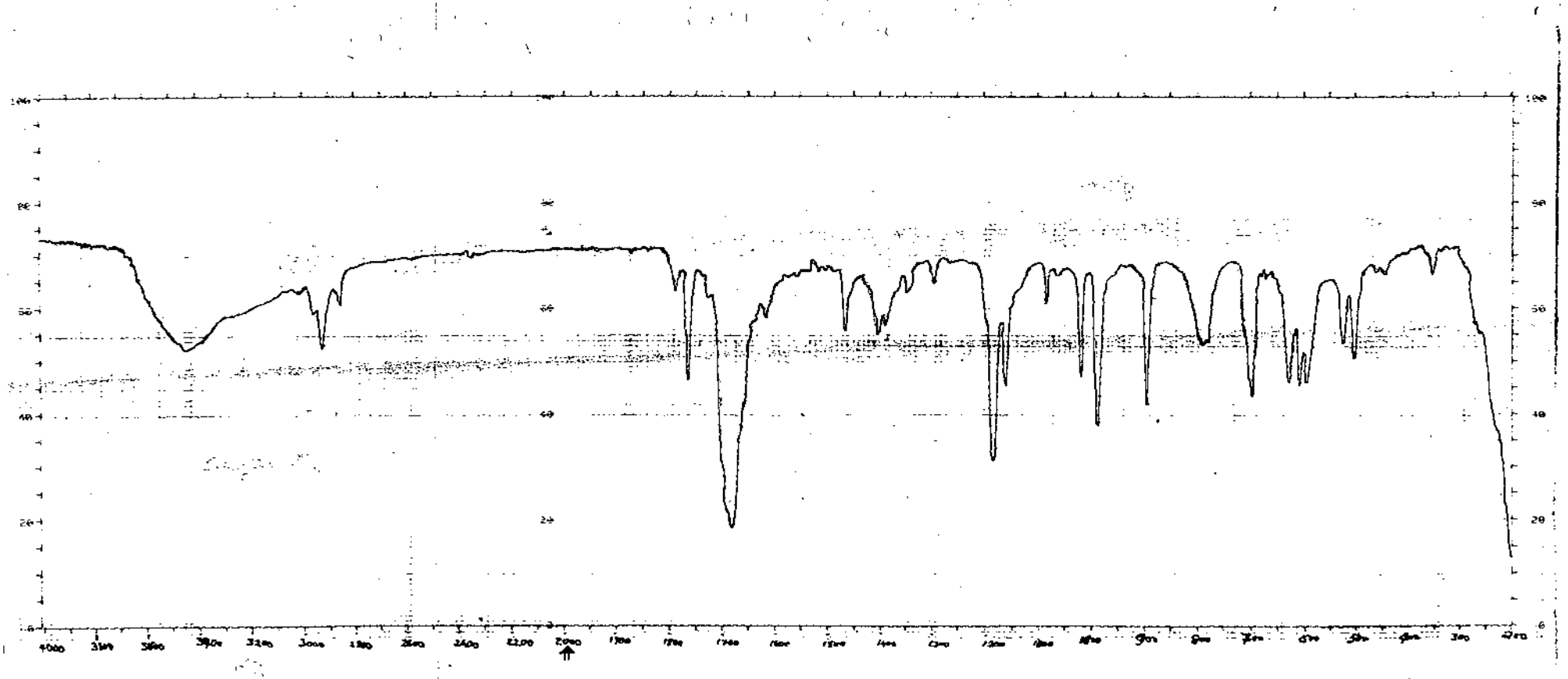
Found :	C 37.74	H 2.95	N 4.10	Sn 37.12
Calcd :	C 37.61	H 3.13	N 4.38	Sn 37.30

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

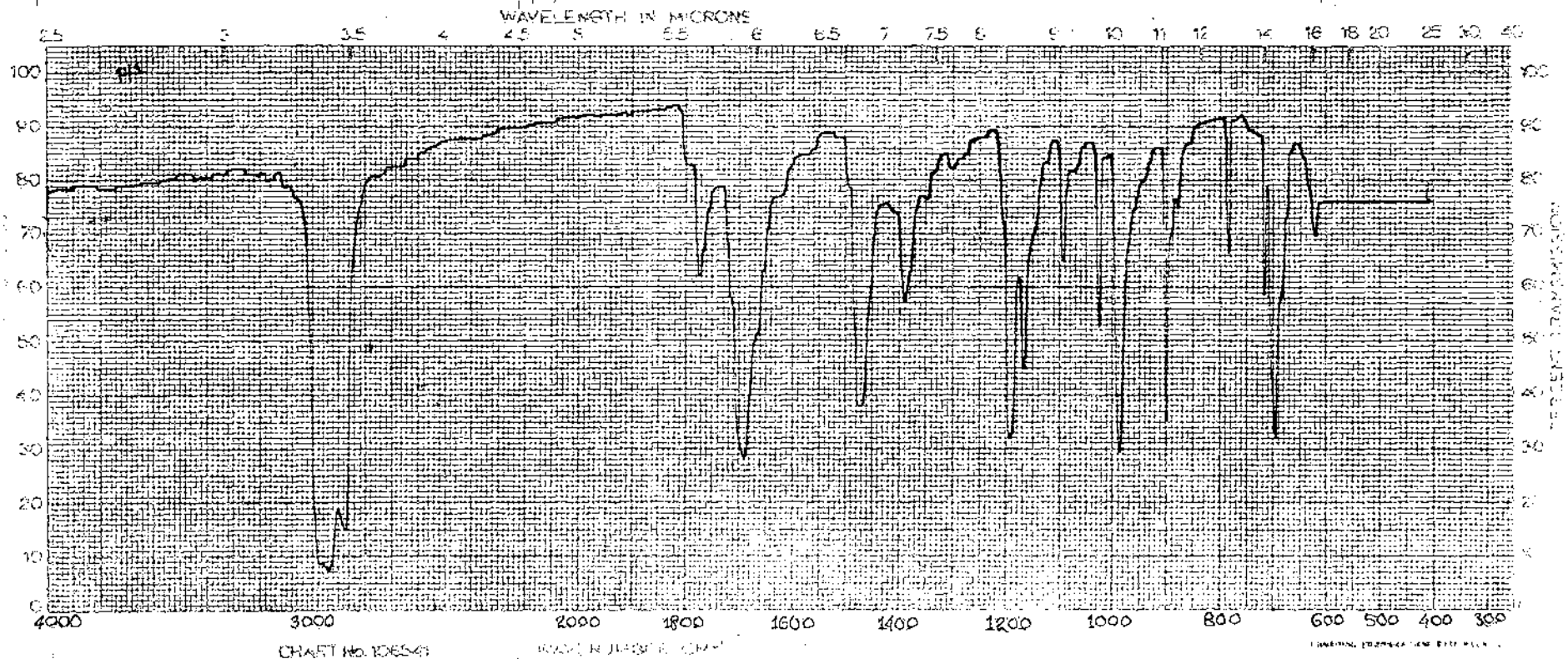
1763(m), 1677(s), 1181(s), 1158(m), 1083(w), 1077(m), 984(s), 892(s), 786(m), 776(m), 696(m), 671(m), 627(m), 607(m), 594(m), 521(m), 500(m), 496(w), 441(w), 351(w).

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

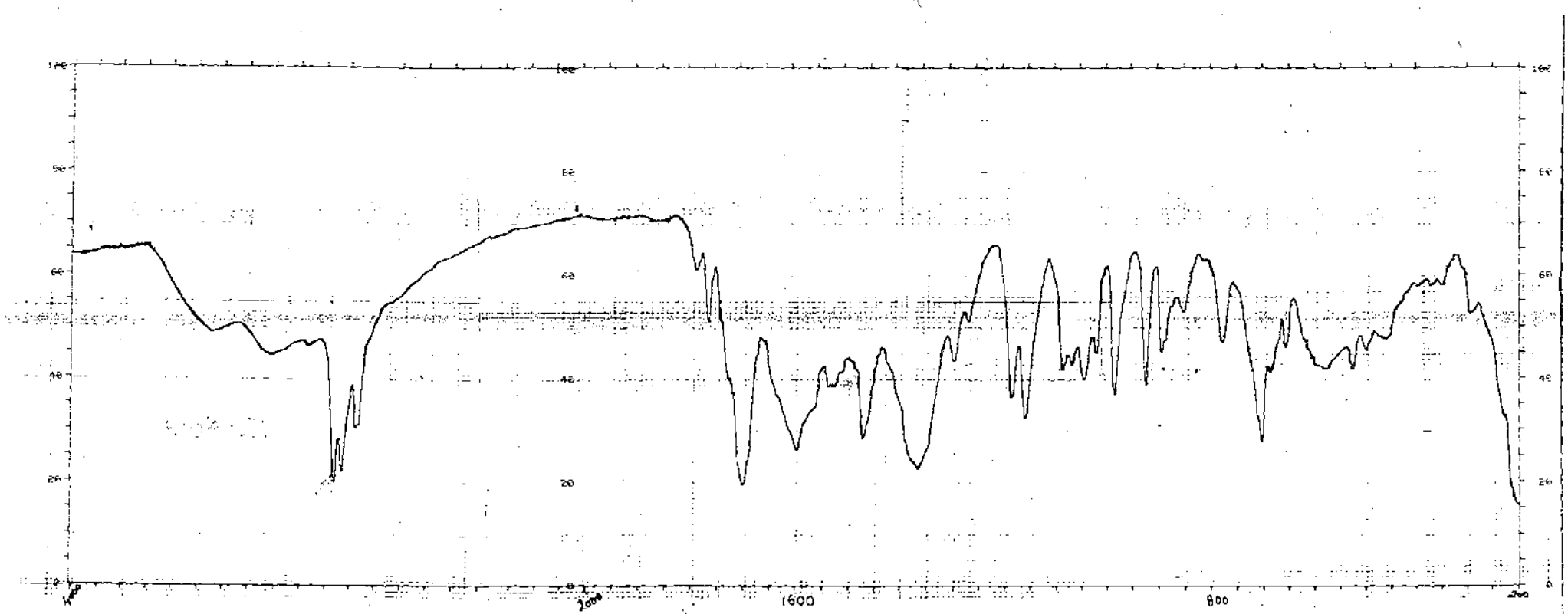
A mixture of dibutyl tin oxide (996 mg; ~4 m.moles) and N-hydroxy phthalimide (652 mg; ~ 4 m.moles) was taken in a 250 ml round bottom flask. 150 ml benzene was added to it. The mixture was refluxed for 4 hours equipped with Dean Stark Water Separator.



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 $C_{32}H_{44}O_7N_2Sn_2$:

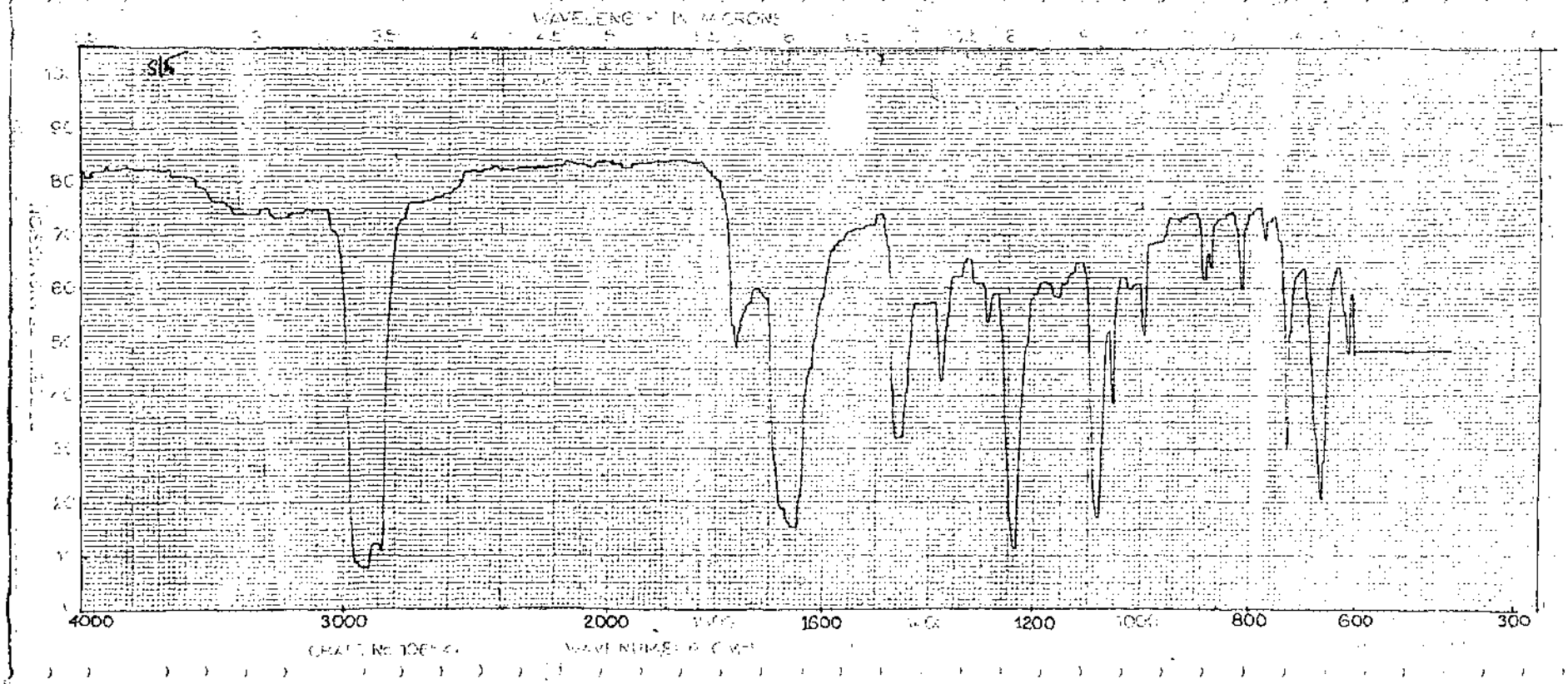
Found	:	C 47.77	H 5.65	N 3.43	Sn 29.62
Calcd	:	C 47.64	H 5.45	N 3.47	Sn 29.52

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

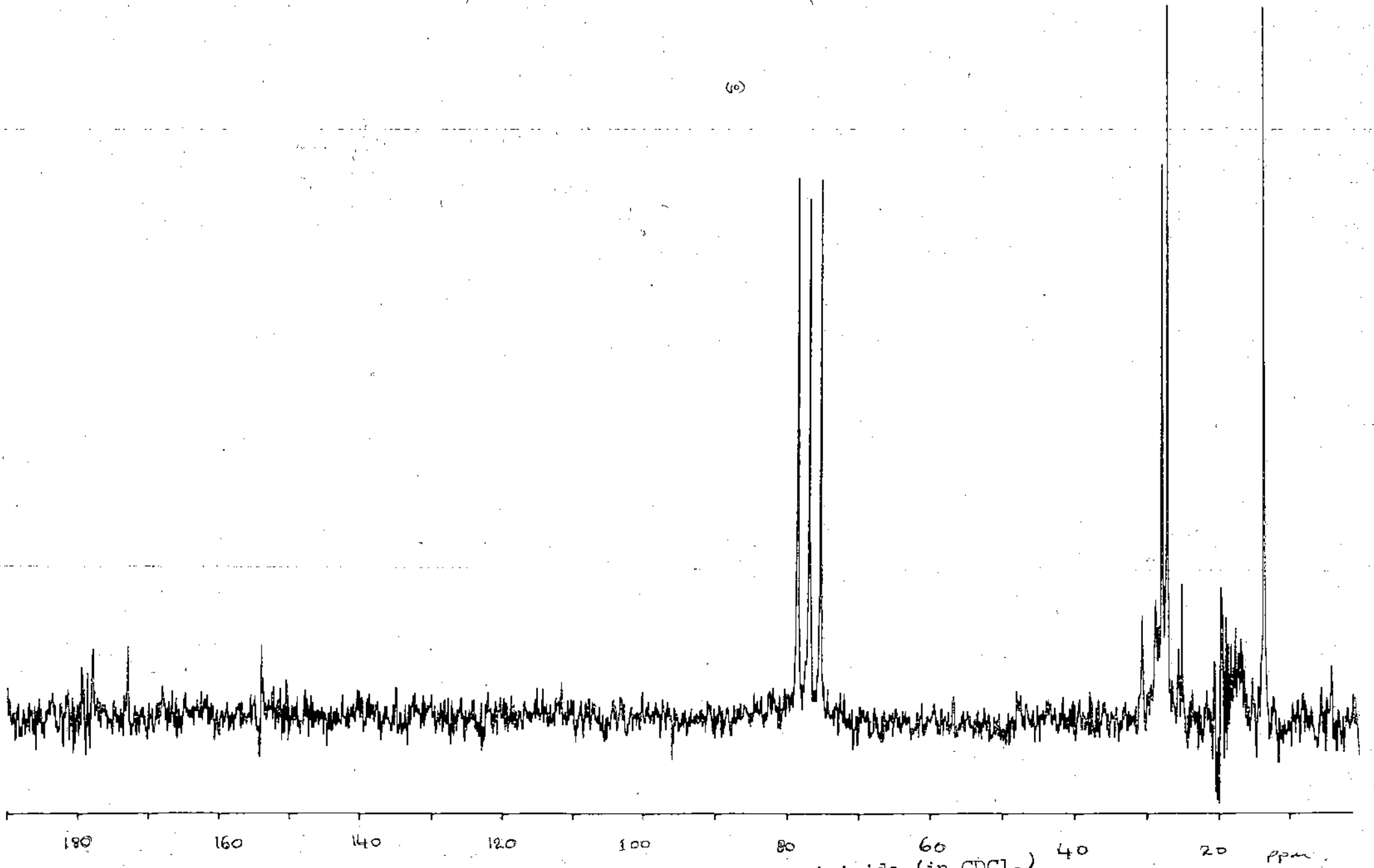
1761(m), 1697(s), 1359(s), 1292(m), 1264(w), 1182(m), 1156(s), 1082(m), 1040(m), 1016(m), 980(m), 921(m), 890(w), 776(m), 700(s), 684(m), 654(m), 576(m), 522(m), 497(w), 460(w), 397(w), 371(w), 384(w), 289(w).

12. Tri butyl tin N-hydroxy succinimide

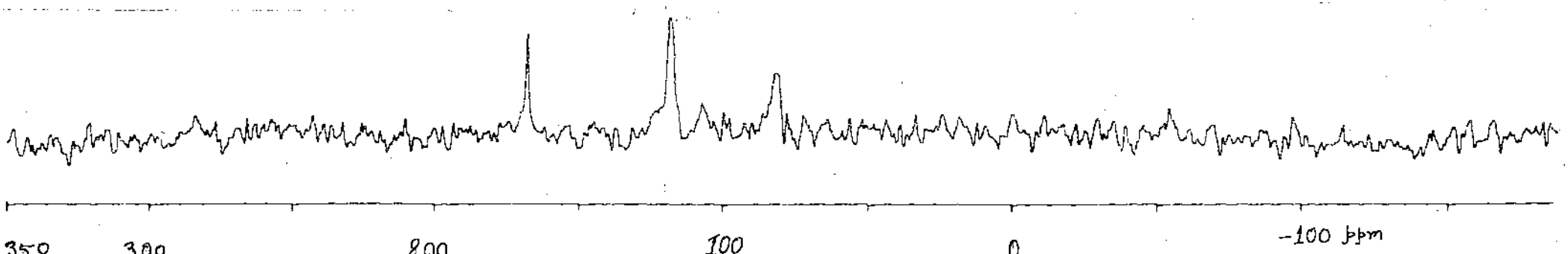
N-Hydroxy succinimide (460 mg; ~ 4 m.moles) and bis tributyl tin oxide (1.192g; ~ 2 m.moles) were taken in a round bottom flask, 150 ml benzene was poured in it. The mixture was refluxed for 4 hours with water separator. The reaction mixture was cooled and filtered. The filtrate was concentrated to about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

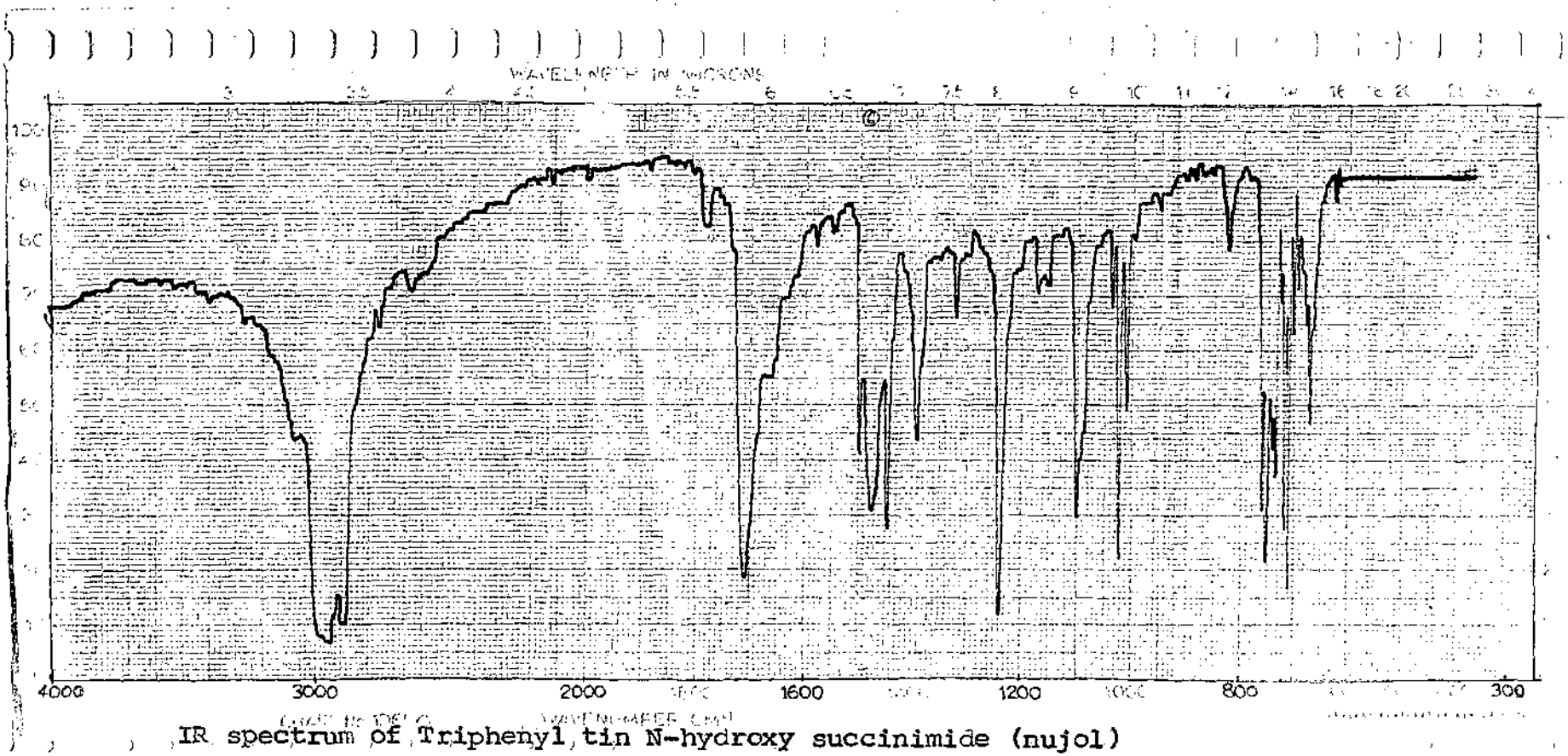
The ^{1}H, ^{13}C and ^{119}Sn NMR spectra indicated impure nature of the compound.

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).

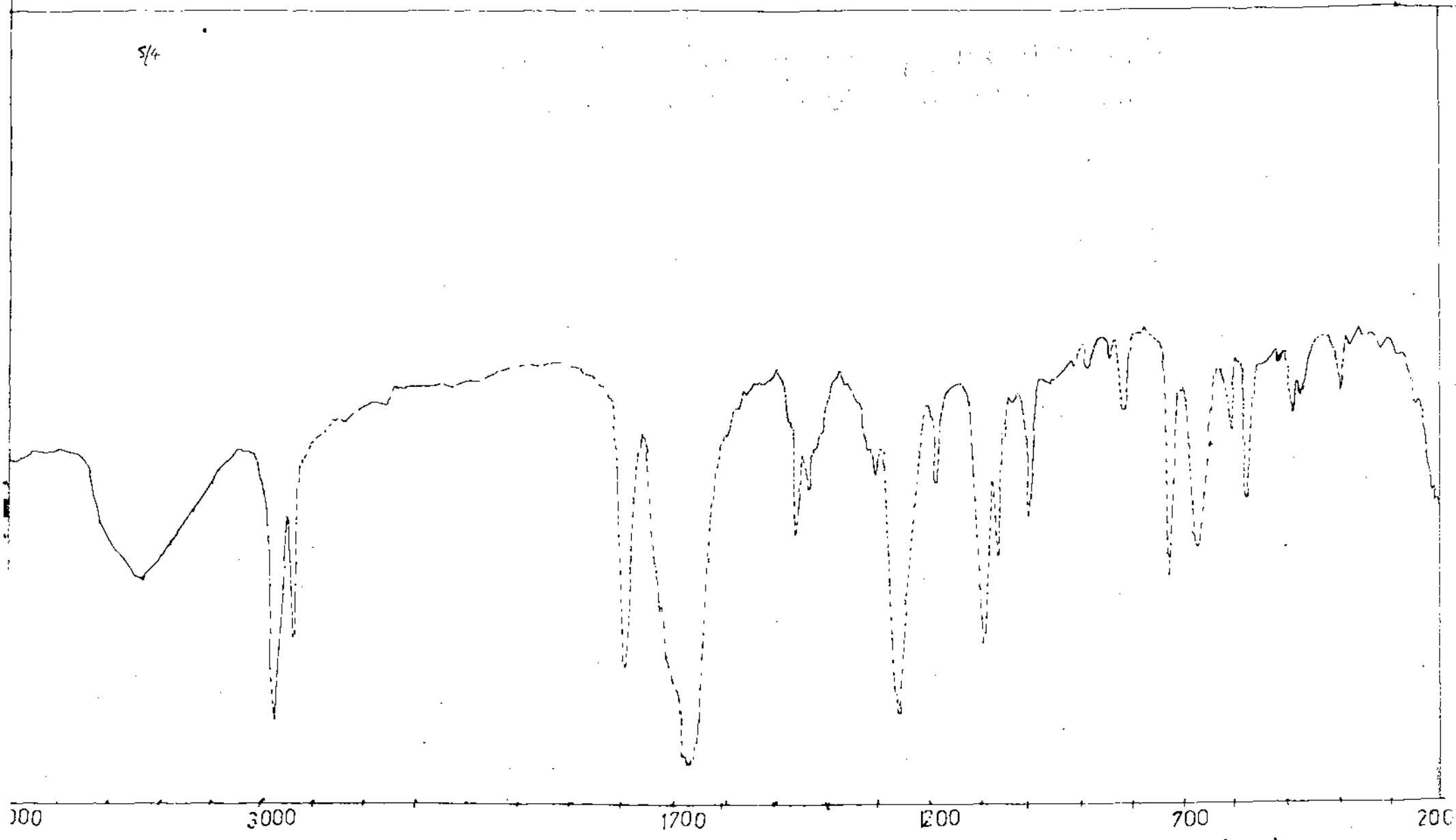
14. Tetracyclohexyl 1:3 di N-hydroxy succinimido distannoxane (Polymeric)

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.

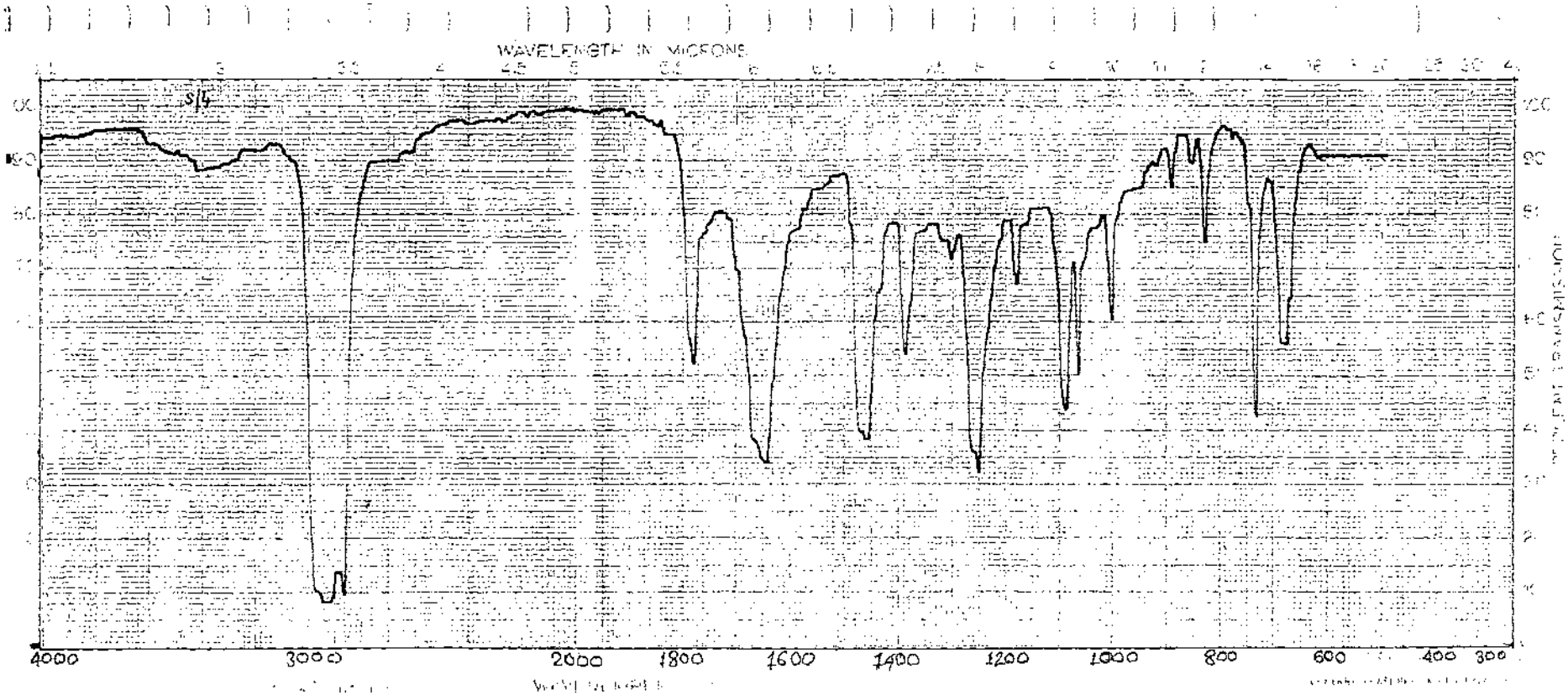
(Yield = ~50%)

% 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%)

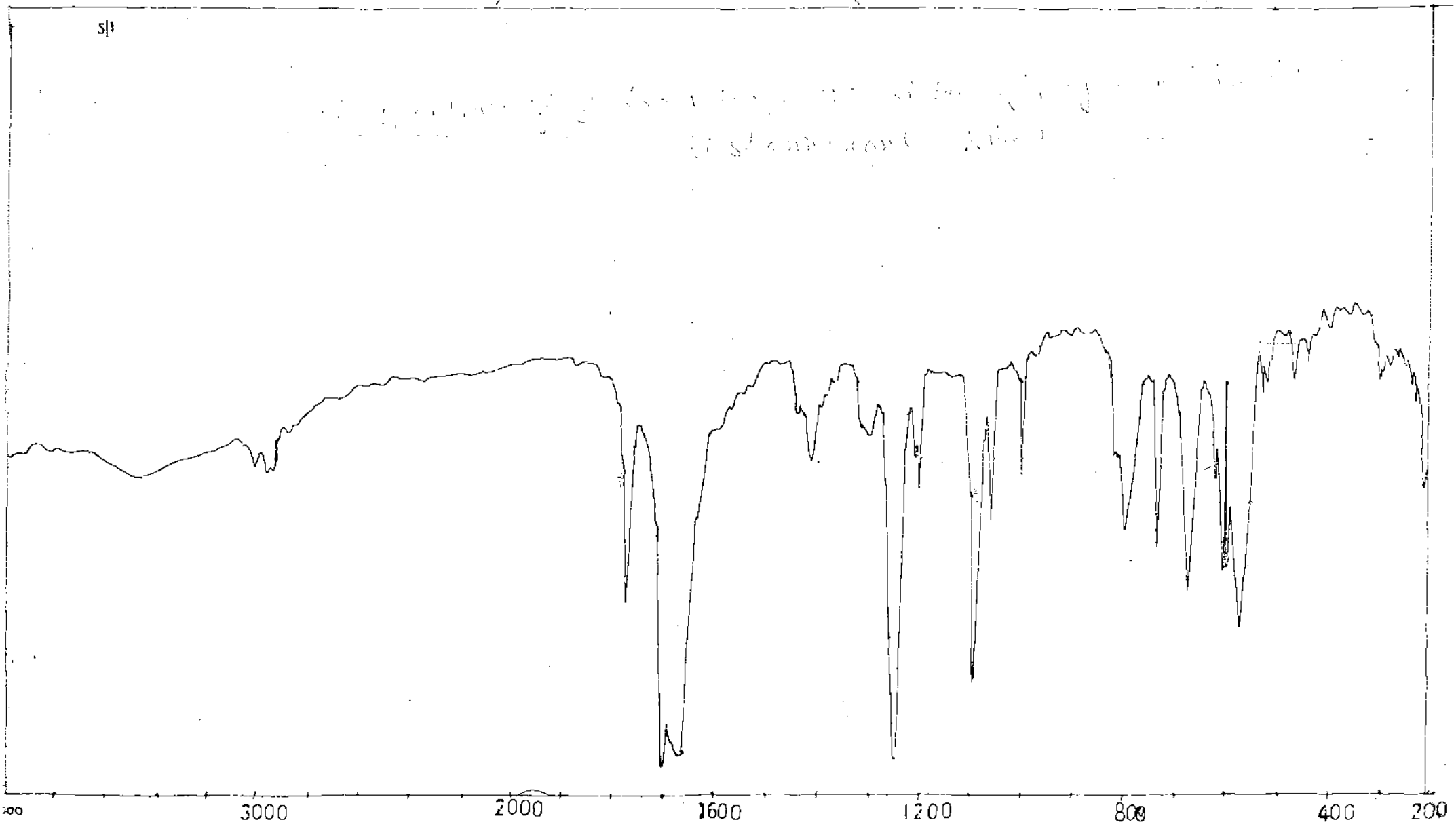
The compound decomposed at 189-90°C.

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

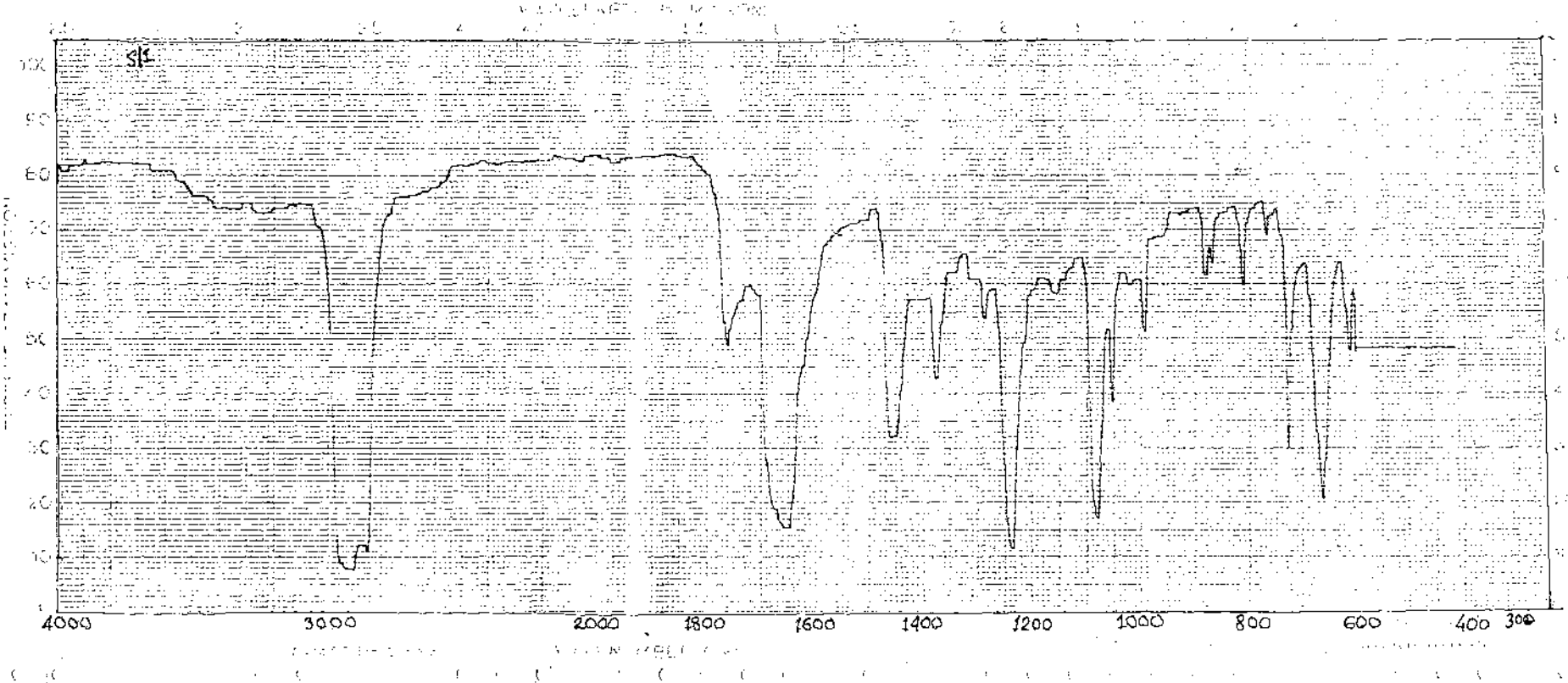
Found :	C 26.43	H 3.30	N 5.21	Sn 44.18
Calcd :	C 26.56	N 3.69	N 5.16	Sn 43.91

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 $C_{24}H_{44}O_7N_2Sn_2$:

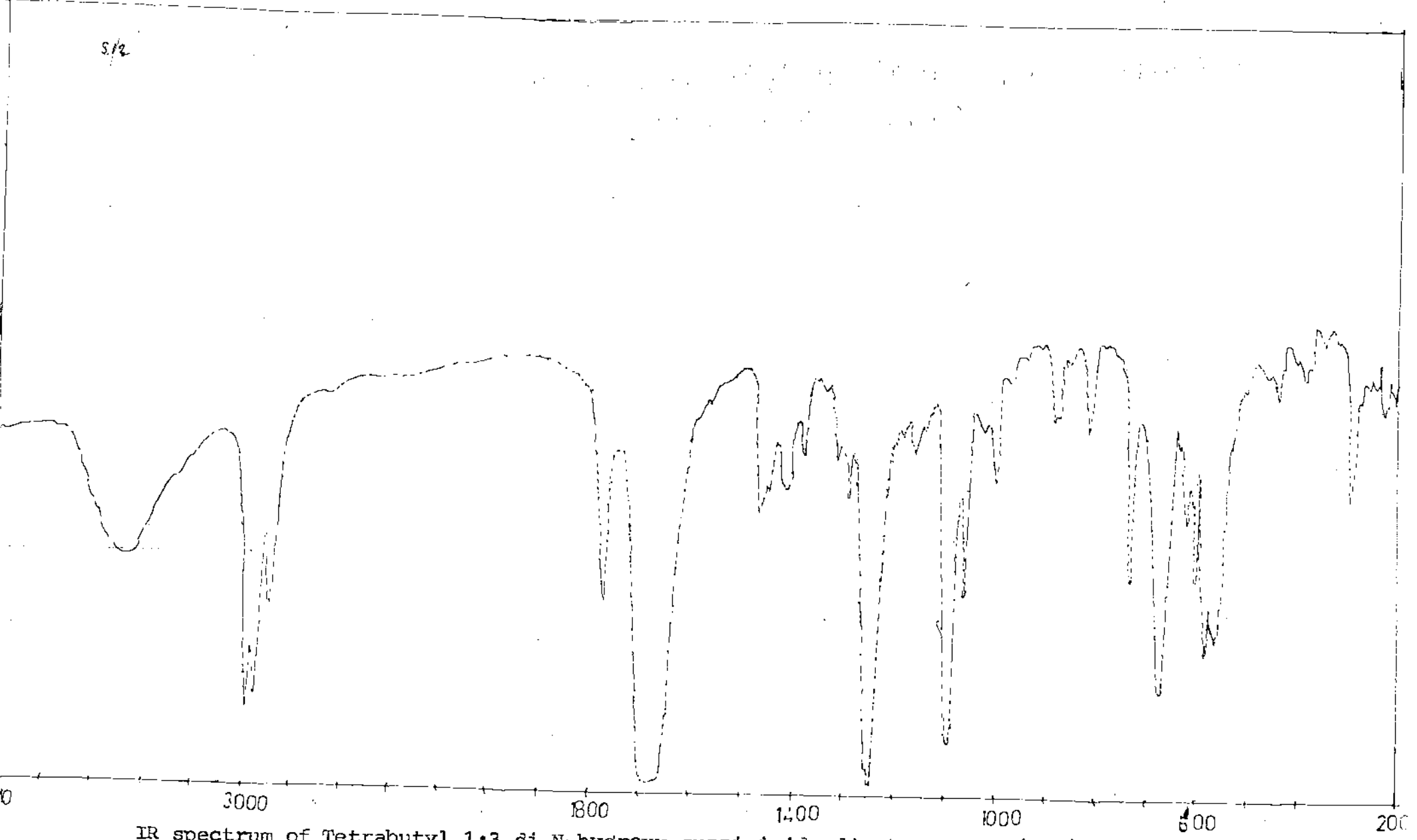
Found :	C 40.49	H 6.06	N 3.74	Sn 33.17
Calcd :	C 40.56	H 6.19	N 3.94	Sn 33.52

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

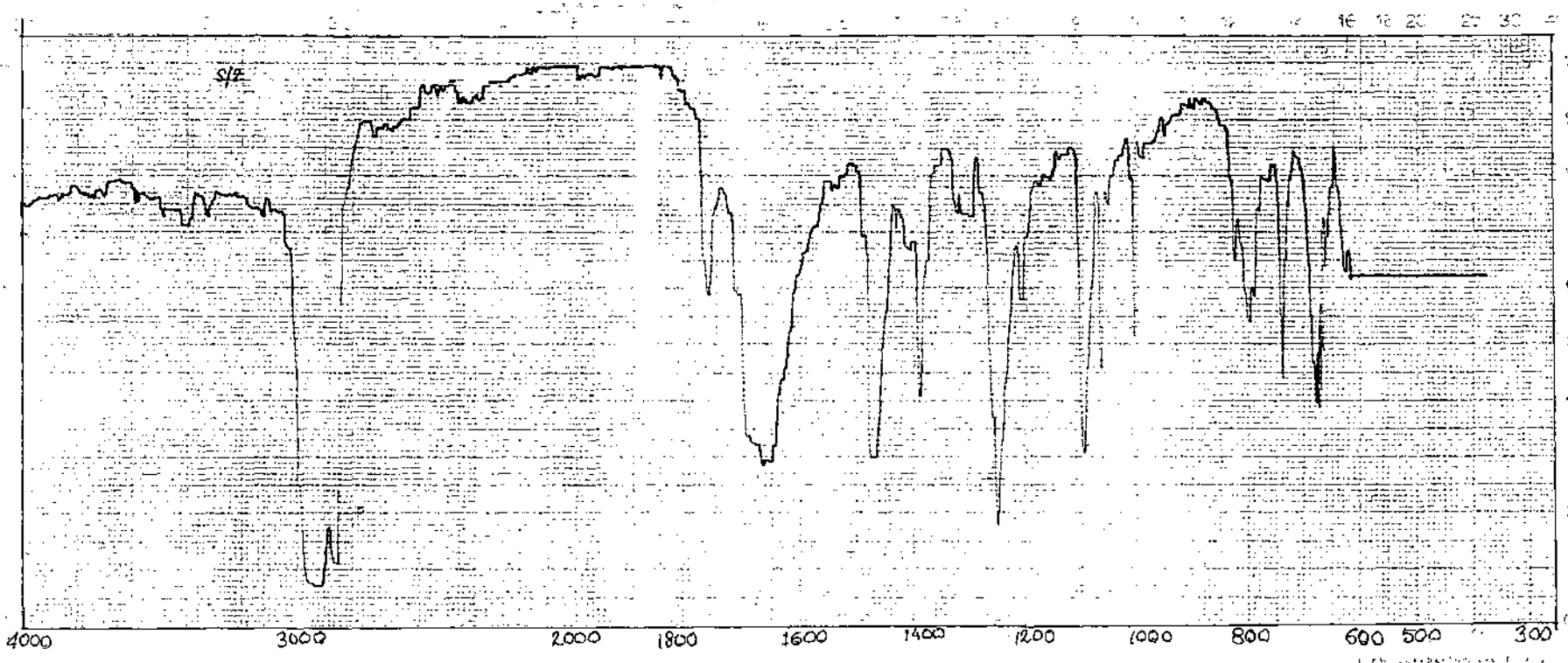
1780(s), 1690(s), 1240(s), 1090(s), 1000(m), 890(m), 820(m), 735(m), 670(s), 620(m), 580(m), 560(s), 440(w), 380(w), 300(w).

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

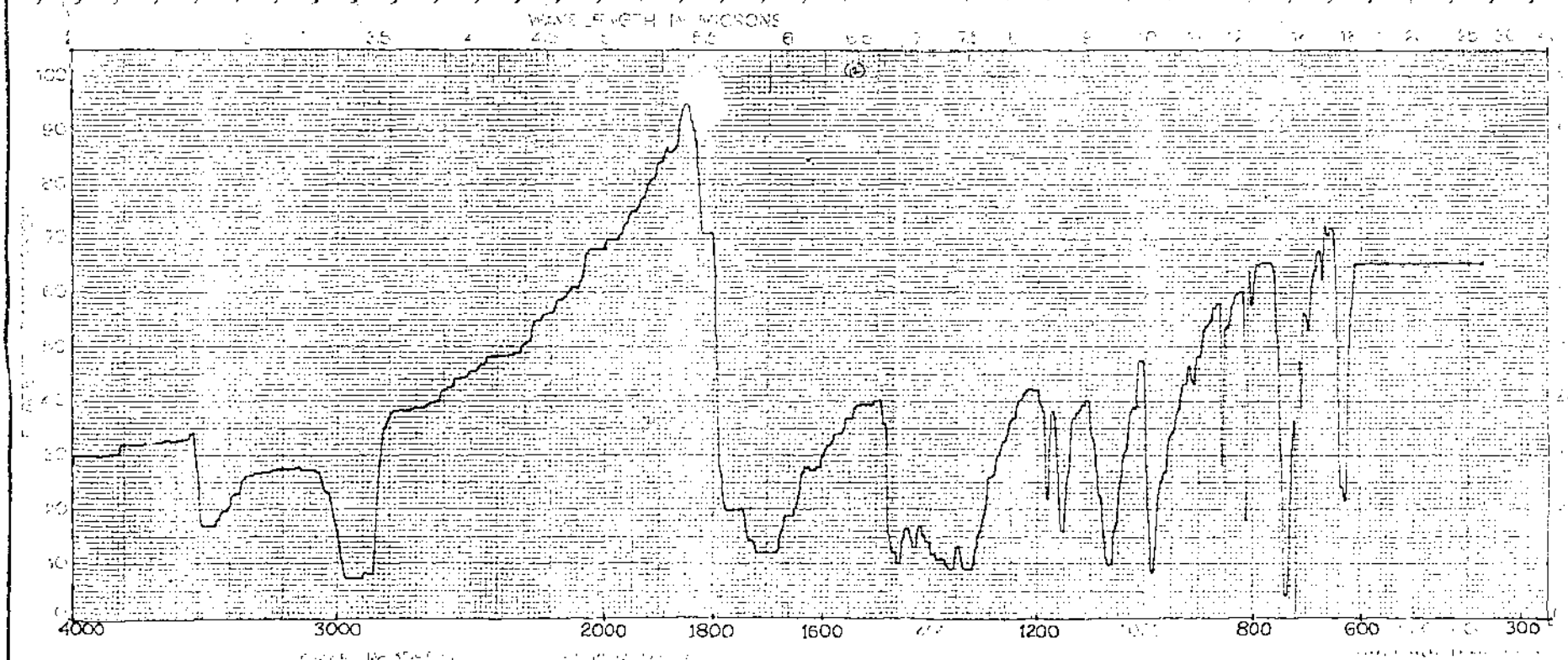
Compound	Molecular weight	
	Found	Calcd (for monomer)
Tributyl tin N-hydroxy phthalimide	446	452
Triphenyl tin N-hydroxy phthalimide	501	512
Tricyclohexyl tin N-hydroxy phthalimide	555	530
Tetrabutyl 1:3 di N-hydroxy phthalimido distannoxane	478	796
Triphenyl tin N-hydroxy succinimide	442	464
Tetrachyclohexyl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

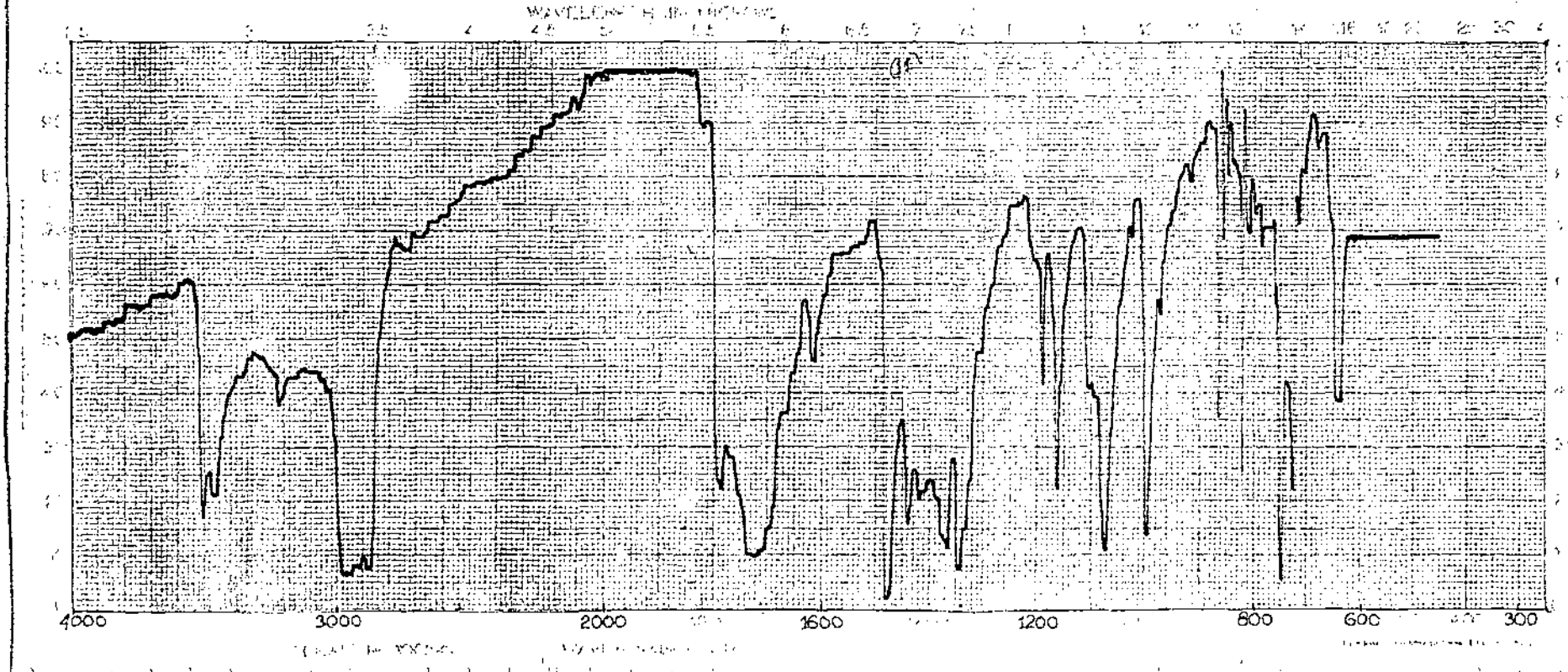
Reactions of N-(hydroxy methyl) phthalimide with diorganotin oxides

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 :

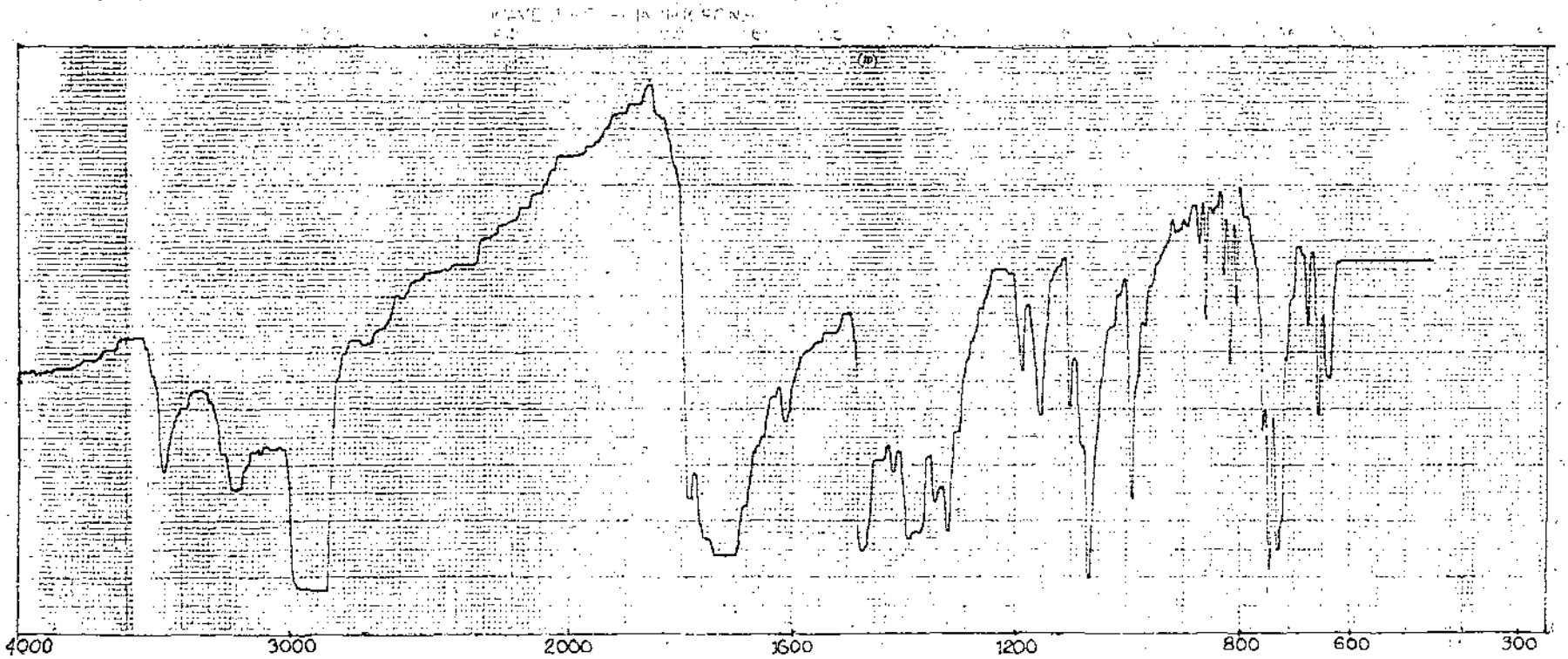
Reaction of dibutyl tin oxide and N-(hydroxy methyl) phthalimide was also carried out in 1:1 molar ratio in refluxing benzene for four hours. A white crystalline product was isolated (mp 190-192°C). The product was washed with chloroform and dried. The elemental analyses gave the following data.

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

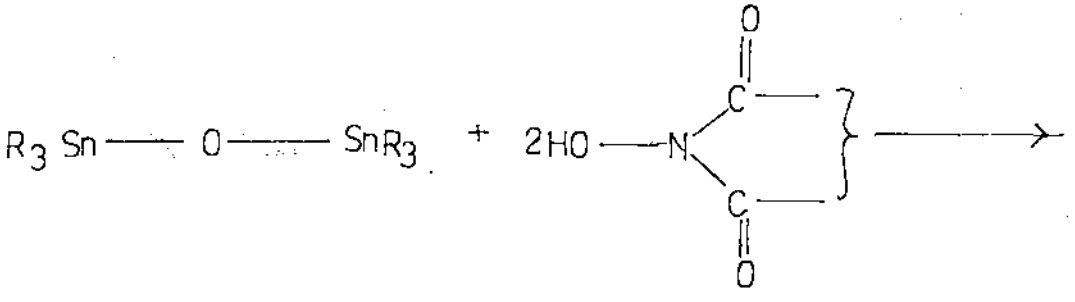
bis (Triorganotin) oxides or polymeric diorganotin oxides generally react with bidentate ligands (H_nL) like β-diketones, 8-hydroxy quinolines, substituted hydroxamic acids, diphenyl carbazones, diphenythiocarbazones etc in the following manners:

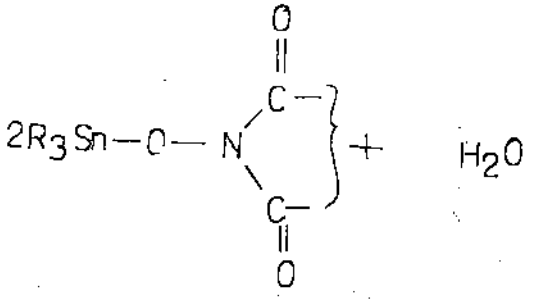
$$R_3Sn - O - SnR_3 + 2\ H_nL \longrightarrow 2R_3SnL + nH_2O$$

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

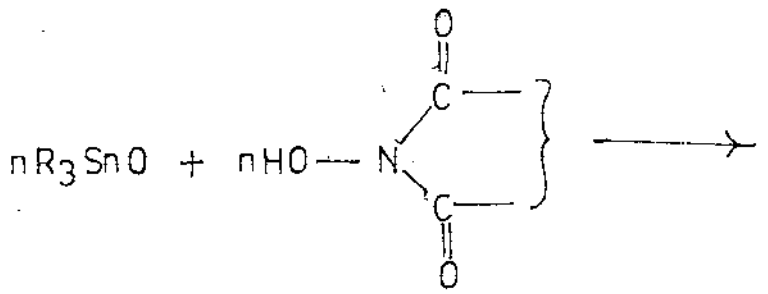
(L = chelate ligands)

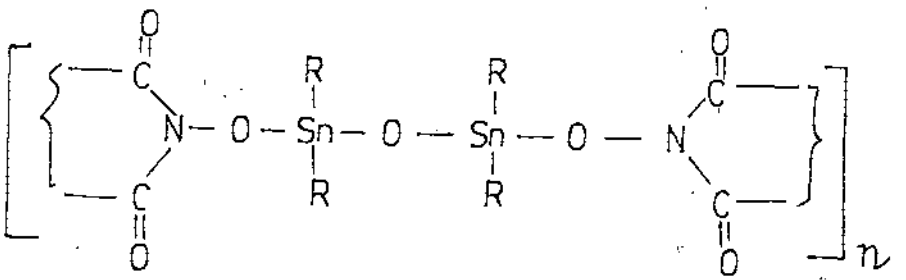
During the reactions between bis (triorganotin) oxides with N-hydroxy succinimide or N-hydroxy phthalimide, it was observed that the triorganotin derivatives of these ligands do not form any chelated species nor these derivatives contain any Sn-O-Sn bonds. These reactions can be illustrated as follows:





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.

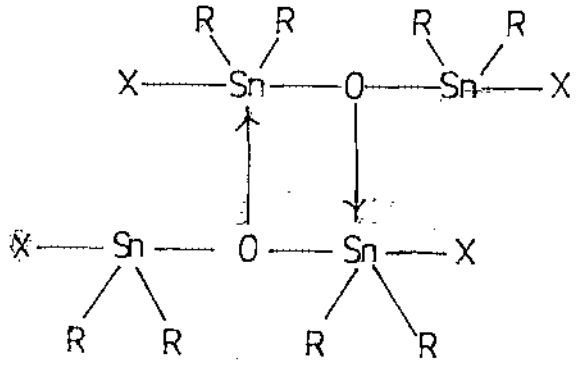




The ^{119}Sn spectra of some of the diorganotin derivatives indicated two types of tin atoms in the compounds.

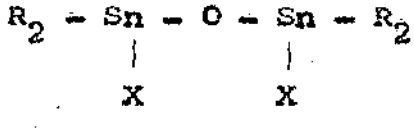
Organo stannoxanes containing Sn-O-Sn bonds are known for last few decades. A number of organo stannoxanes have been reported (138). The characteristic properties due to the Sn-O-Sn bond was discussed by Okawara (139) for tetraalkyl-1,3 di stannoxane $ClR_2SnOSnR_2Cl$ and tetraalkyl 1,3 bis (trimethylsiloxy) 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.

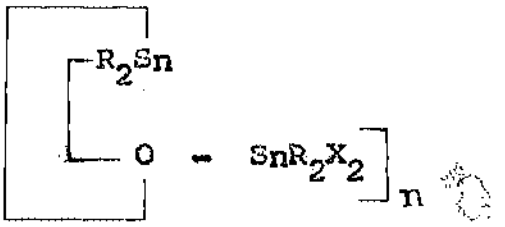


Davies et al (140) reported that the exhaustive hydrolysis of dialkyltin (IV) compounds R_2SnX_2 (X = e.g. halogen or carboxylate) under basic conditions gives the dialkyl tin oxides R_2SnO which are insoluble, amorphous, infusible solids and are usually regarded as high polymers. If however the reaction 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.

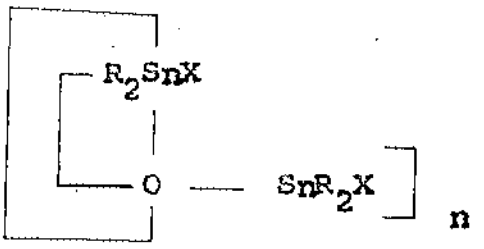
The following structure for $R_4Sn_2X_2O$, was assumed by Pfeiffer & Brach (141).



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

($XR_2SnO-SnR_2X$)

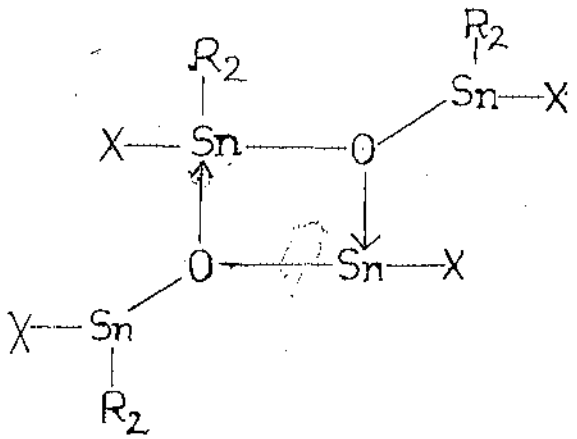
X	R	References
$OSi(CH_3)_3$	$CH_3, C_2H_5, C_3H_7, C_4H_9$	147
F	C_4H_9	148
Cl	$CH_3, C_2H_5, C_3H_7, C_4H_9$	149, 150, 148
Br	C_2H_5, C_3H_7, C_4H_9	150, 148
NCS	C_2H_5, C_3H_7, C_4H_9	148, 151
NCO	CH_3, C_4H_9, C_6H_5	152, 153
OCCR'	CH_3, C_4H_9	149, 150, 154
OC_6H_5	CH_3, C_4H_9	154-156
OC_6H_4Y	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.

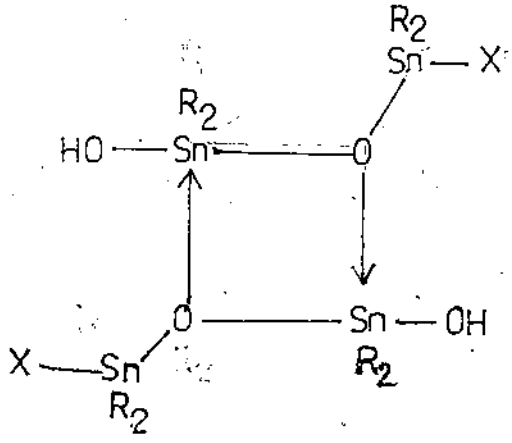
In the dimeric structure of type A distannoxanes there are both tetra coordinated and penta coordinated tin atoms and accordingly, two different kinds of substituents X. This difference is evident in the reaction of $XR_2Sn-O-SnR_2X$ (X = Cl, Br) with an excess of organic base, such as pyridine. One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

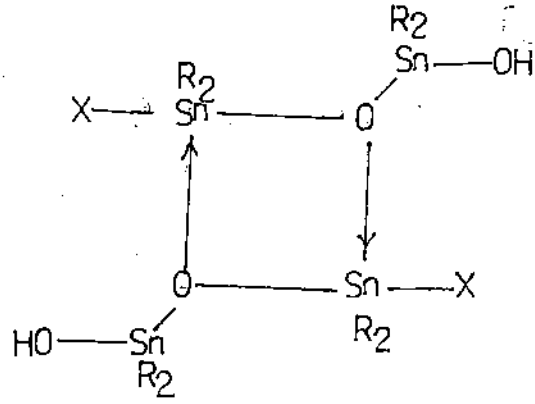
$(C_6H_5O)(C_4H_9)_2Sn-O-Sn(C_4H_9)_2(OC_6H_5)$.

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)

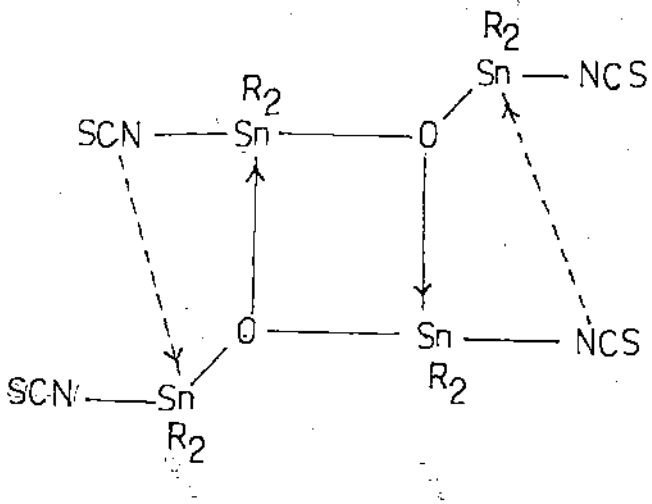


(B)

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.

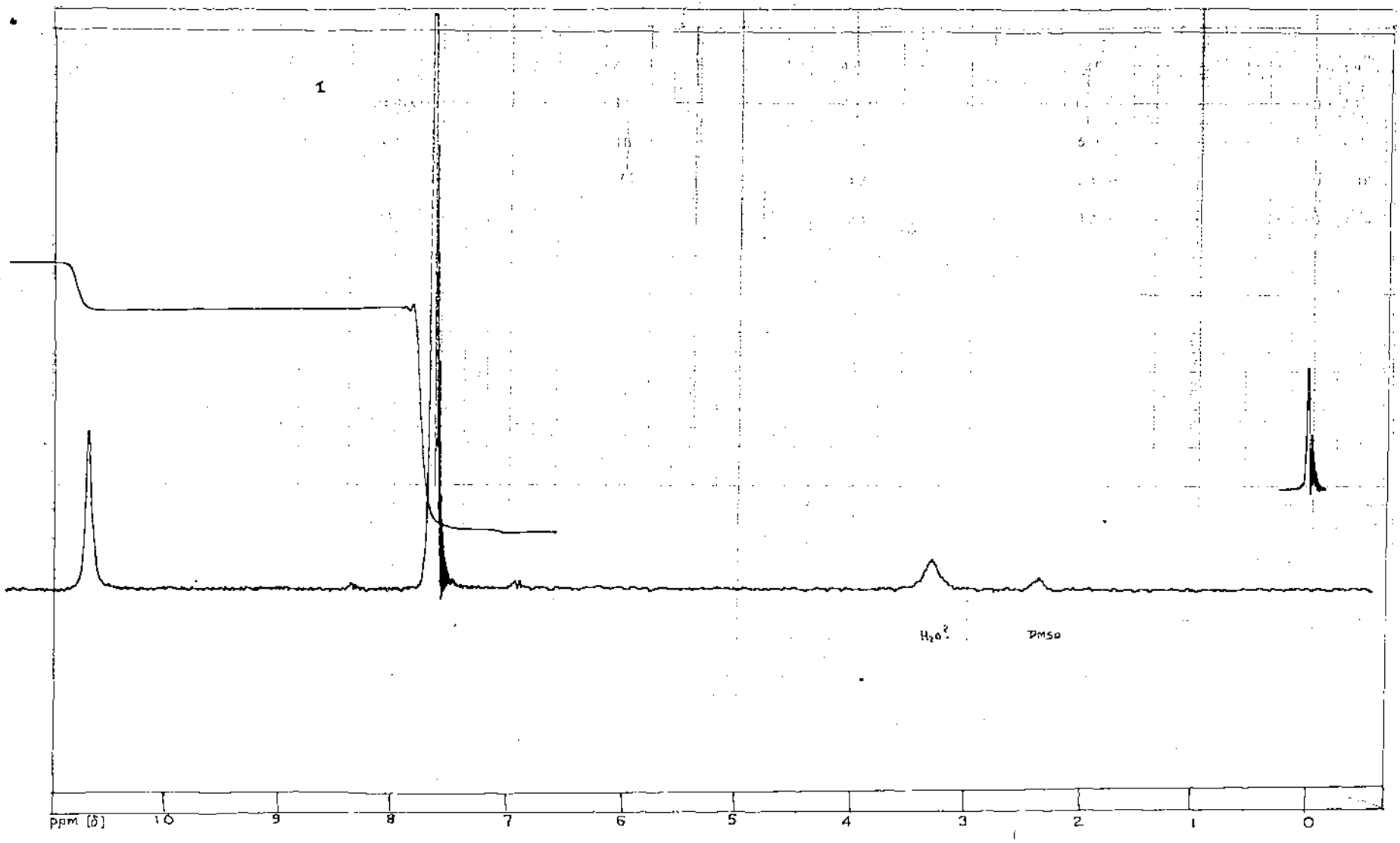
The structure A is favoured upon assumption that, in the partial hydrolysis process from type A compounds, the tin atom which most easily undergoes substitution would be the penta coordinated one (150). Further, the existence of a stable hydroxyl oxygen to the tetra coordinated tin atom similar to that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

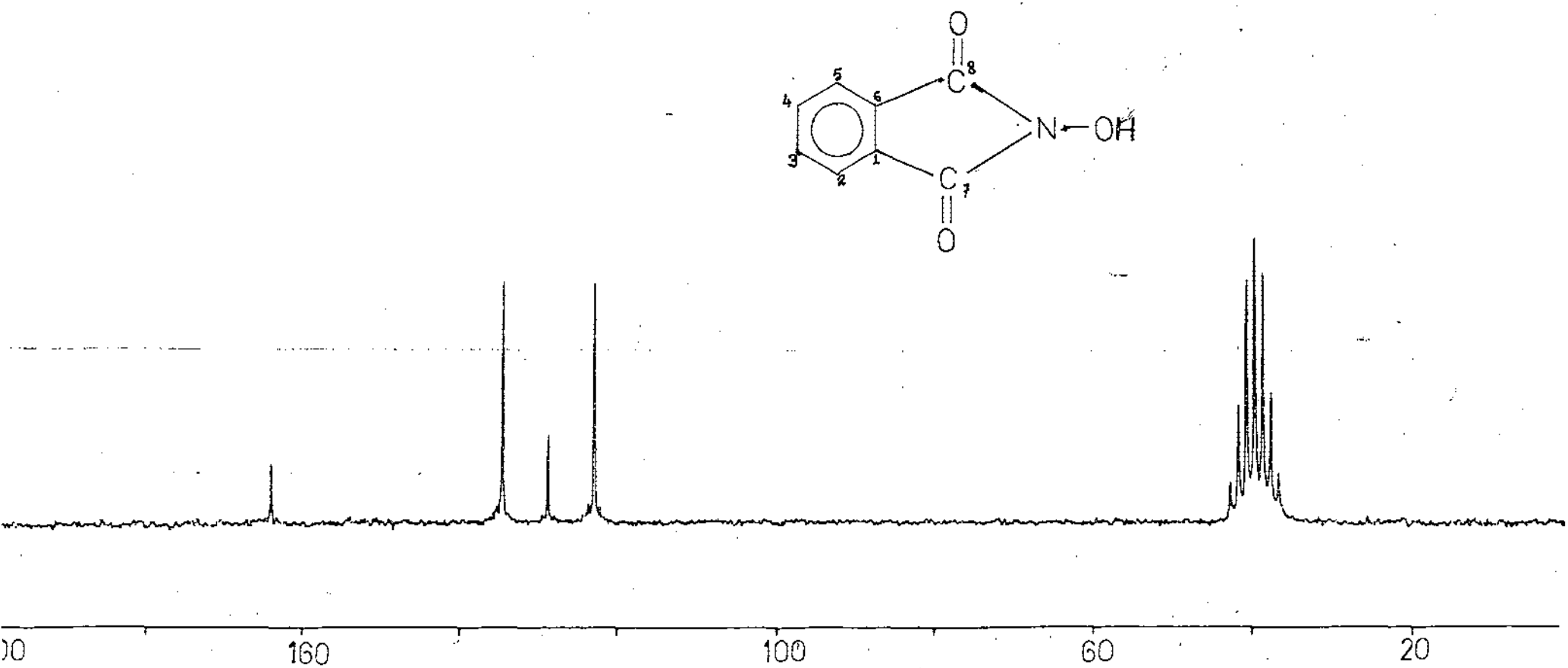


The ladder type structure has been confirmed by an X-ray study of $(CH_3)_3SiO(CH_3)_2Sn\text{-}O\text{-}Sn(CH_3)_2OSi(CH_3)_3$ (162).

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 $C_{20}H_{31}O_3NSn$.

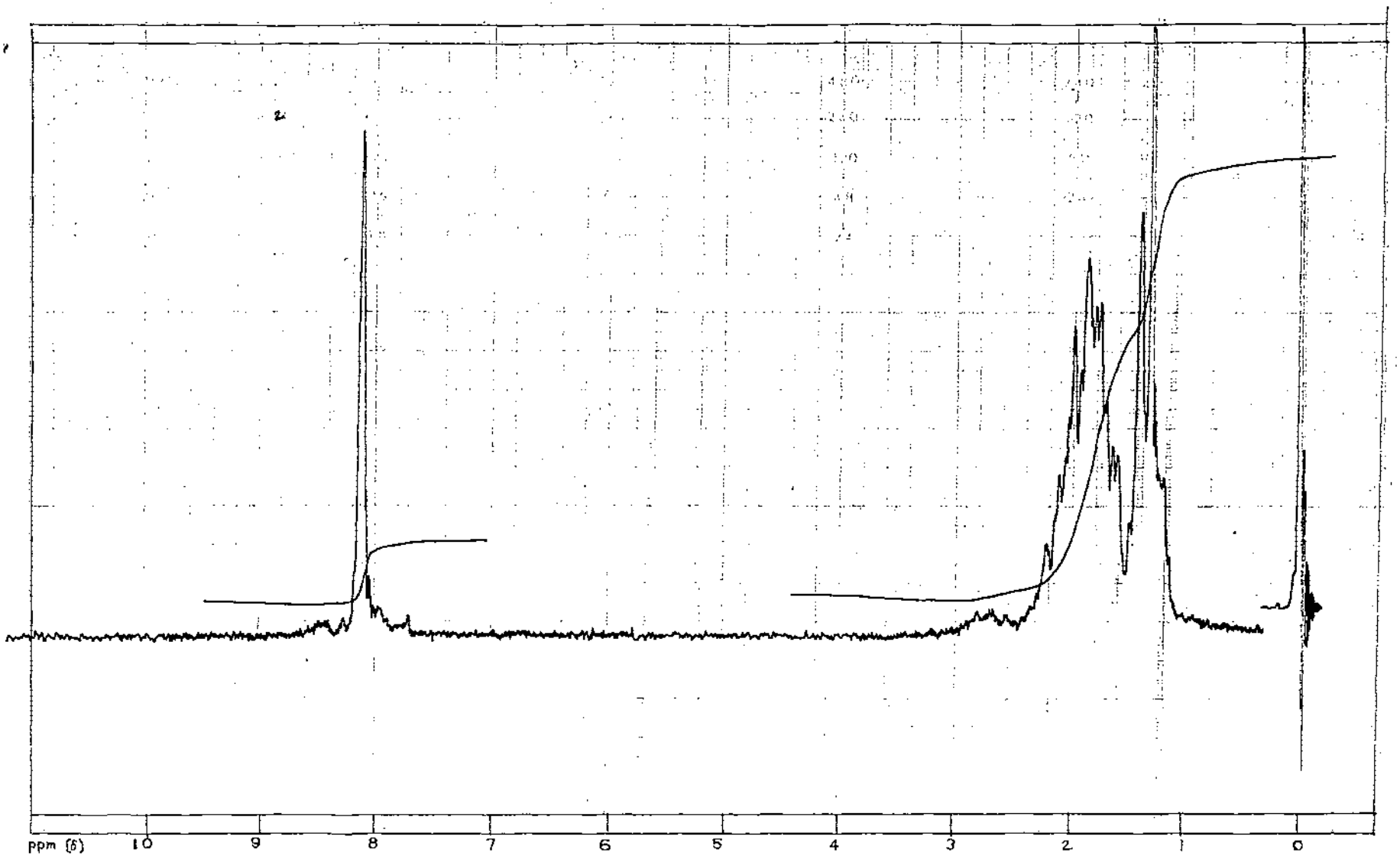
Mol. wt. (Rast Method) Found 446

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.

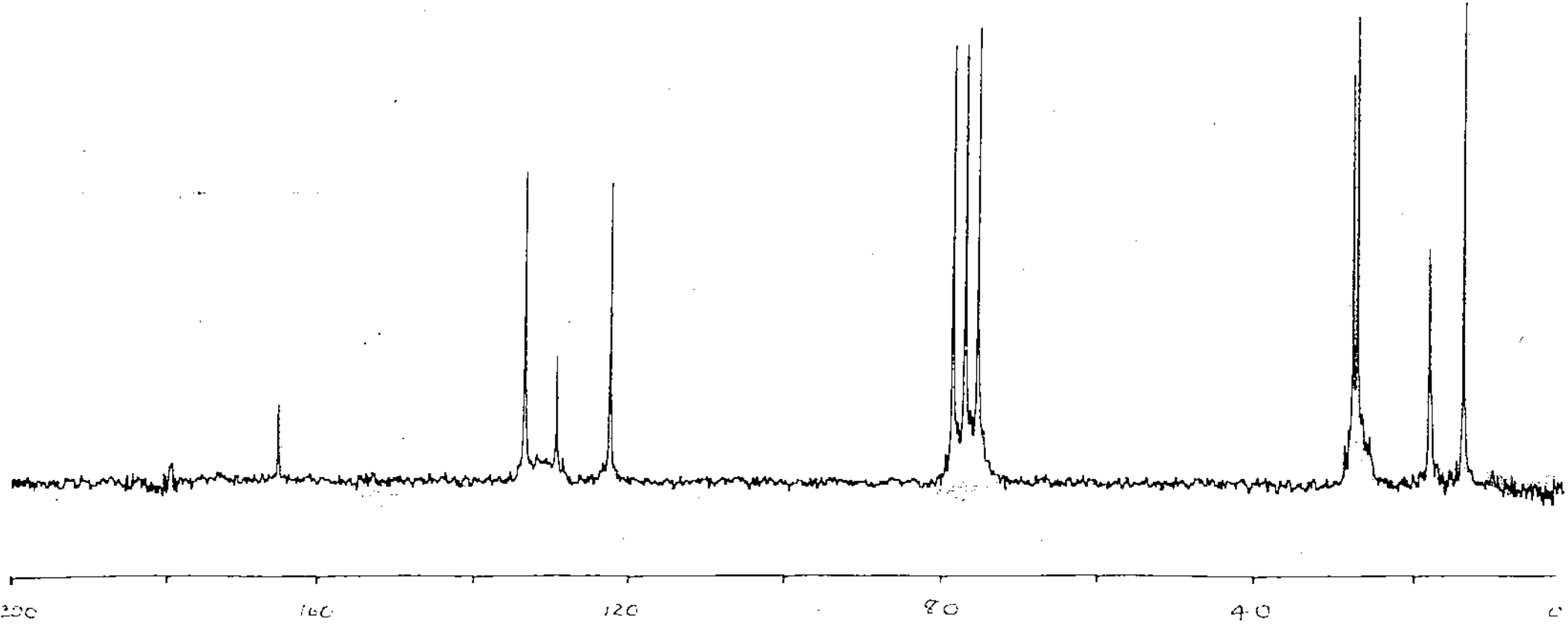
The carbonyl peaks of this compound appeared at 1770 cm^{-1} and 1700 cm^{-1} compared to the carbonyl peaks of N-hydroxy phthalimide, which appeared at 1793 cm^{-1} (s) and 1707 cm^{-1})(v.s.). Though the 1793 cm^{-1} peak of N-hydroxy phthalimide shifted somewhat significantly, the more intense 1707 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.

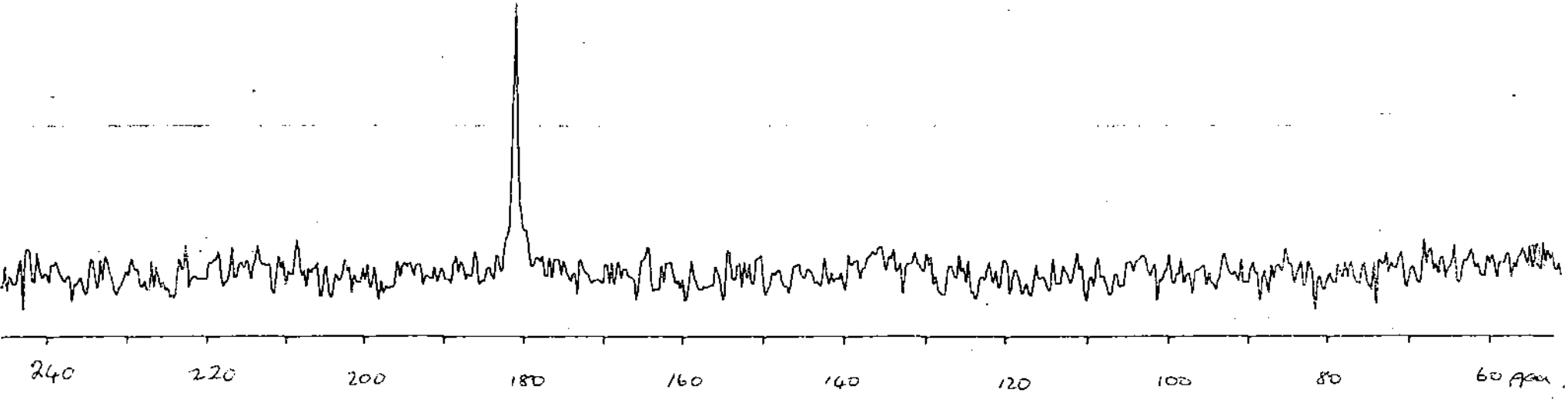
The ^1H NMR spectrum of the compound was recorded at 60 MHz. The methyl protons of the butyl groups appeared at δ 1.38 (9H) while the remaining methylene protons appeared as complex patterns between δ 1.39 - 2.9 (18H). The aromatic protons appeared 7.9 - 8.25 (Ar-4H).



^{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.

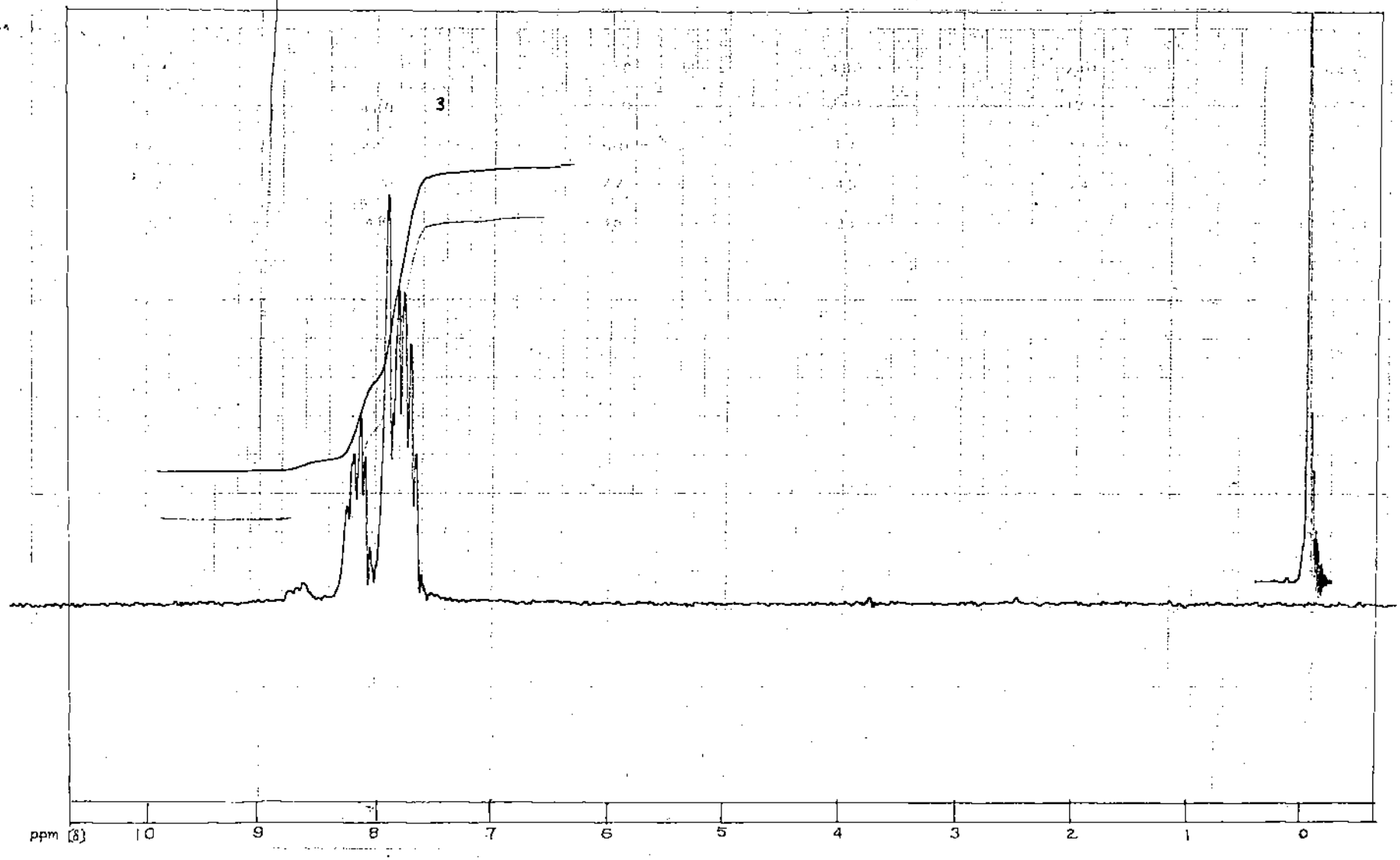
The ^{13}C NMR spectrum and IR spectrum of bis (tricyclohexyl tin) succinyl bis N-phenyl hydroxamate showed strong evidence of chelate formation. In ^{13}C NMR spectrum showed strong shielding effect

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.

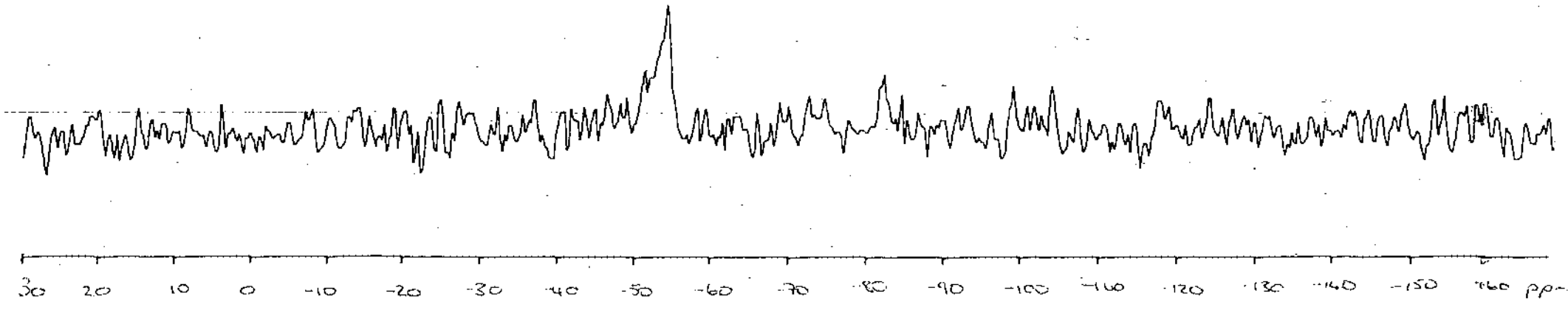
But if we compare the above data with those of the tributyl tin N-hydroxy phthalimide and N-hydroxy phthalimide the question of intramolecular coordination of the carbonyl groups to tin atom probably does not arise. Hence the tributyl tin N-hydroxy phthalimide is not a chelate complex but it is most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

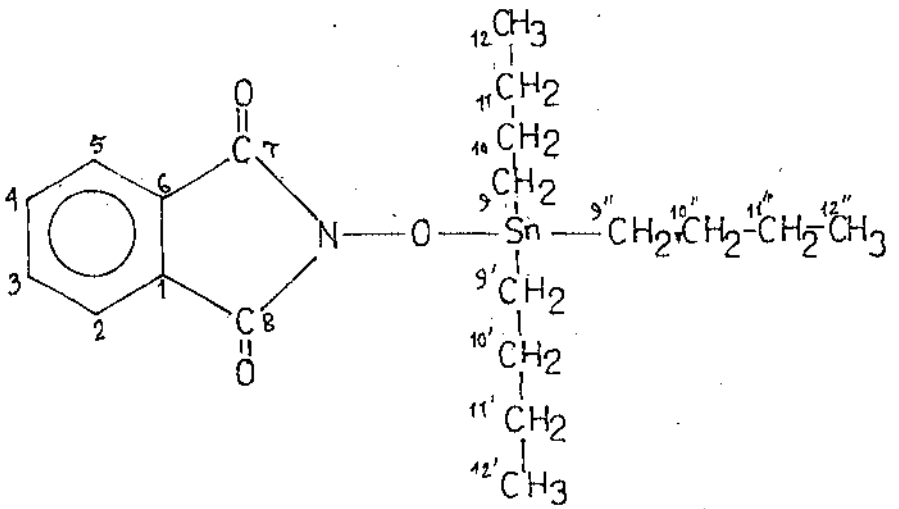
On the basis of the above data the structure of this compound tentatively can be suggested as follows:



^{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

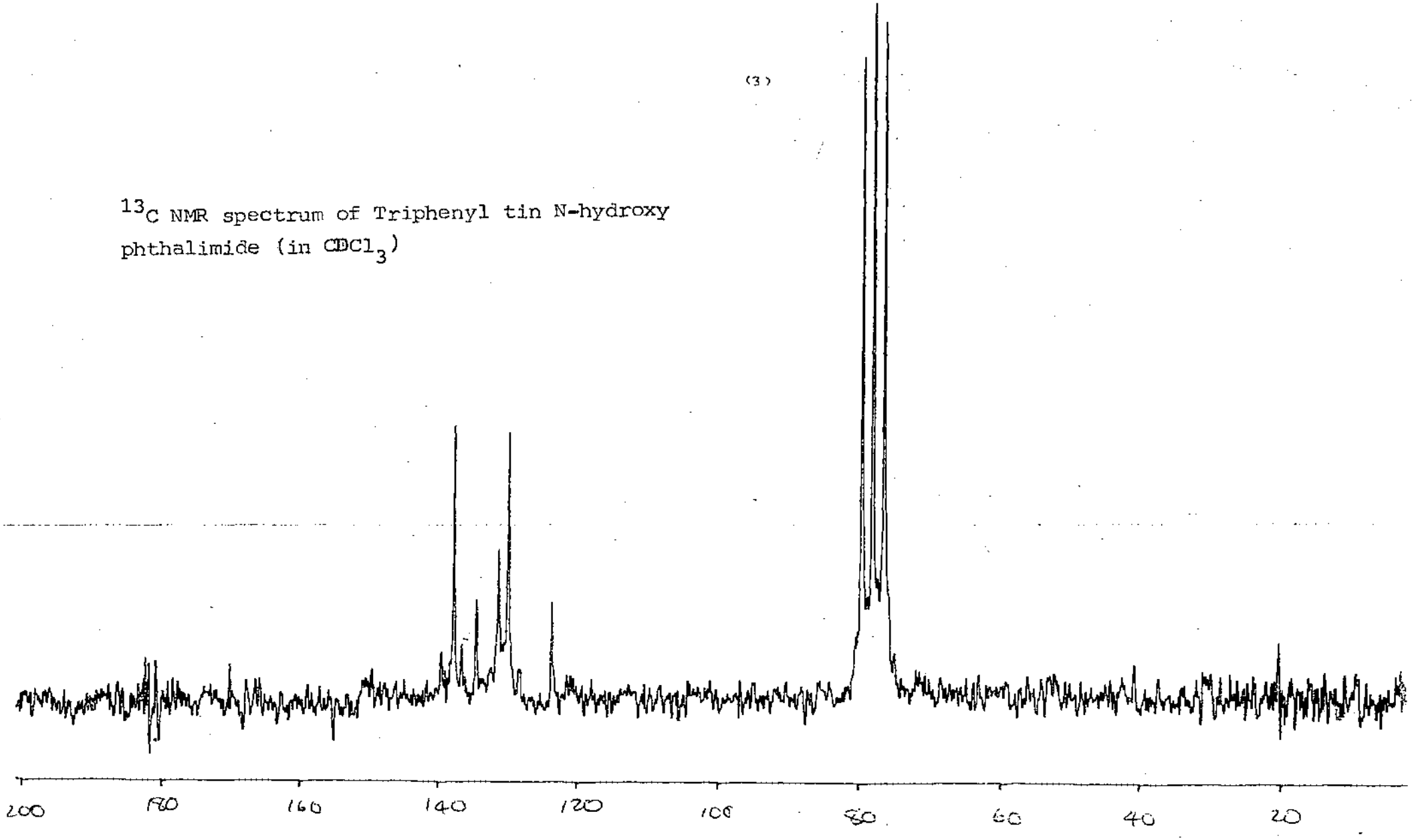
Elemental analyses of this compound showed an empirical formula of $C_{24}H_{19}O_3NSn$.

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 $CDCl_3$)



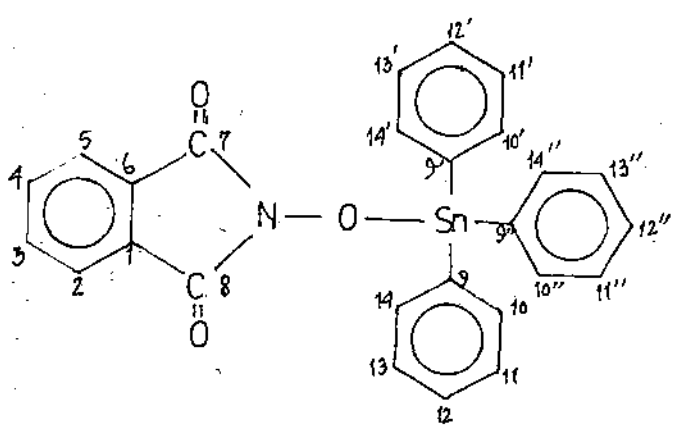
The ^{1}H NMR spectrum showed a group of peaks at δ 7.6 - 8.0; 8.04 - 8.16 and 8.45 - 8.80. It was not possible to assign ligand aromatic protons and tin aromatic protons in a conclusive manner from the spectrum obtained. However, the spectrum showed absence of hydroxyl proton of the ligand in the triphenyl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

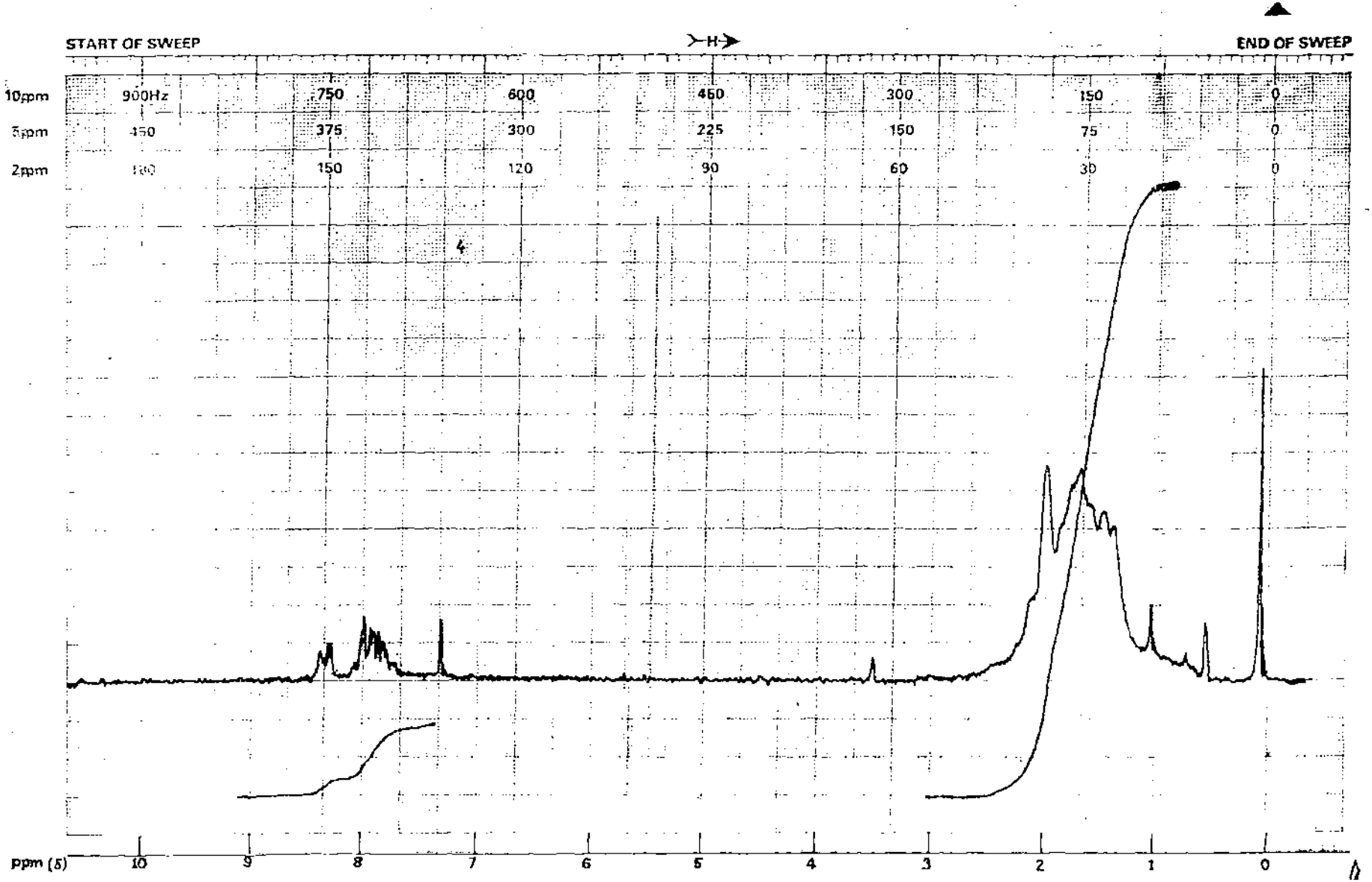
The IR spectrum showed the absence of -OH stretching frequency of the ligand indicating the substitution of the hydroxyl proton by tricyclohexyl tin group.

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.

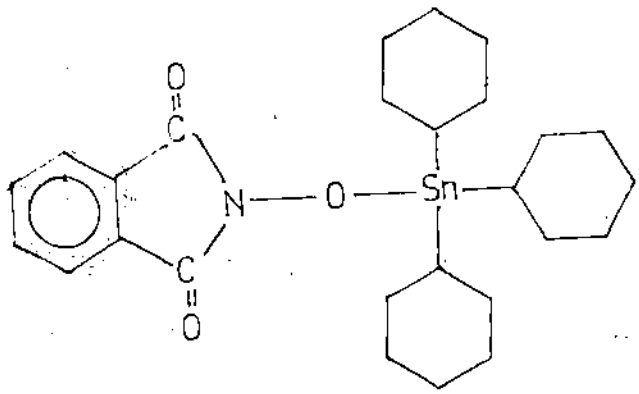
The ^1H NMR spectrum showed a group of complex peaks in the region δ 1.0 to 2.4 (for 33H). The aromatic protons appeared in the region of δ 7.6-8.3 (for 4H) as complex pattern.

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.

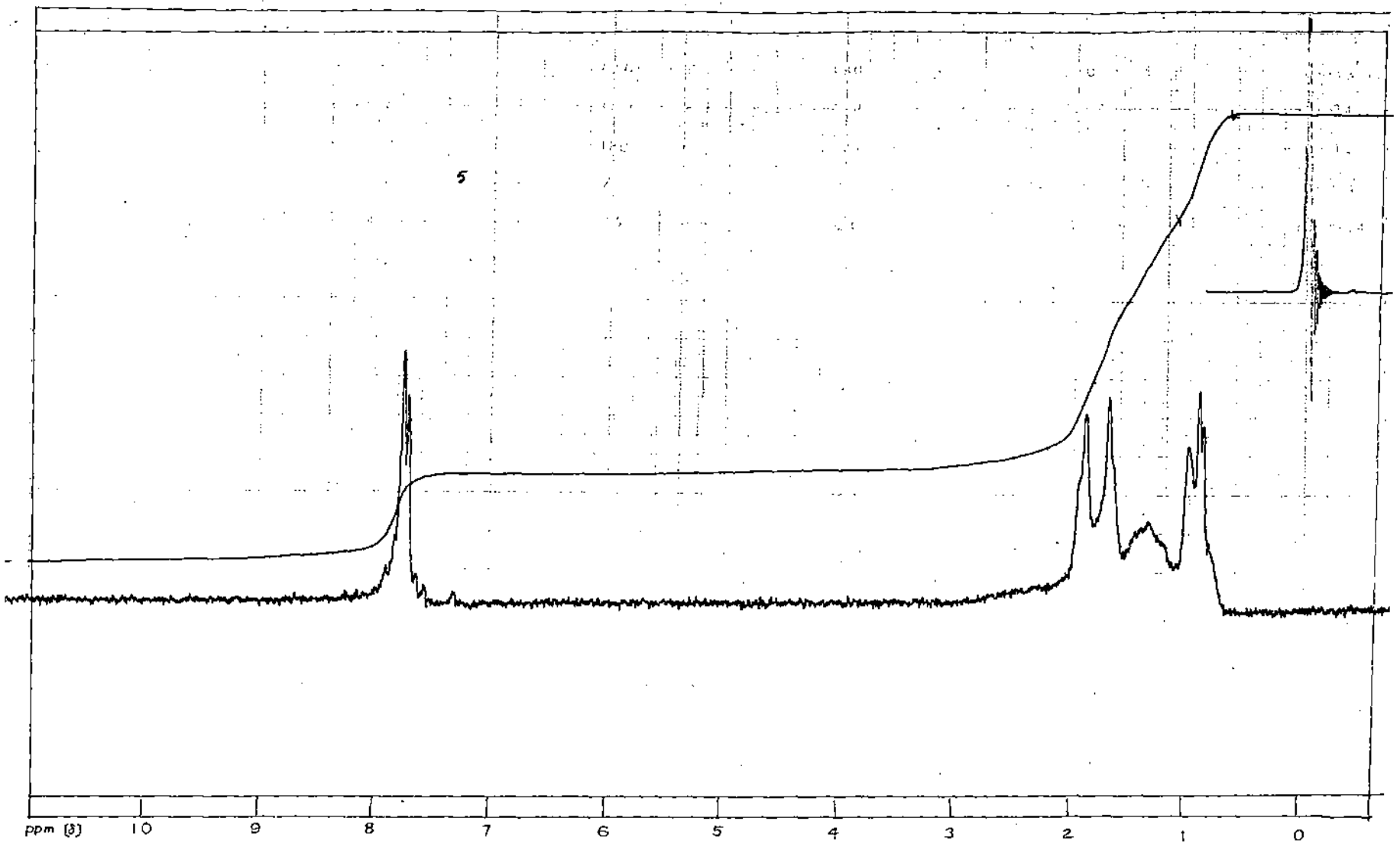
The N-C-O coupled vibration may be at 1182 cm^{-1} and 1156 cm^{-1}.

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

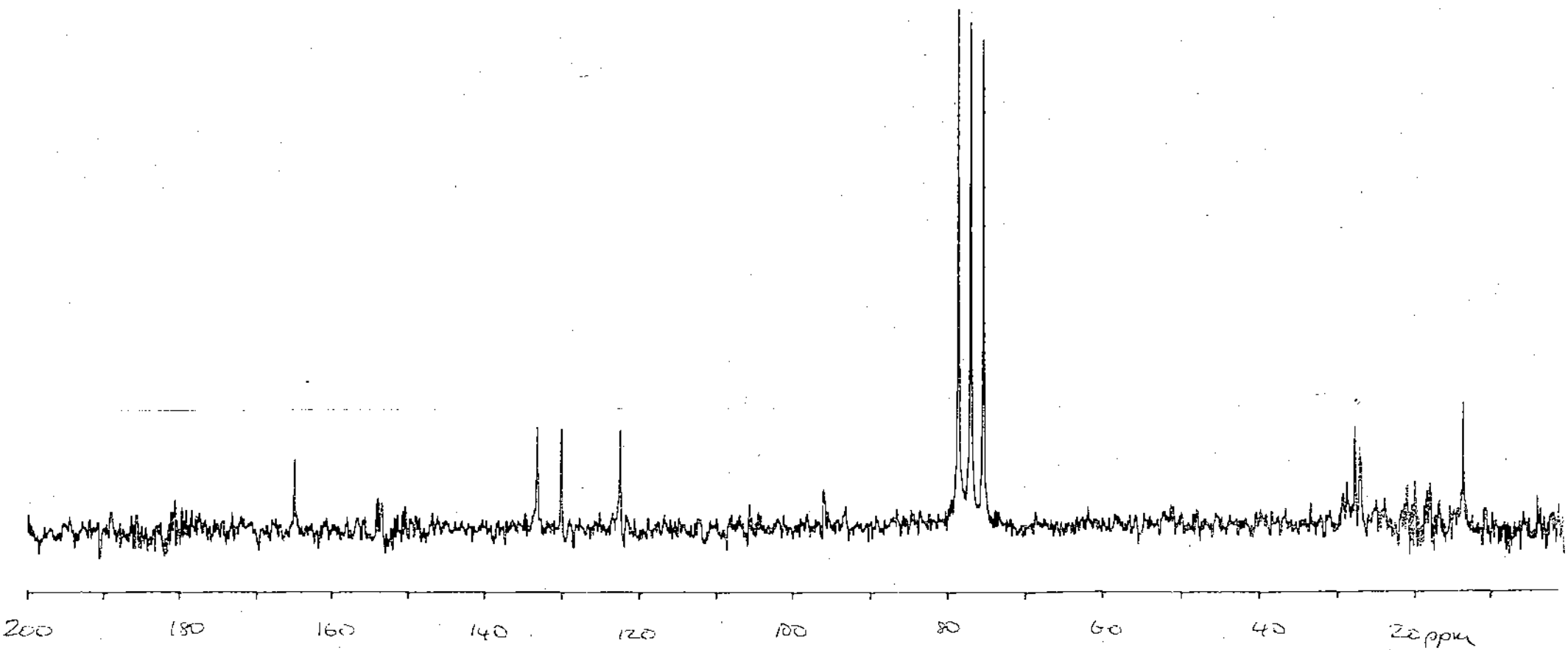
Sn-C stretching frequency appeared at 497 cm^{-1}.

^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.

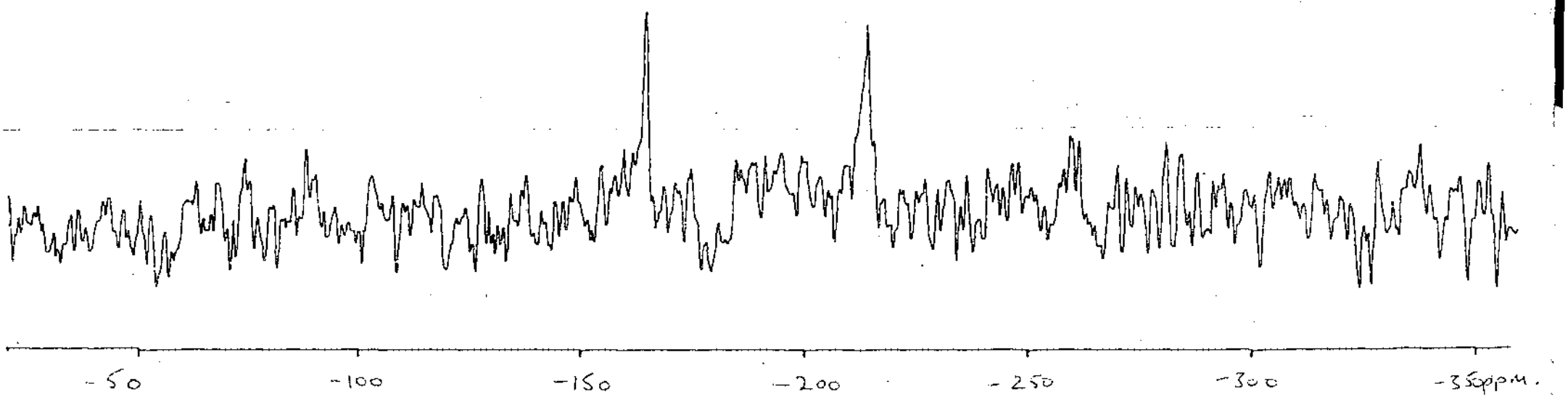
In the ^{13}C NMR spectrum methyl carbons (C_{12}, etc) appeared at δ 13.54, other methylene carbon peaks may be assigned (163) as δ 26.76, 26.89 and 27.52 for (C_9 & etc), (C_{11} & etc) and (C_{10} & etc)



^{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 $CDCl_3$)

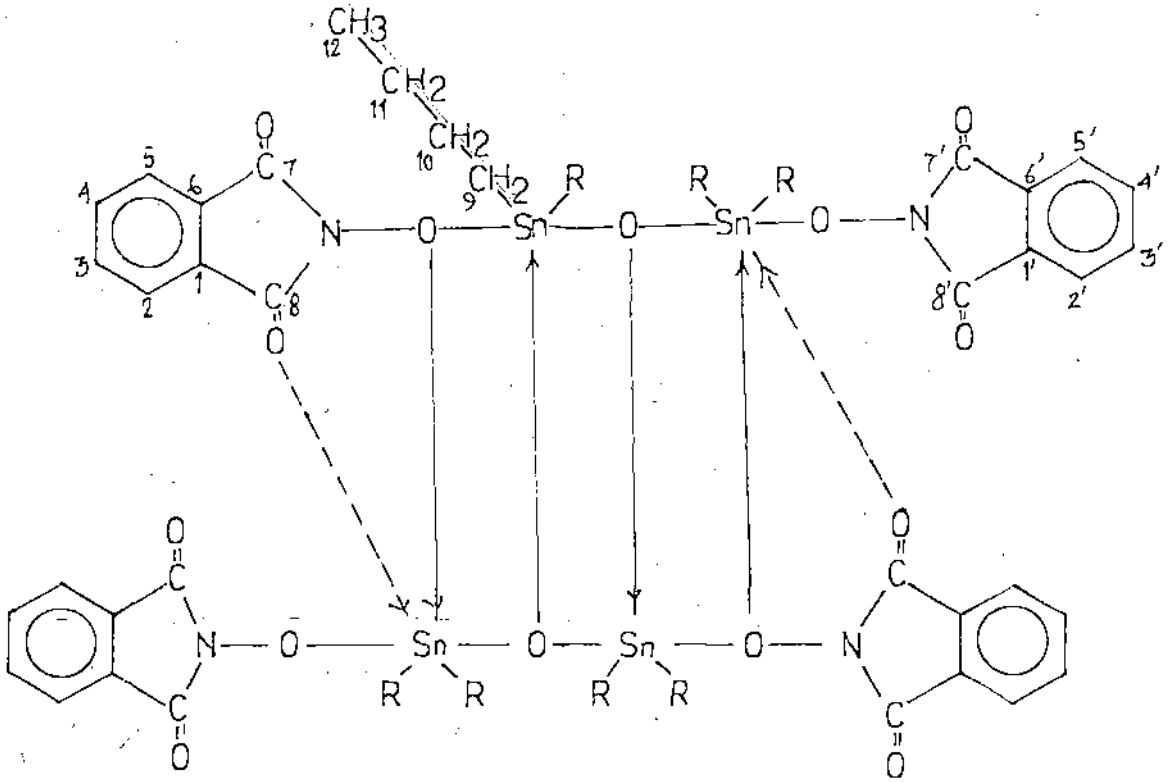
respectively. The aromatic carbons showed signals at δ 122.48, 130.05 and 133.18 which may be assigned (164) as (C_1,C_6 & etc), (C_2,C_5) and (C_3,C_4 & etc) respectively. The carbonyl carbons (C_7,C_8) appeared at δ 164.84.

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.

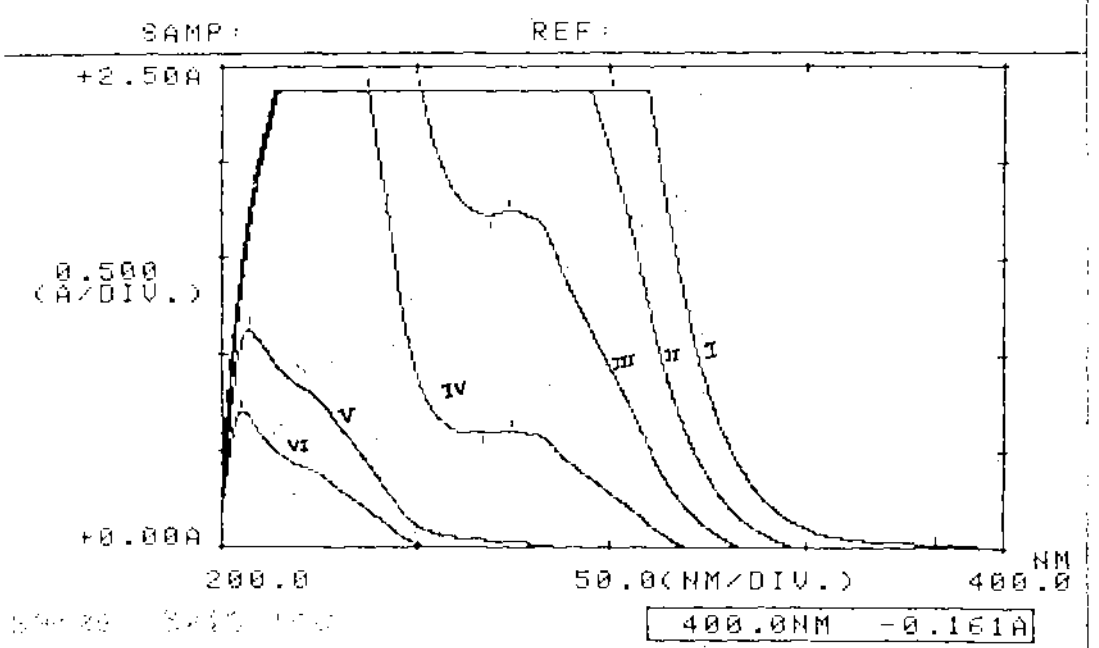
With N-hydroxy phthalimide, diorganotin oxides, yield organotin compounds which contained Sn-O-Sn linkages, as indicated by the presence of an additional peak at ~575 cm^{-1}. Diorganotin oxides in many cases form hexa coordinated monomeric R_2SnL_2 (LH_n = 8 hydroxy quinoline, substituted hydroxamic 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.

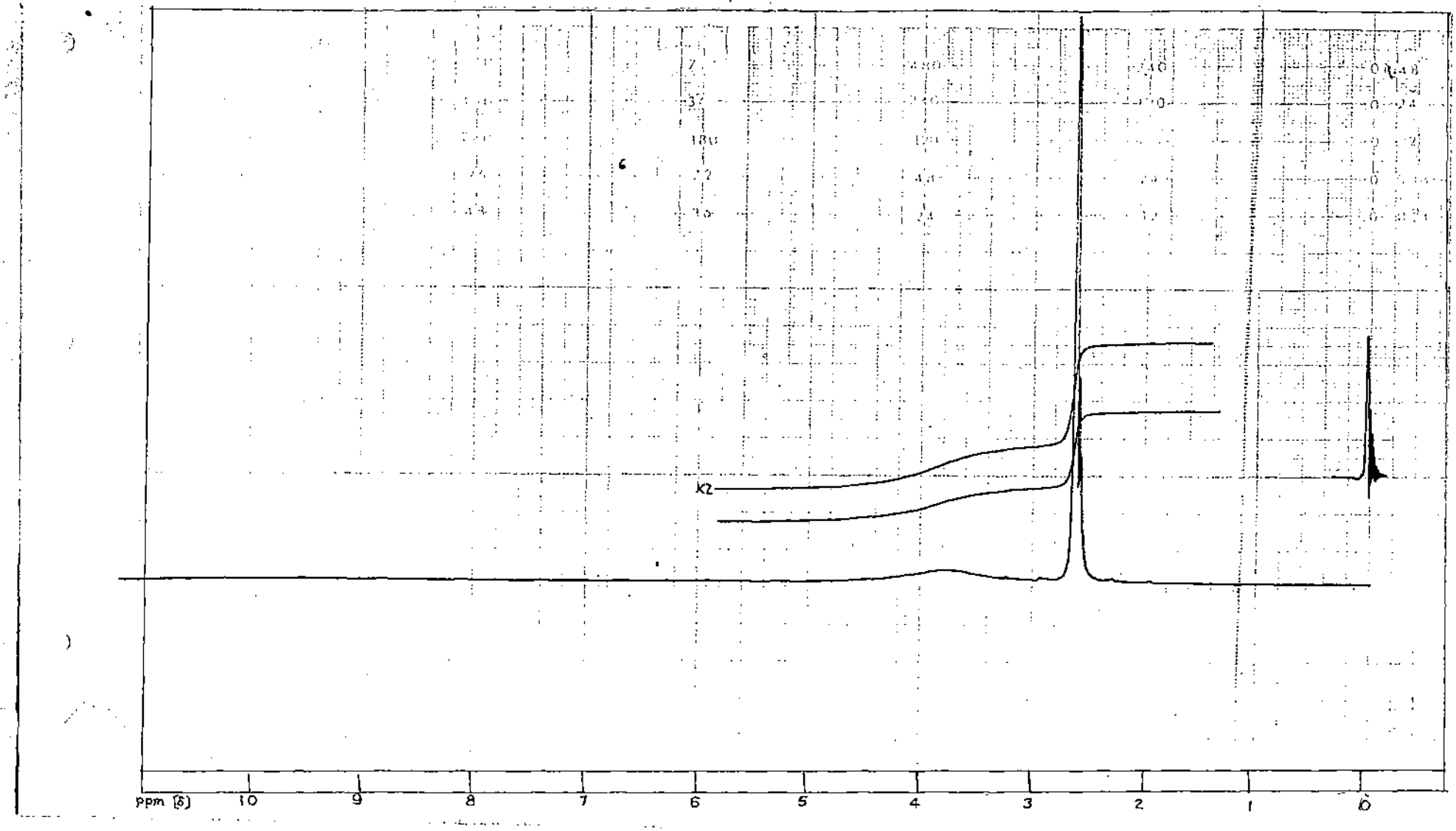
6. Triphenyl tin N-hydroxy succinimide

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

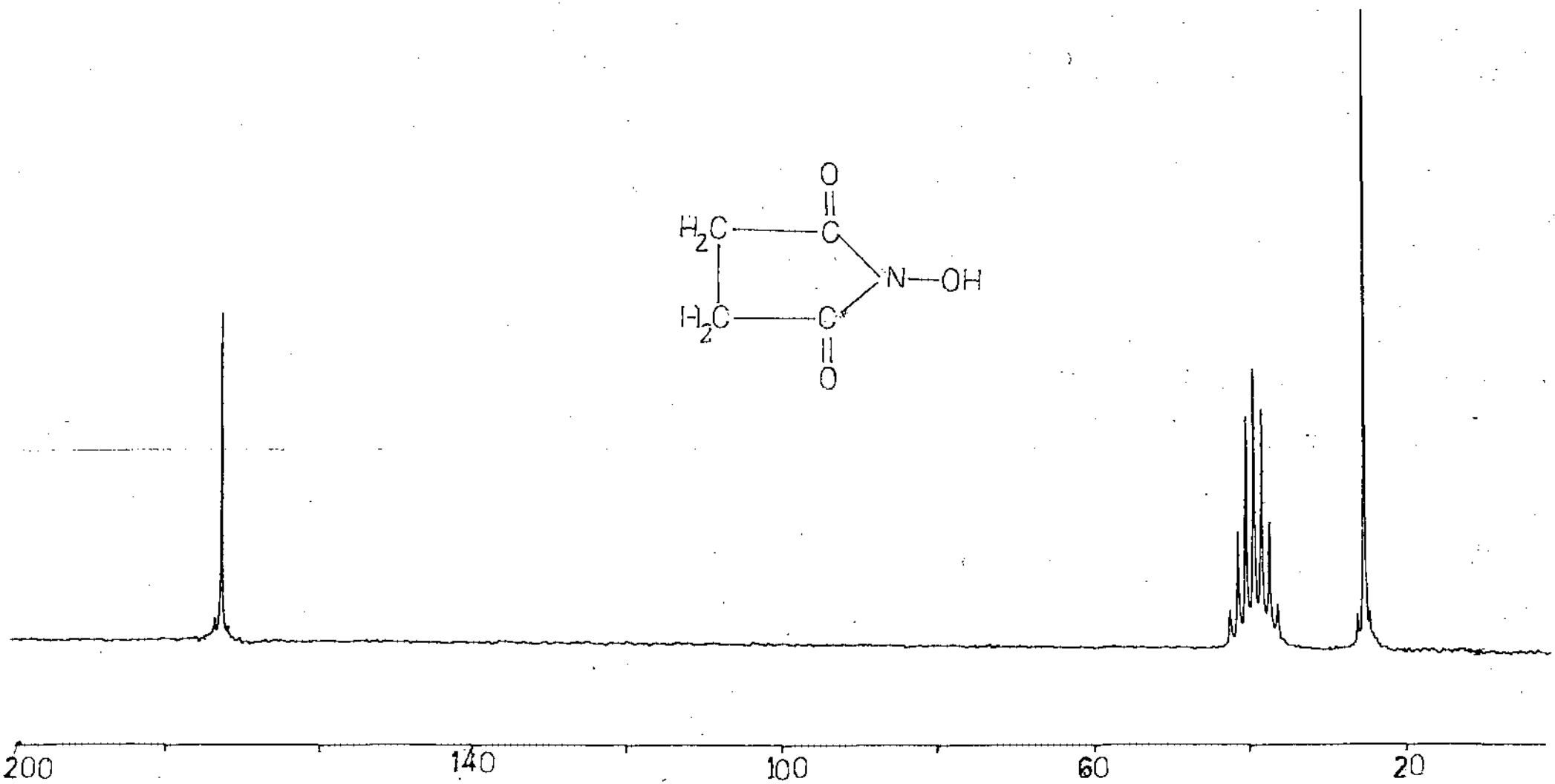
Apparent molecular weight (Rast method)

Found 442, Calcd (monomer) 464.

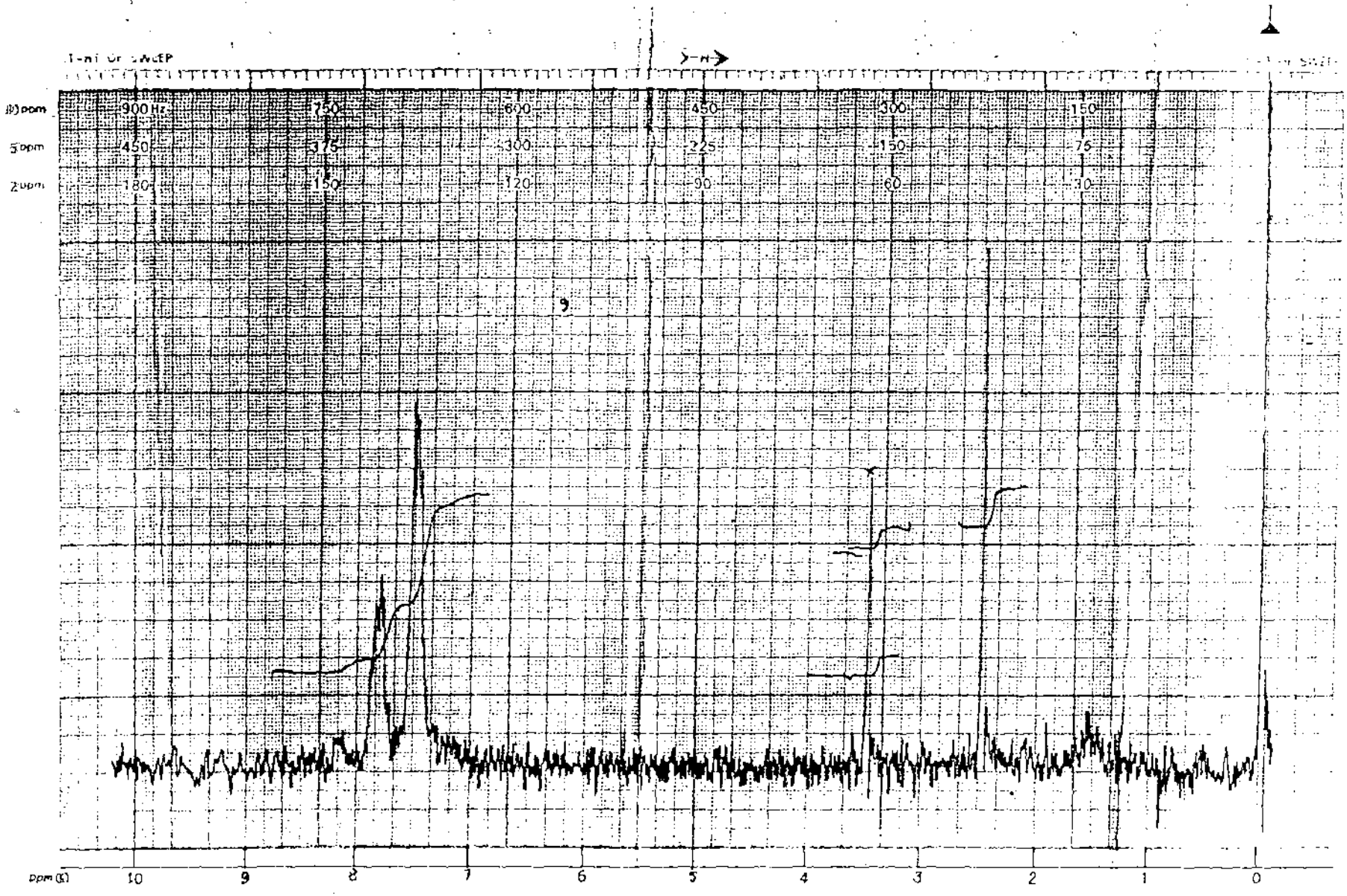
In the IR spectrum of N-hydroxy succinimide-OH stretching frequency absorption occurred at 3000 cm^{-1}. But in the triphenyl



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

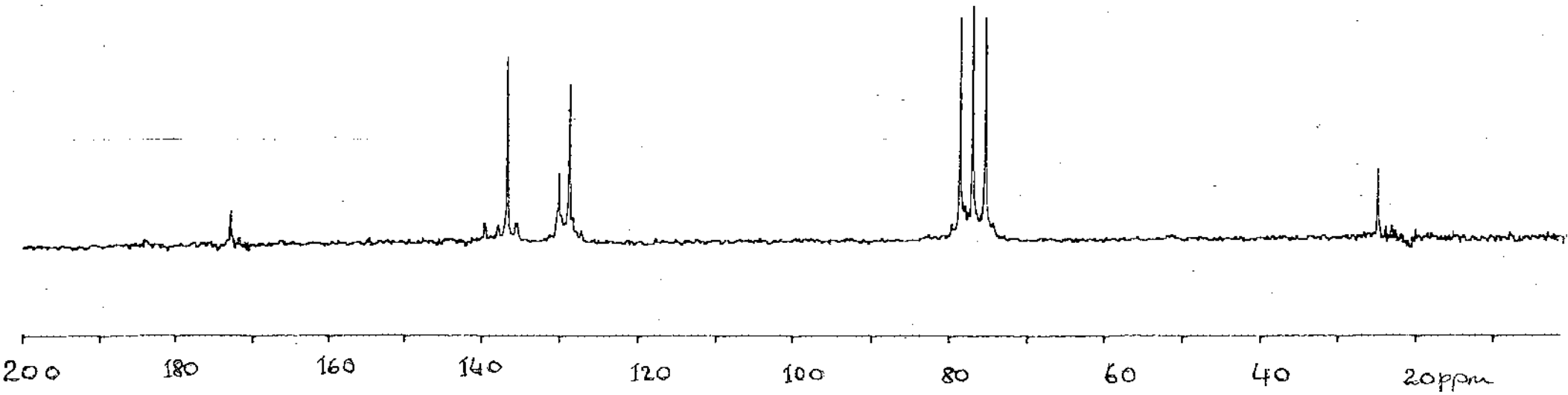


^{13}C NMR spectrum of N-hydroxysuccinimide (in d6 DMSO)



^{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.

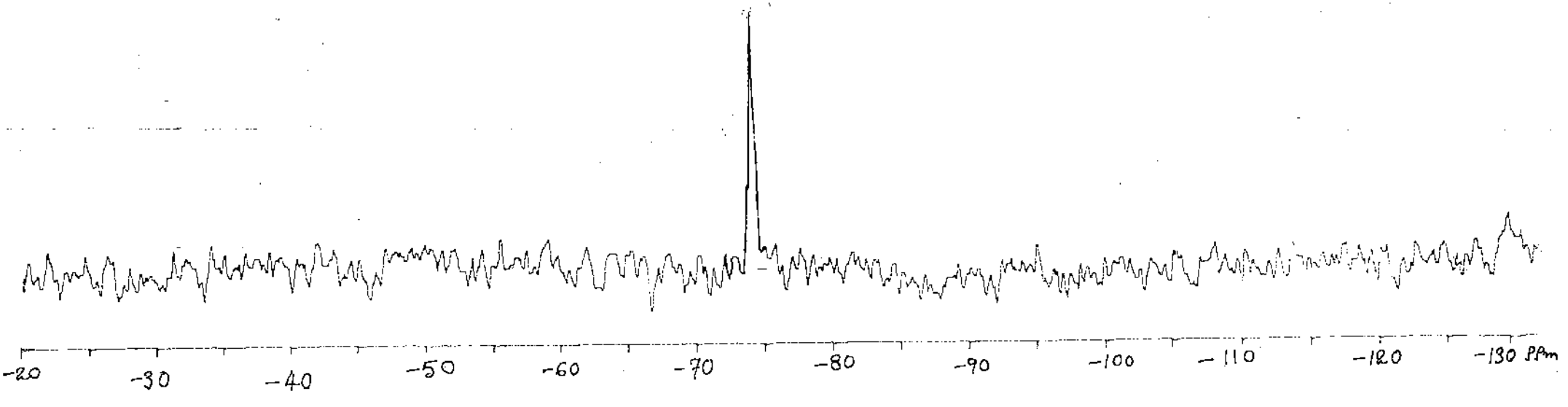
The band at 1240 cm^{-1} may be due to NCO coupled vibration.

^{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).

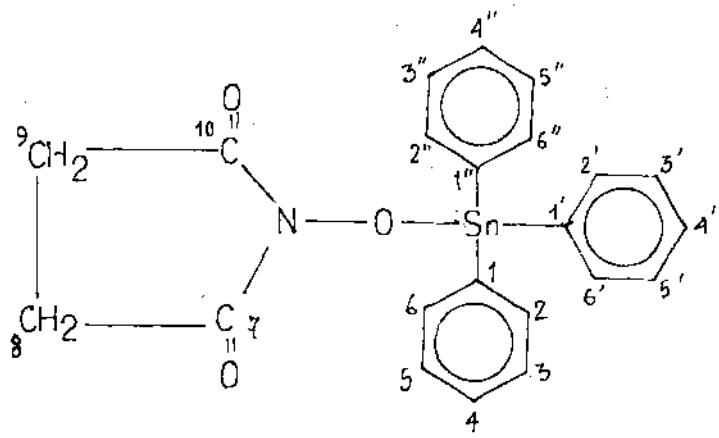
In the ^{13}C NMR spectrum of the ligand N-hydroxy succinimide, carbonyl carbons appeared at δ 172.74 and a single signal for the methylene carbons appeared at δ 25.12. In case of the triphenyl tin N-hydroxy succinimide, methylene carbons (C_8,C_9) appeared at δ 24.25. The signals for aromatic carbons 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 $C_{32}H_{52}O_7N_2Sn_2$.

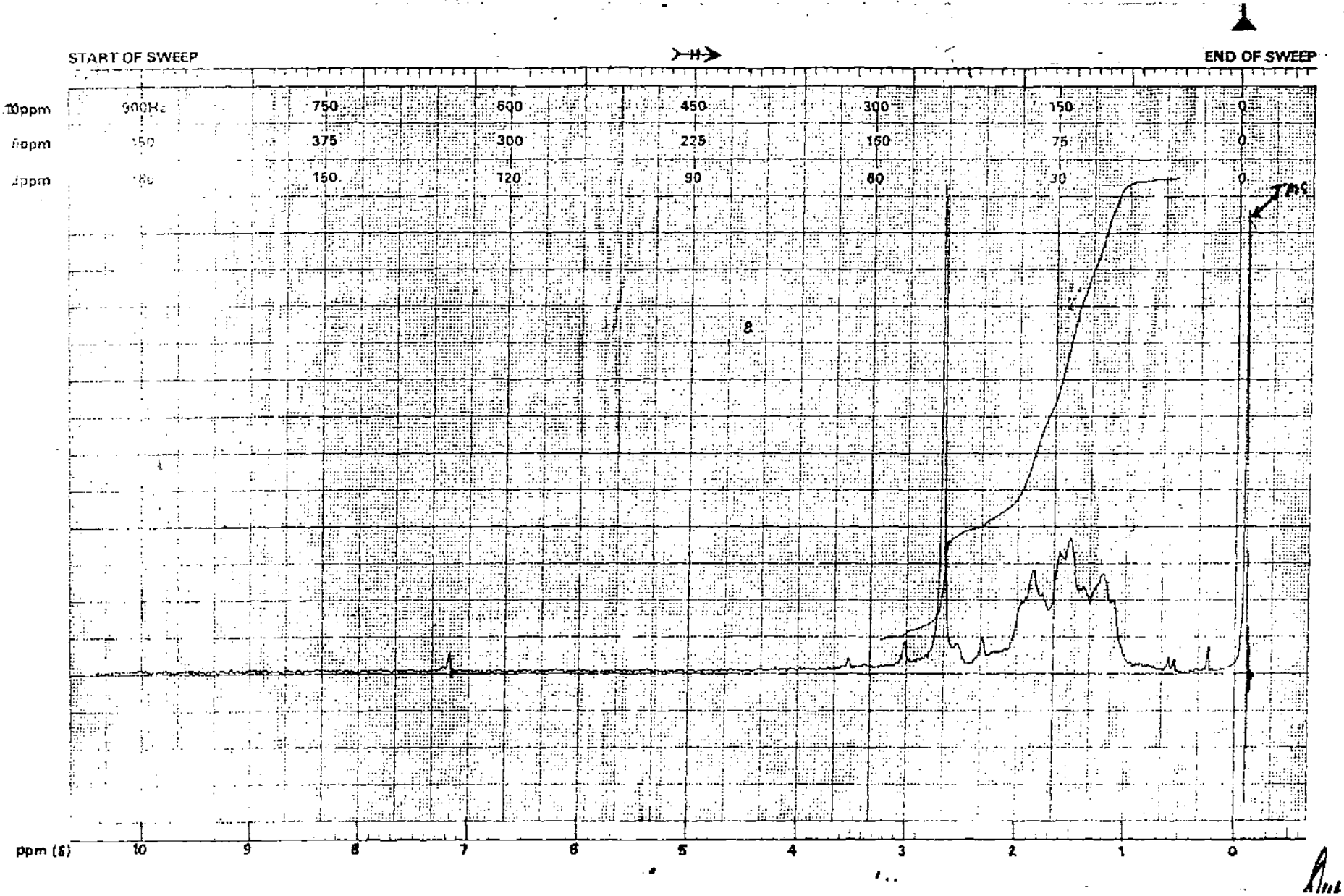
Apparent molecular weight (Rast method)

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.

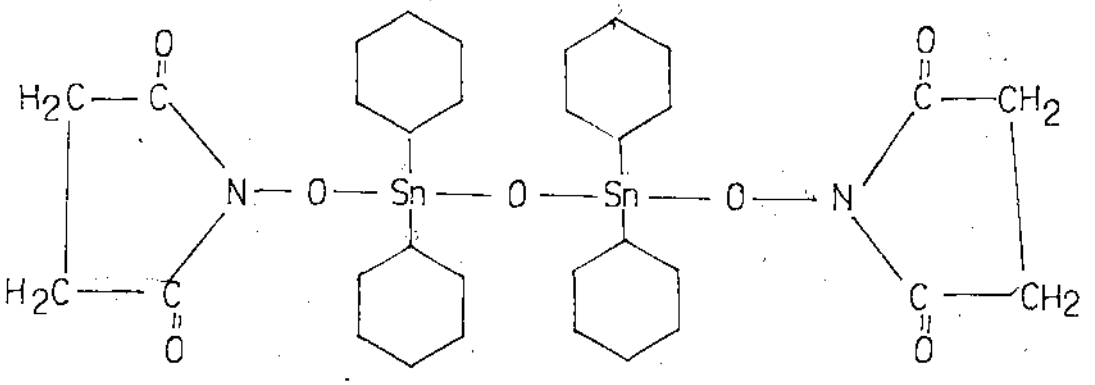


^{1}H NMR spectrum of Tetracyclohexyl 1:3$_{di}$N-hydroxy succinimido distannoxane

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.

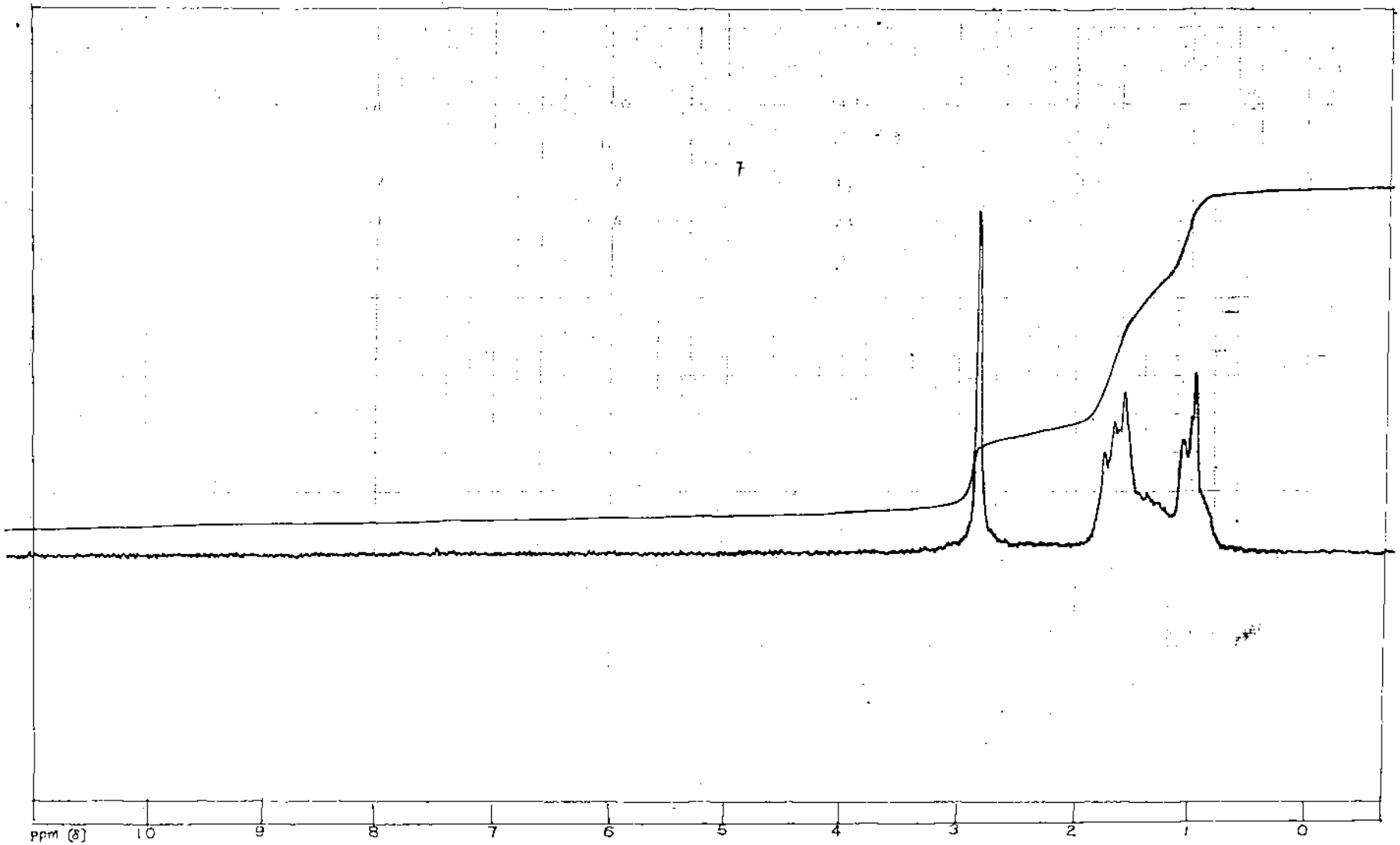
In the IR spectrum of the compound carbonyl absorption bands appeared at 1780 cm^{-1} and 1690 cm^{-1}. Carbonyl absorption did not shift significantly compared to the ligand carbonyl absorption bands.

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

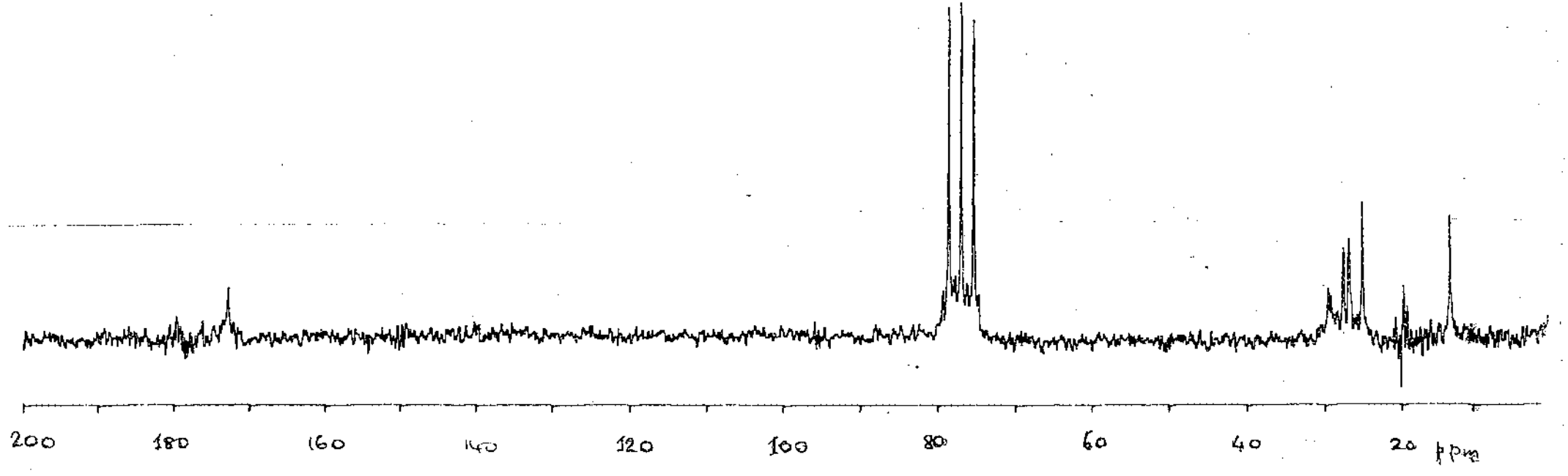
Absorption due to Sn-O-Sn bond found at 580 cm^{-1} and Sn-C stretching band appeared at 560 cm^{-1}.

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,)

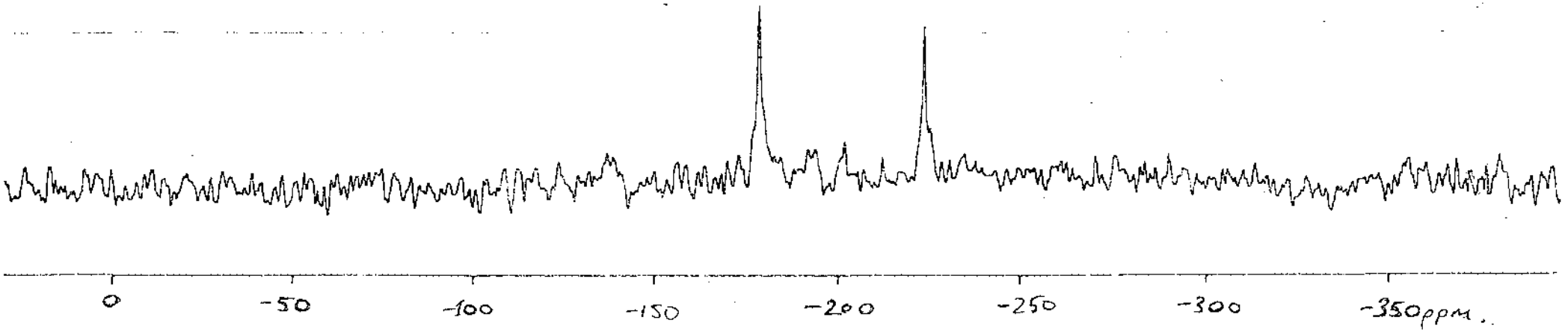


$^{1}_{H}$ NMR spectrum of Tetrabutyl 1 : 3 di N-hydroxy succinimido distannoxane



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

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



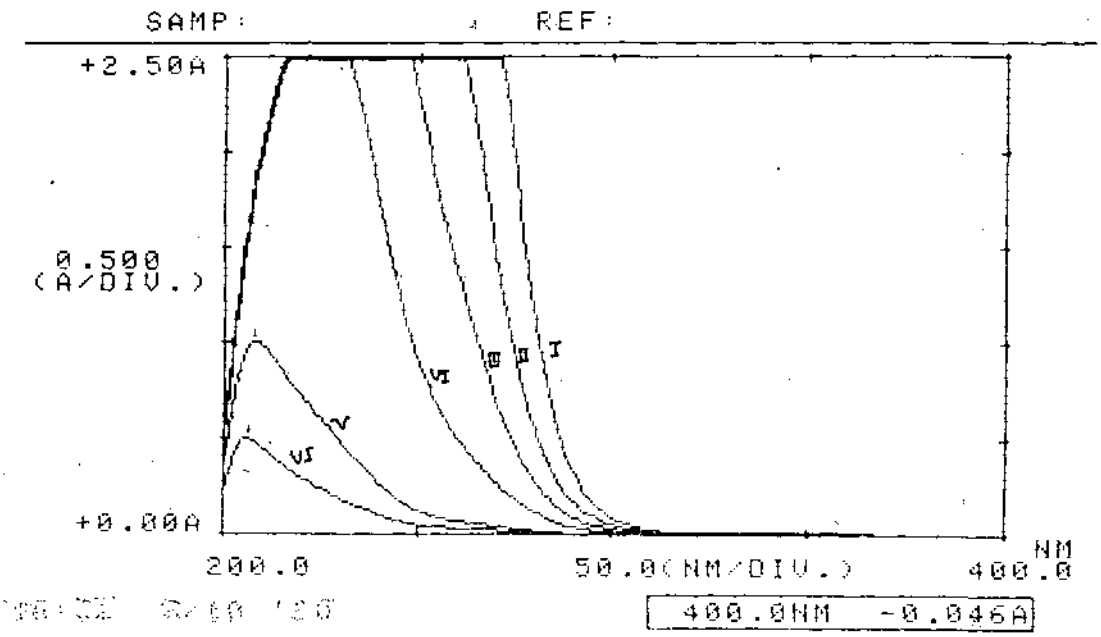
^{119}Sn NMR spectrum of Tetrabutyl 1 : 3 di N-hydroxy succinimido distannoxane (in $CDCl_3$)

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.



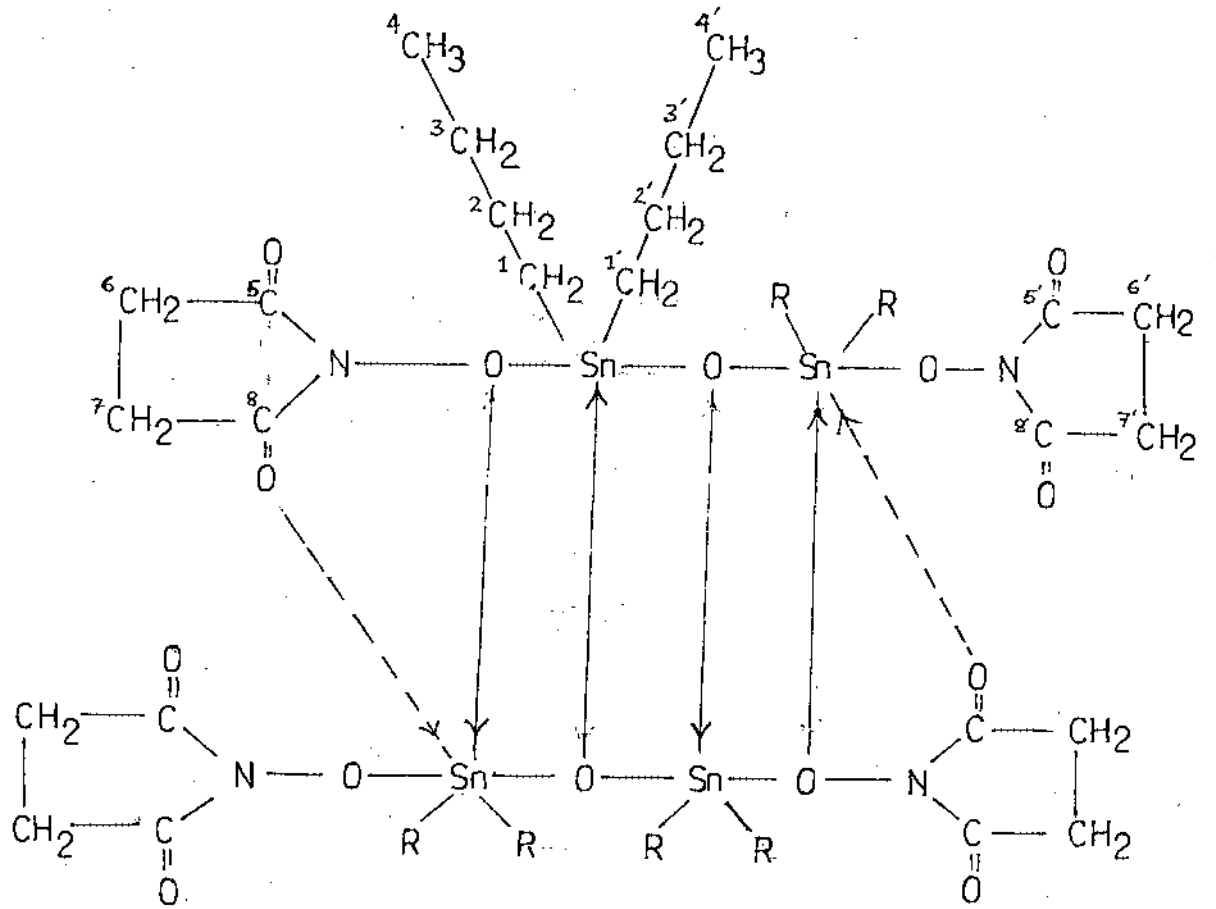
UV spectra of Tetrabutyl 1:3 di N-hydroxy succinimido distannoxane [I-5.6 x 10^{-4}(M)] diluted subsequently 10 times in each step (II, III, IV, V and IV).

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

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