PART - II

INTRODUCTION

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

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

Preparative Methods of Organotin Carboxylates

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

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

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

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

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

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

$$2Bu_3SnOCOCH_2ON = CRR' + H_2O$$

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

$$(Bu_3Sn)_2O \ + 2\,0 - HOC_6H_4COOH \xrightarrow{100-110^{\circ}C}$$

$$2\ Bu_3SnOCOC_6H_4OH{-}0 + H_2O$$

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

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

$$(M = Na,\ K,\ Ag)$$

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

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

$$+ Et_2SiO$$

$$(R = Me,\ Et)$$

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

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

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

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

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

I

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

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

II

products irrespective of the conditions used (55).

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

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

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

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

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

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

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

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

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

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

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

Table

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

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

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

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

Table

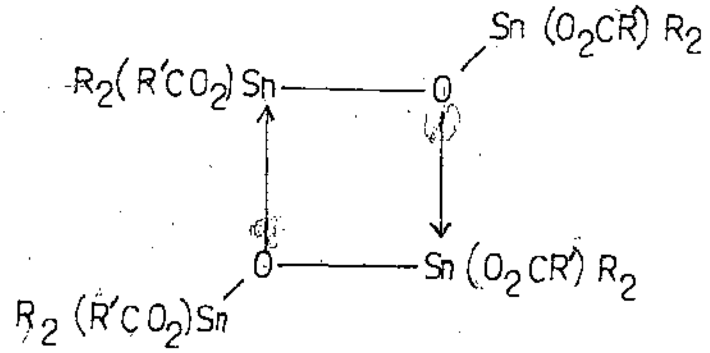
R_2SnXY compounds

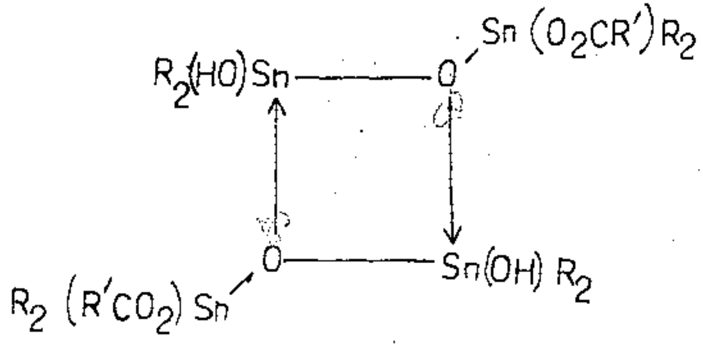
R	X	Y	Ref.
$n\text{-}C_4H_9$	H	O_2CCH_3	31,32
CH_3	Cl	O_2CH	33
CH_3	Cl	O_2CCH_3	33,34
CH_3	Cl	$O_2CC_2H_5$	35
CH_3	Br	O_2CCH_3	35
CH_3	I	O_2CCH_3	35
C_2H_5	Cl	O_2CH[a]	36
C_2H_5	Cl	O_2CCH_3	36
$n\text{-}C_3H_7$	Cl	O_2CH[a]	36
$n\text{-}C_3H_7$	Cl	O_2CCH_3	36
$n\text{-}C_4H_9$	Cl	O_2CH[a]	36
$n\text{-}C_4H_9$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

[a] Each compound has one molecule of water

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

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





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

Khoo and Smith (49) have been prepared some carboxylate derivatives of amino substituted benzoic acid. These are (O-aminobenzoato) triphenyl tin, $Ph_3Sn[O-(H_2N)C_6H_4CO_2]$ and (p-aminobenzoato) triphenyltin, $Ph_3Sn[p\text{-}(NH_2)C_6H_4CO_2]$. Reaction of bis (triphenyltin)oxide with o-amino benzoic acid in refluxing benzene solution gave (o-amino benzoato) triphenyl tin. Similarly when p-amino benzoic acid was used as a reactant the (p-amino benzoato) triphenyl tin derivative obtained. Following the above method another compound [o-(dimethylamino)benzoato] triphenyl tin has been obtainted (50). The triphenyl tin esters of hydroxy substituted benzoic acid have been reported (51) (o-Hydroxy benzoato) triphenyl tin, $Ph_3Sn[o\text{-}(OH)C_6H_4CO_2]$ has been prepared in refluxing benzene. In a similar fashion (o-methoxy benzoato) triphenyl tin, $Ph_3Sn[o\text{-}(CH_3O)C_6H_4CO_2]$; [p-(methylthio)benzoato] triphenyltin, $Ph_3Sn[p\text{-}(CH_3S)C_6H_4CO_2]$; (o-thiobenzoato) diphenyltin, $Ph_2Sn[o\text{-}(S)C_6H_4CO_2]$ have been prepared. The nuclear magnetic resonance spectral studies and X-ray crystallographic studies have been made thoroughly on these compounds.

Physical properties of Organotin Carboxylates

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

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

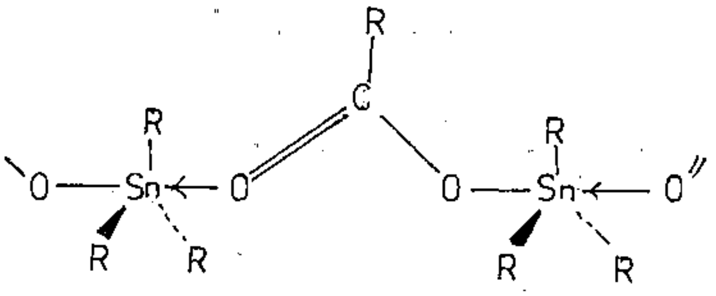
Structural aspects

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

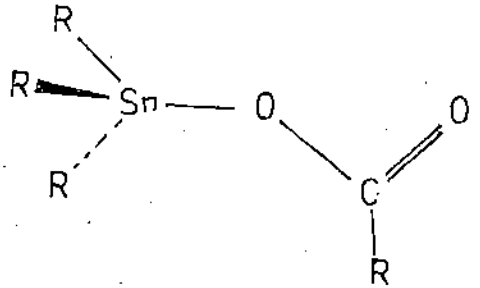
Infrared Spectroscopy

Carbonyl group absorption:

A comparison of the IR spectra $Me_3SnOOCCH_3$ with that of $Me_3SiOOCCH_3$ points to the essential difference of structures between these two class of compounds. The trimethyl silyl derivative possess normal ester structure as evidenced by the appearance of assymmetric stretching frequency of the carbonyl group ($\nu_{as}CCO$) at 1725 cm^{-1} (57,58). The trimethyl stannyl acetate, on the other hand, show $\nu_{as}(OCO)$ at 1576 cm^{-1}, the absorption frequency being similar to $\nu_{as}(OCO)$ of 1578 cm^{-1} in $NaOOCCH_3$. Presence of a symmetrical carbonyl group of the ionised $RCOO^-$ type $[\nu_{as}(OCO)$ 1550-1610 cm^{-1} and $\nu_s(OCO)$ 1300-1400 $cm^{-1}]$ is, therefore indicated. All carboxylates of the type $R_3SnOOCR'$ and $R_2Sn(OOCR')_2$ (R = alkyl/aryl group) show such symmetric and assymmetric carbonyl absorption in solid state. On dissolving the compounds in non polar non-coordinating solvents, the assymmetric stretching frequencies are raised to the region 1650-1700 cm^{-1} while the symmetric frequencies are lowered to a relatively small extent indicating that in solution the molecules possess ester like structures. Further, the difference between the asymmetric and symmetric stretching frequency $\Delta\nu(\nu_{as}\,OCO - \nu_s OCO)$ is generally found to be less than 200 cm^{-1} in solid state and greater than 250 cm^{-1} in solution (58,59). This has been interpreted in terms of bidentate and an almost symmetrical carbonyl group forming intermolecular bridges in solid state giving rise to polymeric carboxylates (VA) while in solution depolymerisation occurs resulting in ester like monomeric species (VB) (60-65) having a monodentate carboxyl group. Molecular weights of the carboxylates also supports monomeric structure (VB) in solution with the exception of trimethyl tin formate which exists as an equilibrium of associated and unassociated forms in $CHCl_3$ (61). On the other hand when the group R bonded to the tin atom is too bulky or when there is branching at the carbon atom α-to the tin atom (e.g. triphenyl tin 2-ethyl hexoate) the compounds assume monomeric ester like structures in solid state as a result of steric hindrance exerted by the bulky organic groups (57,66-70). Thus, tricyclohexyl,

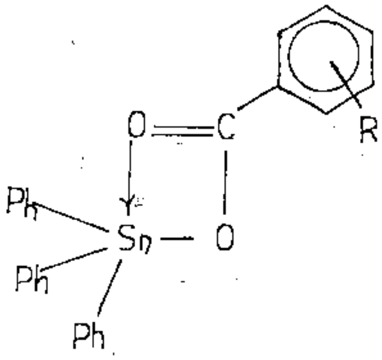


(VA)

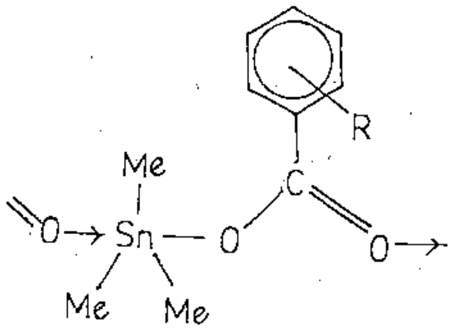


(VB)

triisopropyl, trineopentyl and tri-α-napthyl tin acetates absorb at 1645 cm^{-1} both in solid state and in solution confirming monomeric structures in both phases. Steric interaction between the alkyl or aryl groups bonded to tin and "tail" of the carboxylate group can also prevent polymerisation. For Ph$_3$Sn derivatives while Ph$_3$SnOOCCHMe$_2$ and Ph$_3$SnOOCH = CH$_2$ are penta coordinated polymers. Ph$_3$SnOOCCMe$_3$. Ph$_3$SnOOCCMe = CH$_2$ and Ph$_3$SnOOCCl$_3$ are tetra coordinate monomers in the solid state (71). Recently it has also been claimed that triphenyl tin derivatives of chlorobenzoic acid, salicyclic acid and o-anisic acid are discrete five coordinated form in the solid state (64,65,72). In contrast, trimethyl tin derivatives of these carboxylic acids are in the intermolecular chain structures (72). Intramolecular carbonyl coordination takes place in case of triphenyl tin derivatives (Fig. A) whereas intermolecular carbonyl coordination occurs in case of trimethyl tin derivatives (Fig. B). An analogous situation is also observed in the oxinate carboxylates e.g. $RSn(Ox)_2OOCR'$ which also have monomeric structures in solid state (73). Trimethyl tin glycinate also has a polymeric chain structure in solid state (ν_{as}OCO and ν_{s}OCO are 1630 and 1398 cm^{-1} respectively). but bridging occurs via the NH_2 groups (74).



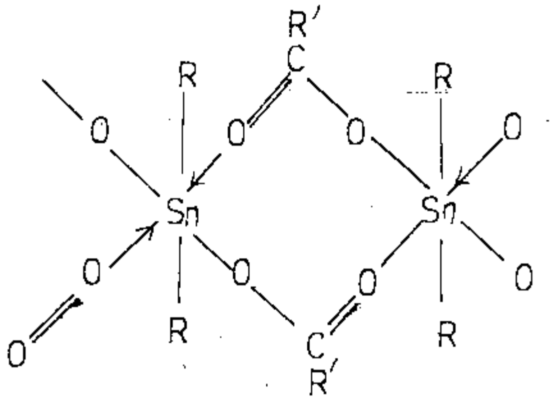
(A)



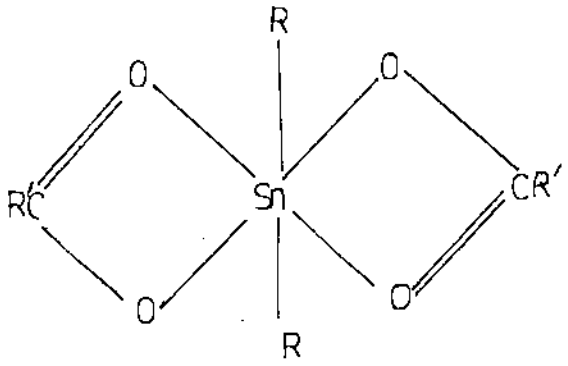
(B)

R = Cl, OH, NH_2

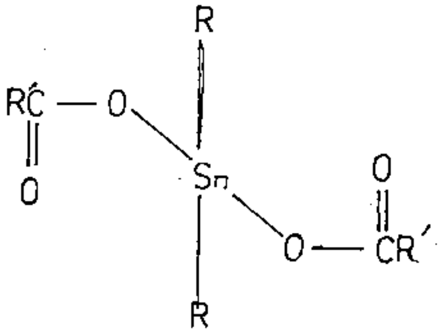
The structure of dialkyltin dicarboxylate was first suggested for dimethyl tin diformate by Okawara (33) which included a linear Me_2Sn cation and a formate anion. Further studies have been carried out on dialkyltin diacetates (75,35) which suggest that in the neat liquid or solid state, those adopt a polymeric structure (VIA) with intermolecularly bridging carboxylate groups and an octahedral <u>trans</u> R_2SnX_4 tin atom geometry. In solution, these compounds are monomeric on evidenced by raising of ν_{as}(OCO) frequencies. The molecules have been suggested to be octahedral with intramolecularly chelated carbonyl groups (VIB)(2). It is, however, equally likely that these compounds assume a non-chelated ester like structure in solution (VIC). The dialkyl chlorotin carboxylates $R_2Sn(OCOR')Cl$ are also believed to possess inter and intra molecularly chelated structures in the solid state (VIIA) and solution (VIIB) respectively with the tin atom occupying a trigonal bipyramidal cis R_2SnX_3 geometry (76).



(VI A)



(VI B)



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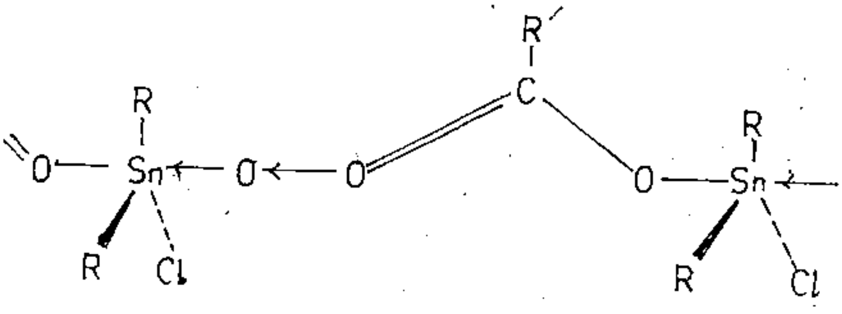
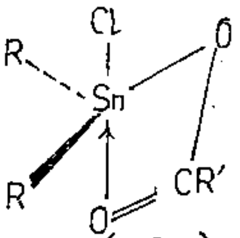


(VII A)

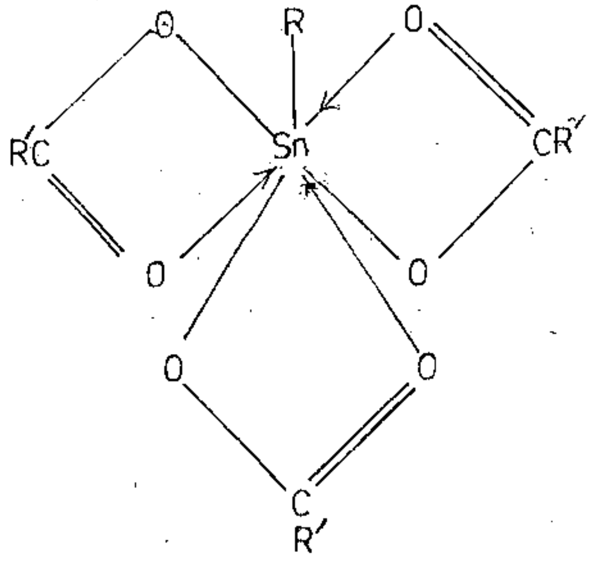


(VII B)

The structure of bis (trimethyl stannyl) ester of a dicarboxylic acid (malonic acid) has been determined and shows that in $Me_3SnOOCCH_2COOSnMe_3$, each carbonyl group links planar Me_3Sn moieties intermolecularly to form a three dimensional polymeric net work (77).

The IR spectra of a number of mono organotin tricarboxylates in CCl_4 show coordinated carbonyl stretching bands, and additionally

$BuSn(OOCMe)_3$ and $BuSn(OOCEt)_3$ were found to be monomeric in camphor solution (78). This is indicative of a 7-coordinated tin atom geometry for these compounds (VIII).



(VIII)

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

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

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

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

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

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

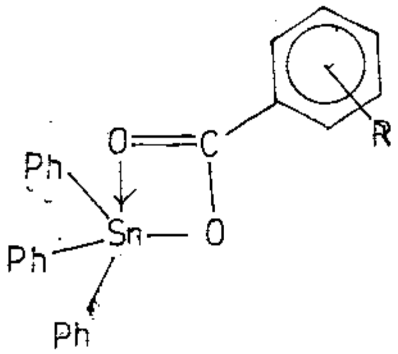
The role of ^{13}C NMR spectra was exploited by Lycka et al (65,80) for elucidation of structures of some triorganotin carboxylates.

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

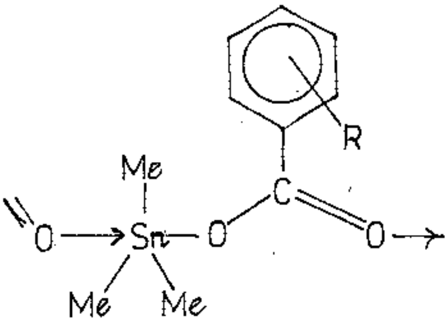
Utilising the above tools, Holmes et al (50,51,72,82), has established the structures of a number of organotin carboxylates. They studied the structures of the following compounds:

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

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



(A)

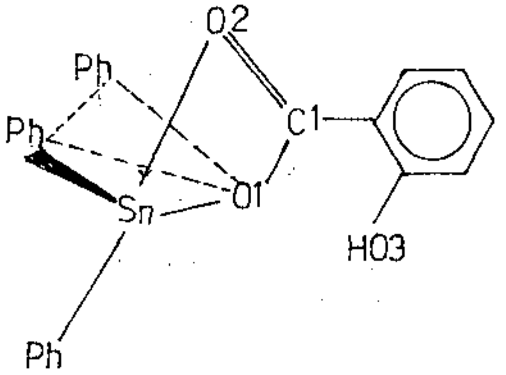


(B)

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

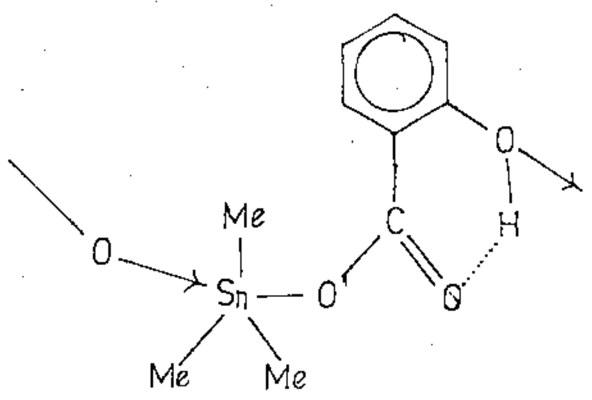
The basic structure of (o-hydroxy benzoato) triphenyl tin ester, results from a distortion from tetrahedral geometry induced by the approach of an oxygen atom, O2 or of the carboxylate group at a tetrahedral face opposite one of the tin phenyl groups. The distortion is toward trigonal bipyramid that contains O2 and the latter phenyl group at axial sites. The axial Sn - O2 lengths are considerably longer than the equitorial Sn - O1 bond length . Tin

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



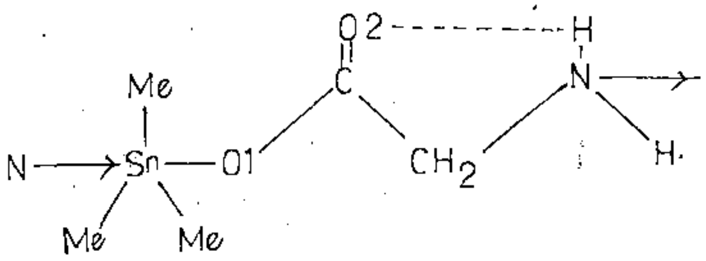
The intramolecular hydrogen bond formed from the orthohydroxy group of salicyclic acid [02...... H_3 = 1.93 A°] contributes in causing the longer Sn - 02 bond length.

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



(C)

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



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

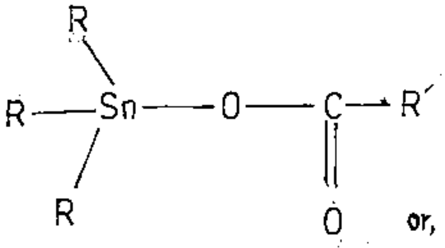
The infrared data are most instructive in comparing solid and solution state structures. For the anisic acid derivative, changes in the carbonyl group stretch ν_{COO}, and an increase in the number of tin methyl group stretches, ν_{SnC_3}, on going from the solid to a chloroform solution imply a greater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

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

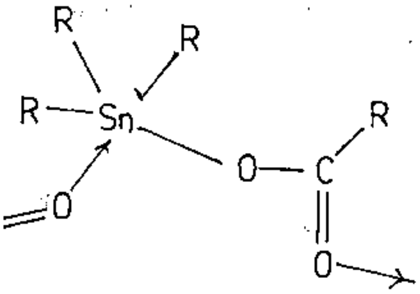
The diorganotin derivatives of carboxylic acids are less in number, there is only one reported compound, (o-thiobenzoato) diphenyltin (51) without any structural details.

SCOPE AND OBJECTIVE

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



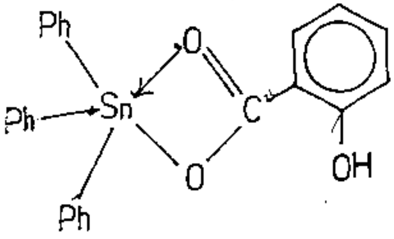
(A)



(B)

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

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



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

EXPERIMENTAL

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

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

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

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

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

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

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

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

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

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

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

Preparation of starting materials

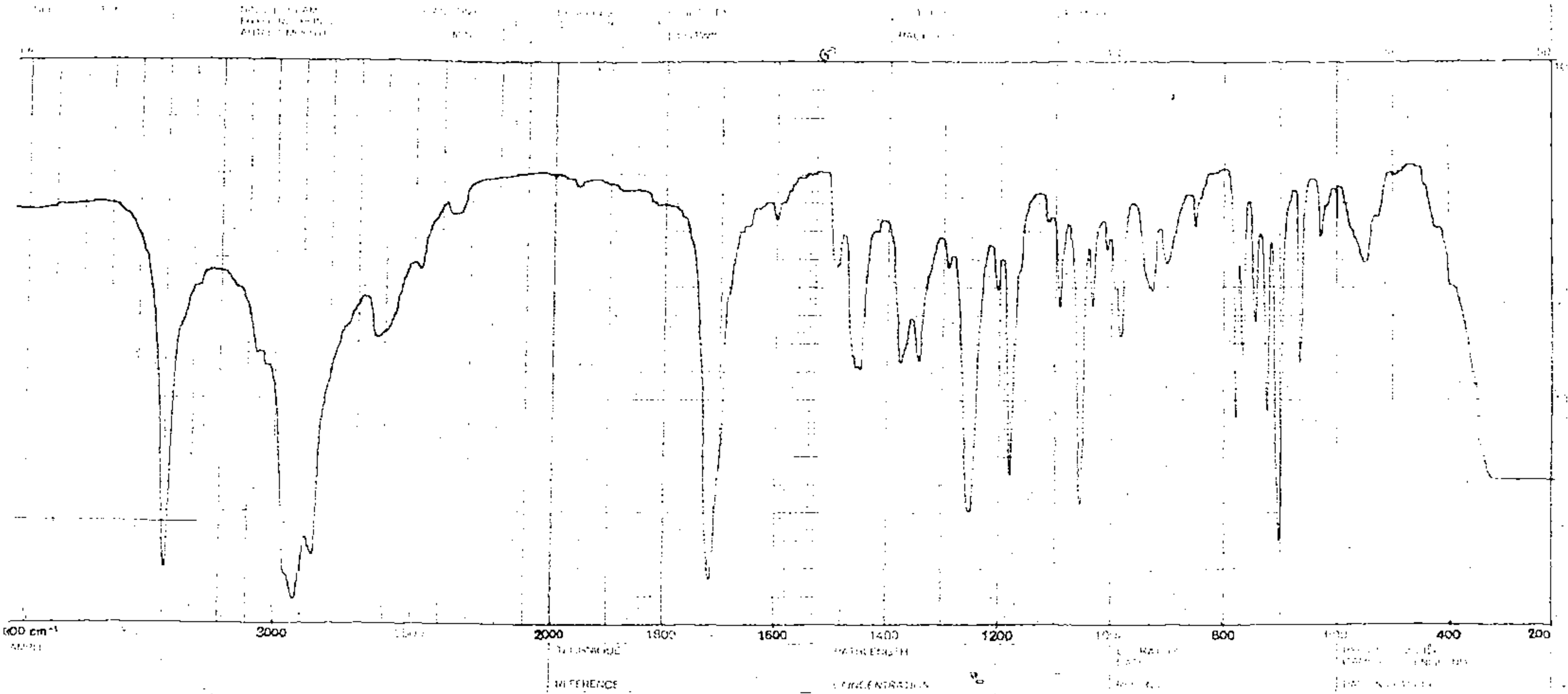
All the solvents required in this experiment have been purified and dried accordingly as described earlier.

1. Diphenyl glycolic Acid

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

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

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



IR spectrum of Diphenyl glycolic acid (nujol)

2. Dibutyl tin diphenyl glycolate

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

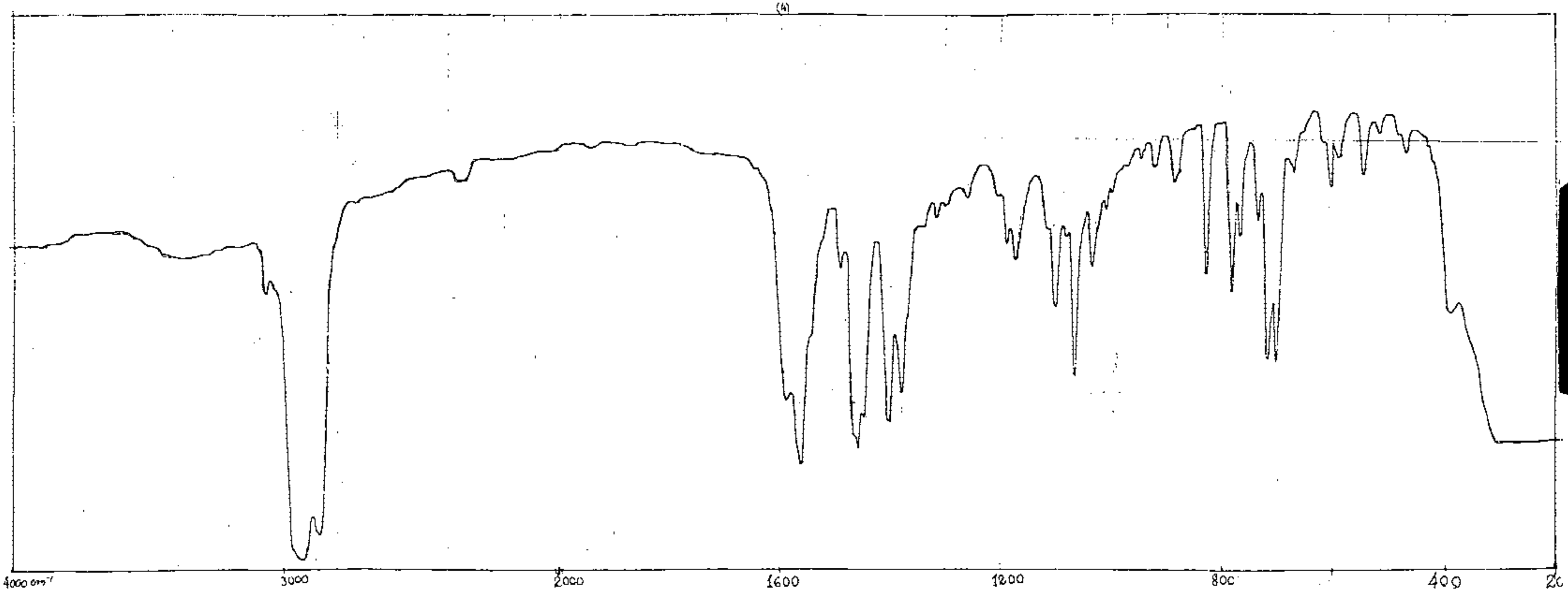
The compound melted at 313°C.

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

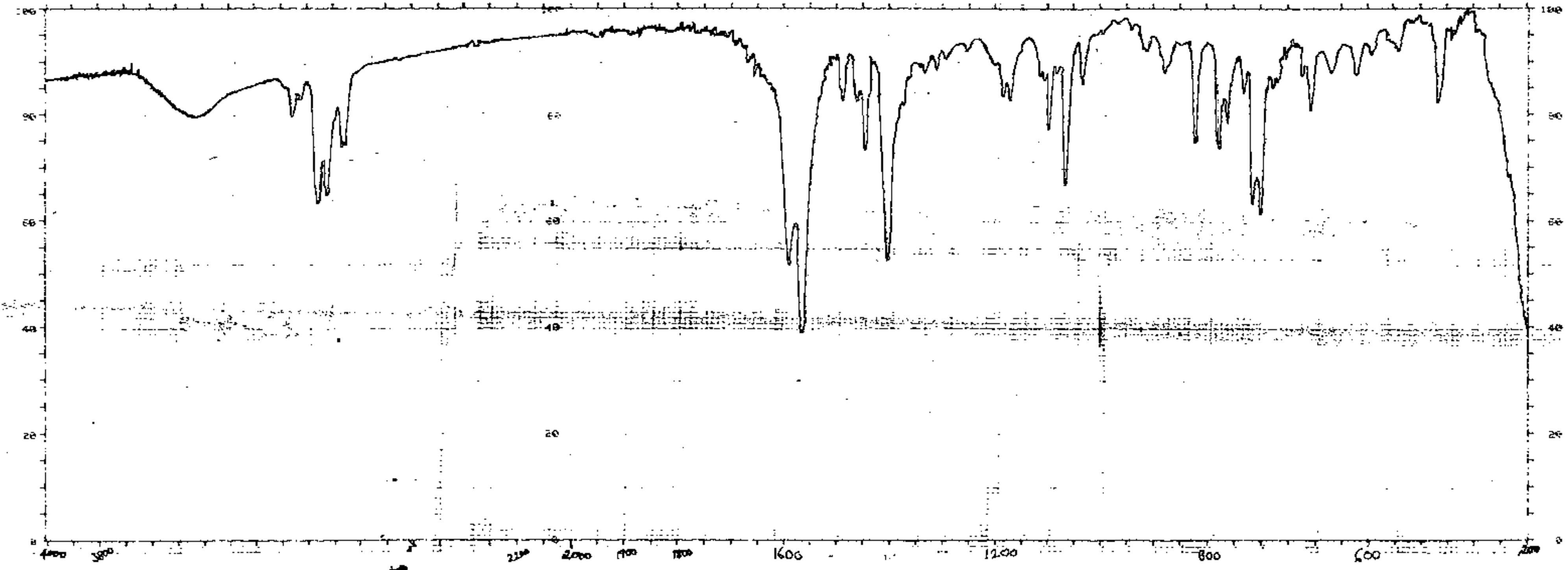
Found	:	C 57.49	H 6.29	Sn 26.02
Calcd	:	C 57.51	H 6.10	Sn 25.92

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

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



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



IR spectrum of Dibutyl tin diphenyl glycolate (solution)

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

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

(Yield ≈ 62%)

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

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

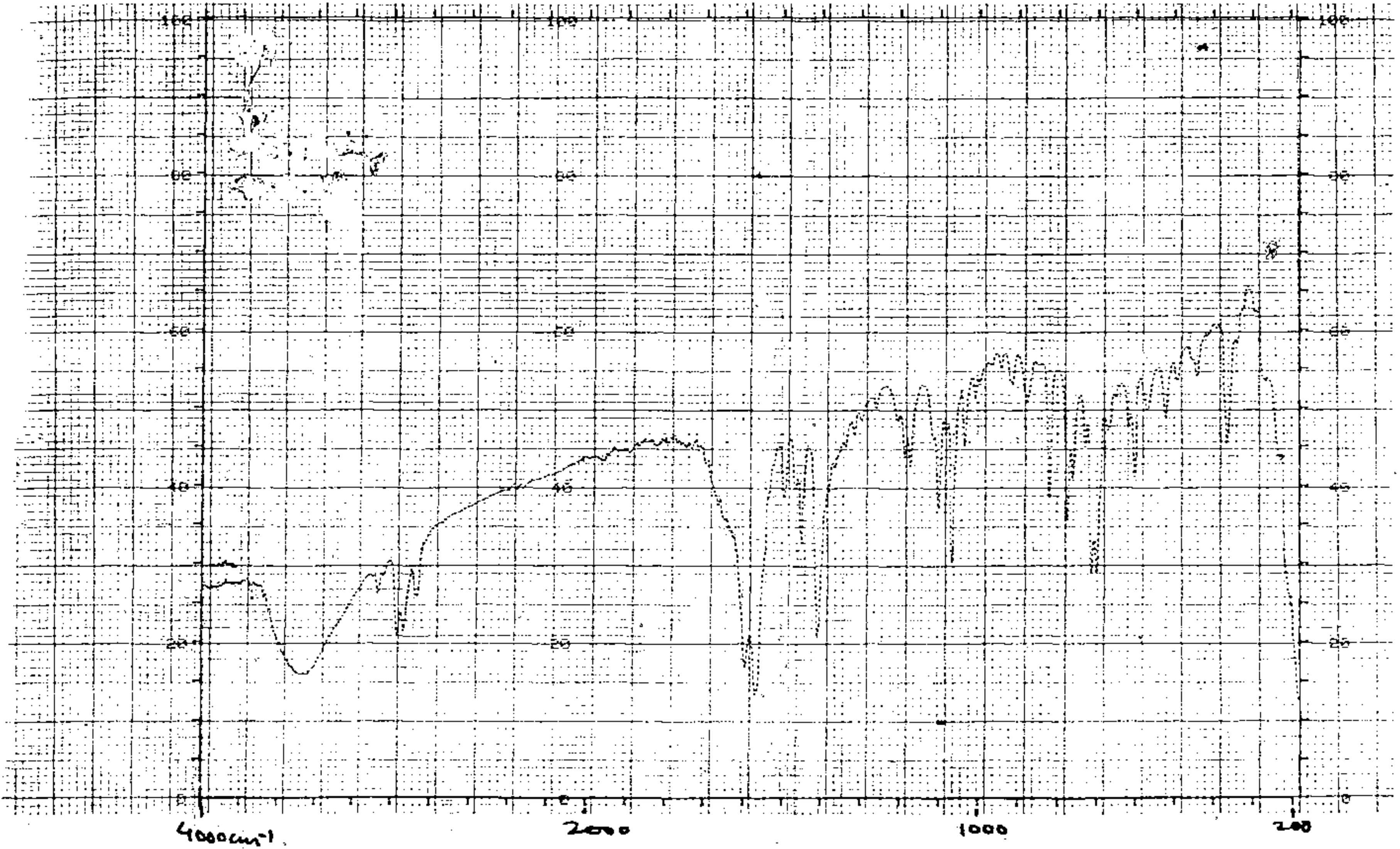
Found	:	C 56.86	H 5.92	Sn 24.90
Calcd	:	C 57.51	H 6.10	Sn 25.92

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

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

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

So these two compounds are same.



IR spectrum of Dibutyl tin diphenyl glycolate (KBr)

3. Diphenyl tin diphenyl glycolate

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

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

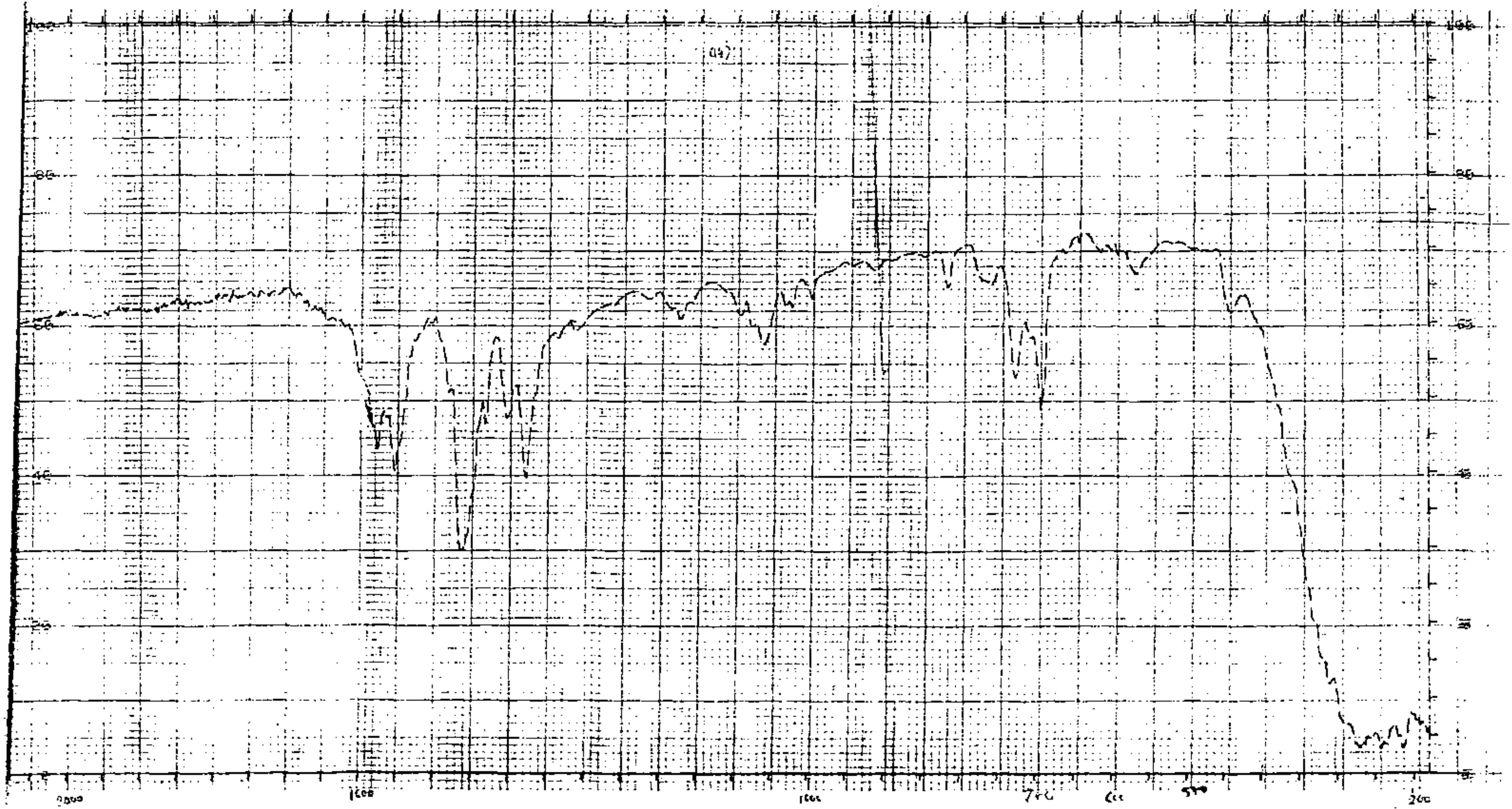
The compound decomposed after 282°C.

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

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

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

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



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

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

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

(Yield = ~55%).

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

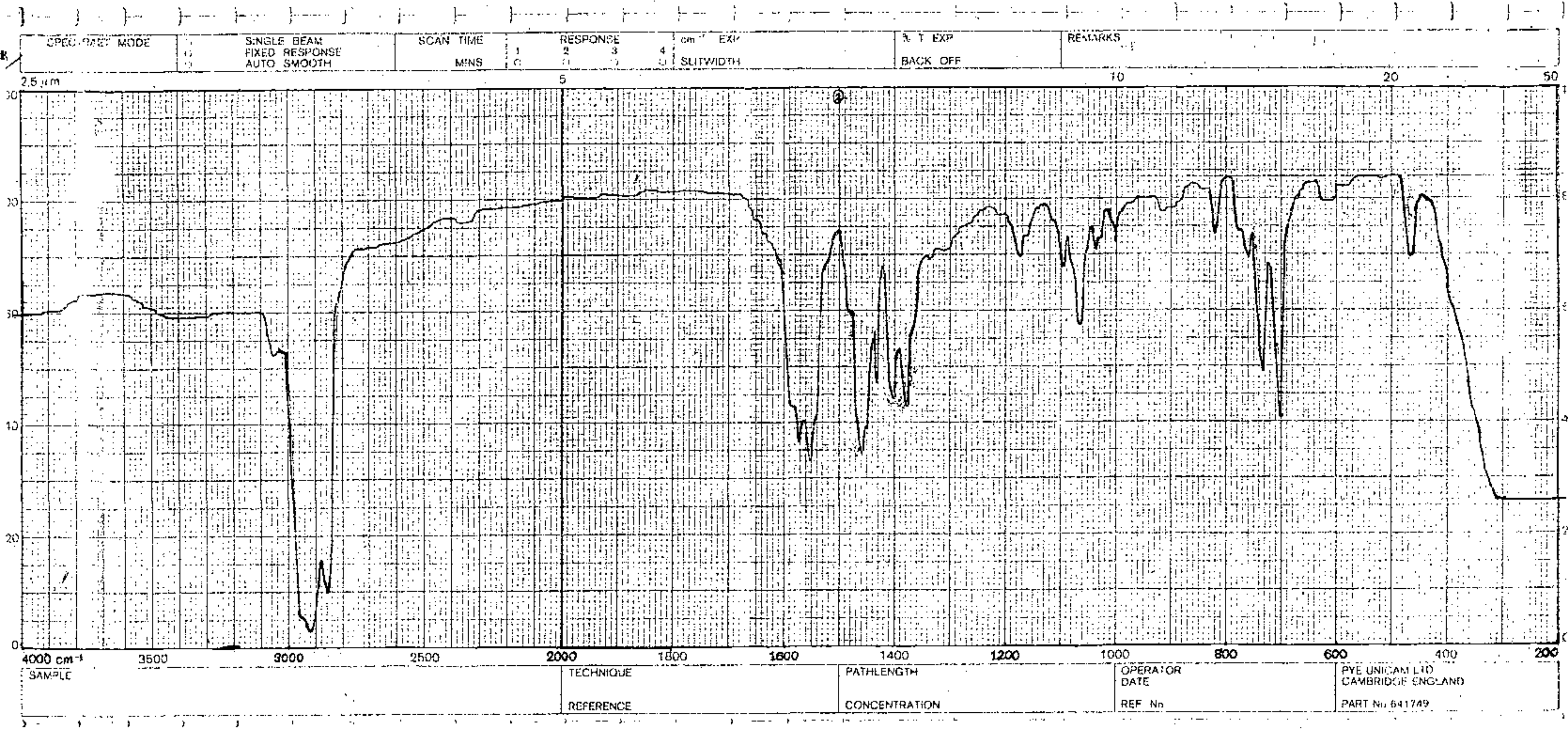
The compound decomposed at 280-282°C.

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

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

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

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



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

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

4. Dibenzyl tin diphenyl glycolate

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

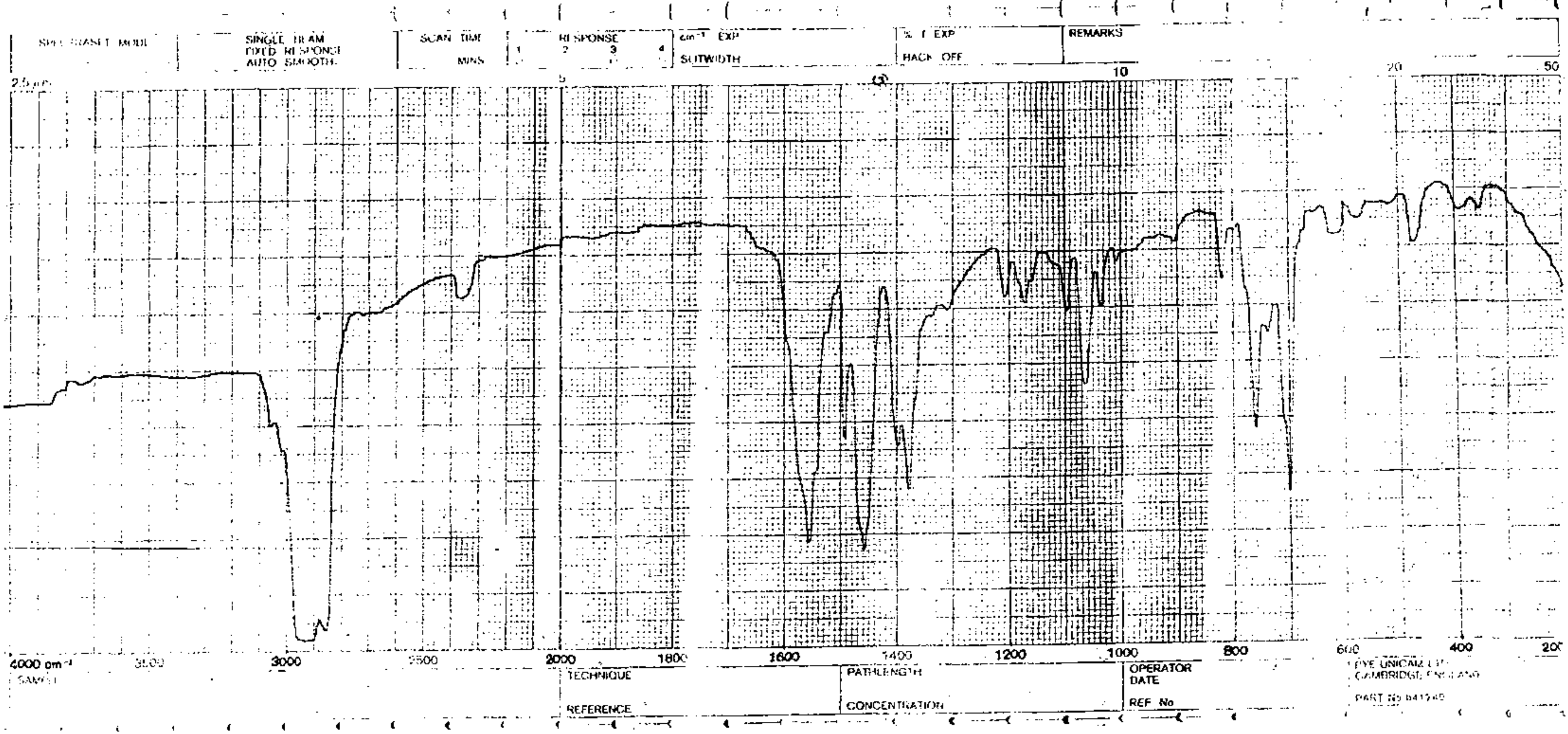
Purification have been done by washing several times with warm chloroform.

(Yield = ~50%).

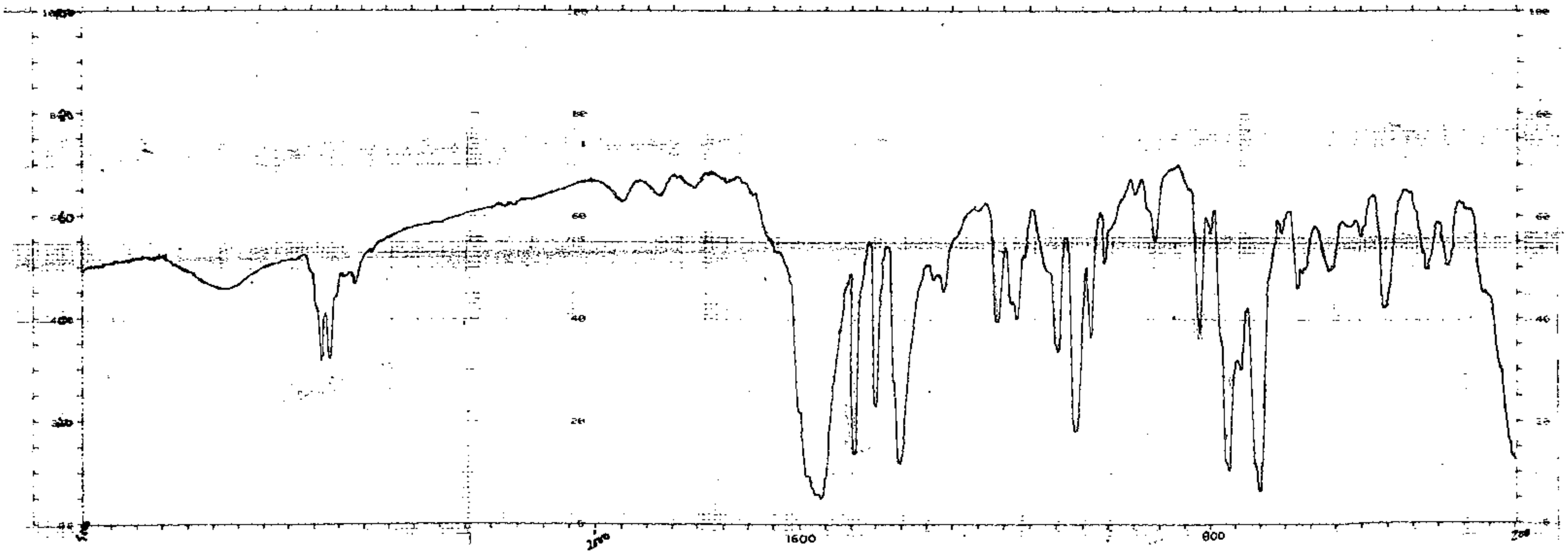
The compound melted at 226°C and decomposed after this temperature.

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

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



IR spectrum of Dibenzyl tin diphenyl glycolate (nujol)



IR spectrum of Dibenzyl tin diphenyl glycolate (Solution)

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

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

5. Dimethyl tin *bis* (diphenyl glycolate)

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

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

(Yield = ~55%).

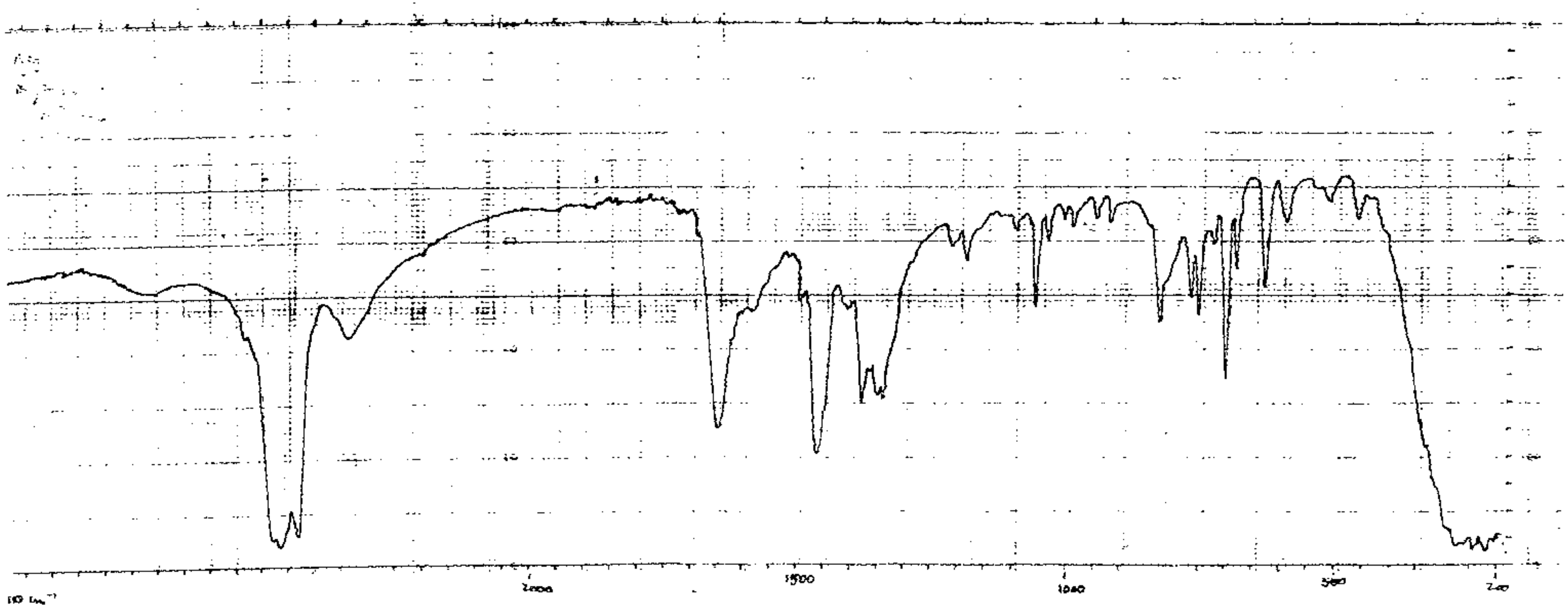
The compound was purified by repeated crystallisation from chloroform and finally dried in vacuum.

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

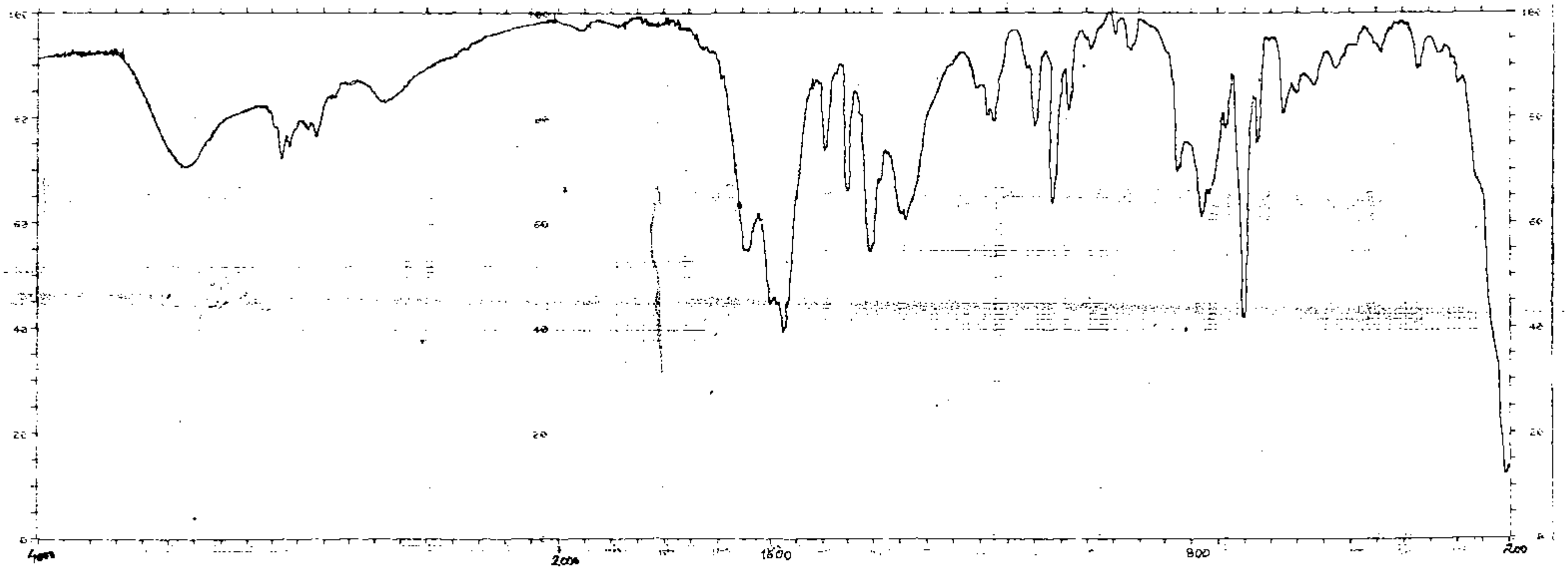
The same compound was found, when the reactants were used in 1:1 molar proportion, though the yield was rather poor.

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

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



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



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

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

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

6. Dicyclohexyl tin diphenyl glycolate

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

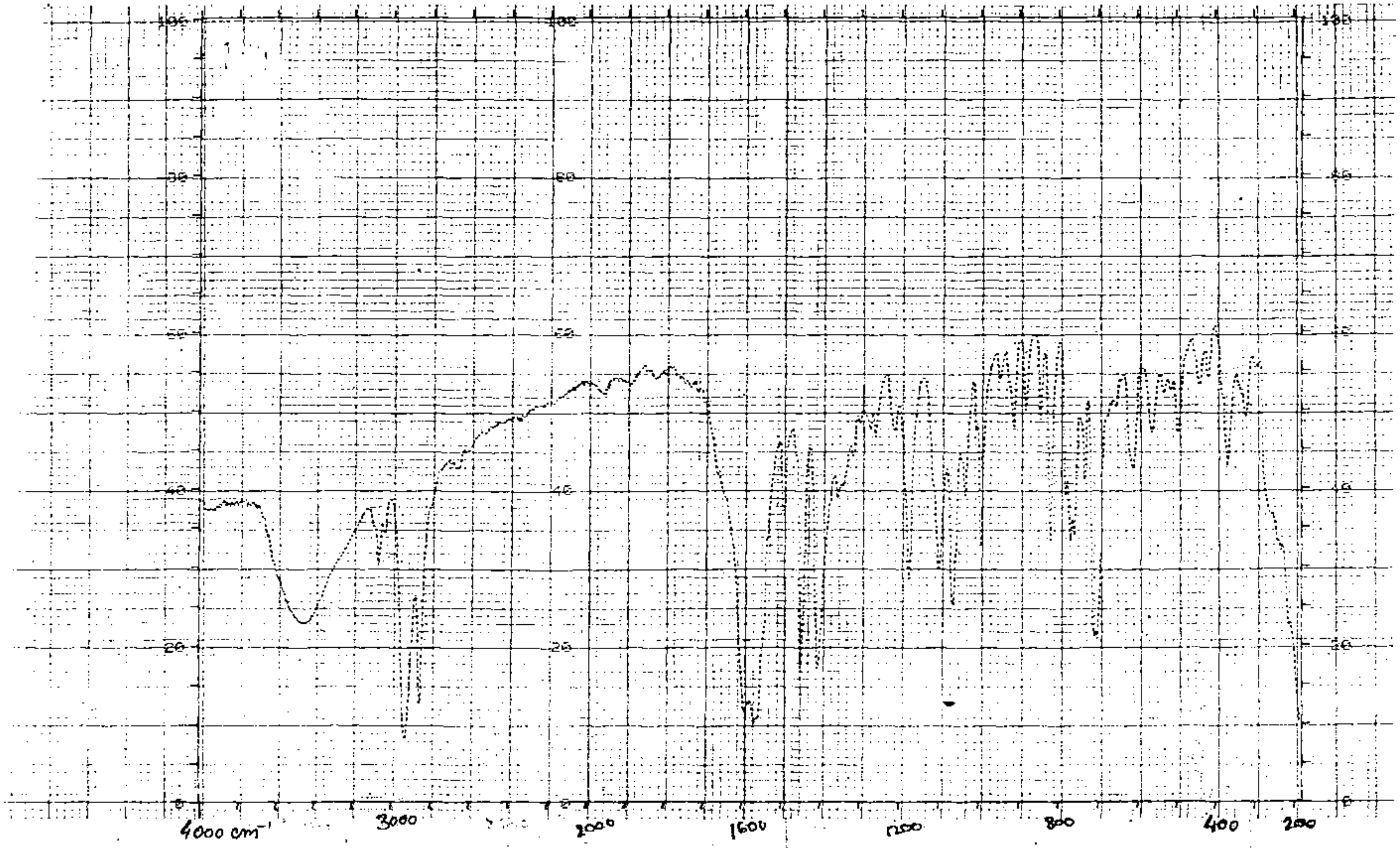
After reaction the mixture was cooled and filtered off the unreacted suspensions. The clean solution was concentrated to about 15 ml and kept overnight. A white crystalline product appeared. Purified by washing with hot chloroform and then dried in vacuum.

(Yield = ~52%).

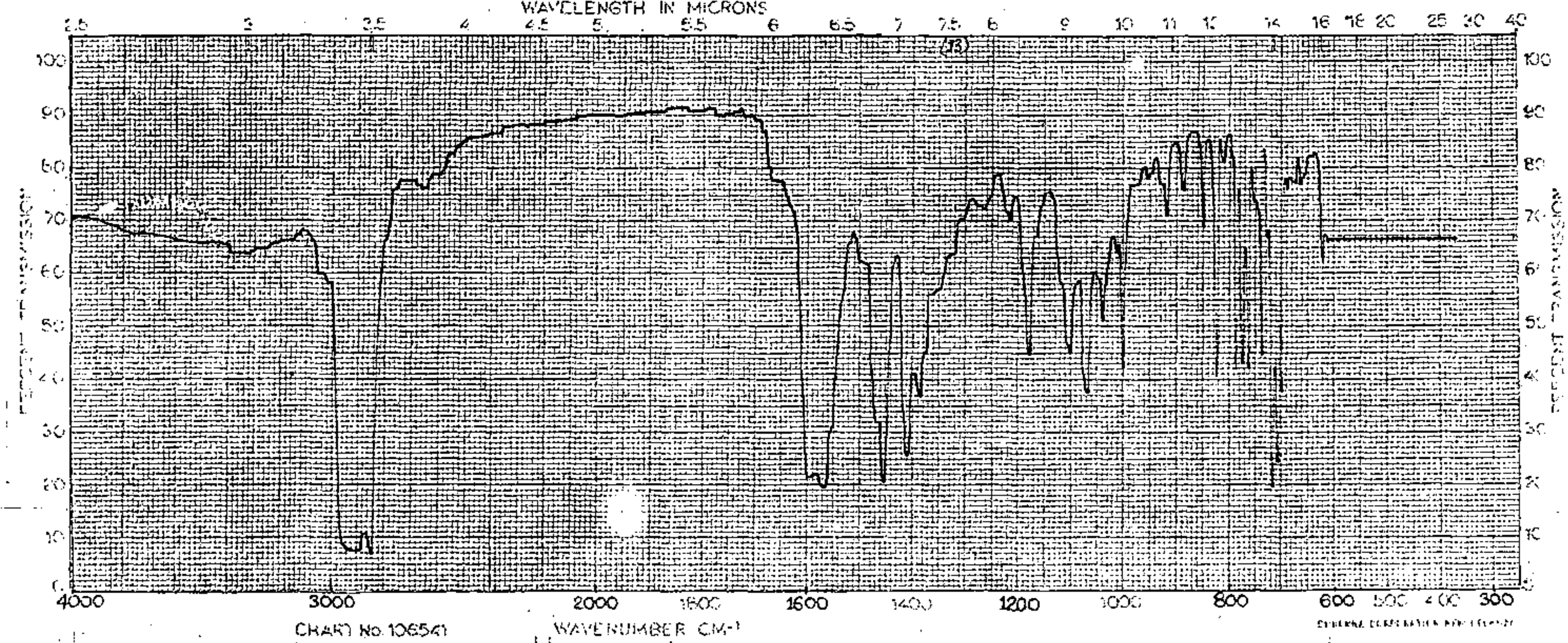
Melting point was found at 320°C.

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

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



IR spectrum of Dicyclohexyl tin diphenyl glycolate (KBr)



IR spectrum of Dicyclohexyl tin diphenyl glycolate (nujol)

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

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

7. Dipropyl tin diphenyl glycolate

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

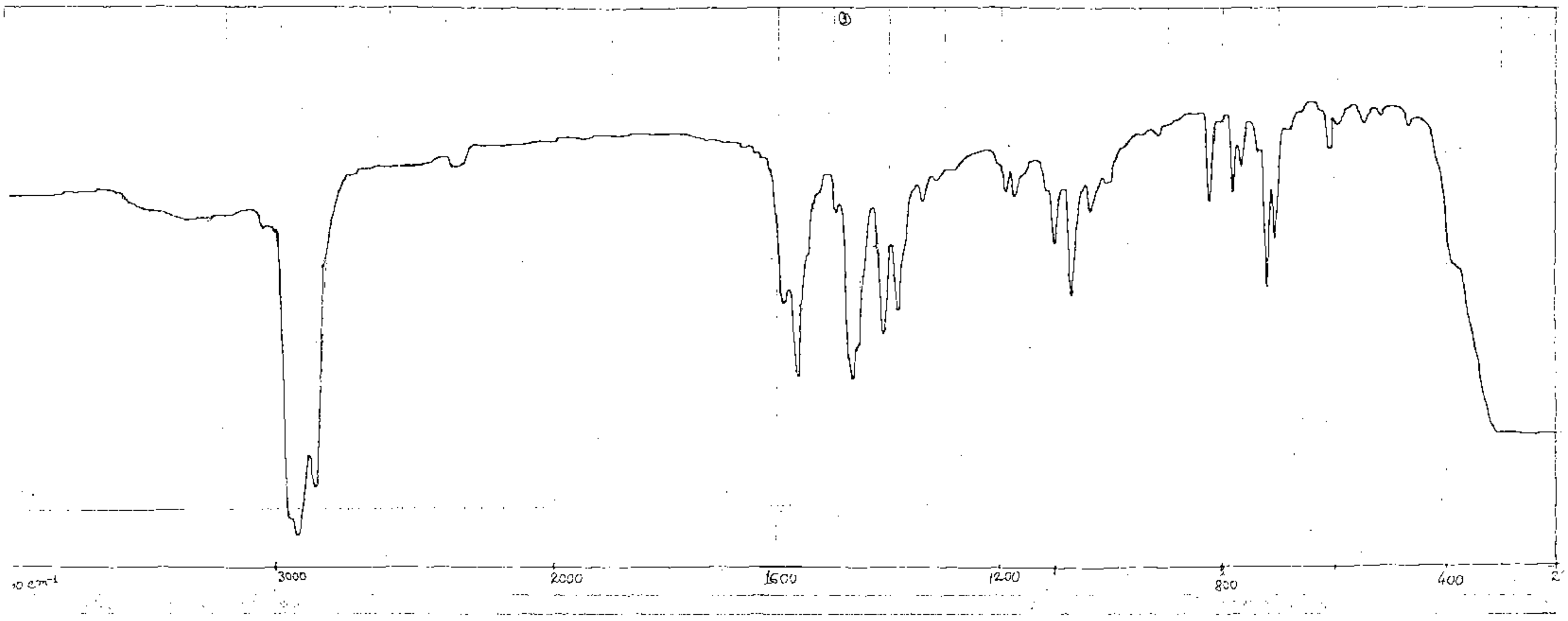
The compound was purified by repeated washing with hot chloroform.

(Yield = ~50%)

The compound decomposed after 230°C.

% Analysis for $C_{20}H_{24}O_{3}Sn$

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



IR spectrum of Dipropyl tin diphenyl glycolate (nujol)

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

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

Some Attempted Reactions

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

TABLE I

MOLAR CONDUCTANCE OF SOME OF THE COMPOUNDS

Temp. 25°C

Solvent : DMSO

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

TABLE II

^{1}H NUCLEAR MAGNETIC RESONANCE SPECTRAL DATA

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

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

TABLE III

^{13}C NUCLEAR MAGNETIC RESONANCE SPECTRAL DATA

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

TABLE IV

^{119}Sn NUCLEAR MAGNETIC RESONANCE SPECTRAL DATA

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

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

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

TABLE V

APPARENT MOLECULAR WEIGHT DATA

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

TABLE VI

SOME INFRARED SPECTRAL DATA IN SOLUTION

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

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

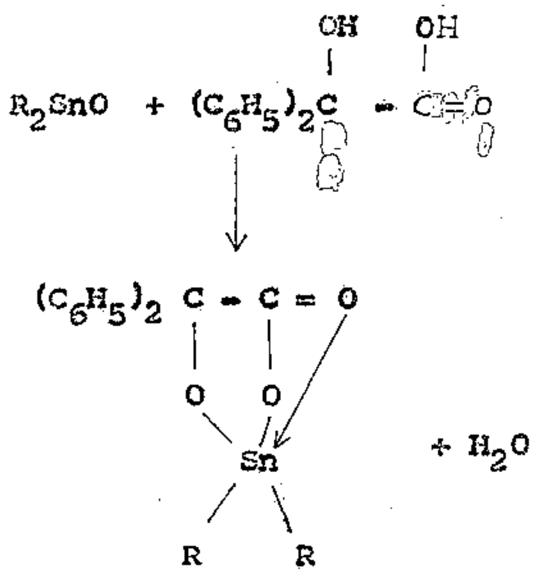
TABLE VII

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

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

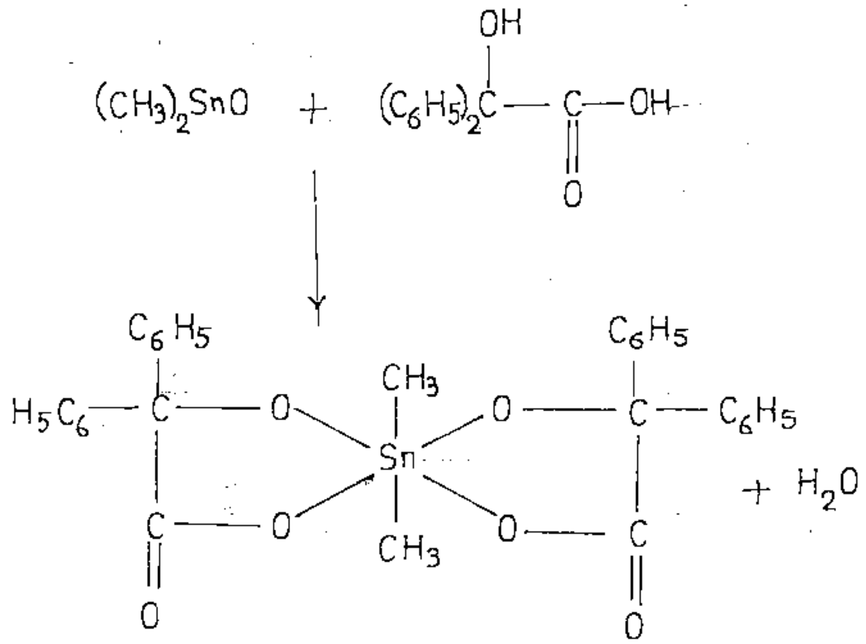
DISCUSSION

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



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

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



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

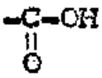
The elemental analyses gave satisfactory data for the suggested molecular composition of these compounds. The infrared spectra of the compounds were recorded.

Infrared spectra

The ν —OH peak of diphenyl glycolic acid was found absent in all these organotin derivatives, suggesting replacement of both of the hydroxyl and carboxyl protons of the ligand. Several IR spectra of the derivatives have been recorded upto 200 cm^{-1} in Nujol, KBr and in T.H.F. There are number of peaks in the region of 300-600 cm^{-1}, some of which could possibly due to $\nu_{\text{Sn-C}}$ and $\nu_{\text{Sn-O}}$ frequencies but due to some confusing nature of these peaks, we refrain from unambiguous assignments of $\nu_{\text{Sn-C}}$ and $\nu_{\text{Sn-O}}$ peaks in these organotin derivatives. These spectra certainly indicate characteristic peaks from some ligand and organotin moieties but we would like to concentrate on the peaks due to carbonyl groups of the ligand and organotin derivatives.

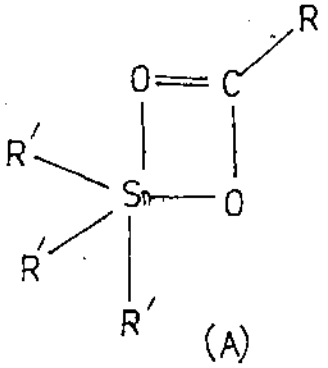
ν_{CO} peaks of the ligand and organotin derivatives (cm^{-1})

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

Compared to carbonyl peak of Diphenyl glycolic acid, the carbonyl peaks of the organotin derivatives were shifted considerably indicating the formation of the esters. However in most cases, two peaks appeared, one in the range of 1585-1600 cm^{-1} while the other band appeared $\sim$ 1560-1570 cm^{-1}. The latter bands are more intense than the former ones. In case of Dimethyl tin bis (diphenyl glycolate), only one band appeared at 1650 cm^{-1} in nujol, but in T.H.F. solution the same compound gave a peak at 1650 cm^{-1} and a group of three bands around 1570 cm^{-1}. The shifting of carbonyl bands from 1715 cm^{-1} to around 1570 cm^{-1} for most of the compounds may be due to coordination of $C = 0$ group to tin atom, in addition to the replacement of the proton of  $-\underset{\underset{O}{\|}}{C}-OH$ group. The ^{119}Sn spectra which will be discussed later, support such suggestion for most of the organotin derivatives except for the dimethyltin derivative. The infrared spectra do not show any significant spectral changes between the solid and solution state for most of diorganotin derivatives.

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

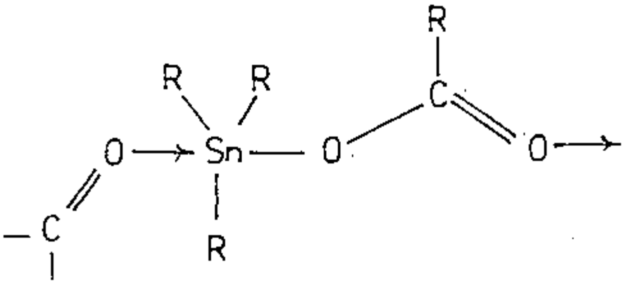
In 1960 Okawara et al (30) investigated the infrared spectra of some methyltin acetates and formates. They interpreted the spectra of trimethyl tin carboxylates e.g. $(CH_3)_3SnOOCR'$ ($R' = H, CH_3$) in terms of ionic structures, since the spectra showed the existence of a planar trimethyl tin group and indicated an ionic type carboxylate group. However Beattie and Gilson pointed out that the spectroscopic evidence might also be interpreted in terms of either bridging carboxylate groups or simple acetate ions (53). Viscosity measurements by Jansen et al (54) supported the bridging structure. The X-ray diffraction of trimethyltin formate indicated that the structure consisted a planar trimethyl tin and a formoxy group arranged alternately along a helix chain. The tin atoms are penta coordinated by three carbon atoms and two oxygen atoms (25). Recently, a number of workers have studied different types of organotin carboxylates by IR, ^{13}C and ^{119}Sn NMR and X-ray diffraction studies. From their results, it may be concluded that organotin carboxylates can be classified into two major groups. These may be monomeric discrete intramolecular chelated carboxylates (82)



(A)

R = alkyl or aryl
R' = aryl

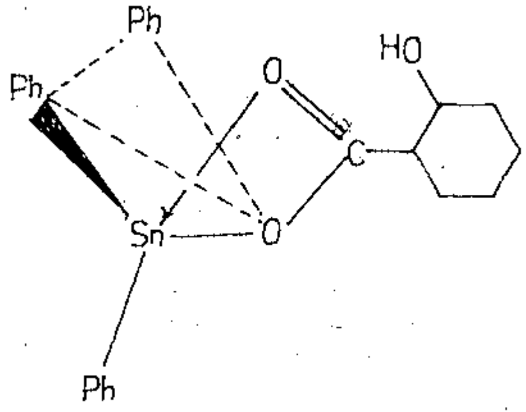
associated arrangements containing five coordinated tin atoms.



(B)

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

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

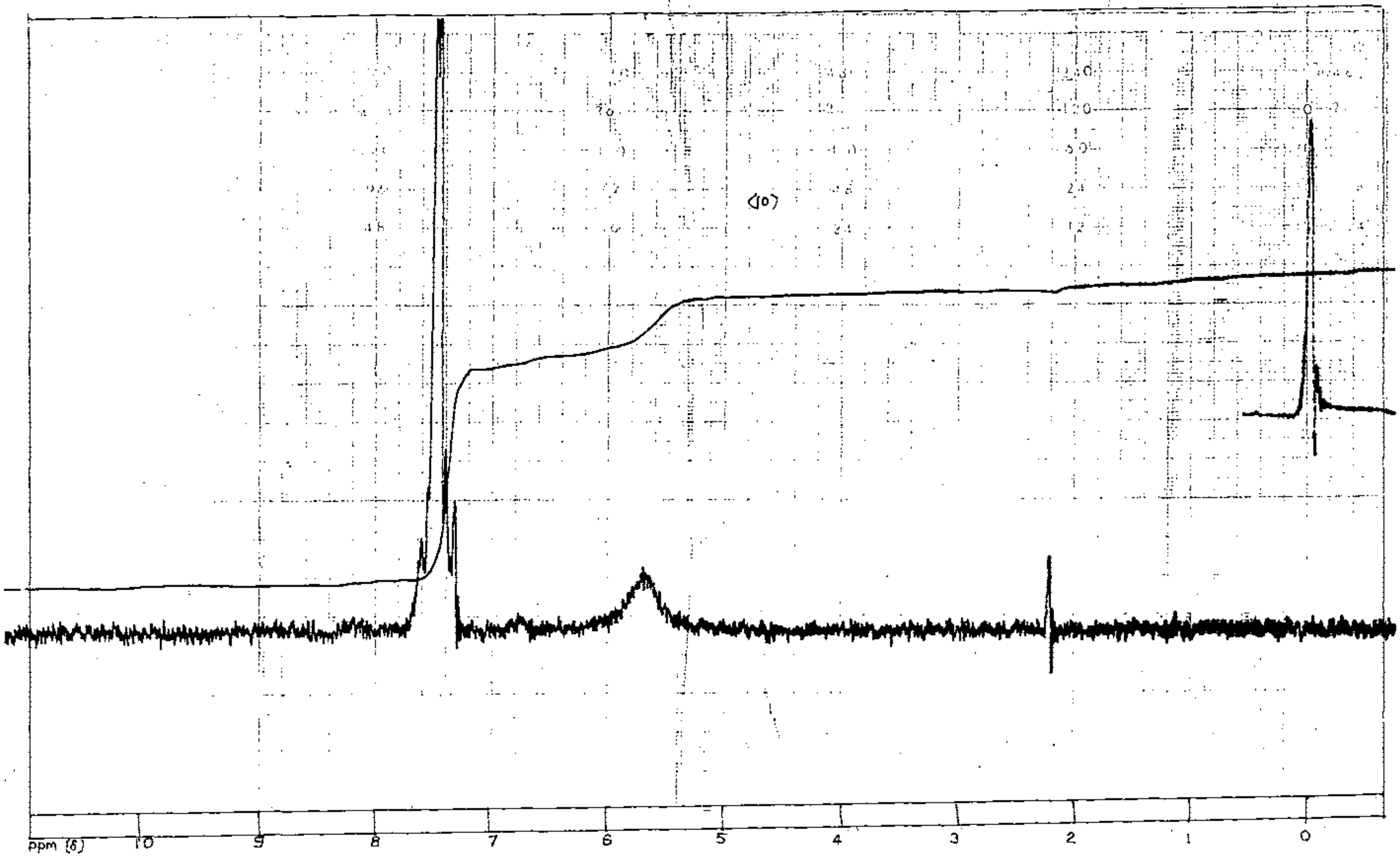


Similar type of intramolecular chelated structures are present with a number of organotin carboxylates.

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

^{1}H NMR spectra

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



^{1}H NMR spectrum of Diphenyl glycolic acid

Dibutyl tin diphenyl glycolate (in d^6 DMSO)

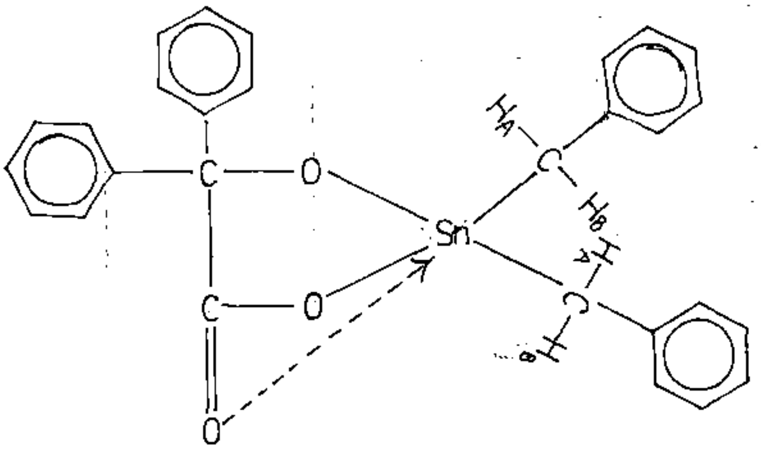
Carboxyl and hydroxyl protons were found to be completely absent and the alkyl protons appeared as triplet at δ 0.62-1.00 (butyl methyl -6H) and methelene protons appeared as complex pattern in between δ 1.02-1.9 (butyl methylene protons 12H). The aromatic protons appeared as complex pattern in between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

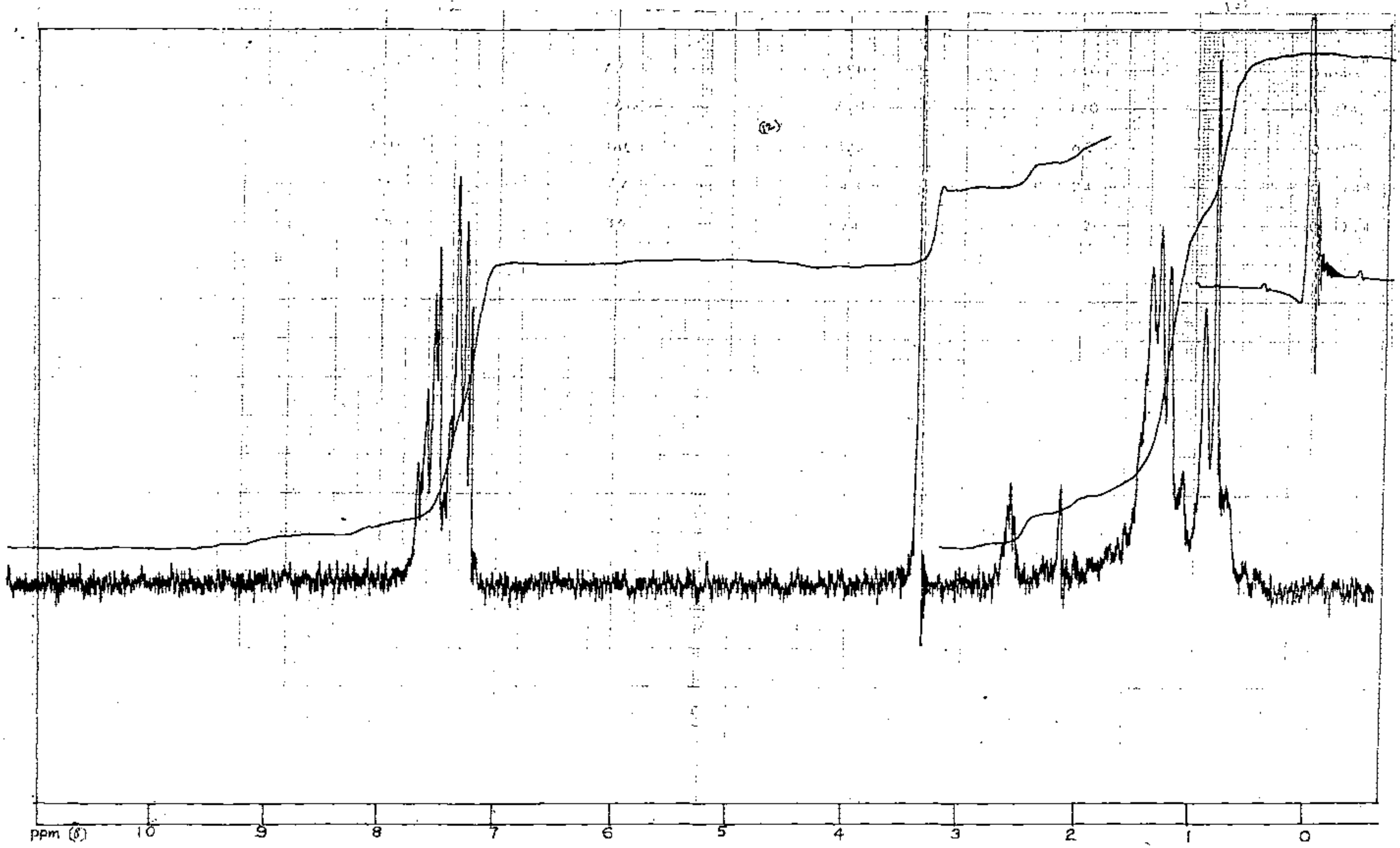
Diphenyl tin diphenyl glycolate

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

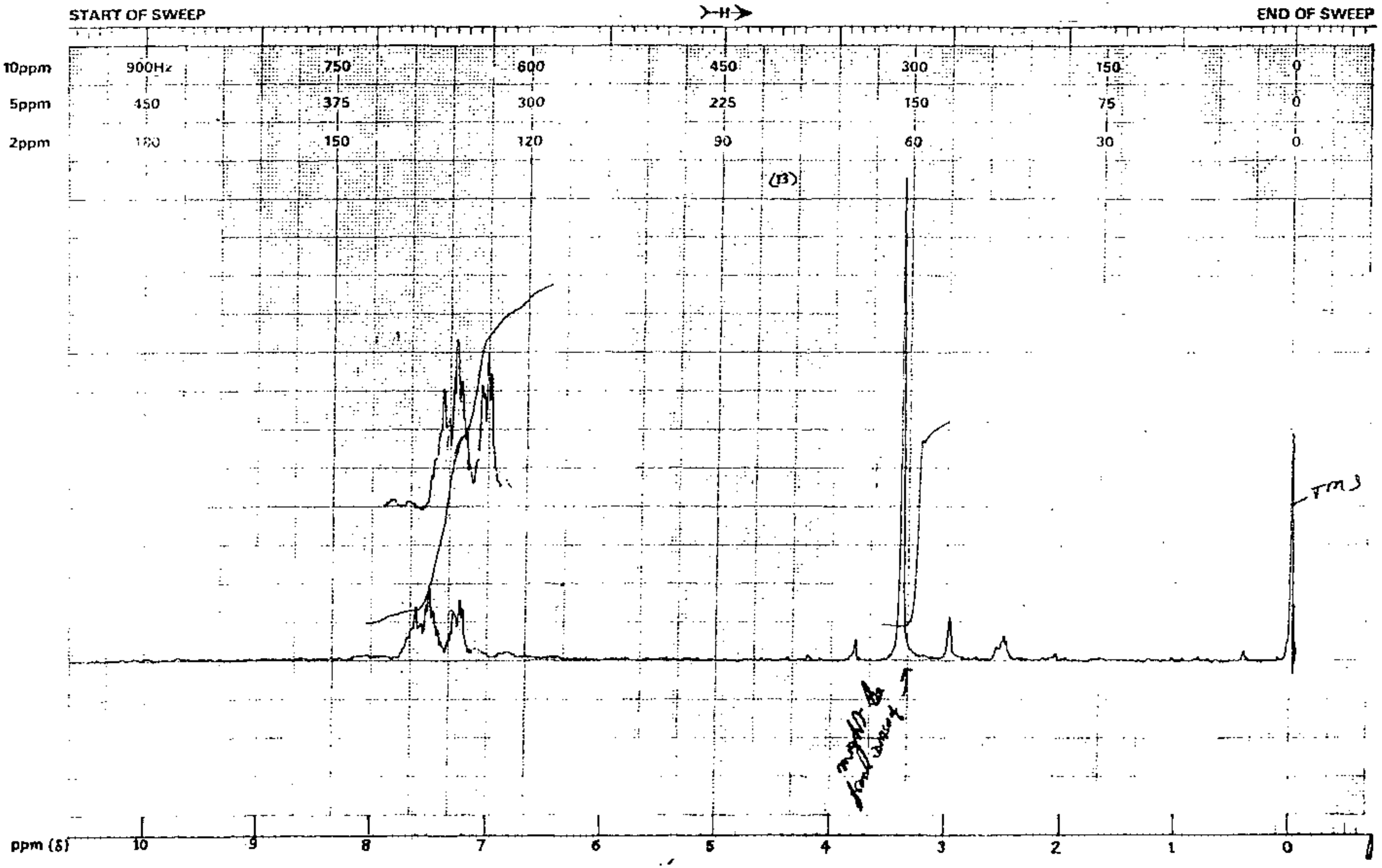
Dibenzyl tin diphenyl glycolate

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

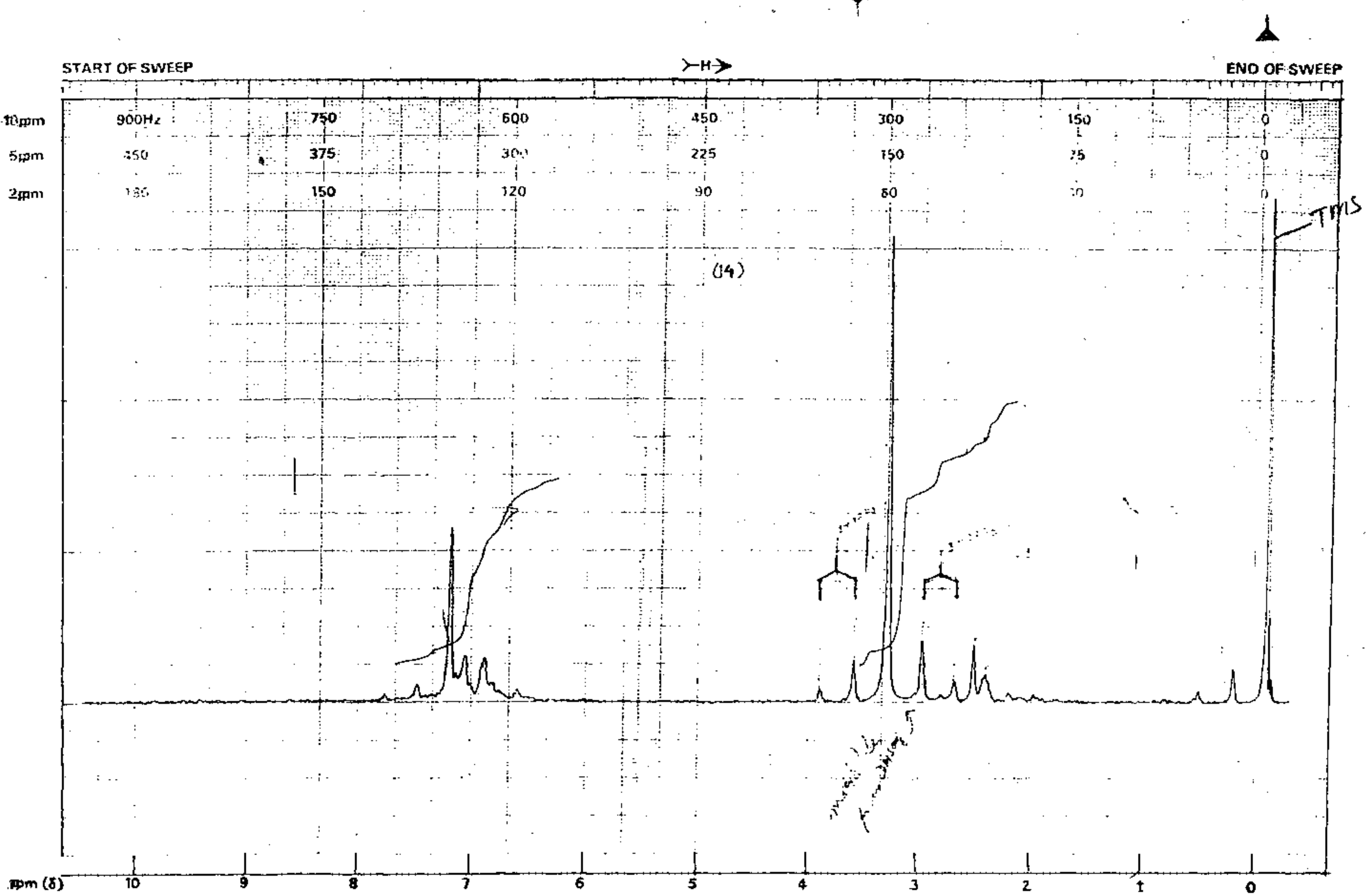




^{1}H NMR spectrum of Dibutyl tin diphenyl glycolate



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



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

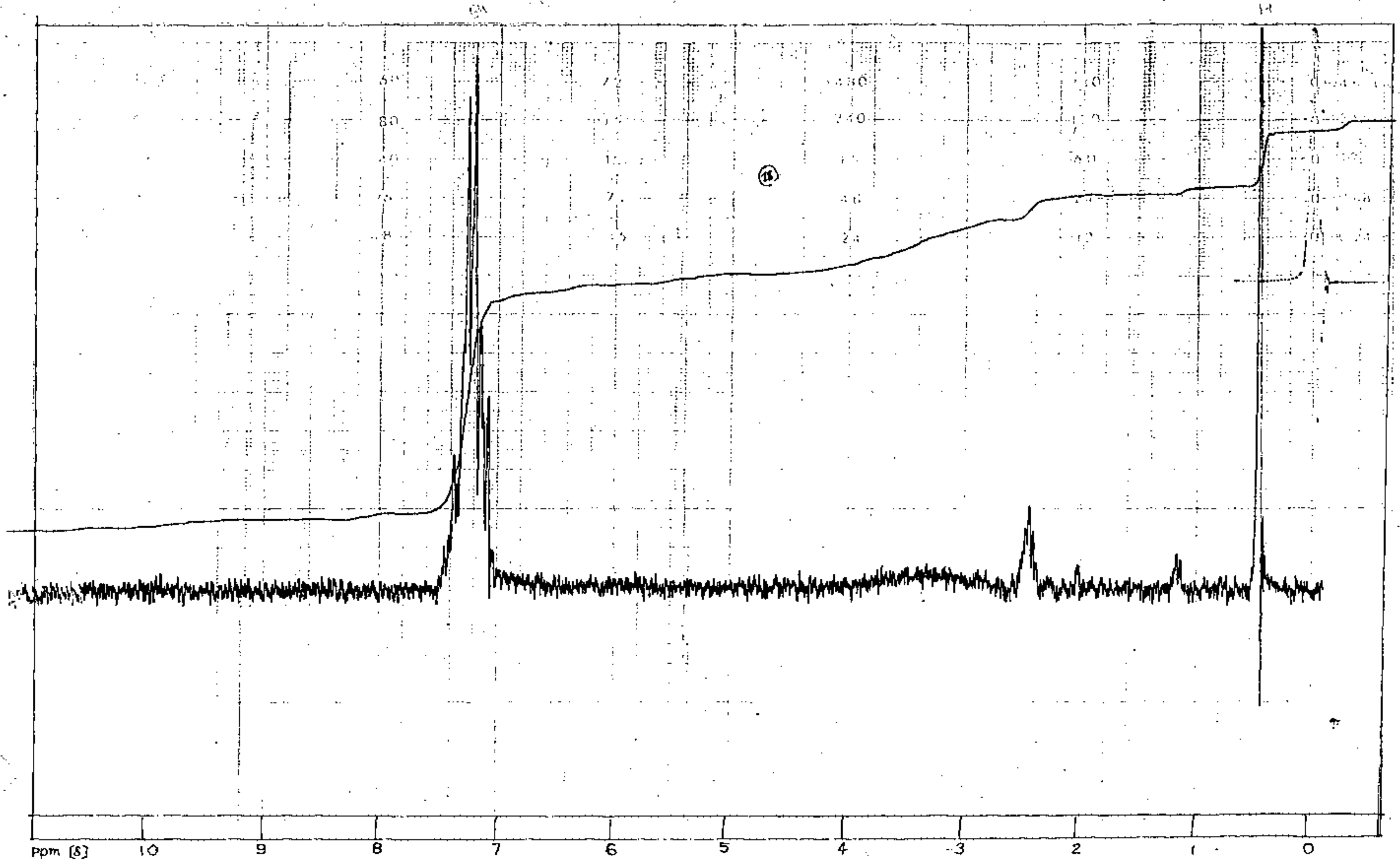
The aromatic protons appeared at δ 6.9-7.4 (ArH = 20H) as complex pattern. Here also it was not possible to assign individual type of aromatic protons.

Dimethyl tin bis (diphenyl glycolate)

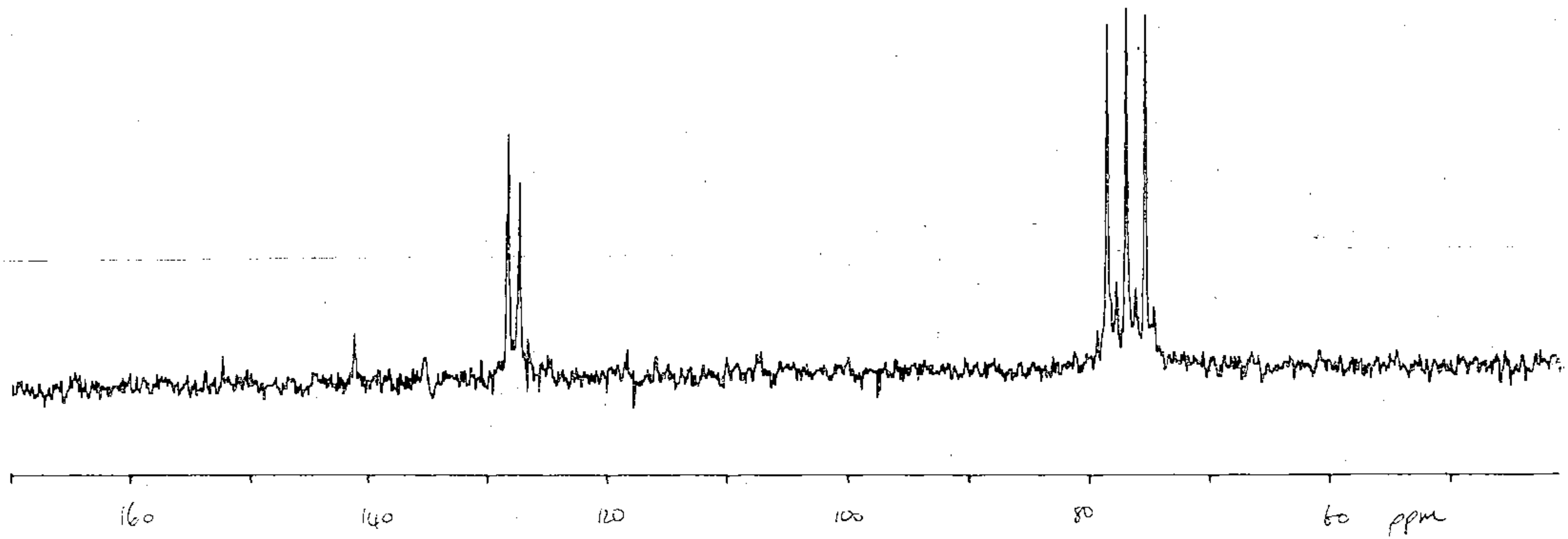
Here also carbonyl and hydroxyl protons were absent. The dimethyl tin protons appeared as singlet at δ 0.42 (methylene protons -6H), suggesting trans disposition of the methyl groups. The aromatic protons appeared as complex pattern in between δ 7.02-7.5 (ArH = 20H). The ratio of aromatic and aliphatic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

^{13}C NMR spectra

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

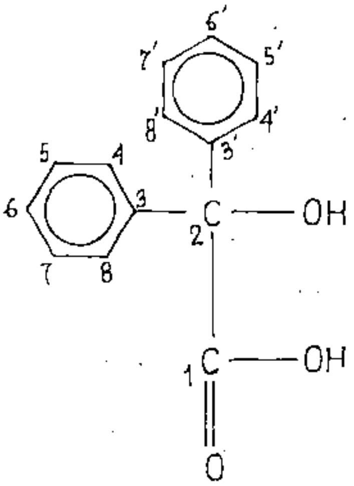


^{1}H NMR spectrum of Dimethyl tin <u>bis</u> (diphenyl glycolate)



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

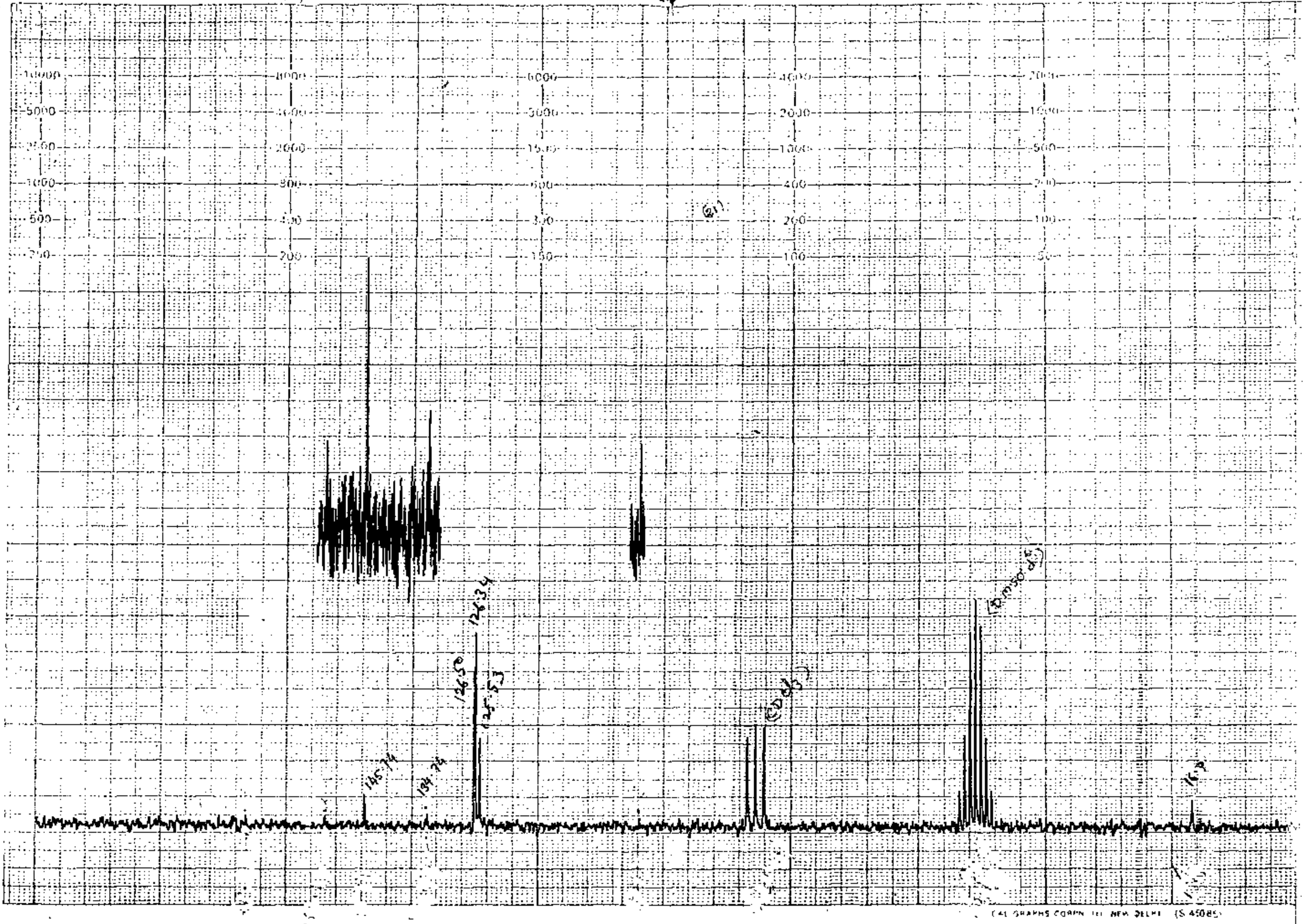
four peaks at δ 127.35 (C_5, $C_{5'}$, C_7 & $C_{7'}$), 127.87 (C_4, $C_{4'}$, C_8 & $C_{8'}$), 128.30 (C_3 & $C_{3'}$) and 128.41 (C_6 & $C_{6'}$) aromatic carbon atoms.



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

Dimethyl tin bis (diphenyl glycolate)

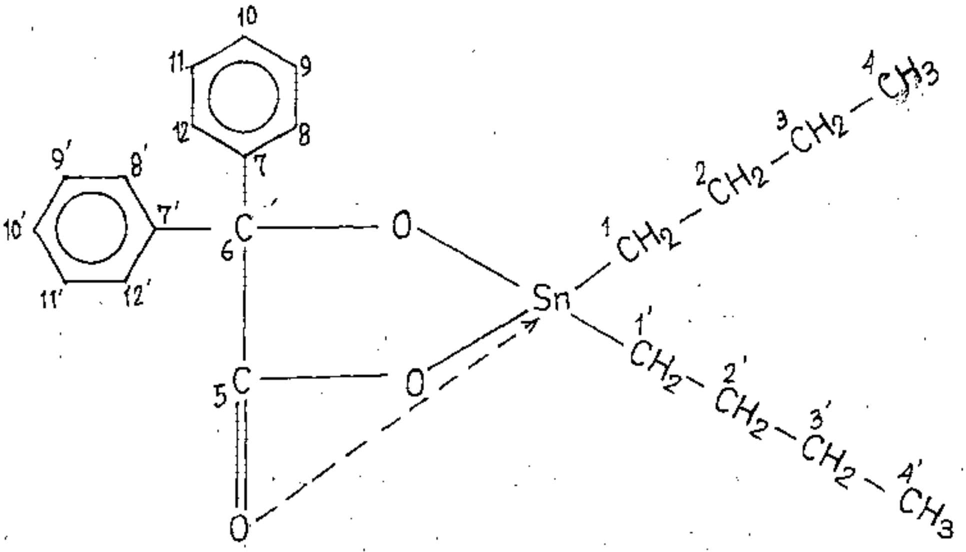
The ^{13}C NMR spectrum gave a number of characteristic peaks. The methyl carbon atoms appeared as a single peak at δ 16.9 while $-\overset{|}{\underset{|}{C}}-$ OH carbon atom appeared at δ 134.74 and $O = \overset{|}{C} -$ OH carbon atom appeared at δ 145.74. The shielding of $= \overset{|}{C}-OH$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



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

Dibutyltin diphenyl glycolate

The aliphatic peaks appeared in between δ13.29-26.38 and may be assigned (80) as follows:



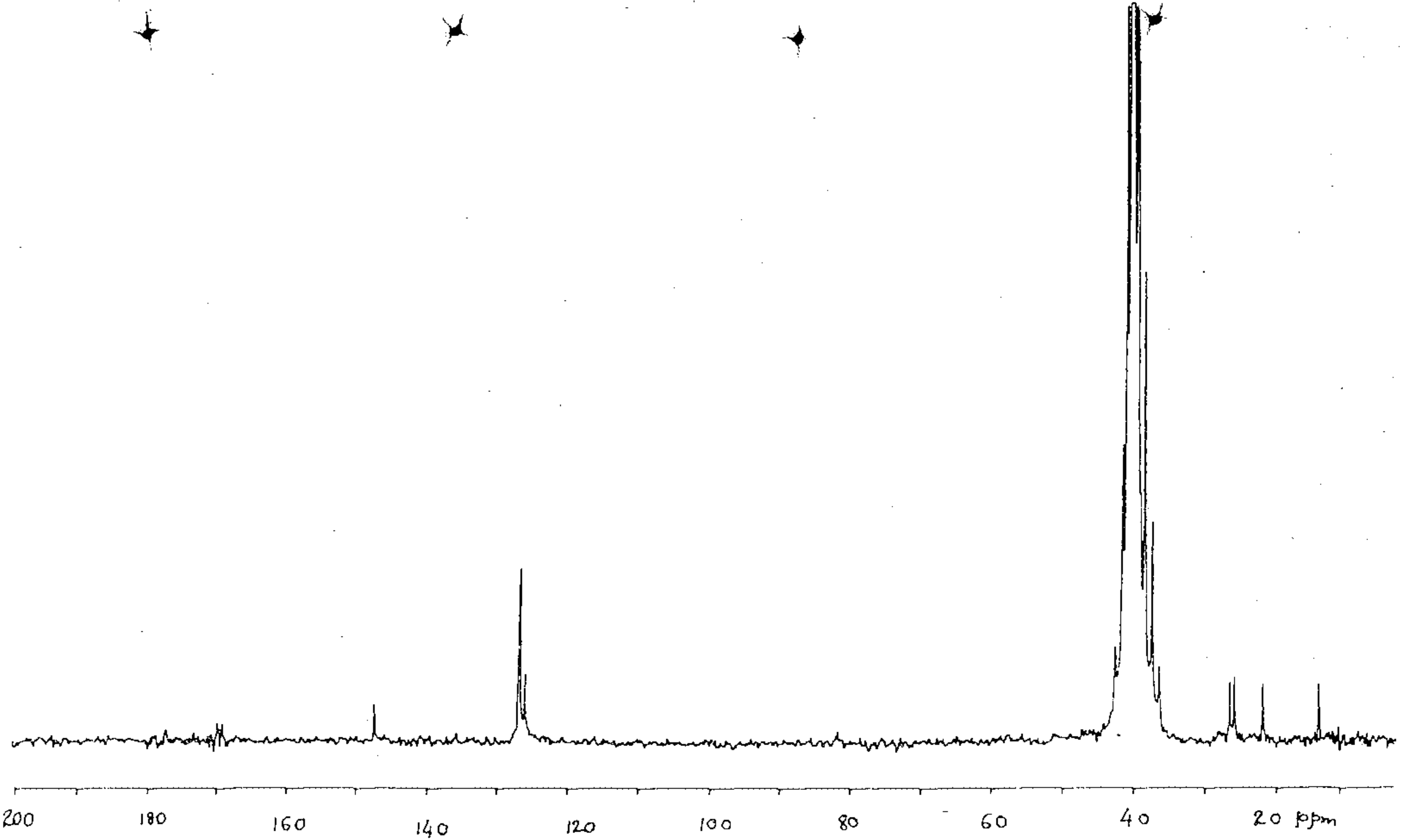
δ 13.29 $C_4, C_{4'}$

δ 21.78 $C_1, C_{1'}$

δ 25.26 $C_3, C_{3'}$

δ 26.38 $C_2, C_{2'}$

The C_5 carbon atom appeared at δ147.40 while due to poor intensity of the spectrum the C_6 carbon atom peak could not be

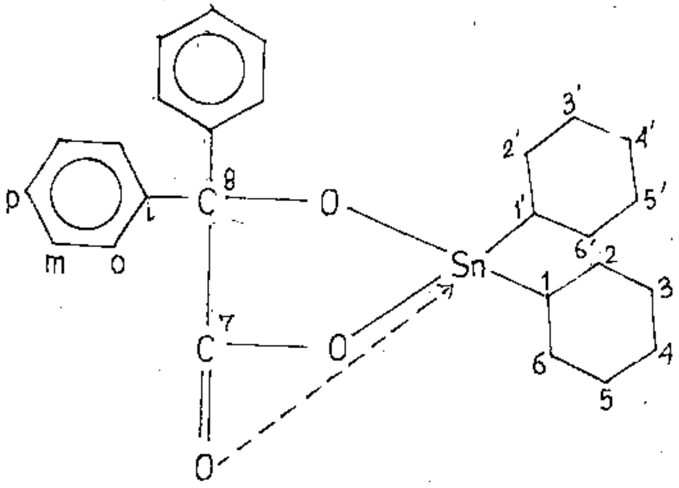


^{13}C NMR spectrum of dibutyl tin diphenyl glycolate (in d^6 DMSO) unambiguously assigned. Compared to ligand, the C_5 carbon atom peak showed considerable shielding.

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

Dicyclohexyltin diphenyl glycolate

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

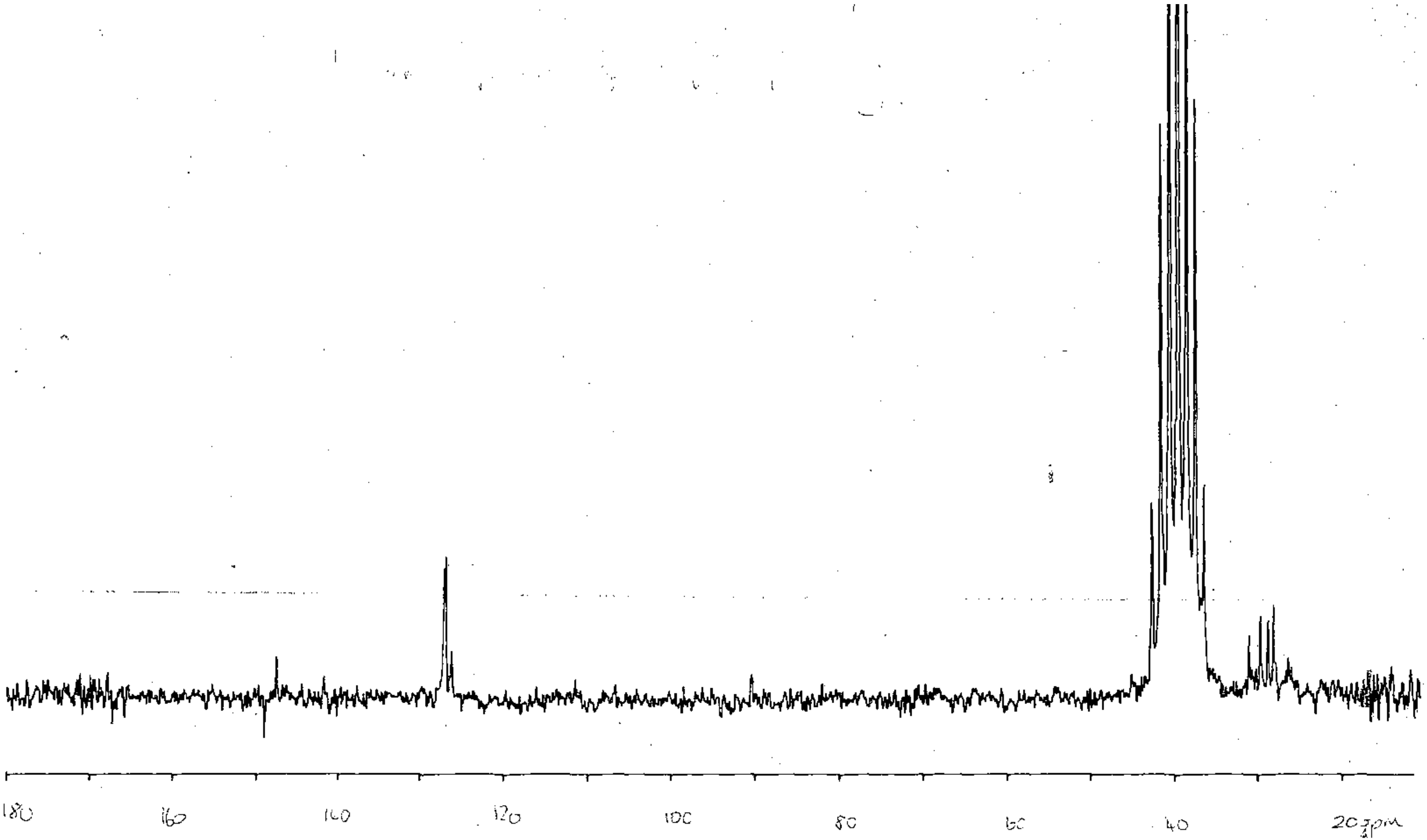


δ 27.95 – C_4, $C_{4'}$

δ 28.58 – C_1, $C_{1'}$

δ 29.50 – C_3, $C_{3'}$, C_5, $C_{5'}$

δ 30.90 – C_2, $C_{2'}$, C_6, $C_{6'}$



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

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

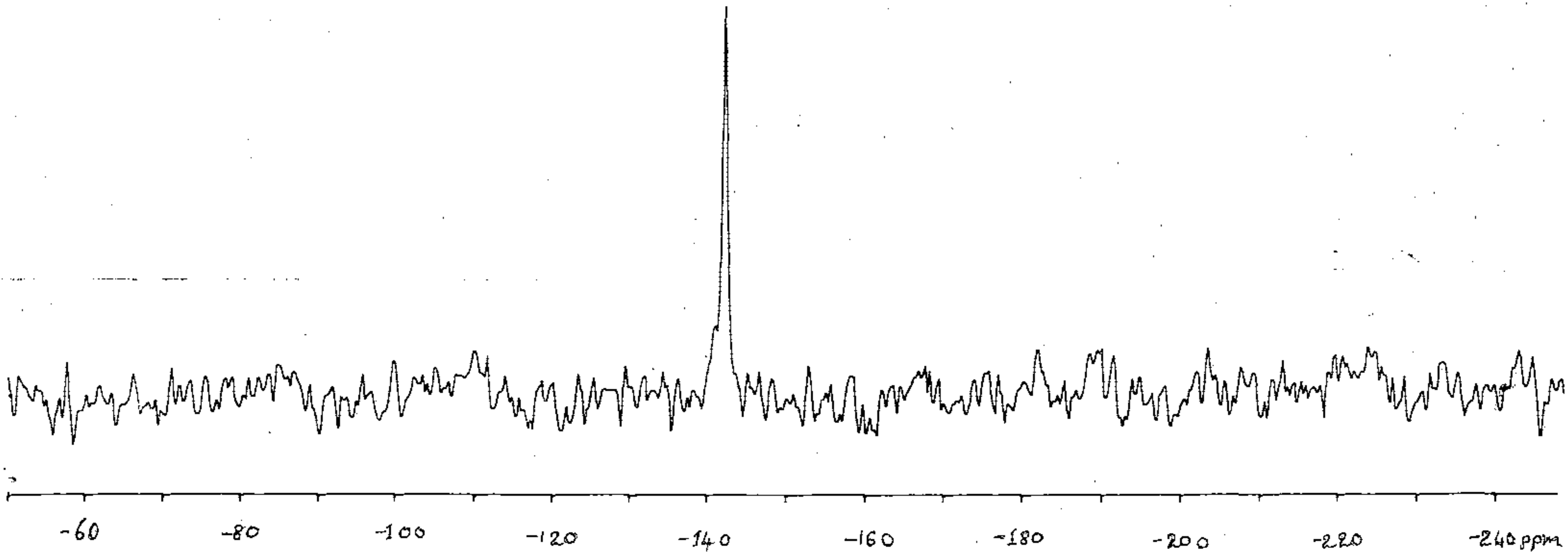
δ 126.17 (m)
δ 126.40 (p)
δ 126.94 (o)
δ 127.10 (i)

^{119}Sn NMR spectra

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

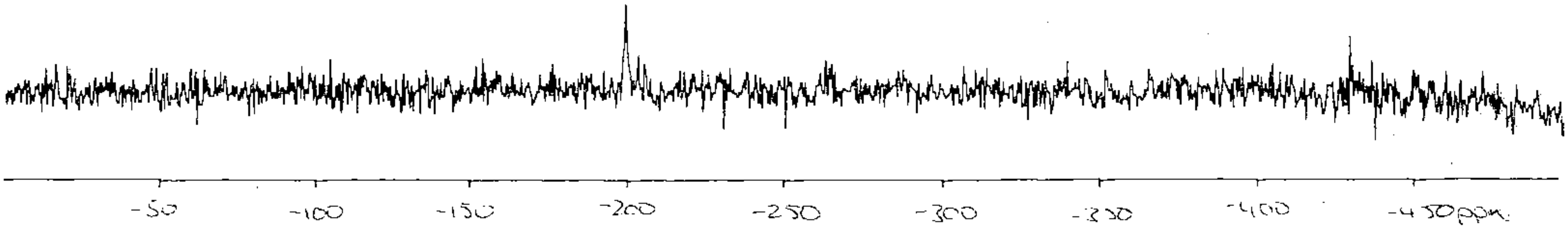
^{119}Sn NMR spectral data

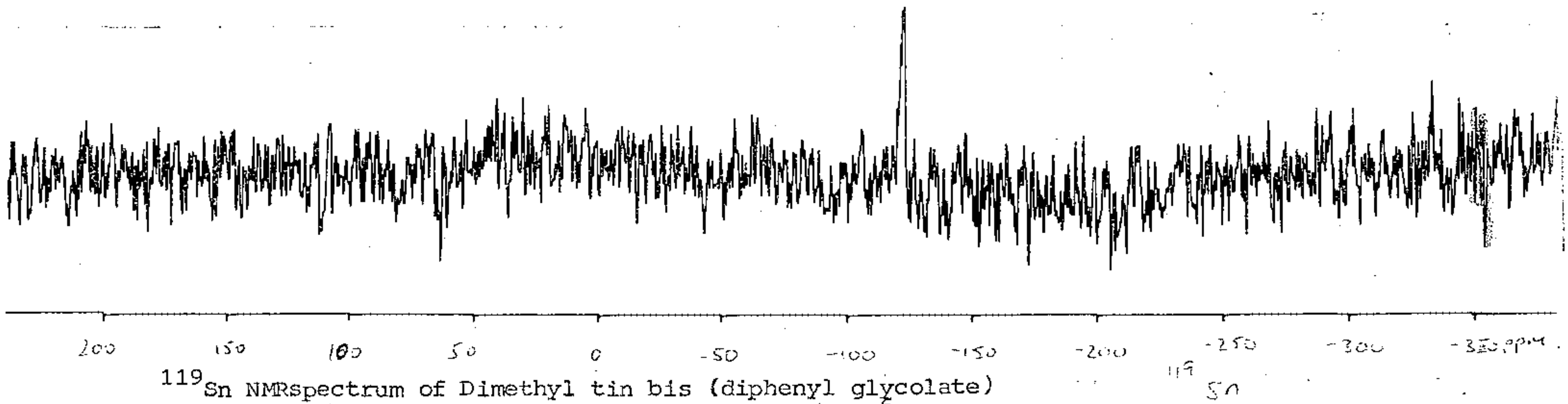
Compound	Chemical shift (δ)
Dibutyl tin diphenyl glycolate	-142.12
Dicyclohexyl tin diphenyl glycolate	-199.37
Dimethyl tin <u>bis</u> (diphenyl glycolate)	-123.02



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

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

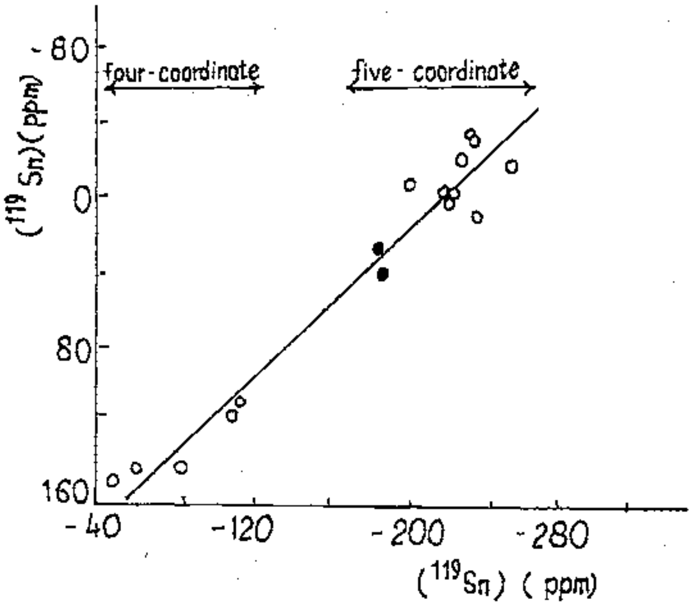




^{119}Sn NMRspectrum of Dimethyl tin bis (diphenyl glycolate) (in d^6 DMSO)

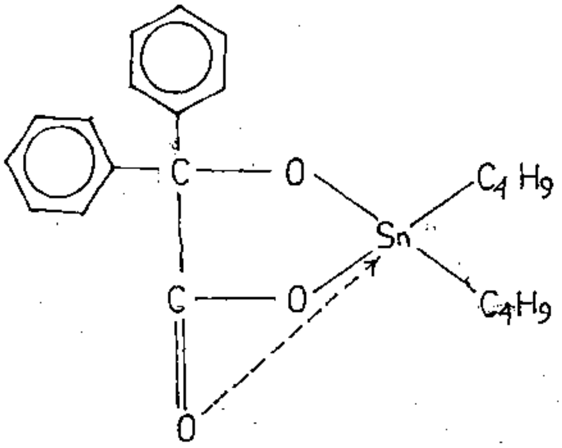
The dibutyl tin diphenyl glycolate had ^{119}Sn signal at δ -142.12 indicating penta coordinating nature.

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



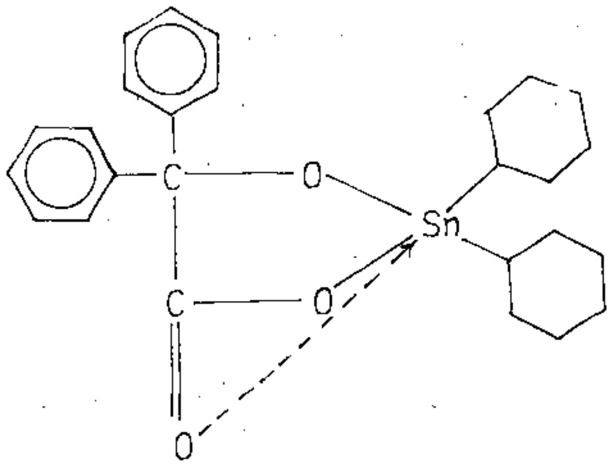
Correlation of ^{119}Sn chemical shifts in tri n-butyl tin (IV) compounds with ^{119}Sn chemical shifts in triphenyltin (IV) analogues.

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



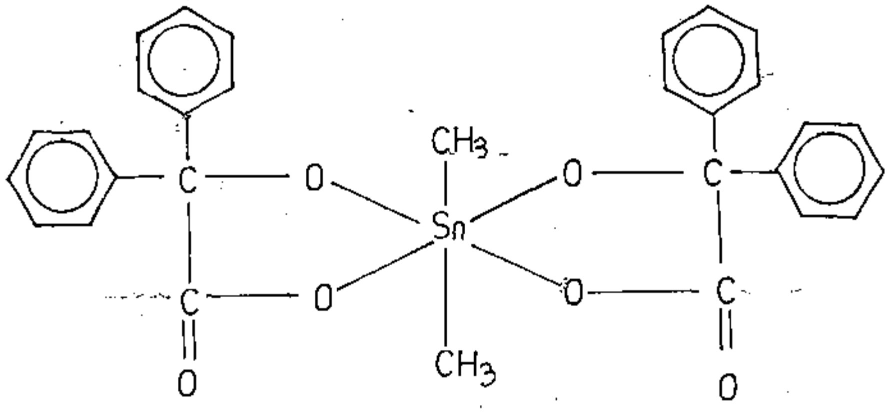
The CO_2 absorption frequency in IR spectra showed an unusually strong shift from 1715 cm^{-1} to $\sim$ 1570 cm^{-1} indicating strong coordination from $>C = O$ group of the carboxylate ion, which supports $\delta(^{119}Sn)$ value.

The ^{119}Sn spectra of dicyclohexyl tin diphenyl glycolate was also recorded in d^6 DMSO solvent. The ^{119}Sn peak appeared at δ -199.37 indicating a similar structure like the above dibutyl derivatives. The IR shift is also similar here for CO_2 group. Hence we may tentatively suggest the structure of Dicyclohexyl tin diphenyl glycolate as follows



Though detailed data are lacking for other diorganotin diphenyl glycolates. These may have similar structures like dibutyl or dicyclohexyl tin derivatives.

The Dimethyl tin derivative is somewhat different from the other diorganotin derivatives, having two diphenyl glycolic acid residues. Elemental analyses, molecular weight and ^{1}H NMR spectra strongly support the formation of Dimethyl tin bis (diphenyl glycolate). The ^{119}Sn peak for this compound appeared at δ -123.02. This may be due to hexa coordinated tin atom of the following type:



In this compound, coordination from the carbonyl oxygen of acid groups may be absent, otherwise it would render the tin atom either hepta or octa coordinating. In that case, we would expect much higher upfield shift of ^{119}Sn signal. Moreover, the CO_2 shift is much smaller, compared to other diorganotin derivatives. It shifts from 1715 cm^{-1} to 1650 cm^{-1} only compared to ~1570 cm^{-1} as in other diorganotin derivatives.

In absence of X-ray data (for which we had no access) all these structures may be considered somewhat tentative in nature.

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