ORGANOTIN DERIVATIVES OF DIPHENYL CARBAZONE

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by
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SUMMARY

In recent years extensive investigations have been carried out in the field of organotin co-ordination compounds. These studies are primarily directed towards preparation and characterisation by various physico-chemical methods of organotin co-ordination complexes. Organotins are commercially used as biocidal agents for the last two decades or more, apart from their use as P.V.C. stabilisers.

First a short discussion of organotin co-ordination compounds has been given. Compounds of a number of ligands such as phenanthroline, oximes, schiff bases, oxine, β-diketones, pyridine carboxylic acid, dithizone, substituted hydroxamic acids etc. with organotins have been described. Some of these compounds have been characterised by various spectral measurements and X-ray crystal structure determinations etc.

In the Part I of the present investigation, the preparation of twenty new organotin diphenyl carbazonates have been described. No solid organotin diphenyl carbazonate (L) have been reported so far. The compounds isolated and characterised under the present investigation are of the following types:

(a) R_3SnL (R = propyl, butyl, cyclohexyl, phenyl, p-tolyl and benzyl).

(b) R_2SnL_2 (R = methyl, butyl, cyclohexyl, phenyl, p-tolyl, benzyl)

(c) R_2SnLX (R = methyl, butyl, phenyl, p-tolyl)

(d) $RSnL_3$ (R = phenyl)

These compounds have been characterised by elemental analysis, visible, I.R., P.M.R. spectra. Some of these organotin compounds showed a single absorption in the region of 530-550 nm in their visible spectra instead of two absorption bands (455 nm and 565 nm) noticed in the case of diphenyl carbazone in the visible region. The I.R. spectra of all organotin compounds showed interesting changes in 3100-3400 cm^{-1} region and the absence of 1707 cm^{-1} and 1650 cm^{-1} bands of diphenyl carbazone. Appearances of new bands at $\sim$1540 cm^{-1} and a broad band around 1200 cm^{-1} clearly indicates the chelating nature of organotin diphenyl carbazonates.

The P.M.R. spectra of organotin diphenyl carbazonates showed some interesting observations. The alkyl and aryl protons of organotin diphenyl carbazonates showed significant chemical shifts compared to parent compounds. The position of imino protons was found to be variable possibly due to the nature and extent of hydrogen bonding.

All evidences clearly indicated that organotin moieties can replace only one imino proton of diphenyl carbazone in such complexes, similar to organotin dithizonates.

In second part, some ligand exchange reactions have been investigated to obtain an idea of the relative stabilities of different organotin co-ordination complexes. The ligands were diphenyl carbazone, dithizone, oxine, substituted benzohydroxamic acids. It has been found that one ligand (e.g., dithizone) can replace another ligand (oxine) from an organotin oxinate under reflux conditions for 2 hours. From the investigations carried out presently, we possibly can conclude that organotin compounds have definite soft acid character as they form stronger complexes with N-S donors than N-O donors and O-O donors, though some earlier workers believed the hard acid character of organotin compounds.

In the last part, the fungicidal properties of triphenyl tin diphenyl carbazonate, bis-(triphenyl tin) oxide and dithizone have been described against inhibition of conidial germination of *Aspergillus niger*, *Penicillium jenseni*, *Verticillium albo-atrum*, *Helminthosporium oryzae* . Results obtained indicated extremely high fungitoxic nature of triphenyl tin diphenyl carbazonate against these fungi. An attempt has been made to get a preliminary idea about the effect of co-ordination on triphenyl tin moiety. Though more work is necessary, it may be stated that triphenyl tin diphenyl carbazonate retains most of the fungitoxic character of bis-triphenyl tin oxide, if we consider the actual tin content of such compounds.

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PART II - LIGAND EXCHANGE STUDIES

PART III - FUNGITOXIC PROPERTIES

A SHORT DISCUSSION OF ORGANOTIN CO-ORDINATION COMPOUNDS

Introduction

The Chemistry of organotin compounds has been studied extensively during last few decades due to their unique physico-chemical, structural, biocidal and other properties.

Historically, Frankland (1-2) in 1849 first reported an organotin compound though he could not characterise it properly until 1853. Lowig (3) in 1852 isolated the first organotin compound from the reaction of sodium-tin alloy on ethyl iodide. These initial investigations soon initiated more work in the field of organometallic chemistry in general and organotins in particular.

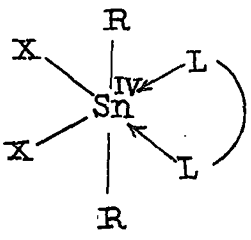
A number of review articles in this area have been published. The first comprehensive review covering the literature upto 1935 was done by Krause and Von Grosse (4). Ingham, Rosenberg and Gilman (5) extended the literature work upto 1959. The list of organotin compounds covering the literature from 1937 to 1964 was done by Weiss (6). From 1964, few literatures of organotin chemistry have been published in annual surveys (7-16). The tin annual survey covering the year 1974 has been published (17). Harrison published two reviews — one is of organotin derivatives of tin and lead (18) and another of organotin compounds in 1973 (19). Apart from these review articles, several books have been published (20-23).

After the discovery, organotin compounds long remained of purely scientific interest, but in recent years these have been put into large scale commercial exploitations. The present annual world consumption of organotin compounds is about 30,000 tons, though the production in 1948 was maximally a few tons. Most of these productions are utilised for P.V.C. Stabilisation, the remainder being shared between several biocidal and catalytic uses of organotin compounds.

The applications of organotin compounds are diverse (24-26) in nature and some of which may be indicated as follows:

For stabilisation of poly vinyl chloride (P.V.C.), di-organotin and mono organotin compounds are currently used. P.V.C. for its processing is subjected to temperature between 150-200°C. At this temperature, decomposition of P.V.C. takes place unless it is protected by appropriate stabiliser. Apart from organotins, metallic soaps and some pure organic compounds are also used as stabilisers for P.V.C. The organotin stabilisers are most powerful though it is more expensive. When a perfectly clear and colourless product is required or extreme temperature is used in processing, the organotin stabilisers are mostly used.

Apart from the use of organotin compounds for P.V.C. stabilisation, there are a large number of biological applications of organotin compounds. The biological effects of organotin compounds was systematically studied since 1950. These compounds have been found very active against a number of fungi and bacteria, marine organisms, parasitic worms, aquatic snells and insects. Investigations in these area have led to proposals for practical applications, some of which have been successfully realised. A comprehensive review of such applications has been written by Luijten (27). Recently an interesting potential use of organotin complexes have been indicated by the effectiveness of a series of organotin dihalides complexes for anti tumour activities. The compounds are of the type $R_2SnX_2 \cdot L_2$(I) where R = Me, Et, n-Pr, n-Bu, Ph; X = Cl, Br, I, NCS; L = O- or N-donor ligand have been tested for antitumour activity (28). These compounds were modelled on the original active platinum compounds (29) Cis-$Pt(NH_3)_2Cl_4$ (II) and Cis-$Pt(NH_3)_2Cl_2$ (III).



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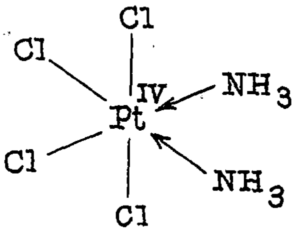

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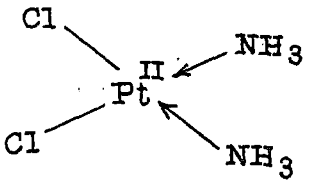


III

The diorganotin complexes chosen for test contain Cis-halogen groups and some of these compounds inhibit P388 Leukaemia in mice.

In recent years, the co-ordination chemistry of organotin compounds has been extensively studied. Tin differs from the lighter group IVA elements 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 co-ordination number above four. As a consequence, many organotin compounds form stable adducts with Lewis bases. Reactions involving nucleophilic attack at tin are also facilitated by the formation of co-ordinated intermediates.

The ability of tin compounds to form complexes is largely dependent on the electronegativity of the substituents. Thus the acceptor strengths of the halides are in the order $SnCl_4 \gg SnBr_4 > SnI_4$. When the electronegative chlorine atoms of $SnCl_4$ are replaced by relatively electropositive organic group, the acceptor strength of tin declines as indicated by the sequences $SnCl_4 > RSnCl_3 > R_2SnCl_2 > R_3SnCl$; $Ph_3SnCl > Bu_3SnCl$; and $PhSnCl_3 > MeSnCl_3 > BuSnCl_3$. No adducts of tetraalkyl or aryl tin compounds have yet been reported and attempts to detect interaction between tetra ethyl- or tetra phenyl tin and dioxanes by dipole moment measurements gave negative results (30).

A large number of most commonly used ligands are those with donor atoms from the first row of periodic table particularly oxygen and nitrogen, as it is widely accepted that tin (IV) is a class A acceptor (hard acid) (31).

Kumar Das (32) has prepared complexes of the type $R_3SnX.L$ (where R = Me, Ph; X = Cl, NO_3 and L = hexamethyl phosphoric triamide (HMPA), dimethyl Sulphoxide (DMSO), 1:10 phenanthroline (Phen) etc. 1:1 complex of HMPA with Ph_3SnX (X = Cl, Br, I, N_3, CN) have been prepared (33-34) by the general reaction

$$Ph_3SnX + HMPA \xrightarrow[\text{or pet ether}]{\text{chloroform}} Ph_3SnX.\ HMPA$$

That, the $Ph_3SnNO_3.L$ (L = HMPA, DMSO and phen) complexes are relatively good electrolytes in absolute alcohol, indicate a weak co-ordination of nitrate group to the tin atom. I.R. spectral data support it and these three complexes have been found to be penta co-ordinated by Mössbauer spectral data (35).

A large number of 1:1 adducts of substituted pyridine N-oxides with triphenyl tin chloride have also been prepared (36). These compounds are precipitated by mixing together an equimolecular amount of the reactants (37). Stability constant measurements of the compounds $Me_3SnCl.L$ (L = substituted pyridine N-oxide) clearly indicate the formation of stable adducts by these ligands with Me_3SnCl.

The formation of 1:1 complexes of triorganotin chlorides and thiocyanates with some tridentate chelating agents have been reported by Smith and Liengme (38). The chelating agents are

3-[2-(1,10-phenanthrolyl)]-5,6-diphenyl-1,2,4-triazine (I) and 3-[2-(1,10-phenanthrolyl)]-5,6-dimethyl-1,2,4-triazine (II). The isolated complexes were $(CH_3)_3SnCl.L$; and $(C_6H_5)_3SnCl.L$ (L = I and II) and $(C_6H_5)_3Sn(NCS).L$ (L = I). These complexes are stable crystalline solids and behave as non-electrolytes in nitrobenzene.

A number of complexes like $Me_2SnCl_2.2Py$; Me_2SnCl_2 . phen (39,40); Me_2SnX_2. Bipy (X = Cl, Br, I); $2R_2SnX_2$. Terpy (41) (R = Me, Ph; X = Cl, Br, I) have been obtained by the action of ligands such as Pyridine (Py), bipyridyl (Bipy), Phenanthroline (Phen), terpyridyl (Terpy) etc. upon diorganotin halides.

Reutov et al have summarised a large number of crystalline complexes of the general formula $R_{4-n}MX_n$. L where L is a neutral donor ligand (31). In that summary, they also discussed the structures of such complexes containing monodentate and bidentate ligands. In recent years a large number of organotin complexes with various bidentate ligands have been extensively studied. A brief review of some representatives of these complexes may be described as follows:

Organotin derivatives of oximes and Schiff Bases:

The oxime derivatives of organotin compounds have been reviewed by Mehrotra and his co-workers (42). Organotin oximates are prepared either by the action of sodium or lithium Salts on organotin halides (43-45)

$$\begin{array}{c} R_{4-n}SnCl_n + nNa(Li)ON = CR'R'' \\ \downarrow \\ R_{4-n}Sn(ON = CR'R'') + nNaCl(LiCl) \end{array}$$

or by azeotropic distillation of water from a mixture of organotin oxide or hydroxide with oxime in benzene or toluene (43-45).

$$\begin{array}{c} (R_3Sn)_2O + 2HON = CR'R'' \\ \downarrow \\ 2R_3SnON = CR'R'' + H_2O \end{array}$$

$$R_3SnOH + HON = CR'R'' \longrightarrow R_3SnON = CR'R'' + H_2O$$

Reactions of alkyl tin alkoxides with oximes (42-43, 46,47) take place as

$$\begin{array}{c} R_{4-n}Sn(OR')_n + nHON = CR''R''' \\ \downarrow \\ nR'OH + R_{4-n}Sn(ON = CR''R''')_n \end{array}$$

From the action of diorganotin dichloride with the silver salt of oxime, Koheler et al (48) was able to prepare diorganotin derivatives of a dicyanoformaldehyde.

Mehrotra et al (49) have also prepared various types of butyl tin derivatives of alkanolamines. Organotin derivatives of oxime can react with acyl or benzoyl halides and o-acyl or o-benzoyl oxime (42).

$$R_{4-n}Sn(ON = CR'R'')_n + nR'''COX \downarrow R_{4-n}SnX_n + nR'R''C = NOCoR'''$$

Organotin halides or oxides can react with bidentate, tridentate and tetradentate Schiff bases.

$RSnCl_3$ reacts with $HOC_6H_4CH : NR'$ (where R = Et, n-Bu and Ph; R' = Me, Et and Ph) in cyclohexane and forms 1:2 adducts (50). Molar conductance measurements in nitrobenzene have shown the non-electrolytic nature of these adducts. Infrared and Mössbauer spectral studies suggest octahedral structures for these adducts.

$(CH_3)_2SnCl_2$ reacts with tridentate Schiff bases N-(2-hydroxyl phenyl) salicylaldimine $OH. C_6H_4CH = N. C_6H_4 .OH$ or its derivatives to form penta co-ordinated structures (51). Triphenyl tin hydroxide reacts with N-(2-hydroxy phenyl)-salicylaldimine to form hexa co-ordinated complex. The structure of N-(2-hydroxy phenyl)-salicylaldimine has been determined and found to be heavily distorted with organic groups occupying equitorial positions (52).

Diorganotin oxides react with tetradentate Schiff Bases to yield R_2Sn(Salen), R_2Sn(aceto-salen) and R_2Sn(benzo salen) where R = n-Bu, n-octyl and benzyl ; [salen = bis-(2-hydroxy-5-methyl acetophenone) ethylene diamine; benzo salen = bis-(2-hydroxy-5-methyl benzophenone) ethylene diamine].

The compound R_2Sn (aceto salen) and R_2Sn(benzo salen) exist in trans form both in solid and in solution whereas R_2Sn(salen) exist both in cis and in trans forms (53).

Organotin Oxinates:

Organotin oxinates (oxine = 8-hydroxy quinoline) are stable and well defined compounds. These have been studied extensively. These organotin oxinates are generally of the following types:

$R_3Sn(OX)$, $R_2Sn(OX)_2$, $RSn(OX)_3$, $R_2Sn(OX)X$ and $RSn(OX)_2X$, where R = organic group, OXH = 8-hydroxy quinoline, X = halogens, isothiocyanate and carboxylates.

The simple organotin oxinates of the type $R_{4-n}SnOX_n$ (n = 1,2,3) are prepared either from the organotin halides and sodium oxinate (54)

$$R_2SnCl_2 + 2NaOX \longrightarrow R_2Sn(OX)_2 + 2NaCl$$

$$n\text{-}BuSnCl_3 + 3NaOX \longrightarrow n\text{-}BuSn(OX)_3 + 3NaCl$$

or from organotin halide and oxine, the hydrogen halide formed during the reaction is removed by neutralising with the help of a base such as ammonia (55).

$$R_2SnCl_2 + 2OXH + 2NH_3 \longrightarrow R_2Sn(OX)_2 + 2NH_4Cl$$

and organotin oxide with oxine (56,57)

$$(Ph_3Sn)_2O + 2OXH \longrightarrow 2Ph_3SnOX + H_2O$$

Triorganotin oxinates have also been prepared by the reaction of triorganotin chloride with a mixture of oxine and sodium methoxide (54).

By refluxing (58) a mixture of tetra [bis-(penta fluoro phenyl) ~~tin~~ or tris-(penta fluoro phenyl)] tin chloride and an excess of oxine in ethanol, (bis-penta fluoro-phenyl) tin bis oxinates have been prepared. The crystal structure of dimethyl tin bis-(8-hydroxy-quinolinate) has been determined (59). The compound assumes a structure with cis-dimethyl tin groups (110.7^{o}) in which the oxygen atoms appear trans (the θ-Sn-θ angle seems not to be listed) and the nitrogen atoms are Cis (N-Sn-N = 75.8^{o}). The nearly tetrahedral dimethyl tin groupings has tin-carbon internuclear distances that are the same as those observed for the tetrahedral tin compounds, $(CH_3)_nSnX_{4-n}$ and CH_3SnH_3. In the bonding of the oxinate ligand to tin, it seems that the tin oxygen distances are shorter by 0.25A^{0} than the tin-nitrogen distances.

By the reaction of diphenyl tin dichloride and oxine in benzene in absence of a base in 1:1 molar ratio, halo oxinate is formed (60,54):

$$R_2SnCl_2 + OXH \longrightarrow R_2SnCl(OX) + HCl$$

Halo oxinate compounds can also be obtained through disproportionation of a dihalide and a dioxinate in refluxing benzene or ethanol (61,54).

$$R_2SnCl_2 + R_2Sn(OX)_2 \longrightarrow 2R_2SnCl(OX)$$

or, by the reaction of dioxinate and silver halide (60).

$$R_2Sn(OX)_2 + AgX \longrightarrow R_2SnX(OX) + Ag(OX).$$

Dimethyl chlorotin oxinate have been prepared by McGrady et al. (62) by the disproportionation reaction of dimethyl tin dichloride and dimethyl tin dioxinate in refluxing benzene. Dialkyl tin isothiocyanate oxinate and acetate oxinate have similarly been prepared (60). Dialkyl tin nitrate oxinate and sulfate oxinate are prepared by the following methods (60)

$$R_2Sn(OX)_2 + AgNO_3 \xrightarrow{\text{in } CH_3OH} R_2Sn(NO_3)(OX) + Ag(OX)$$

$$2R_2SnCl(OX) + Ag_2SO_4 \longrightarrow [R_2Sn(OX)_2]SO_4 + 2AgCl.$$

In other halogen substitution reaction the product disproportionates (63) as

$$R_2SnCl(OX) + I^- \longrightarrow [R_2Sn(I)(OX)] + Cl^-$$

$$2[R_2SnI(OX)] \longrightarrow R_2SnI_2 + R_2Sn(OX)_2$$

The halogen atom of penta co-ordinated tin halo oxinate undergo ready exchange with groups such as butyl, alkoxy or even with chelating agents e.g. acetyl acetonates (54,63) which may disproportionate into diorganotin derivatives, e.g.

$$R_2SnCl(OX) + Tl{-}OC_2H_5 \longrightarrow R_2Sn(OC_2H_5)(OX) + TlCl$$

$$\begin{tikzcd} R_2SnCl(OX) + n\text{-}BuLi \arrow[r] & R_2Sn(n\text{-}Bu)(OX) + LiCl \arrow[d, shift right] \\ & R_2Sn(OX)_2 + R_2Sn(n\text{-}Bu)_2 \arrow[u, shift right] \end{tikzcd}$$

$$\begin{tikzcd} R_2SnCl(OX) + Tl\text{-}acetate \arrow[r] & R_2Sn(acac)(OX) + TlCl \arrow[d, shift right] \\ & R_2Sn(OX)_2 + R_2Sn(acac)_2 \arrow[u, shift right] \end{tikzcd}$$

Datta (64) have prepared phenyl tin halo oxinates by the reaction of diphenyl tin dioxinate with mercuric halides in ether at room temperature.

$$Ph_2Sn(OX)_2 + HgCl_2 \longrightarrow PhSnCl(OX)_2 + PhHgCl$$

Phenyl tin acetate dioxinate has been prepared by Roy (65) by the displacement of chlorine atom from phenyl tin chloro oxinate with sodium acetate. He has also prepared $PhSn(OCOC_2H_5)(OX)_2$, $PhSn(OCOCH_2Cl)(OX)_2$ and $PhSn(OCOCF_3)(OX)_2$ complexes by similar methods.

A novel compound, $[n\text{-}C_4H_9Sn(OX)_2]S$ has been prepared from the reaction of n-butyl tin sesquisulfide and oxine in boiling toluene (66).

Mehrotra et al (67) have synthesised butyl tin-isopropoxy oxinates $[BuSn(OPr^{i})_{3-n}(OX)_n]$ by the reaction of butyl tin tris-isopropoxide and oxine and the isopropanol formed in the reaction was removed by azeotropic fractionation with refluxing benzene.

Ghosh and co-workers (68) have examined the action of mercuric halides on organotin oxinates and probable mechanisms of these reactions have been given. Triphenyl tin oxinate has been shown to react readily with HgX_2 (X = Cl, Br, I) at room temperatures. The hexa co-ordinated diphenyltin dioxinate is attacked by HgX_2 only when refluxed in benzene or ether. In both the cases, $PhSn(OX)_2X$ have been found. It has also been shown that $Ph_2SnCl(OX)$ can react with mercuric chloride with the complete cleavage of the tin-phenyl bond, producing $Sn(OX)_2Cl_2$, PhHgCl and Ph_2SnCl_2.

Organotin derivatives of substituted oxines, e.g., some diaryl tin bis oxinates/2-methyl oxinates and diaryl tin chloride oxinate/2-methyl oxinates have been reported by Srivastava et al (69).

Sen et al (70,71) have prepared and characterised several diorganotin bis-(mono- and disubstituted oxinates) by the reaction of diorganotin dichloride with ligands in 1:2 molar ratio in DMF or ethanol.

Gopinathan et al (72), Kumar Das et al (73), Deb and Ghosh (74) have very recently prepared oxine compounds of ester tins.

Kumar Das et al have also reported and synthesised the compounds of the type $R_2Sn(OX)_2$ and $R_2SnCl(OX)$ (where R = $MeOCOCH_2CH_2$). The former compound has been synthesised by the method of Westlake and Martin (75) and the latter by the reaction of an equivalent amount of diorganotin bis(oxinate) with R_2SnCl_2 in benzene. The compounds were studied by U.V., I.R., P.M.R. and Mössbauer spectroscopy.

It has been proved by P.M.R. data that relative to bis oxinate, the chloro oxinate appears to involve a greater extent of chelation.

Deb and Ghosh (loc cit) have synthesised and characterised co-ordination compounds of β-substituted mono- and dialkyl ester tin compounds with ligands like 8-hydroxy quinoline, substituted 8-hydroxy quinolines, dithizone, alizarin etc. by the reactions of ester tin chlorides with ligands.

Organotin Tropolonates, Kojates, Dithiocarbamates and β-Diketonates:

A number of organotin tropolonate complexes of the types Ph_3SnT, Me_2SnXT, R_2SnT_2, $RSnXT_2$ (R = alkyl or Ph; X = Cl, Br, I; TH = Tropolone) have been prepared where the tropolone acts as bidentate chelating agent bonding through both oxygen atoms.

Diorganotin bis-tropolonates have been prepared (76,77) by the following reactions.

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

$$R_2SnCl_2 + 2TlT \longrightarrow R_2SnT_2 + 2TlCl$$

By the reaction of phenyl tin trichloride in benzene with a solution of tropolone in ether (78), the compounds phenyl tin tris tropolonate and phenyltin chloride bis tropolonate have been prepared.

Organotin complexes with kojic acid, e.g., from methyl tin chloride - and methyl tin bromide bis kojates have been prepared by Otera et al (79).

Organotin dithiocarbamates are prepared by the reaction of sodium-dithiocarbamate with an organotin chloride (80-81).

Organotin compounds can form a number of complexes with bidentate oxygen donor β-diketones. There are several organotin acetyl acetonates. They are generally of the following types: $R_3Sn(acac)$, $R_2Sn(acac)_2$, $RSn(acac)_3$, $RSnX(acac)_2$, $RSnX(OR')(acac)$ and $RSn(acac)_n(OR')_{3-n}$.

R_3SnL [R = Me, Ph; LH = acetylacetone(acac), benzoyl acetone (bzac)] compounds have also been prepared and characterised by I.R., N.M.R. and Mössbauer spectroscopy (82). These compounds have been prepared by Tl(1) salt method (83,84,85) e.g.,

$$R_3SnCl + Tl(acac) \longrightarrow R_3Sn(acac) + TlCl.$$

Diorganotin bis acetyl acetonates, $R_2Sn(acac)_2$ and diorganotin bis (β-diketones) have been prepared either by the addition of acetyl acetone to a mixture of diorganotin dichloride and sodium methoxide in methanol (86) or by direct reaction of the reactants in the presence of a base (83).

Srivastava and Saxena (87) have synthesised some diorganotin bis (acetyl acetonates), $R_2Sn(acac)_2$ (R = Ph, o-, m-, p-tolyl).

Tri and diorganotin complexes of 2-Thenoyl-trifluoro acetone of the types $R_3Sn(TTA)$ (where R = CH_3, C_2H_5, C_4H_9 and HTTA = 2-Thenoyl trifluroacetone) have been synthesised by Bachlas and Jain (88).

$$CH_3oNa + HTTA \longrightarrow \overset{+}{Na}(TTA)^{-} + CH_3OH$$

$$R_3SnCl + \overset{+}{Na}(TTA)^{-} \longrightarrow R_3Sn(TTA) + NaCl$$

$$(R_2SnO)_x + 2XHTTA \longrightarrow XR_2Sn(TTA)_2 + XH_2O$$

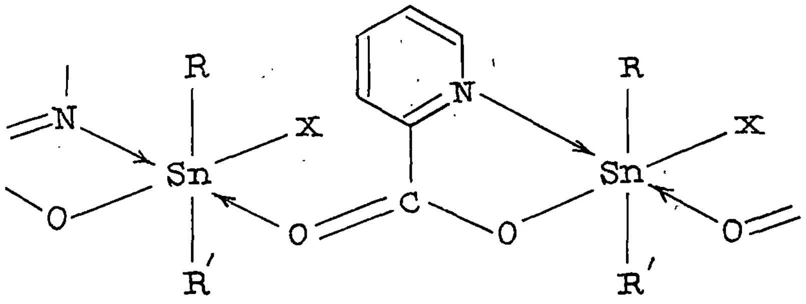
Organotin derivatives of Pyridine carboxylic acids and other ligands:

A series of diorganotin bis (pyridine carboxylates), $R_2Sn\ (O.CO.C_5H_4N\text{-}n)_2$ ($R = Me$, $n = 2\text{-}4$; $R = Ph$, $n = 2$ or 3); diorganochlorotin pyridine carboxylates, $R_2ClSn\ (O.CO.C_5H_4N\text{-}n)$ ($R = Me$ or Ph, $n = 2$; $R = Me$, $n = 4$) and monoorganochlorotin pyridine carboxylates $RCl_2Sn(O.CO.C_5H_4N\text{-}2)$ ($R = Bu$ or Ph) have been synthesised and their structures are investigated by ^{119}Sn Mössbauer and Infra red spectroscopy (89).

The spectra indicates the trans octahedral R_2SnX_4 geometry of the three dimethyl tin bis-(pyridine carboxylates) along with diphenyl tin bis-(3 pyridine carboxylate) and dimethyl chloro and diphenyl chlorotin 2-pyridine carboxylate in the solid state.

Dimethyl chlorotin 4-pyridine carboxylate, however, possesses a five co-ordinated trigonal bipyramidal Cis- R_2SnX_3 stereochemistry while diphenyl tin bis-(2-pyridine carboxylate) has an octahedral Cis-R_2SnX_4 structure, with two bidentate N-chelating pyridine carboxylate groups.

The structure of dimethyl tin bis-(2-pyridine carboxylate) most probably has both bridging and terminal carboxylate groups where co-ordination from pyridine nitrogen atom to tin occurs (Fig. 1).



Stucture of dimethyl tin bis-(2-pyridine carboxylate)
(R= R'=Me ; X=O.CO.C_5H_4N- 2)

(Fig. 1)

Di-ethyl-, di n-octyl- and dicyclohexyl tin derivatives of 2-pyridine carboxylic acid also adopt a similar structure in solid phase as indicated by Nelson (90).

Some mixed chelate compounds of diorganotin (IV) of the type $[SnR_2L'L'')$ involving the chelate ligands N,N-dialkyl dithiocarbamate ($S_2CNR'_2$), 8-quinolinate (oxine), 2-methyl-8-quinolinate (quin) and the anion of bis (p-fluoro benzoyl methane) (fbm) has been synthesised together with the symmetrical bis-chelates $[SnR_2(quin)_2]$ (R = Me, Ph), and The cationic complex $[SnMe_2(PPh_3O)_2(AsPh_3O)_2]^+[BPh_4]^-_2$, containing mixed mono dentate ligands has been prepared (91).

These mixed chelate complexes were prepared according to the reaction scheme:

$$TlL' + [SnR_2ClL'') \longrightarrow [SnR_2L'L''] + TlCl$$

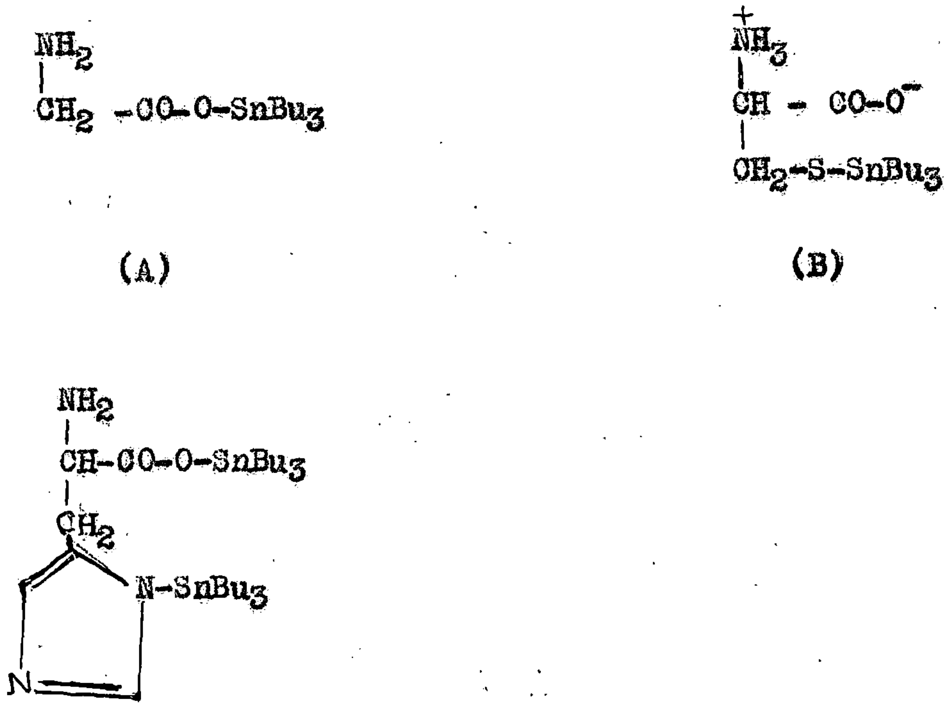
where $R_2 = Me_2, Bu_2, Ph_2$, BuPh and L', L" are as indicated above.

The symmetrical bis chelates, $[SnR_2(quin)_2]$ (R = Me, Ph), were prepared by the method described by Westlake and Martin (75) for the corresponding bis oxinates. The complex, $[SnMe_2(PPh_3O)_2(AsPh_3O)_2]^+[BPh_4]^-$ was obtained immediately by the addition of an ethanolic solution containing the two oxygen donor ligands to an ethanolic solution containing dimethyl tin dichloride and sodium tetraphenyl borate. The reactants were kept in stoichiometric ratio indicated below in the parenthesis:

$[SnMe_2Cl_2]$ (1), $[AsPh_3O]$ (1), $[PPh_3O]$ (3), $[NaBPh_4]$ (2).

Configurational assignments of the Sn-C bonds in the octahedral structures of these complexes have been made (91) by Mossbauer spectroscopy.

A series of air stable s-triorgano stannyl derivatives of L-cysteine and DL-homocysteine have been prepared (92b) by the reaction of appropriate triorganotin hydroxide or bis (triorganotin) oxide with the sulphydryl - containing amino acids in methanol/water at room temperature. Some tributyl stannyl derivatives of types A, B, C formed with glycine, cysteine and histidine are shown in fig. 2.



(A) (B) (C)

Fig. 2 Types of tributyl stannyl derivatives formed from amino acids.

$$(R_3Sn)_2O + 2HS(CH_2)_nCHNH_2COOH$$
$$\longrightarrow 2R_3SnS(CH_2)_nCHNH_2COOH + H_2O$$

($n = 1$, R = Np; $n = 2$, R = Bu or Np)

$$R_3SnOH + HS(CH_2)_nCHNH_2COOH$$
$$\longrightarrow R_3SnS(CH_2)_nCHNH_2COOH + H_2O$$

($n = 1$ or 2, R = Ph or Cy).

Very recently, ^{119}Sn- N.M.R spectra are reported for toluene solutions of tributyl stannyl ethers of 2,3,4,6-tetra-o-methyl-D-glucose, 1,2,3,4-di-o-isopropylidene-α-D-galactopyranose, methyl 2,3-di-o-methyl-α-D-glucopyranoside and the dibutyl stannyl ether of the last mentioned sugar (92a).

The structure of dibutyl stannylene derivative of methyl 4,6-o-benzylidene-α-D-glucopyranoside, which in solid state as well as in solution exists as a dimer as shown in (Fig. 3).

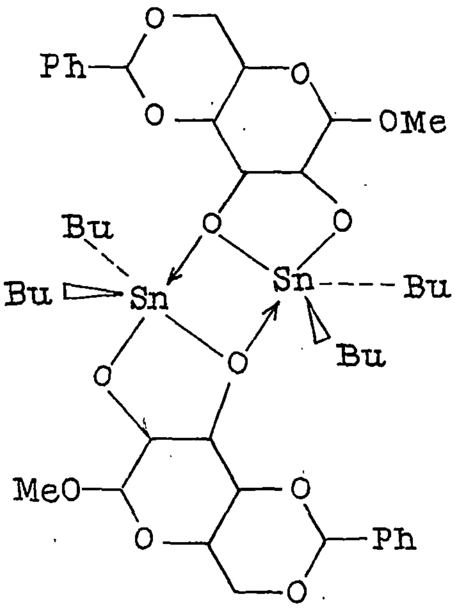


Fig. 3 Structure of dibutyl stannylene derivative of methyl 4,6-o-benzylidene α-D-glucopyranoside.

Organotin hydroxamates

A good number of metal complexes with hydroxamic acids have been prepared by many workers and these hydroxamic acids have been proved to be a very good analytical reagent (93).

Harrison (94,95) has synthesised the hydroxamic acid derivatives of organotin by the azeotropic removal of water from the mixture of appropriate hydroxylamine and the organotin oxides or hydroxides:

$$\begin{array}{l} \frac{1}{2}(R_3Sn)_2O + HONR'R'' \\ \qquad \text{or} \quad \longrightarrow \quad R_3SnONR'R'' + H_2O \\ R_3SnOH + HONR'R'' \nearrow \end{array}$$

(where R = Me, R' = R'' = Et; R = Me, 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 disproportionation reaction, although no pure diphenyl tin derivative could be isolated.

$$Ph_3SnOH + HONHCOPh \xrightarrow{-H_2O} [Ph_3SnONHCOPh]$$
$$\longrightarrow Ph_4Sn + [Ph_2Sn(ONHCOPh)_2]$$

The organotin derivatives of N-benzoyl hydroxyl amines are extremely stable in moisture. The $Ph_3SnONPhCOPh$ is monomeric in both the crystal and solution phases, whereas the trimethyl tin derivatives are associated in the solid (96,94)

Diorganotin derivatives of N-substituted benzo hydroxamic acids have been prepared (97,98,99) according to the following reaction schemes:

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

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

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

Phenyl tin halide bis-(N-phenyl benzohydroxamates) have been prepared by the reaction of triphenyl tin N-phenyl benzohydroxamate with mercuric chloride, mercuric bromide and mercuric iodide (99).

Phenyl tin thiocyanate bis-(N-phenyl benzohydroxamate) has been prepared (loc. cit) 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)

Pradhan and Ghosh (99,99a) have also prepared compounds of the type $R_2SnX(PBHA)$ (where R = Ph, X = Cl, I, SCN; R = Bu, X = SCN) through disproportional reactions.

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

But $Ph_2Sn(SCN)(PBHA)$ has been prepared by the reaction of corresponding chloride complex with KCNS (100)

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

It has been shown by Pradhan and Ghosh (99) that penta co-ordinated diorganotin halide N-phenyl N-benzohydroxamates, on refluxing in non-polar solvent like benzene for a long time, disproportionate to the more stable hexa co-ordinated tin compounds

$$2Ph_2SnX(PBHA) \longrightarrow PhSnX(PBHA)_2 + Ph_3SnX$$

(where X = Cl, SCN).

However, in polar solvents like methanol, ~~change was not found~~. ~~Instead~~ another hexa co-ordinated compound phenyl tin halide methoxy N-phenyl N-benzohydroxamate was formed along with the liberation of one equivalent of benzene (99).

This methoxy compound was also obtained when phenyltin halide bis-N-phenyl-N-benzohydroxamate was refluxed in methanol with the liberation of one mole of ligand.

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

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

Some mono organotin derivatives of hydroxamic acids were prepared by Narula and Gupta (100).

Five, six and seven co-ordinated mono organotin derivatives of hydroxamic acids have been synthesised by them. They isolated the compounds having the general formulae $R_2Sn_2O_2L_2$, $(RSnL_2)O$

(LH = hydroxamic acid derivative).

Recently Harrison et al (98) have prepared a number of new organotin hydroxamates following the usual procedures (94, 95). These compounds are of the types: R_2SnL_2 (where R = Me, nBu*, 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)

Organotin Dithizonates

Alridge and Cremer (101) showed that on extraction with dithizone from a borate-buffer triethyl tin compound gave a yellow complex and that of diethyl tin compound gave an orange complex in solution. The complexes formed had ϵ_{max} = 23300 at 435 and

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* Reported earlier by Pradhan and Ghosh (loc. cit)

ϵ_{max} = 70500 at 510 nm respectively. Irving and Cox (102) have suggested a 1:1 complex for the former compound and 1:2 for the latter. Similar complex compound in solution of tri n-propyl- and tri n-butyl tin, dibutyl - and dioctyl tin compounds were reported.

Skeel and Bricker (103) confirmed that dibutyl tin dichloride reacts with dithizone, but noted that λ_{max} appeared to depend on the pH, the concentration, and the composition of the buffer system employed. This unexpected effect has recently been explained by Kahara and Takei (104) who showed that whereas a 1:2 complex $Bu_2Sn(HDZ)_2$ with ϵ_{max} = 63500 at 479 nm is extracted from a phosphate buffer, a 1:1 complex of $Bu_2Sn(HDZ)X$ (where X = CH_2Cl, COO^-) is extracted from monochloroacetate buffer, and a mixture of the two (X = $HCOO^-$ or $MeCOO^-$) from a formate and acetate buffer. All these mixed complexes had λ_{max} in the range 496-499 nm, with ϵ_{max} = 36600-38300. The complexes formed by Pr_2Sn^{2+} had almost identical properties.

Recently Ghosh and Ghosh (105) reported the isolation and characterisation of a number of crystalline organotin dithizonates. These are of the following types:

R_3SnHDZ (where R = Pr, Bu, Ph) and $R_2Sn(HDZ)_2$
(where R may be Me, Pr, Bu, Ph, p-tolyl, Benzyl).

These triorgano- and diorganotin derivatives were characterised by visible, I.R., P.M.R. spectroscopy and elemental analysis. In all these derivatives dithizone acts as a mono basic acid and the second hydrogen could not be replaced.

Besides these a number of diorgano halo-dithizonates ($R_2SnXHDZ$ where R = Ph, Bu, Me, Benzyl, p-tolyl; X = Cl, Br, I, SCN) and some mono organo halo mixed ligand dithizonates [RSnXLHDZ where R = Ph; X = Cl, I; L = N phenyl benzohydroxamate and H_2DZ is dithizone] have been prepared (106).

All these derivatives are beautifully crystalline in nature and are highly coloured with sharp melting points.

Diphenyl carbazone (Diazene carboxylic acid, 2-phenyl hydrazide) has been used as analytical reagent for various metals for a long time.

Skeel and Bricker (107) used diphenyl carbazone as a reagent for spectrophotometric determination of dibutyltin dichloride in presence of mono-, tri- and tetrabutyltin compounds by measuring the absorbance of dibutyl tin-diphenyl carbazonate complex. They noticed that $BuSnCl_3$ interferes the determination of dibutyl tin content and suppressed the $BuSnCl_3$ by addition of ethylene diamine tetraacetic acid. By controlling the pH, they reported that 3-150 γ of Bu_2SnCl_2 can be determined spectrophotometrically.

Badoz-lamburg, Herlem and Thiebault (108) reported that diphenyl carbazone acts as a mono basic acid in liquid ammonia.

They reported that the pK value of diphenyl-carbazone is between 9.5-11.

Diphenyl carbazone forms a large number of derivatives of the metals like Zn^{2+}, Ni^{2+}, Pb^{2+}, Cd^{2+}, Cu^{2+}, Co^{2+}, Hg^{2+} etc (109, 110). Kemula and Janowski reported that the $\nu(>C = O)$ band observed in diphenyl carbazone disappears and new intense bands at ~1200 cm^{-1} and ~1550 cm^{-1} appears. They also concluded, in metal derivatives, metal- oxygen bond is present and there is also intramolecular hydrogen bond N—H·····N in the complexes. Van Dalen and Balt also observed disappearance of $\nu >C = O$ frequency from 5.85 μ.

Though a large number of metallic derivatives of diphenyl carbazone have been prepared, so far, there is no report of any solid organotin diphenyl carbazonate.

In view of the fact, a large number of crystalline organotin dithizonates could be synthesised and characterised, it was considered desirable to attempt similar derivatives of diphenyl carbazone with organotin compounds, as we can consider diphenyl carbazone is an oxygen analogoue of dithizone. We also wanted to prepare diphenyl carbazone derivatives of organo tin compounds in order to test their fungicidal properties, since it was observed in this laboratory that triphenyltin dithizonate has excellent fungitoxicity against a number of plant pathogenic fungi (111).

From the crystal structure determination, it was observed, in dithizone, coplanar N-N-C-N-N bonds are delocalised and the presence of $>C = S$ group in dithizone could not be definitely established but the crystal structure determination conclusively showed the presence of $>C = O$ group in diphenyl carbazone and one hydrazo chain bond is delocalised and hence it was considered interesting whether the presence of $>C = O$ in organotin diphenyl carbazonates could be confirmed. Moreover, it would be highly interesting to investigate the relative stabilities of organotin dithizonates and diphenyl carbazonates so that some idea of the nature of organotin compounds in the light of HSAB concept can be obtained. It is expected that diphenyl carbazone is a harder acid than dithizone and so may form weaker complexes with organotinsthan dithizonates (112).

PART - I

ORGANOTIN DIPHENYL CARBAZONATES

EXPERIMENTAL

Diphenyl carbazone G.R., E.Merck was used. All solvents were purified and dried. The petroleum-ether used had boiling range 60-80°C. Dibutyl tin dichloride (Fluka), Dimethyl tin dichloride (Fluka), Dicyclohexyl tin dichloride, Tricyclohexyl tin chloride, Tributyltin acetate (Fluka) were used. Potassium thiocyanate (B.D.H), Potassium iodide (B.D.H) were dried in air oven at 110°C for about 6 hours and stored in a vacuum desiccator. All melting points were uncorrected.

In the preparations of starting materials, the compounds were characterised by mixed melting point determination with authentic samples in most cases.

1. Preparation of Stannic chloride:

Stannic chloride was prepared following the method described in "Hand book of Preparative inorganic chemistry", Vol. 1 by Brauer (113).

The crude product was then left standing for sometime over tin with occasional shaking to remove the dissolved chlorine. The crude product was then separated from the excess metal by distillation in a ground glass apparatus, with careful exclusion of moisture; the boiling point of the pure substance was 114°C [lit (113) b.p. 114°C].

2. Preparation of stannic bromide:

Stannic bromide was prepared by adding directly pure bromide to metallic tin (114). Excess bromine was removed by boiling the crude product for a few minutes until the product became nearly colourless. The crude was then distilled to give pure product which solidified on cooling m.p. 33°C [lit (114) m.p. 33°].

3. Preparation of stannic iodide:

Stannic iodide was prepared by refluxing a mixture of metallic tin and iodine in carbon tetrachloride solution (115). The solution was boiled, filtered hot and cooled to give orange-red, needle shaped crystals, m.p. 143°C [lit (115) m.p. 143·5°C].

4. Preparation of Tetraphenyl tin:

Tetraphenyl tin was prepared by the method of Harris (116). It was recrystallised from benzene and dried in vacuum. The melting point of the compound was 226°C [lit (116) m.p. 225°C].

5. Preparation of Tetra-para-tolyl tin:

Tetraparatolyltin was prepared by Weiss (117). It was finally recrystallised from ethyl acetate and dried in vacuum. M.P. was 238°C [lit (117) m.p. 238°C].

6. Preparation of Triphenyl tin chloride:

Tetraphenyl tin was at first prepared according to the method as mentioned earlier. This was then converted to triphenyl tin chloride according to the method of Gilman et al (118).

Triphenyl tin chloride was finally recrystallised from pet-ether and dried in vacuum, m.p. 106° [lit (118) m.p. 106°].

7. **Preparation of Tribenzyl tin chloride:**

Tribenzyl tin chloride was prepared following the method of Schimitz-Dumont et al (119). This was crystallised from acetone, m.p. 142° [lit (119) m.p. 142-44°].

8. **Preparation of Triparatolyl tin chloride:**

Triparatolyl tin chloride was prepared following the same method as that of triphenyl tin chloride. The crude product was finally crystallised from pet-ether and dried in vacuum, m.p. 98° [lit (120) m.p. 98°]

9. **Preparation of Bis-(Triphenyltin) oxide:**

Bis (Triphenyl tin) oxide was prepared by the reaction between triphenyl tin chloride and ~~50%~~ excess of 50% sodium hydroxide Soln (121). It was dried in air and finally in vacuum at room temperature for 12 hours and had m.p. of 123°C [lit (121) m.p. 124°].

10. **Preparation of Bis(Tripropyl tin) oxide:**

Bis-(tripropyl tin) oxide was prepared by the method of Sasin et al (122). The fraction boiling at 150-155° at 2 mm. Pressure was collec [lit (122) b.p. 142-143° at 1 mm].

11. **Preparation of Diphenyl tin dichloride:**

Diphenyl tin chloride was prepared by the method of Gilman et al (123) and was crystallised from pet-ether. It was air dried and had a m.p. of 42-44° [lit (123) m.p. 42-44°].

12. Preparation of Diparatolyl tin dichloride:

Diparatolyl tin dichloride was prepared according to the method of Kocheshkov et al (124). The solid was crystallised from pet-ether. It was air dried and had m.p. 49° [lit (124) m.p. 49°].

13. Preparation of Dibenzyl tin dichloride:

Dibenzyl tin dichloride was prepared following the method of Sisido et al (125) and was crystallised from ethyl acetate. It was air dried and had m.p. 161° [lit (125) m.p. 164°].

14. Preparation of Diphenyl tin oxide:

Diphenyl tin oxide was polymeric and was prepared by the reaction of diphenyl tin dichloride with ~~50%~~ excess of 50% sodium hydroxide soln as described by Elegbede and McLean (126). This was dried in air and finally in vacuum at room temperature for 12 hours.

15. Preparation of Dibenzyl tin oxide:

Dibenzyl tin oxide was prepared in the same way as that of diphenyl tin oxide (loc. cit.). This was dried in vacuum at room temperature for 12 hours.

16. Preparation of Dibutyl tin oxide:

Dibutyl tin oxide was prepared by the same procedure as that of diphenyl tin oxide (loc. cit). The product obtained was dried in vacuum at room temperature for 12 hours.

17. Preparation of Dimethyl tin oxide:

Dimethyl tin oxide was prepared by the reaction between dimethyl tin dichloride with [illegible] excess of 50% sodium hydroxide soln following the same procedure as diphenyl tin oxide (loc. cit). This was dried in vacuum at room temperature for 12 hours.

18. Preparation of Diparatolyl tin oxide:

Diparatolyl tin oxide was prepared from diparatolyl tin dichloride and 50% sodium-hydroxide soln by the same method as that of diphenyl tin oxide (loc. cit). This was dried in vacuum at room temperature for 12 hours.

19. Preparation of dibutyl tin dithiocyanate:

Dibutyl tin dithiocyanate was prepared according to the method of Seyferth et al (127). 3.04 gms of dibutyl tin dichloride was taken in hot ethanol and to it 1.94g of potassium thiocyanate was added. The mixture was heated for some time and was filtered. The filtrate was evaporated to dryness and the solid was crystallised from benzene. Fine white crystals of m.p. 142-43°C was collected [lit (127) 144-45°].

20. Preparation of Dimethyl tin dithiocyanate:

Dimethyl tin dithiocyanate was prepared by same procedure as dibutyl tin dithiocyanate (loc. cit) . 2.20g of dimethyl tin dichloride was taken in hot ethanol and to it a hot ethanolic

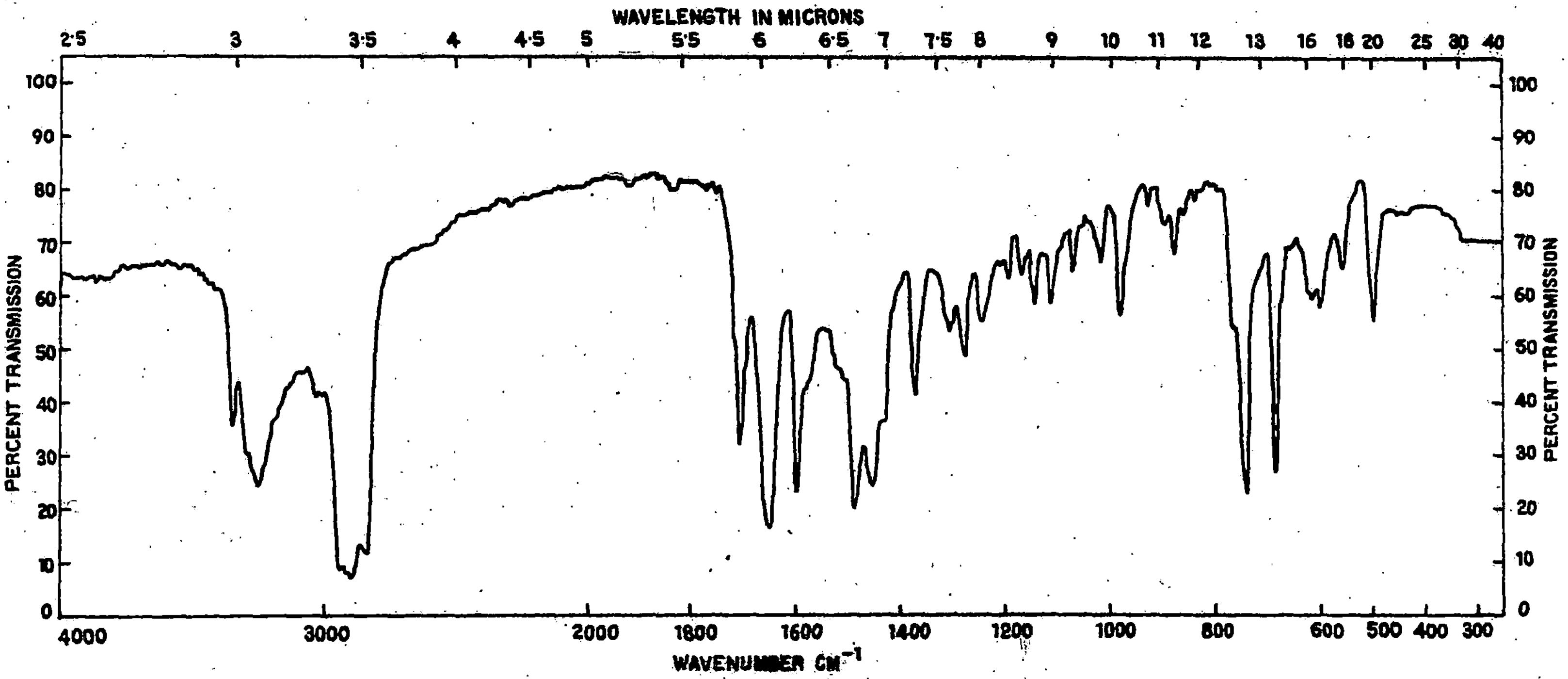

Fig.- 4. I.R. Spectrum of diphenyl carbazone

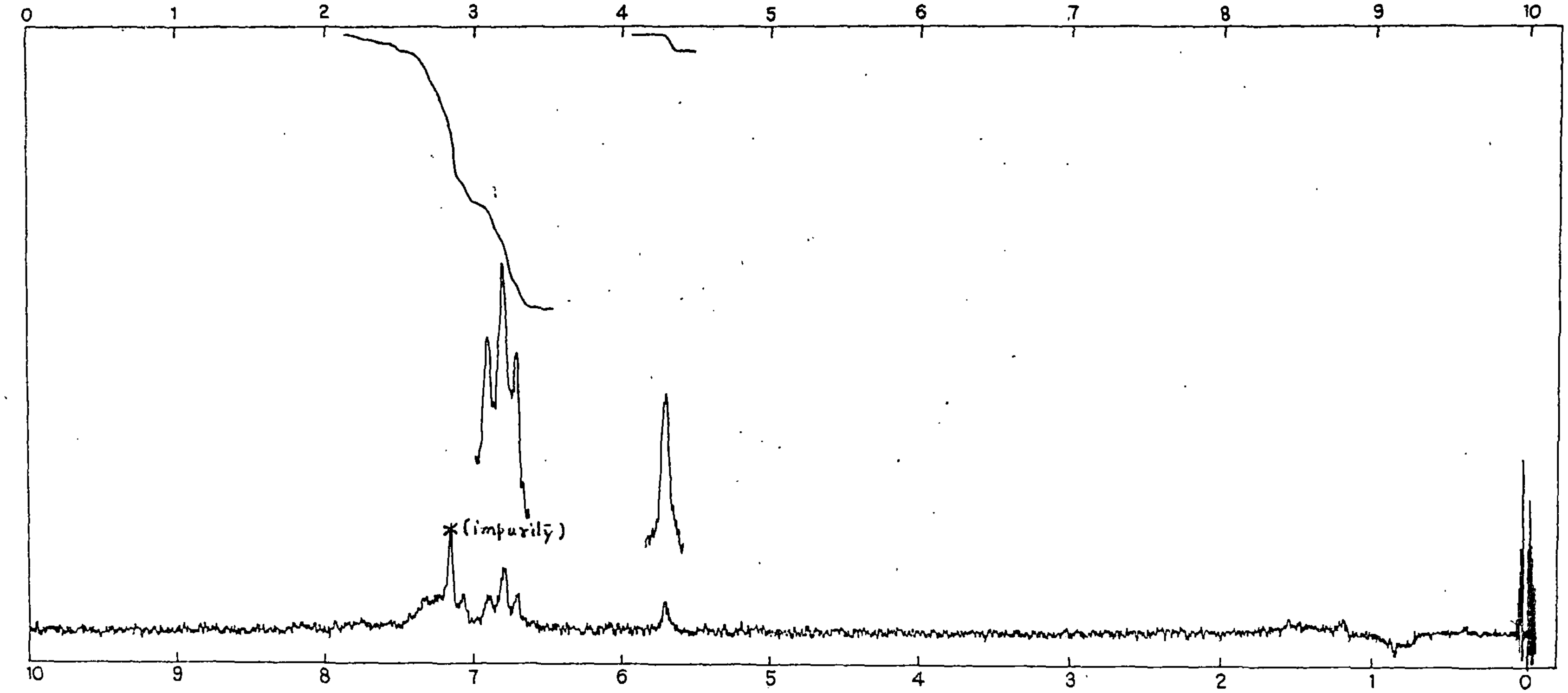

Fig.- 5

PMR Spectrum of diphenyl carbazone

solution of 1.94g of potassium thiocyanate was added. The mixture was filtered and the filtrate was evaporated to dryness. The residue was crystallised from chloroform. Fine shining white crystals (m.p. 194°) were obtained.

21. Tripropyl tin diphenyl carbazonate:

(a) 1.13g of tripropyl tin chloride and 0.96g of diphenyl carbazone was separately dissolved in chloroform. These two solutions were mixed and the mixture was refluxed for two hours. 5-7 drops of ammonium hydroxide (17N) solution was added to the refluxed solution to neutralise the liberated hydrochloric acid and the precipitated ammonium chloride was filtered off. The red filtrate was completely evaporated to a pasty mass on a water bath. To it pet ether (60-80°) was added. This was then boiled and filtered. After boiling the solution thrice with pet ether some insoluble residue was found to be left. This solid was collected and had a melting point 153°C. This solid was confirmed as diphenyl carbazone since it showed no depression of melting point with an authentic sample.

The soluble portion, i.e., the filtrate was completely evaporated to dryness. This solid was dissolved in benzene and to it excess pet ether (60-80°) was added. Beautiful shining reddish crystals of m.p. 162°C were formed. These were collected. On recrystallisation from benzene-pet ether it afforded crystals of m.p. 165°C. The yield was 0.80g.

Found: C = 53.88; H = 6.28; N = 11.26 and
Sn = 24.02 per cent

Calculated for $C_{22}H_{32}N_4OSn$: C = 54.21; H = 6.57; N = 11.50 and
Sn = 24.43 per cent.

(b) 0.51g of bis (tripropyl tin) oxide and 0.48g of diphenyl carbazone were taken in 150 ml benzene. This was refluxed for three hours using a Dean and Stark Water Separator. The colour of the solution became red. The refluxed solution was then filtered and the filtrate was concentrated to about 5 ml on a water bath. To it about 15 ml pet. ether was added. This solution, on standing for sometime, gave beautiful shining red crystals of m.p. 162-63°C. The yield was 0.45g. These crystals on recrystallisation from benzene/Pet ether mixture afforded crystals of m.p. 165-66°C. Mixed melting point of this compound with the previous one (formed from tripropyl tin chloride and diphenyl carbazone) showed no depression.

Found: C = 53.91; H = 6.30; N = 11.24 and
Sn = 24.00 per cent.

Calculated for $C_{22}H_{32}N_4OSn$: C = 54.21; H = 6.57; N = 11.50 and
Sn = 24.43 per cent.

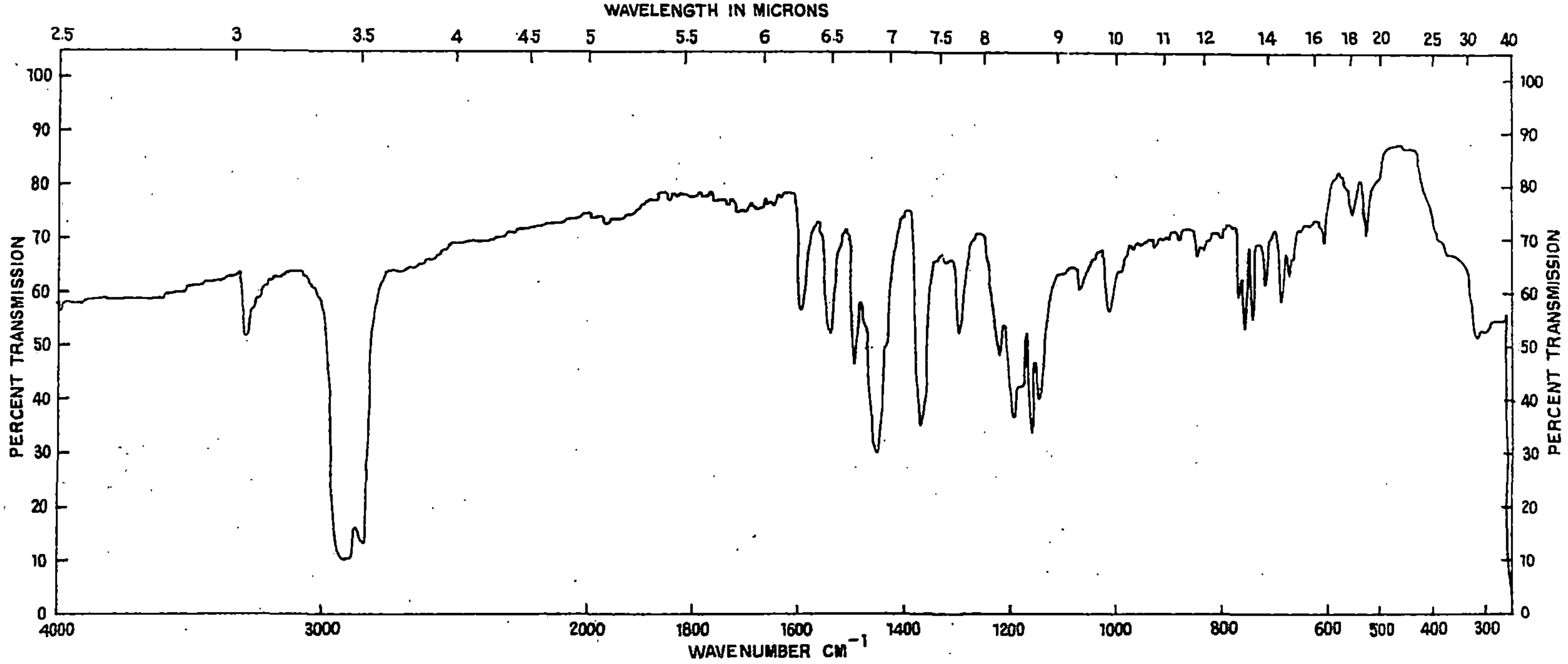

Fig.- 6 I.R. Spectrum of tripropyl tin diphenyl carbazonate

22. Tributyl tin diphenyl carbazonate:

1.04g of tributyl tin acetate and 0.72g of diphenyl carbazone were taken in benzene and the mixture was refluxed for 3 hours. The refluxed solution was filtered and the filtrate was evaporated completely on a water bath. To the residue pet-ether was added. This was then boiled and filtered. The filtrate was concentrated and the concentrated filtrate was kept for some time when violet crystals were formed. The yield was 0.40g. M.P. was 88-90°C. This on recrystallisation for three times from pet ether gave crystals of m.p. 91-92°C.

Found:	C = 56.25; H = 6.97; N = 10.32 and Sn = 22.20 per cent.
Calculated for $C_{25}H_{38}N_4OSn$:	C = 56.71; H = 7.18; N = 10.58 and Sn = 22.49 per cent.

23. Tricyclohexyl tin diphenyl carbazonate:

0.80g of tricyclohexyl tin chloride and 0.48g of diphenyl carbazone was separately dissolved in chloroform. These were then mixed and the mixture was refluxed for two and half hours. A few drops of ammonium hydroxide (17N) solution was added to the mixture to neutralise the liberated hydrochloric acid. The precipitated ammonium chloride was filtered off. The red filtrate was evaporated to a pasty mass. The pasty mass was then boiled with pet ether and the solution was filtered. The filtrate was concentrated to one-

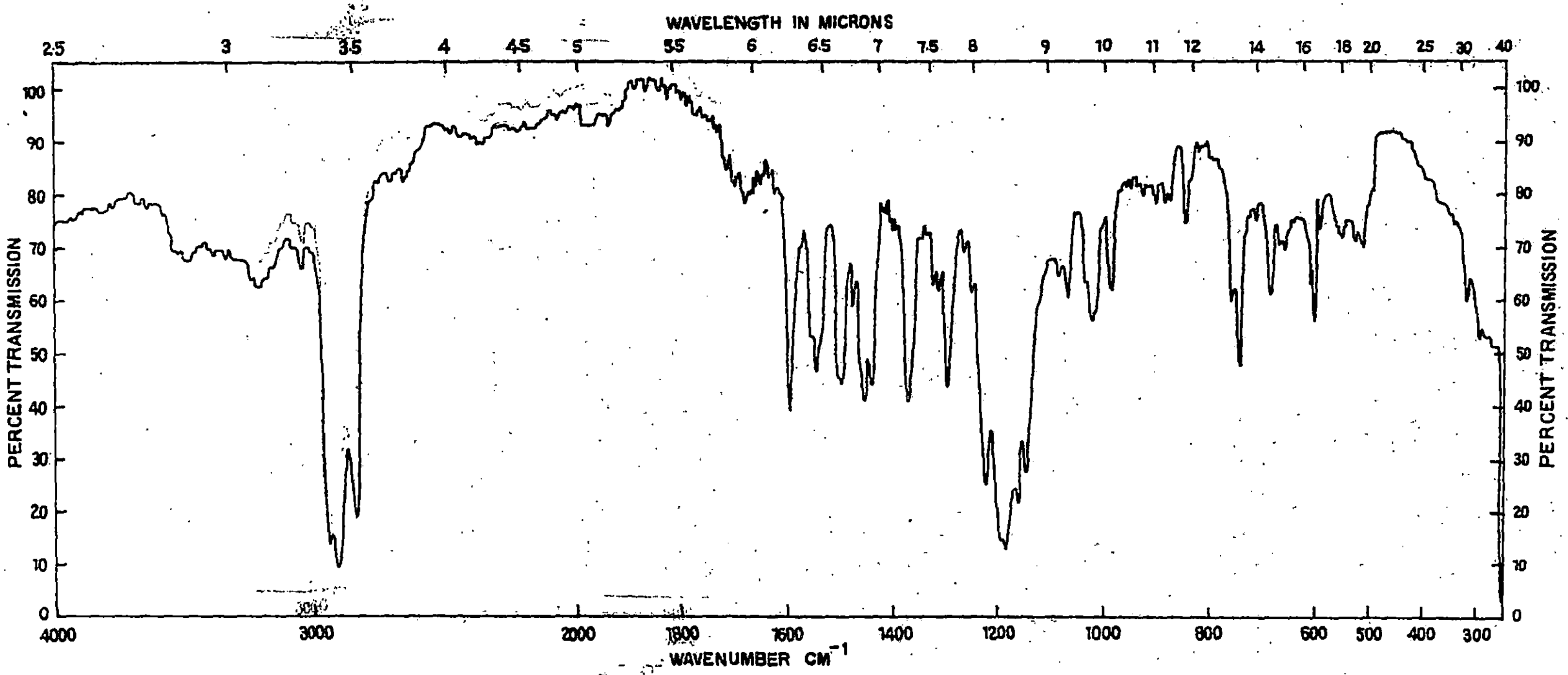

Fig.- 7 I. R. Spectrum of tricyclohexyltin diphenyl carbazonate

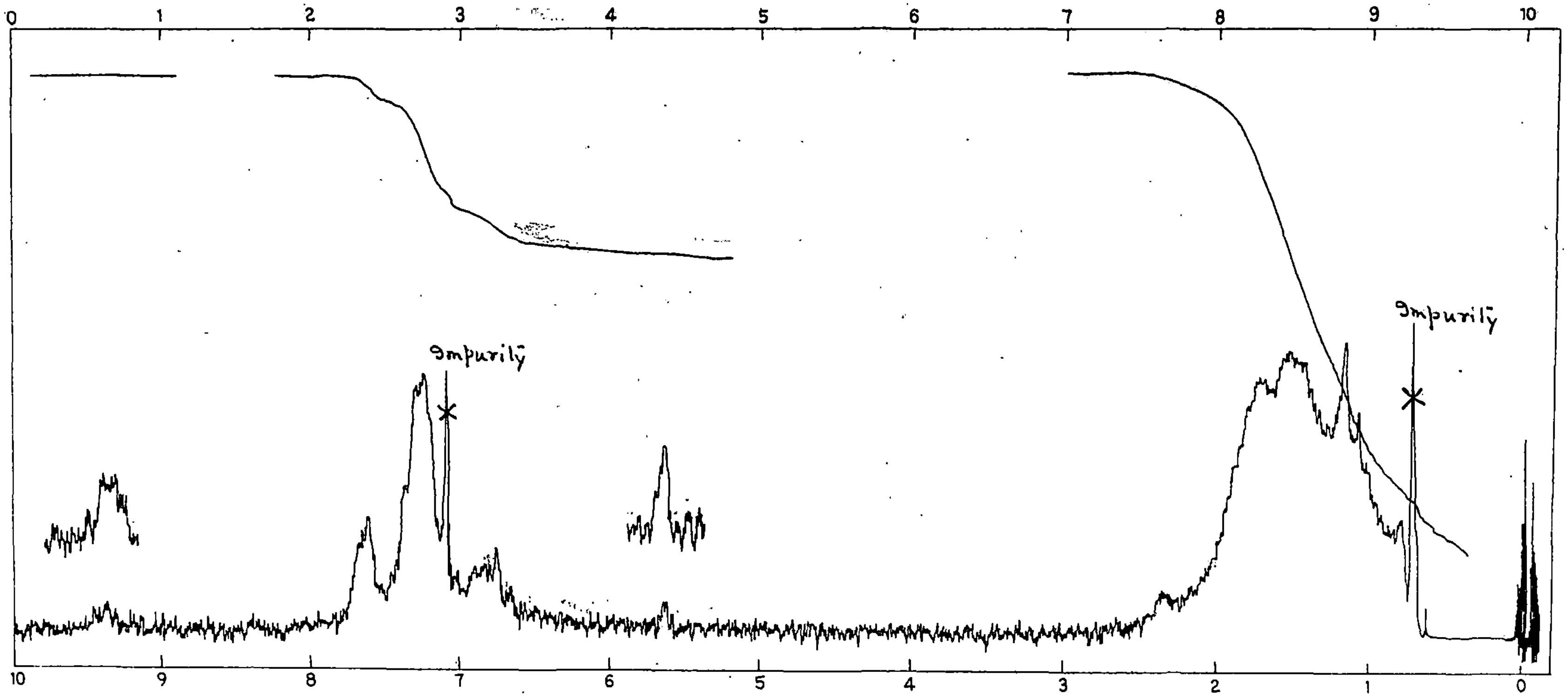

Fig.- **8**

PMR Spectrum of tricyclohexyl tin diphenyl carbazonate third of its original volume and on standing for some time shining reddish crystals appeared and was collected. The yield was 0.70g. The melting point of the crystal was 132-34°C. Recrystallisation from benzene-pet ether afforded crystals of m.p. 136°C.

Found:	C = 60.8; H = 7.08; N = 9.03 and Sn = 19.30 per cent
Calculated for $C_{31}H_{44}N_4OSn$:	C = 61.28; H = 7.25; N = 9.22 and Sn = 19.60 per cent.

24. Triphenyl tin diphenyl carbazonate:

(a) 1.43g of triphenyl tin oxide and 0.96g of diphenyl carbazone was dissolved separately in benzene by heating. The hot solutions were then mixed and the mixture was refluxed for about three and half hours. Dean-Stark Separator was used to remove the water formed during the reaction. The refluxed solution was then concentrated to one-fourth its original volume and the concentrated solution on cooling gave no crystal. To this concentrated solution pet-ether was added till pink coloured crystals of melting point 152-54°C appeared. This was diphenyl carbazone as it showed no depression in melting point with an authentic sample of diphenyl carbazone.

After separating out the diphenyl carbazone the mother liquor was concentrated further and pet ether was added when after some time a bluish-ink coloured crystal of m.p. 165-170°C was formed. Yield was 0.50g. This on further crystallisation from benzene-pet ether for three times afforded crystals of m.p. 169-71°C.

Found:	C = 62.80; H = 4.30; N = 9.32 and Sn = 19.88 per cent
Calculated for $C_{31}H_{26}N_4OSn$:	C = 63.15; H = 4.41; N = 9.50 and Sn = 20.20 per cent.

(b) A mixture of 0.77g of triphenyl tin chloride and 0.48g of diphenyl carbazone were taken in chloroform and the mixture was refluxed for two hours. To this solution a few drops of ammonium hydroxide (17N) solution was added to neutralise the liberated hydrochloric acid and the precipitated ammonium chloride was filtered off. The filtrate was then completely evaporated on a water bath to a pasty mass. The mass was then dissolved in slight hot benzene and to it excess pet ether was added when an orange-coloured crystal appeared which was diphenyl carbazone as was confirmed by mixed melting pointchecking with an authentic sample. After separating out this diphenyl carbazone the mother liquor was further concentrated and kept for a while when fine bluish-pink coloured crystals of melting point 168-70°C was formed. This on further crystallisation from benzene-pet ether mixture afforded crystals of melting point 169-70°C. Yield was 0.30g. Mixed melting point of this crystal with the same obtained in the earlier method showed no depression.

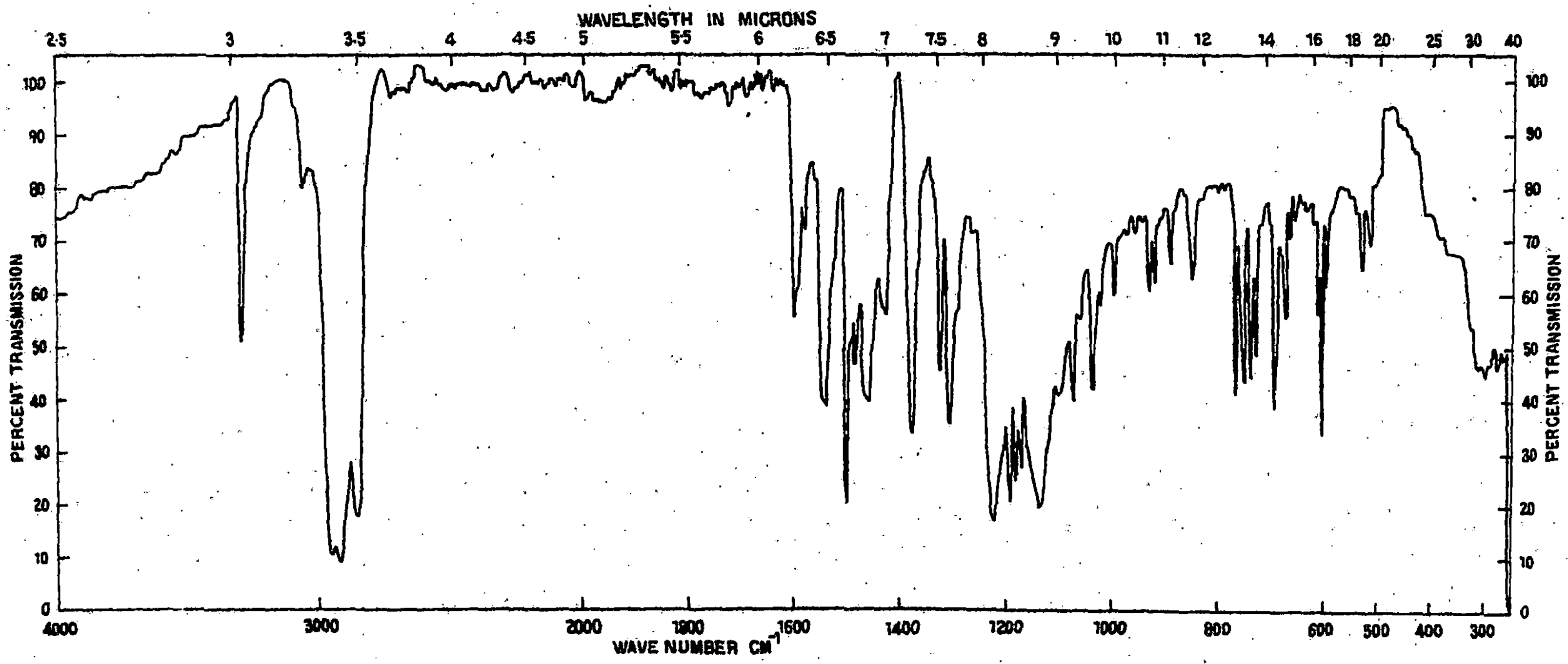

Fig.- 9 I.R.Spectrum of triphenyl tin diphenyl carbazonate.

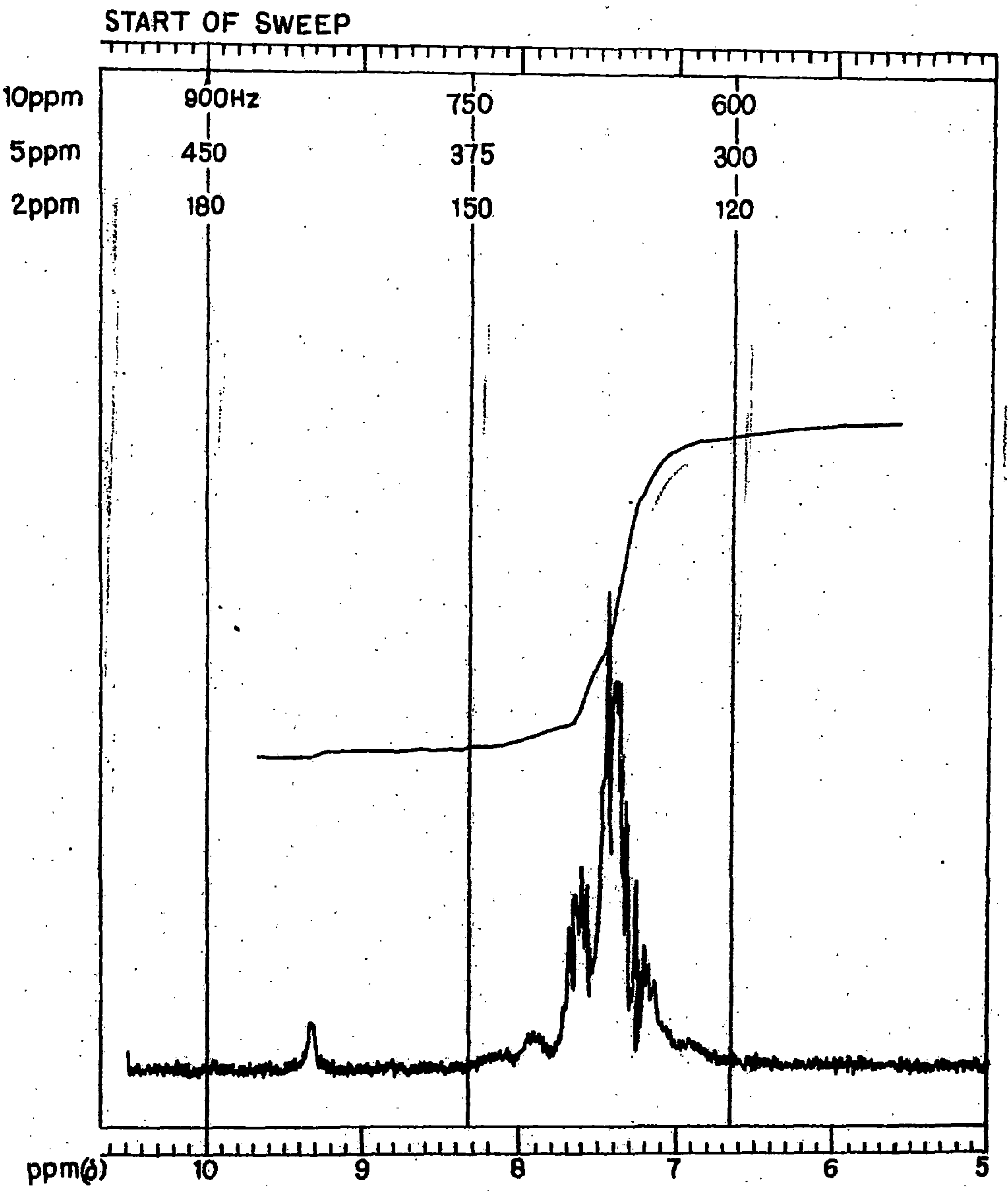

Fig-10 PMR Spectrum of triphenyl tin diphenyl carbazonate

Found: $C = 62.75$; $H = 4.28$; $N = 9.38$ and $Sn = 19.84$ per cent

Calculated for $C_{31}H_{26}N_4OSn$: $C = 63.15$; $H = 4.41$; $N = 9.50$ and $Sn = 20.20$ per cent.

25. Triparatolyl tin diphenyl carbazonate:

0.86g of triparatolyl tin chloride was dissolved in 100 ml chloroform. To it added 0.48g of diphenyl carbazone. The colour of the solution became red. The mixture was then refluxed for two hours. To it a few drops of ammonium-hydroxide (17N) solution was added to neutralise the liberated hydrochloric acid. The precipitated ammonium chloride was filtered off. The red filtrate was completely evaporated to dryness. The mass was boiled with pet ether and the solution was filtered. An insoluble residue in pet ether was found which was confirmed as diphenyl carbazone from the checking of the mixed melting point with an authentic sample. The filtrate was concentrated and the concentrated filtrate was kept for some time when beautiful shining reddish crystals appeared. These were collected. The yield was 0.20g and the melting point was 220-21°C. These on recrystallisation from benzene-pet ether mixture afforded beautiful shining reddish crystals of m.p. 225-26°C.

Found: $C = 64.38$; $H = 5.18$; $N = 8.55$ and $Sn = 18.56$ per cent.

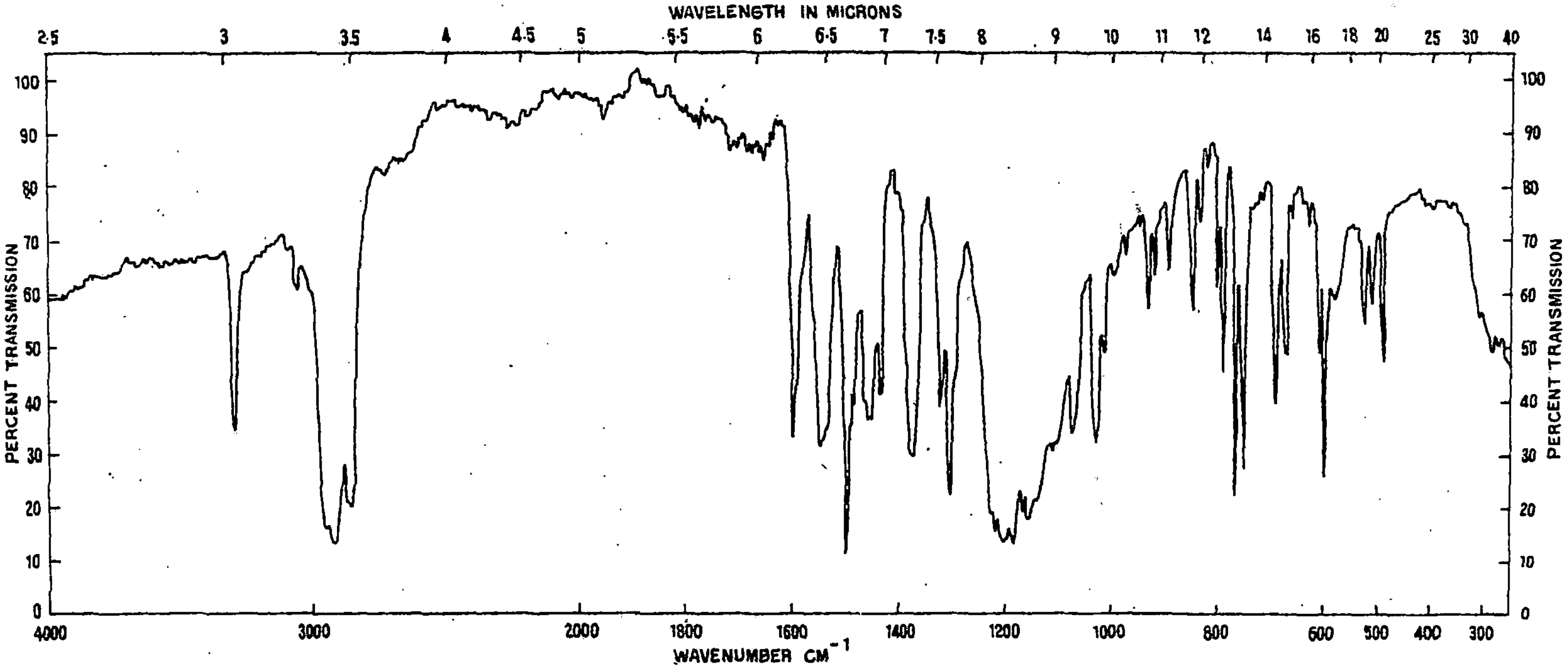

Fig.-11 I.R. Spectrum of tri paratolyl tin diphenyl carbazonate

Calculated for $C_{34}H_{35}N_4OSn$: C = 64.35; H = 5.52; N = 8.83 and Sn = 18.77 per cent.

26. Tribenzyl tin diphenyl carbazonate:

0.85g of tribenzyl tin chloride and 0.24g of diphenyl carbazone were mixed. To it added 100 ml chloroform. The mixture was refluxed for 2 hours. To it added 5-6 drops of ammonium hydroxide (17N) solution to neutralise the liberated hydrochloric acid. The precipitated ammonium chloride was filtered off. The red filtrate was concentrated to about 5 ml and to it 10 ml methanol was added. As no crystals appeared, the solution was further concentrated to one-fourth its volume and was kept for 2 hours when beautiful shining reddish crystals appeared. This was collected. The yield was 0.35g and the melting point was 131-32°C. On recrystallisation from chloroform/methanol mixture it afforded crystals of melting point 134°C.

Found: C = 64.25; H = 4.98; N = 8.42 and Sn = 18.28 per cent

Calculated for $C_{34}H_{32}N_4OSn$: C = 64.66; H = 5.07; N = 8.87 and Sn = 18.86 per cent.

27. Dimethyl tin bis-diphenyl carbazonate:

(a) 0.49g of dimethyl tin oxide and 1.44g of diphenyl carbazone were taken in 100 ml benzene. This mixture was refluxed for three hours using a Dean - Stark Water Separator. The colour of the solution became red. The solution on cooling did not give any crystal. The solution was concentrated on a water bath to about 10 ml . A slight excess of methanol was added to it. No crystals appeared. The mixture was concentrated and the concentrated solution was kept for some time when beautiful shining reddish crystals were formed and collected. Yield was 1.40g. Melting point was found to be 128-30°C. These upon recrystallisation from benzene-methanol mixture afforded crystals of melting point 130-32°C.

Found: $C = 53.28$; $H = 4.36$; $N = 17.66$ and $Sn = 18.80$ per cent

Calculated for $C_{28}H_{28}N_8O_2Sn$: $C = 53.58$; $H = 4.46$; $N = 17.86$ and $Sn = 18.97$ per cent.

(b) A mixture of 0.20g of dimethyl tin dichloride and 0.50g of diphenyl carbazone was separately dissolved in chloroform. These were then mixed and the mixture was refluxed for two hours. 5-7 drops of ammonium hydroxide (17N) solution was added to neutralise the liberated hydrochloric acid and the precipitated ammonium-chloride was filtered off. The red filtrate was concentrated, methanol was added and the mixture was kept for some time when 0.30g of red crystals having m.p. 130-31°C were formed. These were collected. The crystals on recrystallisation from chloroform-methanol mixture afforded crystals of m.p. 132°C. Mixed melting point of this compound with the previous one

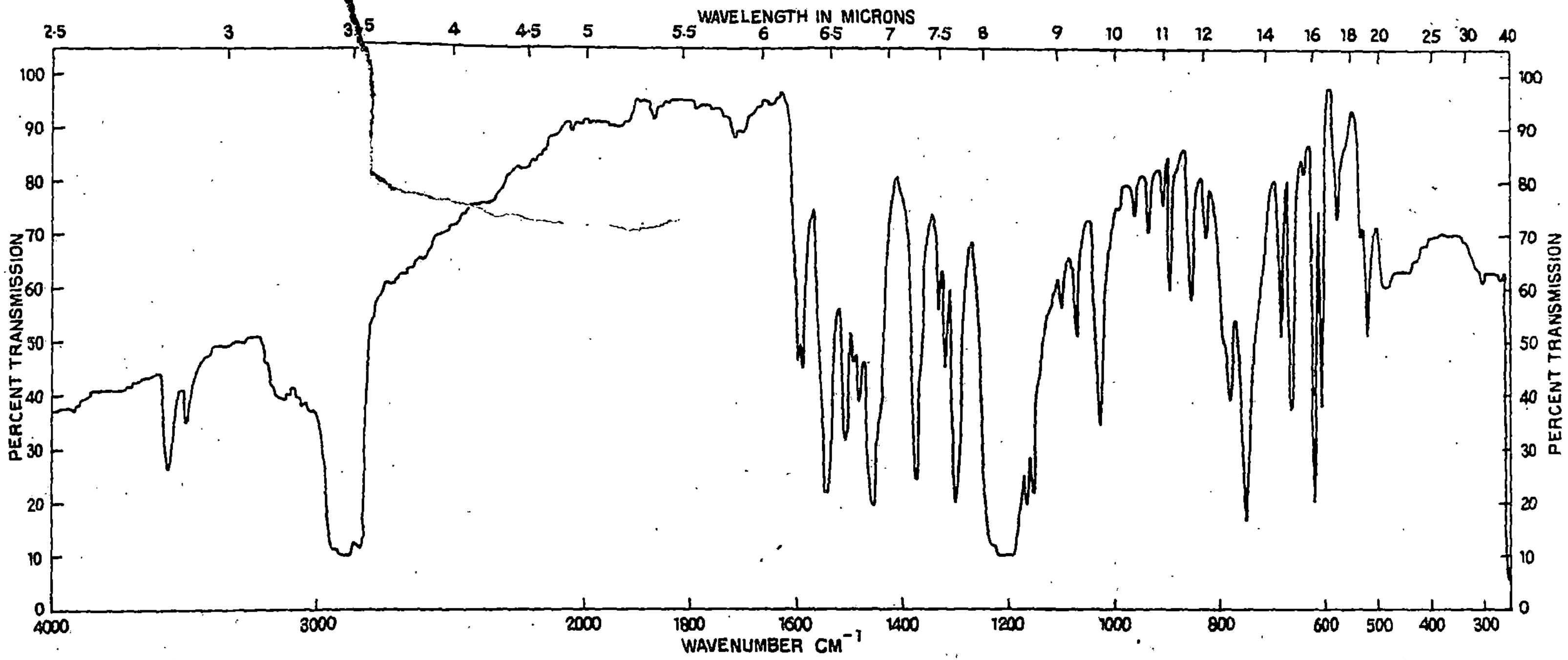

Fig.- 12

I.R. Spectrum of dimethyl tin bis-diphenyl carbazonate .

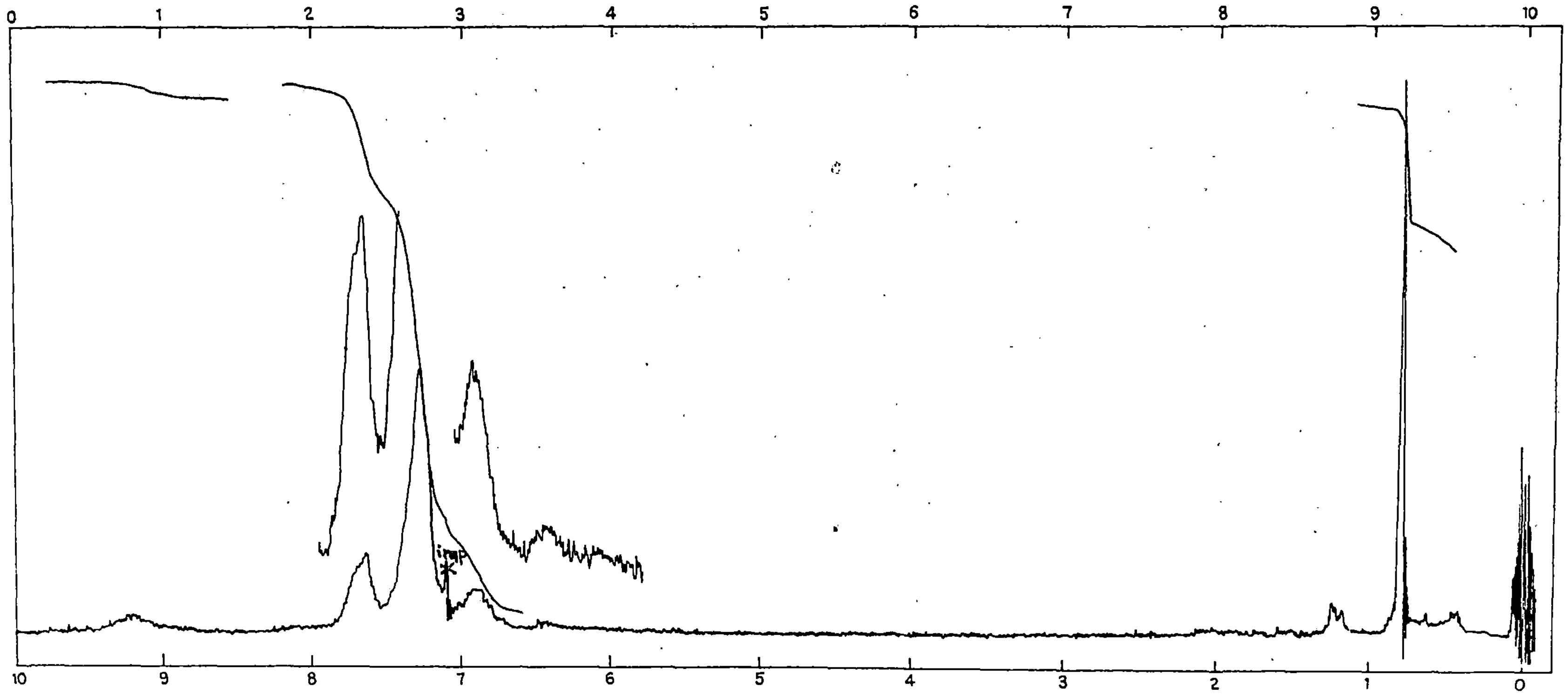

Fig.- 13

PMR Spectrum of dimethyl tin bis- (diphenyl carbazonate) (formed from dimethyl tin oxide and diphenyl carbazone) showed no depression.

Found: C = 53.22; H = 4.32; N = 17.60 and Sn = 18.80 per cent

Calculated for $C_{28}H_{28}N_8O_2Sn$: C = 53.58; H = 4.46; N = 17.86 and Sn = 18.97 per cent.

28. Dibutyl tin bis-diphenyl carbazonate:

(a) 0.74g of dibutyl tin oxide and 1.44g of diphenyl carbazone were mixed. To it 100 ml benzene was added. The mixture was refluxed for 2 hours using a Dean and Stark Water Separator. The refluxed solution was concentrated on a water bath to about 10 ml 20 ml methanol was added to it. The mixture on standing for some time gave beautiful shining reddish crystals of m.p. 120-22°C. Yield was 1.40g. These on recrystallisation from benzene-methanol mixture afforded crystals of m.p. 123-24°C.

Found: C = 57.15; H = 5.48; N = 15.50 and Sn = 16.62 per cent

Calculated for $C_{34}H_{40}N_8O_2Sn$: C = 57.38; H = 5.62; N = 15.75 and Sn = 16.73 per cent.

(b) A mixture of 0.30g of dibutyl tin dichloride and 0.48g of diphenyl carbazone was dissolved in 100 ml chloroform. The solution was refluxed for two hours. A few drops of ammonium

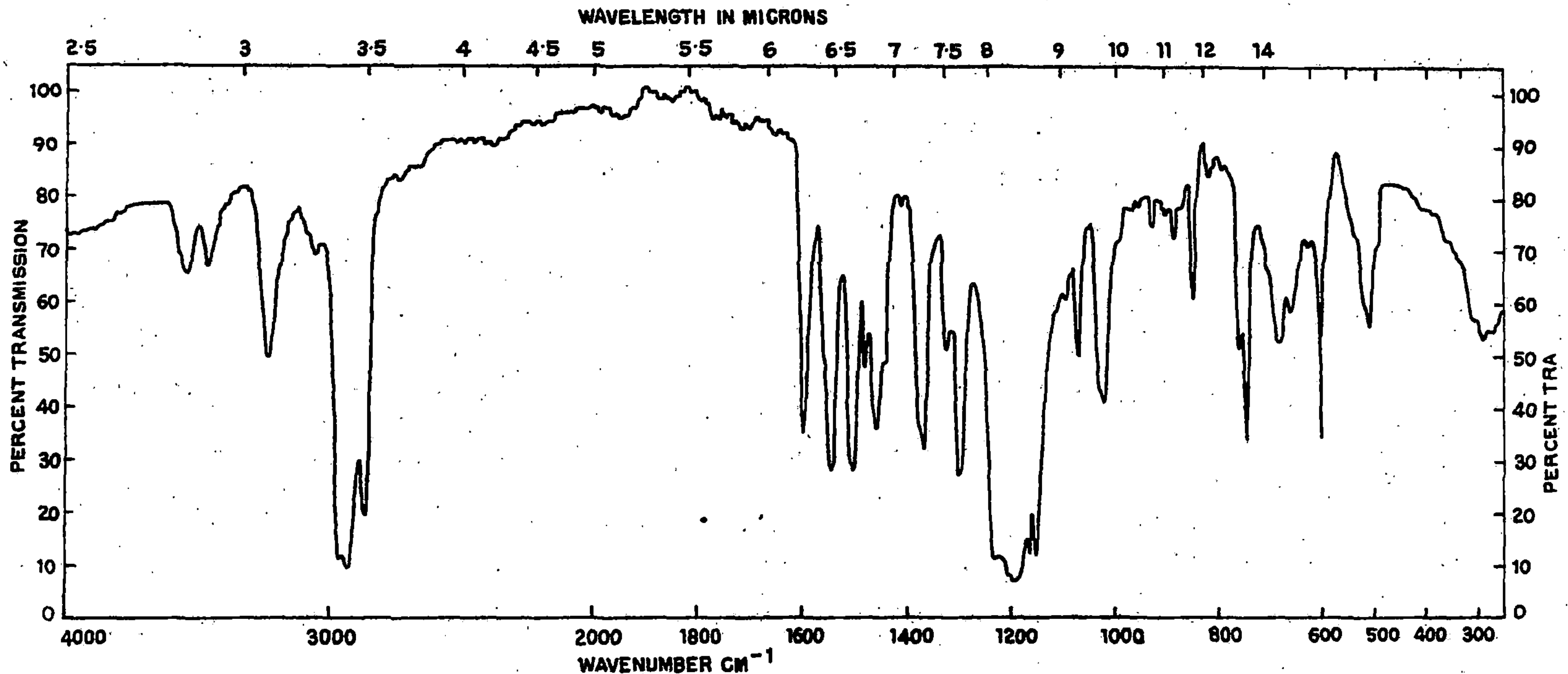

Fig.-14. I.R. Spectrum of dibutyltin bis-diphenyl carbazonate

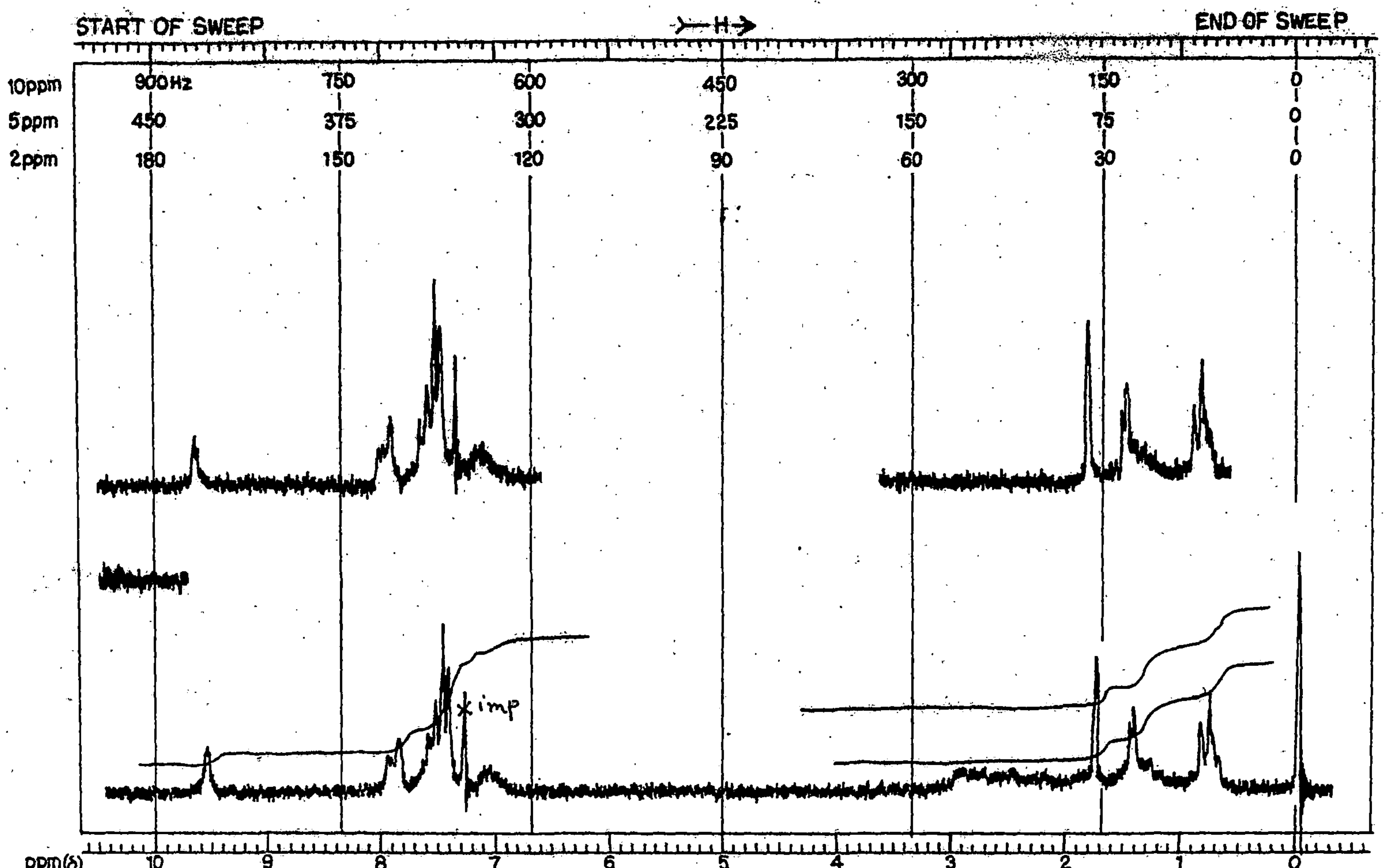

Fig-15 PMR Spectrum of dibutyl tin bis-(diphenyl carbazonate) hydroxide (17N) solution was added to the refluxed solution to neutralise the liberated hydrochloric acid. The precipitated ammonium chloride was filtered off. The red filtrate was concentrated and to it a slight excess of methanol was added. This mixture was allowed to stand for some time when fine shining reddish crystals of m.p. 120-21°C was obtained. These on recrystallisation twice from chloroform-methanol mixture afforded crystals of m.p. 122-24°C. Mixed melting point of this compound with the previous one showed no depression.

Found:	C = 57.07; H = 5.37; N = 15.48 and Sn = 16.58 per cent
Calculated for $C_{34}H_{40}N_8O_2Sn$:	C = 57.38; H = 5.62; N = 15.75 and Sn = 16.73 per cent.

29. <u>Dicyclohexyl tin bis-diphenyl carbazonate:</u>

0.36g of dicyclohexyl tin dichloride and 0.48g of diphenyl carbazone was separately dissolved in chloroform. These two solutions were then mixed. The mixture was refluxed for 2 hours. 5-7 drops of ammonium hydroxide (17N) solution was added to the mixture to neutralise the liberated hydrochloric acid. The precipitated ammonium chloride was filtered off. The filtrate was concentrated and methanol in excess was added to it. The mixture was kept for some time when beautiful shining reddish crystals were formed. This was collected. The yield was 0.42g.

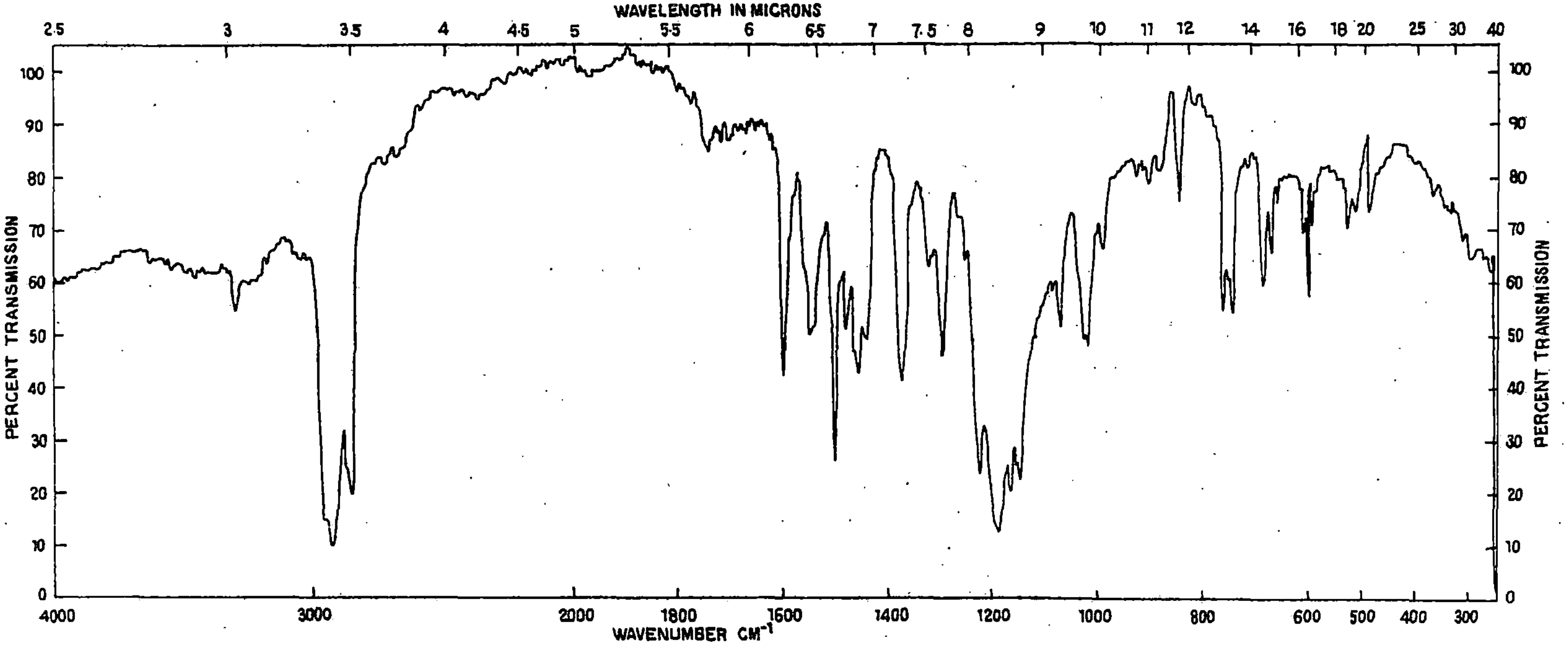

Fig. - 16 I.R. Spectrum of dicyclohexyl tin bis-diphenyl carbazonate.

M.P. was 195-96°C. This on recrystallisation twice from chloroform methanol mixture afforded crystals of m.p. 198°C.

Found :	C = 59.10; H = 5.95; N = 14.32 and Sn = 15.30 per cent
Calculated for $C_{38}H_{44}N_8O_2Sn$:	C = 59.76; H = 5.76; N = 14.68 and Sn = 15.59 per cent.

30. Diphenyl tin bis-diphenyl carbazonate:

(a) 0.58g of diphenyl tin oxide and 0.96g of diphenyl carbazone were taken in 150 ml benzene. This was refluxed for two and half hours using a Dean and Stark Water Separator. The colour of the solution became red. The solution was then filtered and the filtrate was concentrated to about 10 ml on a water bath. To it about 30 ml methanol was added. On standing for some time the solution did not give any crystals. The solution was then concentrated to half its volume and this concentrated solution was kept for some time when beautiful shining crystals of m.p. 222-24°C were formed. These were collected. The yield was 0.92g. These on recrystallisation from benzene-methanol mixture afforded crystals of m.p. 227-28°C.

Found:	C = 61.17; H = 4.30; N = 14.95 and Sn = 15.30 per cent
Calculated for $C_{38}H_{32}N_8O_2Sn$:	C = 60.72; H = 4.26; N = 14.91 and Sn = 15.84 per cent.

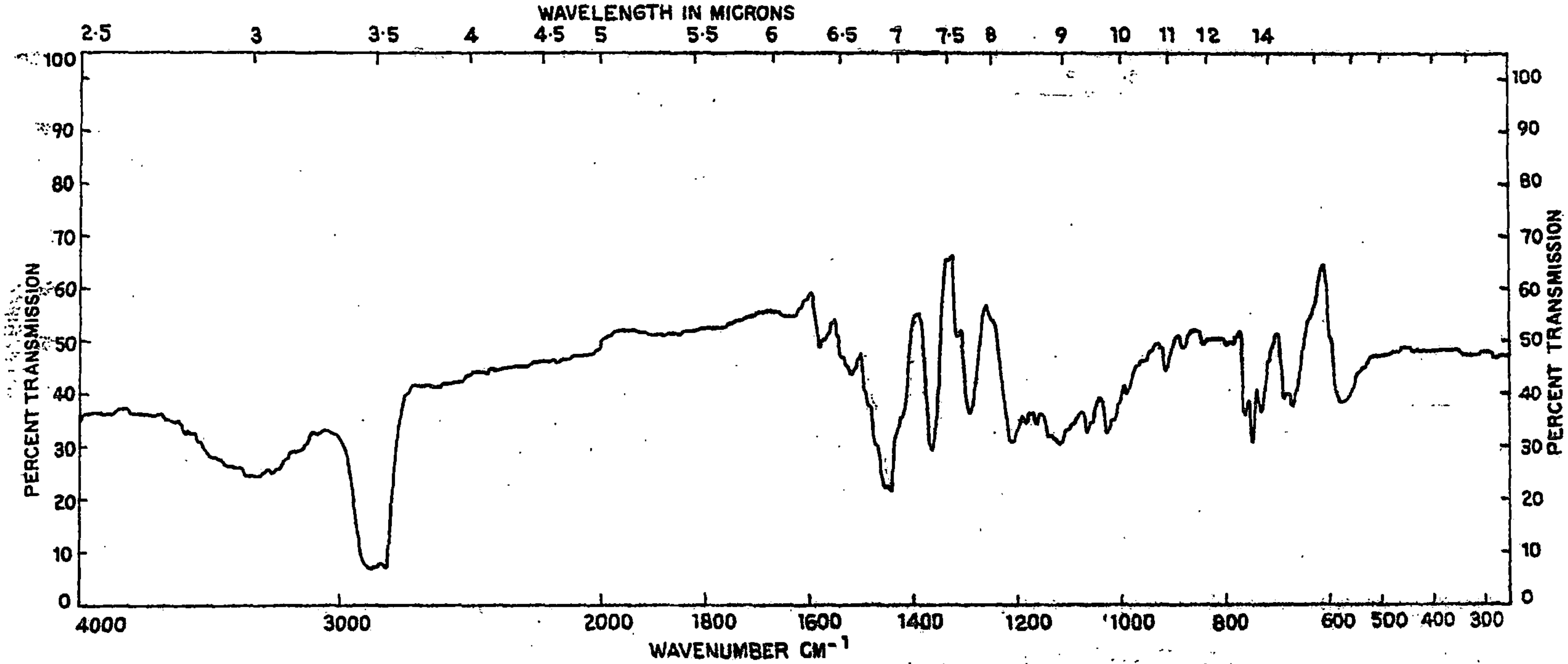

Fig.- 17 I.R. Spectrum of diphenyltin bis- diphenyl carbazonate.

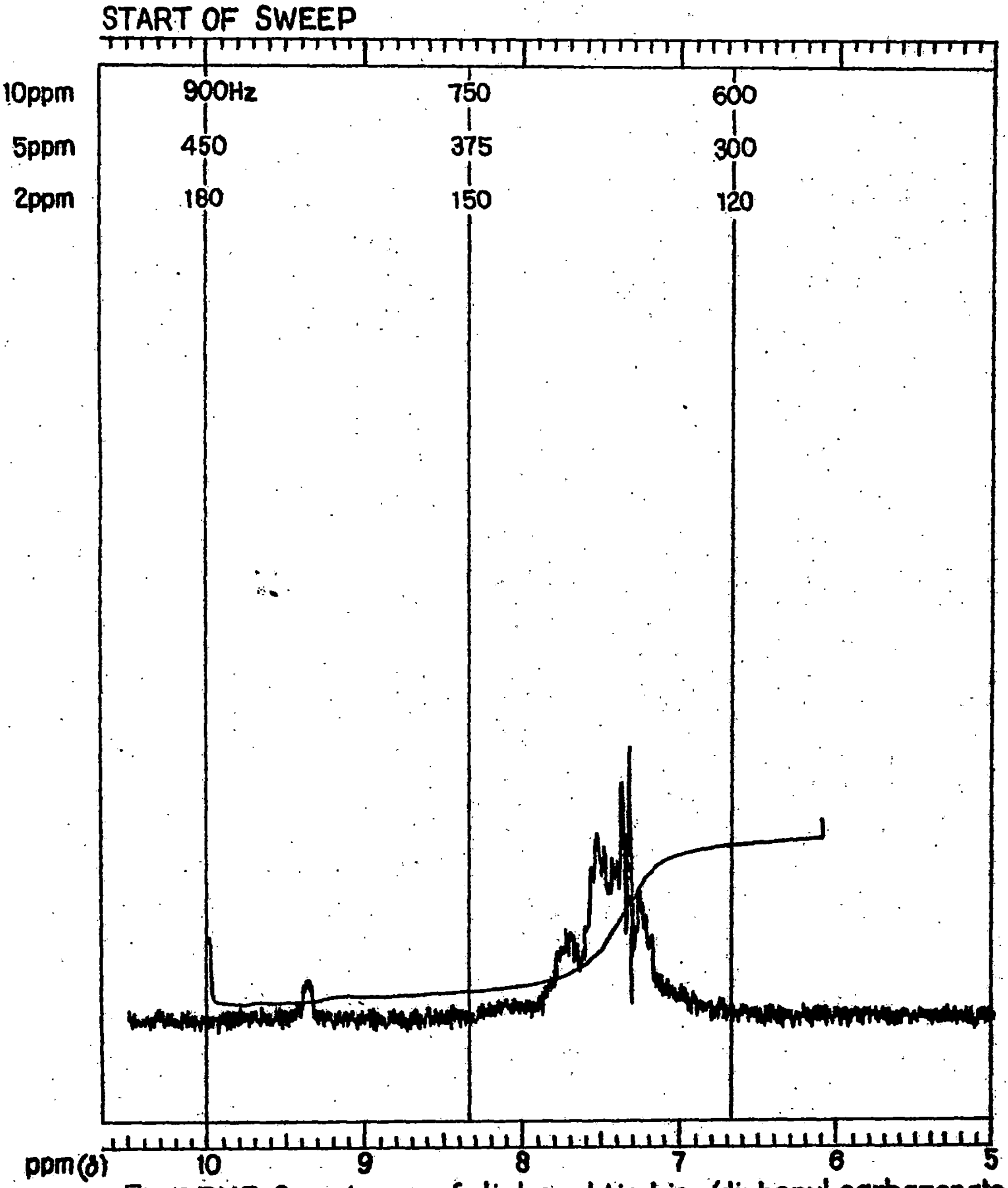

Fig-18. PMR Spectrum of diphenyl tin bis-(diphenyl carbazonate)

(b) 0.69g of diphenyl tin dichloride and 0.96g of diphenyl carbazone was separately dissolved in chloroform. These were mixed and the mixture was refluxed for one hour. 6-7 drops of ammonia (17N) solution was added to the refluxed solution to neutralise the liberated hydrochloric acid. The precipitated ammonium chloride was filtered off. The filtrate was concentrated to one-fourth its original volume. To it slight excess of methanol was added. On standing for some time beautiful shining reddish crystals of m.p. 224-25°C appeared. These were collected and on recrystallisation from chloroform-methanol mixture it afforded crystals of m.p. 227-28°C. Yield was 1.15g. Mixed melting point of this compound with the compound prepared by the previous method showed no depression.

Found: $C = 60.38$; $H = 4.14$; $N = 14.66$ and $Sn = 15.52$ per cent

Calculated for $C_{38}H_{32}N_8O_2Sn$: $C = 60.72$; $H = 4.26$; $N = 14.91$ and $Sn = 15.84$ per cent.

31. Diparatolyl tin bis-diphenyl carbazonate:

(a) 1.44g of diphenyl carbazone was dissolved in 100 ml chloroform. To it added 0.95g of diparatolyl tin oxide and the mixture was shaken. The colour of the mixture changed rapidly from violet to red. The mixture was refluxed for 1 hour and the refluxed solution was filtered. The filtrate was concentrated to one-fourth its original volume on a water bath and methanol was added to it. After some time fine shining pink coloured crystals appeared. These were collected. M.P. was 204-206°C and the yield was 1.2g. This on recrystallisation from chloroform-methanol mixture afforded crystals of m.p. 207-208°C.

Found : C = 60.88; H = 4.69; N = 14.01 and
Sn = 14.87 per cent

Calculated for $C_{40}H_{36}N_8O_2Sn$: C = 61.61; H = 4.62; N = 14.37 and
Sn = 15.27 per cent.

(b) A mixture of 0.37g of diparatolyl tin dichloride and 0.48g of diphenyl carbazone was taken in 100 ml chloroform. The mixture was refluxed for 1 hour. A few drops of ammonium hydroxide (17N) solution was added to the refluxed solution to neutralise the liberated hydrochloric acid. Precipitated ammonium-chloride was filtered off. The filtrate was then concentrated on a water bath to about 10 ml. To it 20 ml methanol was added. After sometime the mixture gave beautiful shining pink coloured crystals of m.p. 202-206°C. These on recrystallisation from chloroform-methanol mixture afforded crystals of m.p. 207-208°C. Mixed melting point of this compound with the previous one showed no depression.

Found : C = 60.90; H = 4.38; N = 14.19 and
Sn = 15.12 per cent

Calculated for $C_{40}H_{36}N_8O_2Sn$: C = 61.61; H = 4.62; N = 14.37 and
Sn = 15.27 per cent.

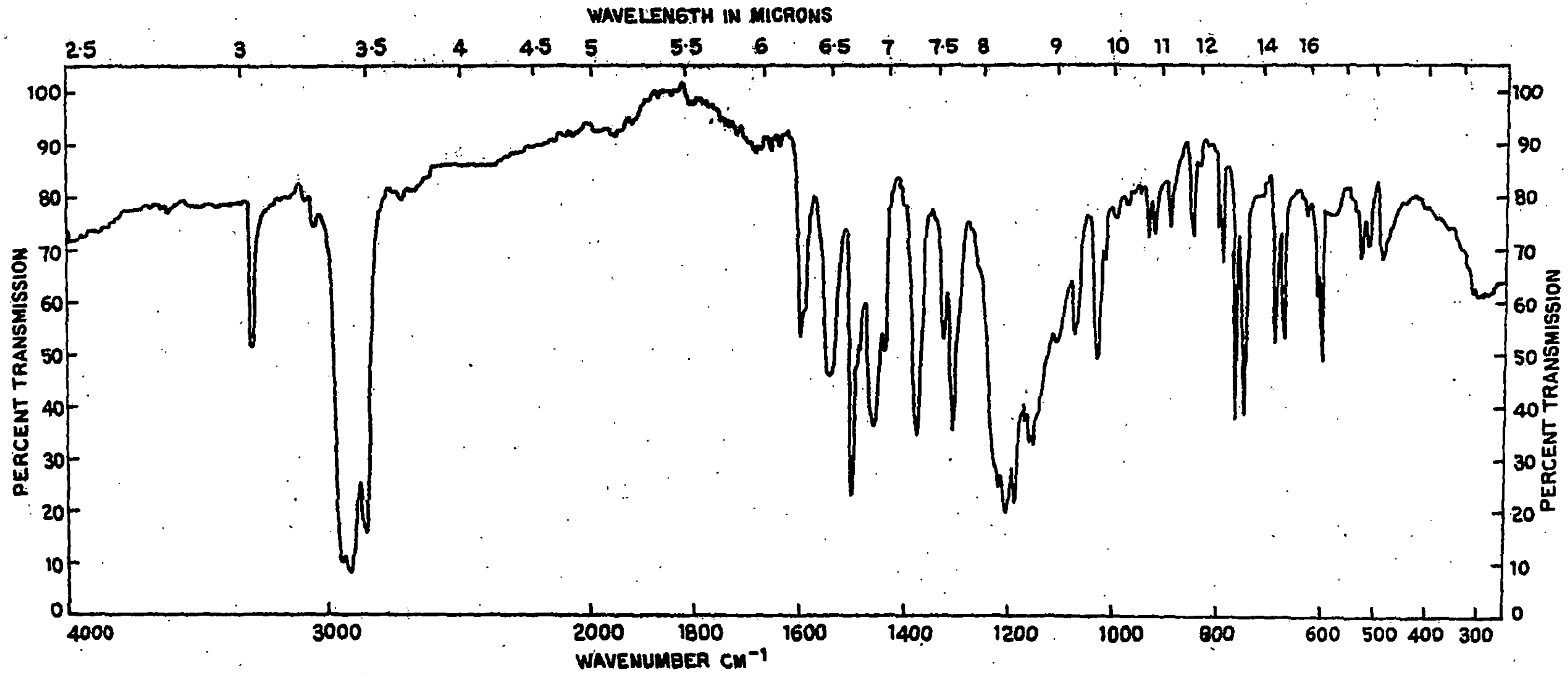

Fig.- 19 I.R. Spectrum of diparatolyltin bis-diphenyl carbazonate

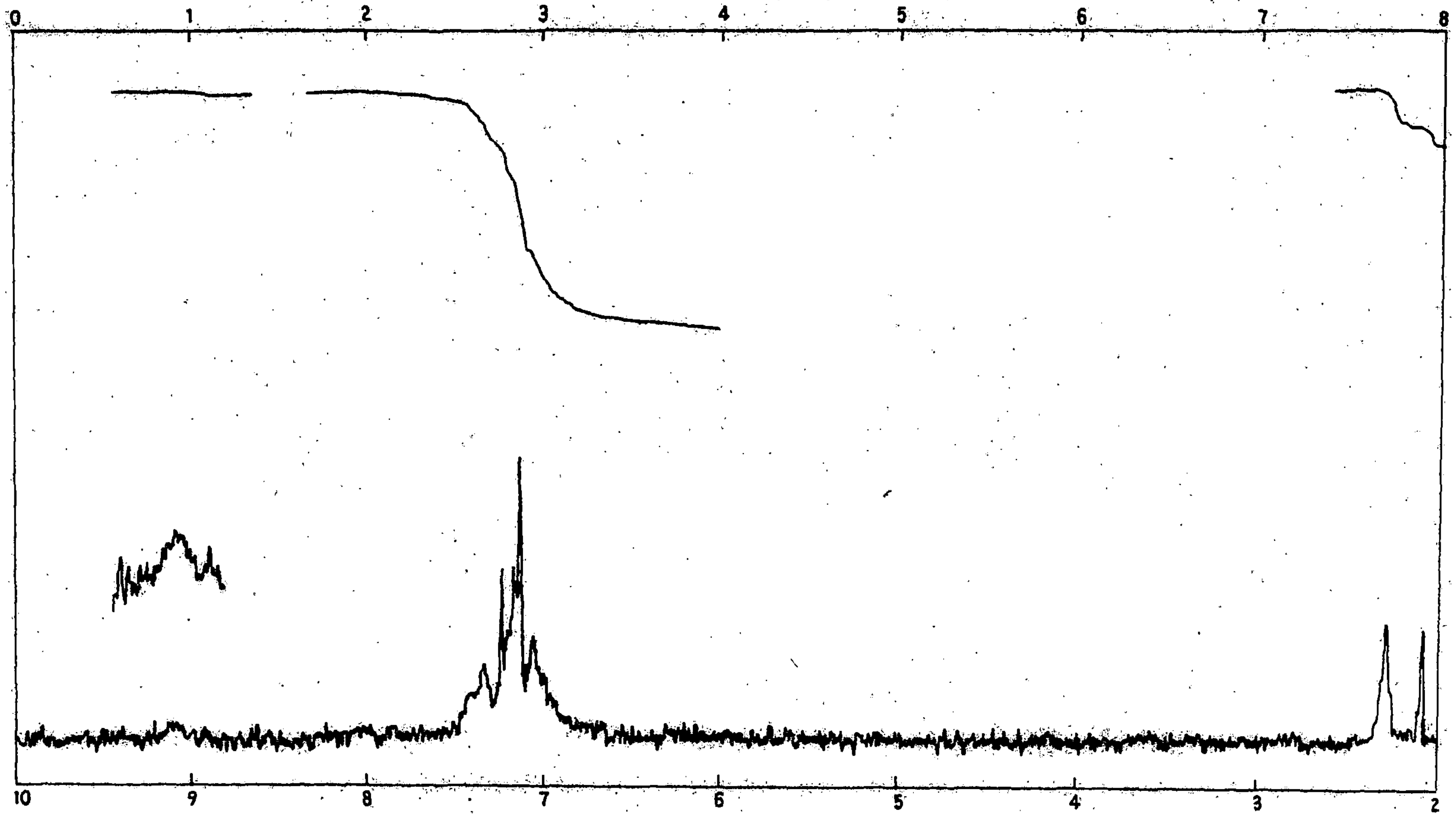

Fig-20. PMR Spectrum of diparatolyl tin bis-(diphenyl carbazonate)

Incorrectword	Correct word	Page	Paragraph	Line
havily	heavily	8	3	7
Reference No.after Kumar Das et al not given	(73)	14	2	1
types	type	19	last	6
glycene	glycine	19	last	6
Collec	Collected	32	5	3
Reference No.after Kemula and Janowski not given		60	last	last
Ambident	Ambient	66		
electrons	electrons	72	2	9
Incomplete sentence		95	1	1
stannes	Stannanes	102	last	3
Unbalanced equation		108		
Reactivity Order not mentioned		125	1	5

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SPNarula
15/9/1983

32. Dibenzyl tin bis-diphenyl carbazonate:

(a) A mixture of 0.31g of dibenzyl tin oxide and 0.48g of diphenyl carbazone was refluxed in 100 ml benzene for two hours using a Dean and Stark Water Separator. The refluxed solution was concentrated to about 10 ml on a water bath. To it added a slight excess of methanol. This, on standing for sometime, gave shining pink coloured crystals of melting point 189-90°C. The yield was 0.30g. These on further crystallisation from benzene-methanol mixture afforded crystals of m.p. 192-93°C.

Found: C = 61.01; H = 4.51; N = 14.22 and Sn = 15.02 per cent

Calculated for $C_{40}H_{36}N_8O_2Sn$: C = 61.61; H = 4.62; N = 14.37 and Sn = 15.27 per cent.

(b) 0.78g of dibenzyl tin dichloride was dissolved in 100 ml chloroform. To it added 0.48g of diphenyl carbazone. The mixture was then refluxed for 1 hour. A few drops of ammonia (17N) solution was added to the refluxed solution to neutralise the liberated hydrochloric acid. Precipitated ammonium chloride was filtered off. The filtrate was concentrated to about one-tenth its original volume. A slight excess of methanol was added to the concentrated filtrate. The mixture did not give any crystals. This mixture was then concentrated and kept for some time when beautiful shining pink coloured crystals of m.p. 191-92°C were formed. These were collected. These on recrystallisation from chloroform-methanol

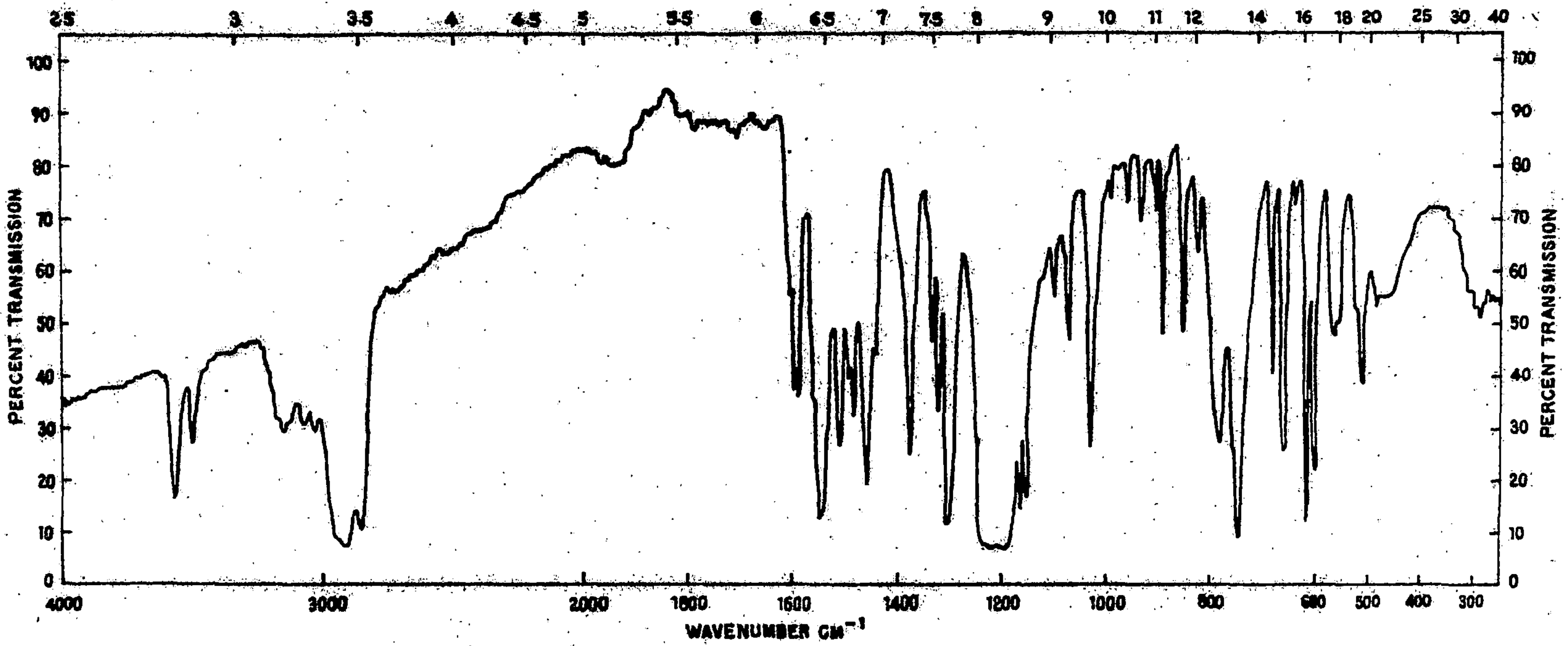


Fig. - 21. I.R. Spectrum of dimethyl chloro-tin-diphenyl carbazonate.

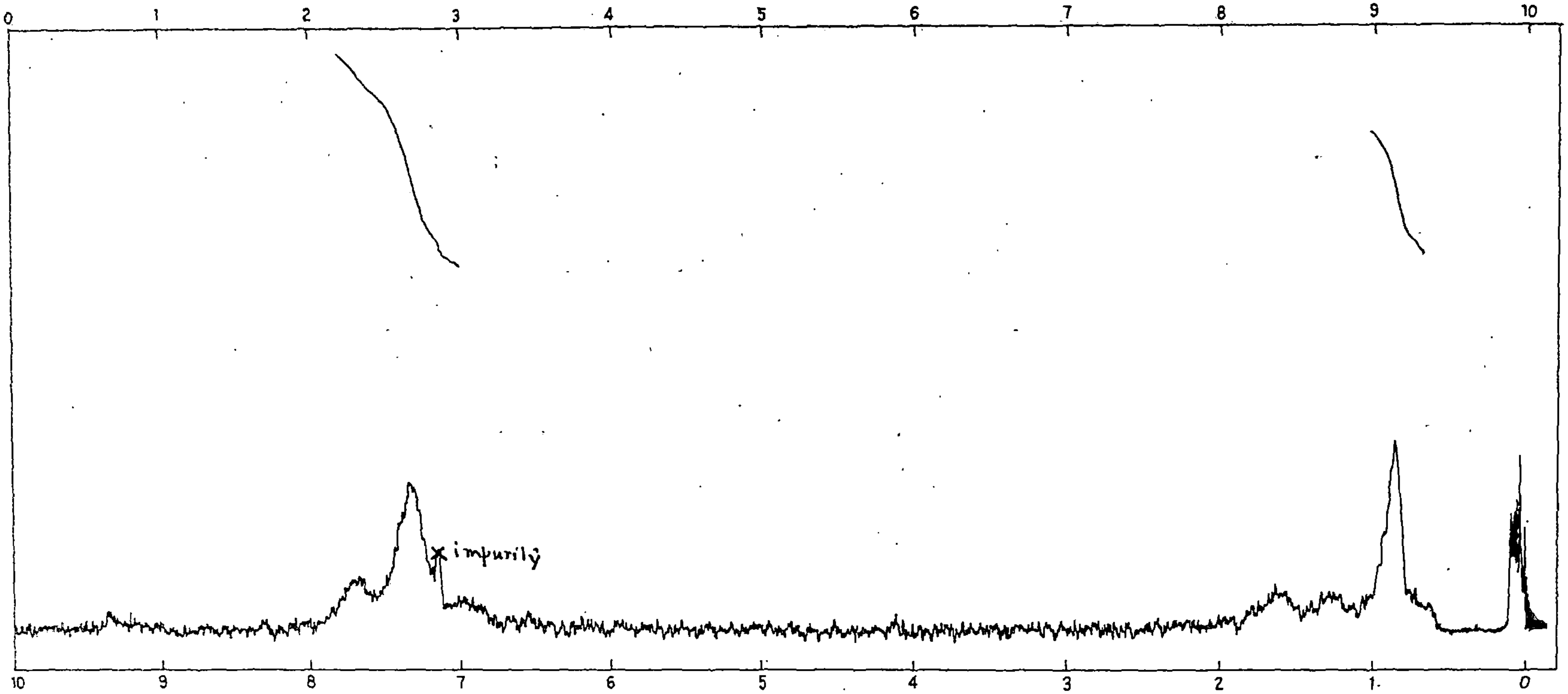


Fig.- **22** PMR Spectrum of dimethyl chlorotin diphenyl carbazonate.

mixture afforded crystals of m.p. 192-93°C. The yield was 0.25g. Mixed melting point of this crystal with the previous one showed no depression.

Found: $C = 60.95$; $H = 4.42$; $N = 14.1$ and
$Sn = 14.98$ per cent

Calculated for $C_{40}H_{36}N_8O_2Sn$: $C = 61.61$; $H = 4.62$; $N = 14.37$ and
$Sn = 15.27$ per cent.

33. <u>Dimethyl chlorotin diphenyl carbazonate</u>:

1.26g of dimethyl tin bis-diphenyl carbazonate and 0.44g of dimethyl tin dichloride were mixed and the mixture was dissolved in minimum volume of benzene. The solution was filtered and the filtrate was concentrated by vacuum pump. Beautiful shining reddish crystals were formed. These were collected. The yield was 0.50g and the m.p. was 126-28°C. This on further crystallisation from benzene gave crystals of m.p. 130°C.

Found: $C = 42.18$; $H = 4.08$; $N = 12.90$ and
$Sn = 27.78$ per cent

$C_{15}H_{17}N_4OClSn$ requires: $C = 42.55$; $H = 4.02$; $N = 13.24$ and
$Sn = 28.01$ per cent.

34. <u>Dimethyl thiocyanato tin diphenyl carbazonate</u>:

0.35g of dimethyl tin dithiocyanate and 0.86g of dimethyl tin bis-diphenyl carbazonate were mixed and the mixture was dissolved in minimum volume of benzene. This solution was

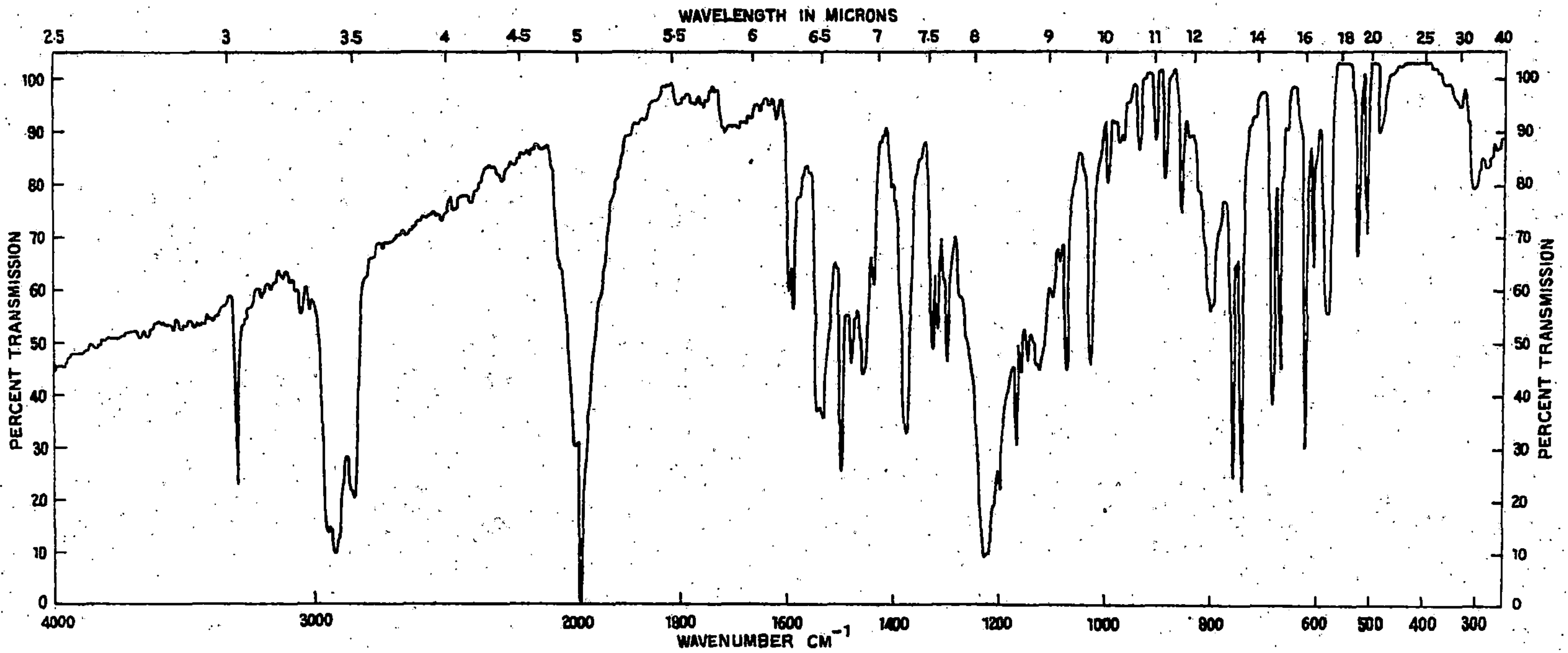


Fig.-23. I.R. Spectrum of dimethyl thiocyanatotin diphenyl carbazonate.

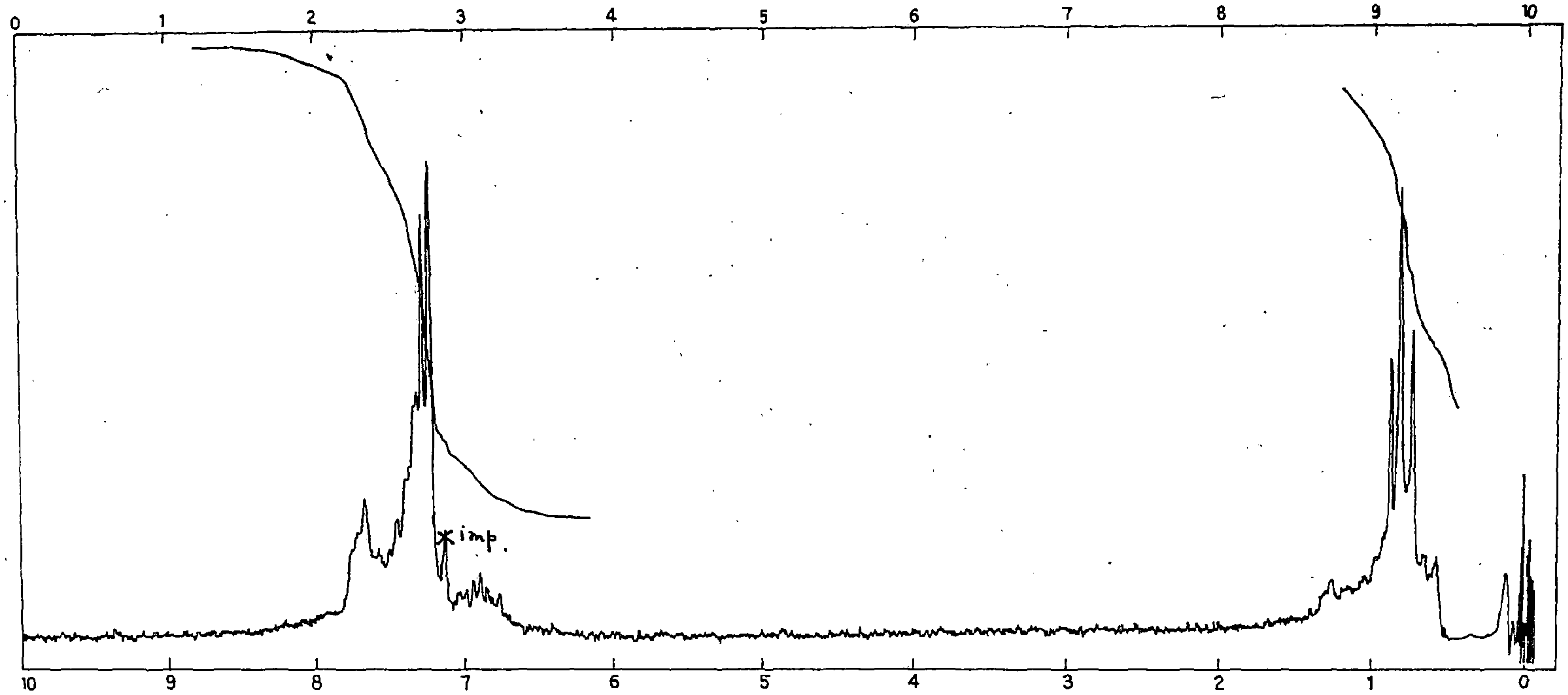


Fig.- 24. PMR Spectrum of dimethyl thiocyanato tin diphenyl carbazonate.

then filtered. The filtrate was concentrated by vacuum pump. The concentrated filtrate was kept for some time when fine shining reddish crystals were formed. This was collected and m.p. was 182-83°C. The yield of the compound was 0.48g. From elemental analysis this compound was found to be dimethyl thiocyanato tin diphenyl carbazonate. After separating these crystals the filtrate was further concentrated and was kept for some time when beautiful shining reddish crystals of m.p. 133-34°C was found to appear. This was collected. This compound was dimethyl tin bis-diphenyl carbazonate as it showed no depression in melting point with an authentic sample.

Analysis found for the compound having m.p. 182-83°C

C = 42.55; H = 4.06; N = 15.46 and Sn = 26.52 per cent

Calculated for $C_{16}H_{17}N_5OSSn$: C = 43.05; H = 3.81; N = 15.69 and Sn = 26.68 per cent.

35. Dibutyl chlorotin diphenyl carbazonate:

0.30g of dibutyl tin dichloride and 0.70g of dibutyl tin bis-diphenyl carbazonate were mixed and a minimum volume of benzene was added just to dissolve the solid mixture. The solution was filtered and the filtrate was concentrated by a vacuum pump. The concentrated filtrate was allowed to stand for sometime when light brownish-red crystals were formed. M.P. was 138-39°C. Recrystallisation of these crystals from benzene afforded crystals of m.p. 140°C. The yield was 0.28g.

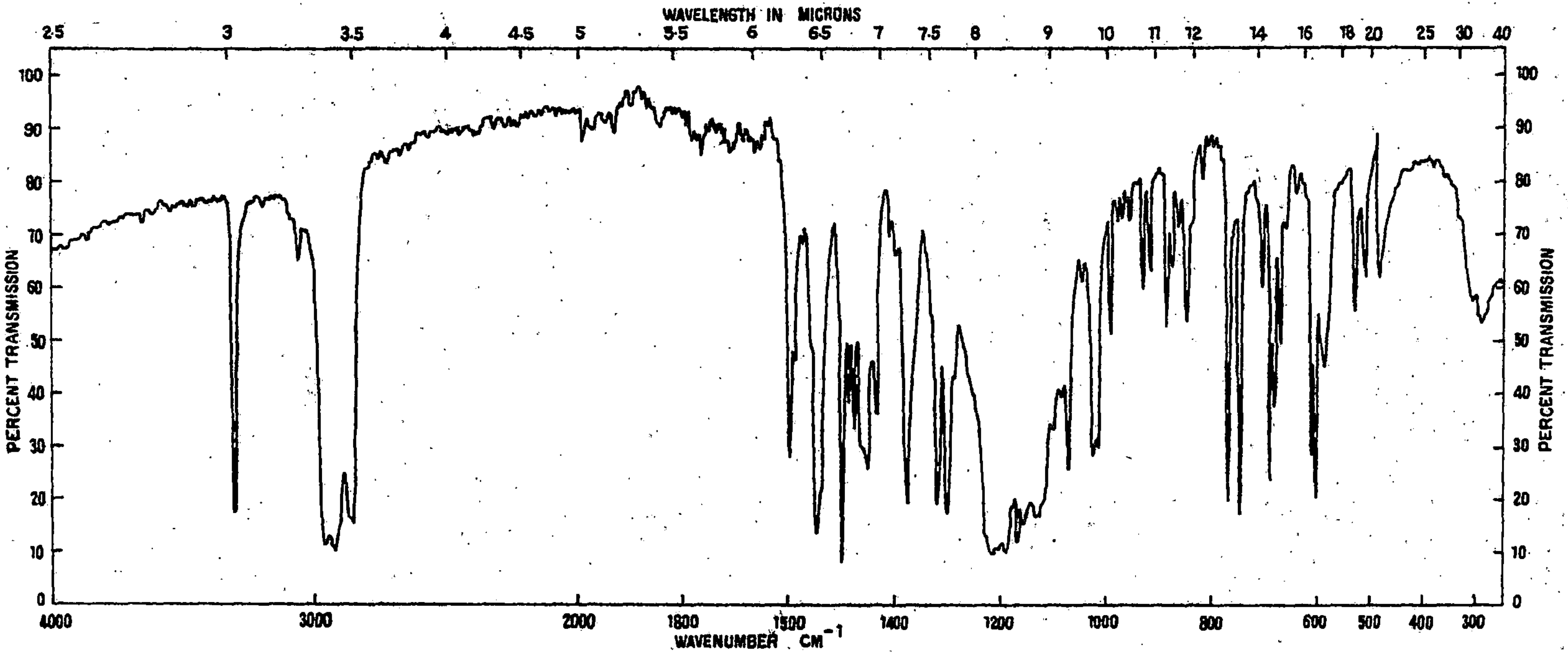


Fig.- 25. I.R. Spectrum of dibutyl chlorotin diphenyl carbazonate

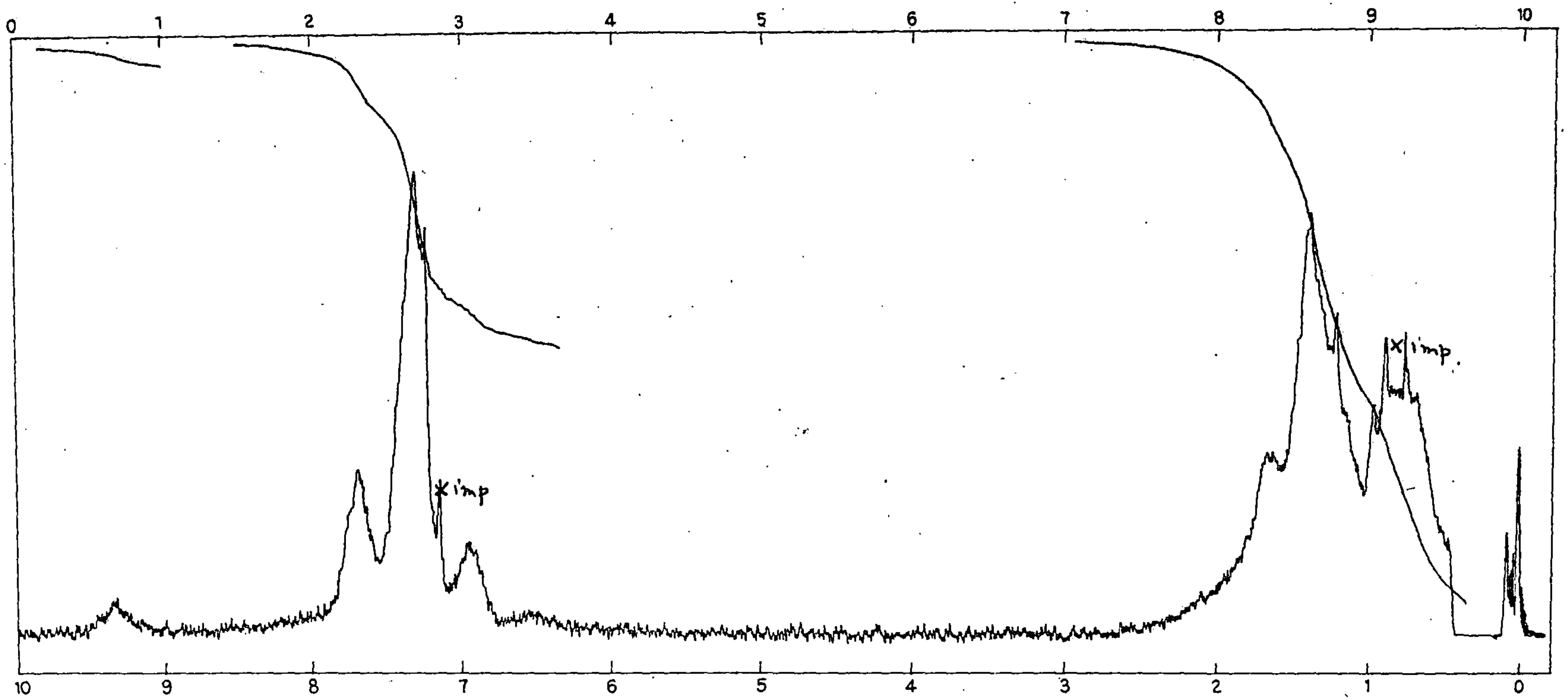


Fig.-**26.** PMR Spectrum of dibutyl chlorotin diphenyl carbazonate.

After separating these crystals the filtrate was further concentrated on vacuum pump when shining reddish crystals of m.p. 124°C appeared. This was collected. This compound was found to be dibutyl tin bis-diphenyl carbazonate as it showed no depression in melting point with an authentic sample as reported earlier in this thesis.

Analysis found for the compound having m.p. 140°C

C = 50.15; H = 5.50; N = 10.74 and Sn = 23.25 per cent

Calculated for $C_{21}H_{29}N_4OClSn$: C = 49.70; H = 5.72; N = 11.04 and Sn = 23.37 per cent.

36. Dibutyl bromotin diphenyl carbazonate:

0.71g of dibutyl tin bis-diphenyl carbazonate and 0.39g of dibutyl tin dibromide was separately dissolved in minimum volume of benzene. These two solutions were mixed. The mixture was concentrated on pump and the concentrated filtrate was allowed to stand for some time when light reddish crystals of m.p. 148-49°C were formed. These on recrystallisation from benzene afforded crystals of melting point 150°C. From elemental analysis this was confirmed as dibutyl bromotin diphenyl carbazonate. After separating this compound the mother liquor was further concentrated on pump when shining reddish crystals of m.p. 123-24°C were formed. By mixed melting point checking with an authentic sample this compound was found to be dibutyl

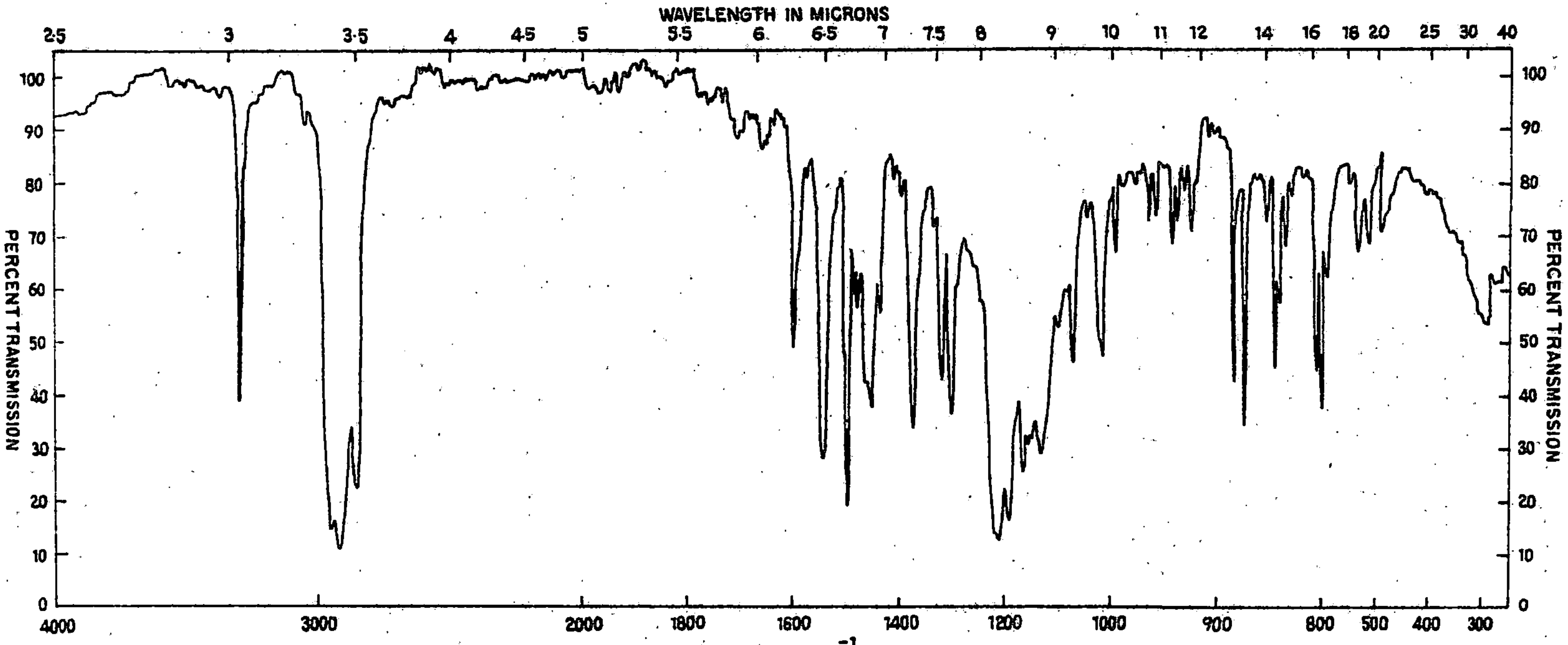


Fig. - 27   I.R. Spectrum of dibutyl-bromo-tin diphenyl carbazonate

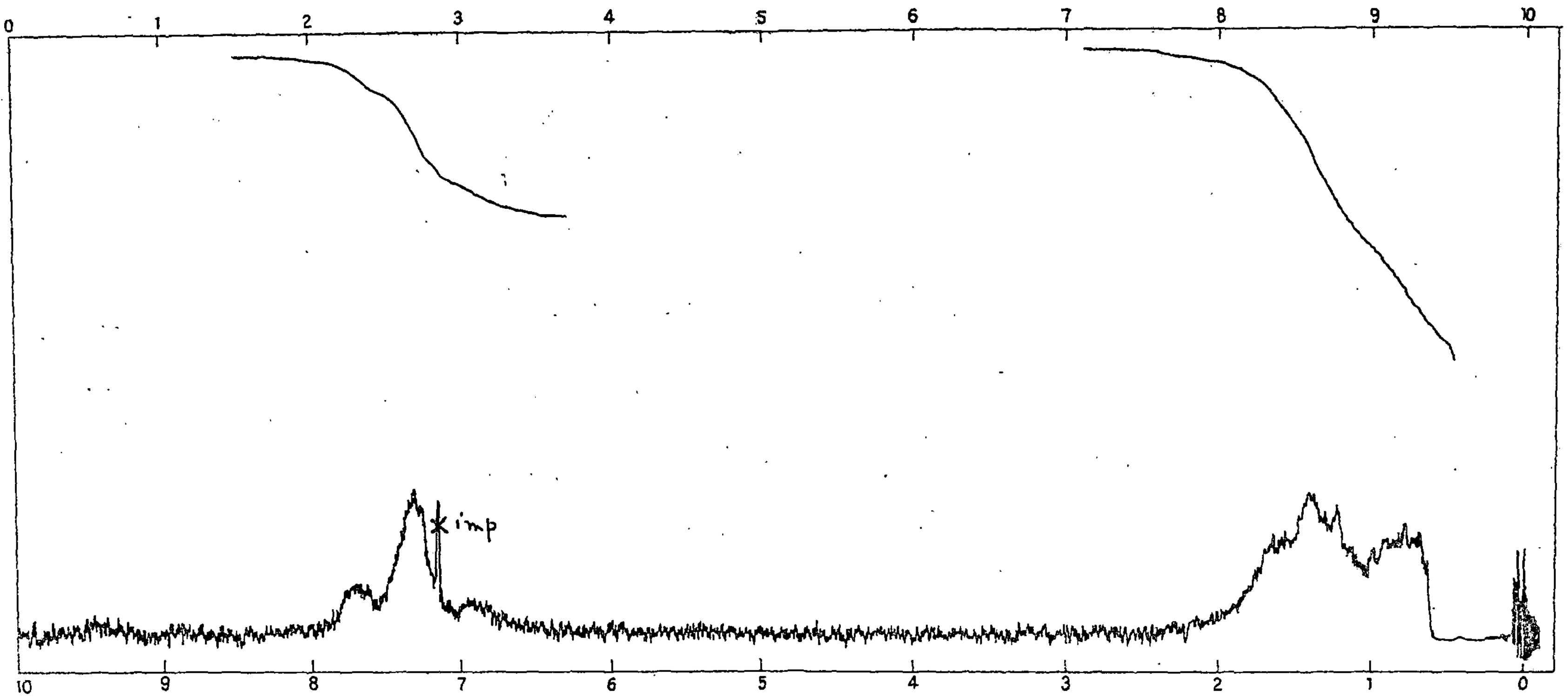


Fig.-28 PMR Spectrum of dibutyl bromotin diphenyl carbazonate tin bis-diphenyl carbazonate. Yield was 0.50g.

Analysis found for the compound having m.p. 150°C

$C = 45.55$; $H = 5.12$; $N = 10.08$ and $Sn = 21.48$ per cent

Calculated for $C_{21}H_{29}N_4OBrSn$: $C = 45.73$; $H = 5.26$; $N = 10.16$ and $Sn = 21.59$ per cent.

37. Dibutyl thiocyanato tin diphenyl carbazonate:

0.35g of dibutyl tin dithiocyanate and 0.71g of dibutyl tin bis-diphenyl carbazonate were mixed. This mixture was just dissolved in benzene. The mixture was filtered and the filtrate was concentrated on pump. This concentrated filtrate, upon standing for sometime, gave shining reddish crystals of m.p. 186-88°C (with decomposition). The yield was 0.22g. From elemental analysis it was found that this compound was dibutyl thiocyanato tin diphenyl carbazonate.

After separating these crystals the mother liquor was further concentrated and the concentrated mother liquor on standing for sometime gave beautiful shining reddish crystals of m.p. 123-24°C. This compound was dibutyl tin bis-diphenyl carbazonate since it showed no depression of melting point with an authentic sample mentioned earlier.

Analysis found for the compound having m.p. 186-88°C :

$C = 49.75$; $H = 5.5$; $N = 13.2$ and $Sn = 22.28$ per cent.

Calculated for $C_{22}H_{29}N_5OSSn$: $C = 49.81$; $H = 5.47$; $N = 13.20$ and $Sn = 22.45$ per cent.

38. Diphenyl chlorotin diphenyl carbazonate:

0.75g of diphenyl tin bis-diphenyl carbazonate and 0.34g of diphenyl tin dichloride was separately dissolved in minimum volume of benzene. These two solutions were then mixed. The mixture on standing did not give any crystal. The mixture was then concentrated by vacuum pump to half its original volume. The concentrated solution on standing for some time gave beautiful shining reddish crystals. These were collected. The yield was 0.40g and the m.p. of the crystal was 168-72°C (with decomposition). This on recrystallisation from benzene afforded crystals of m.p. 172°C.

Found: C = 54.52; H = 3.96; N = 10.01 and Sn = 21.35 per cent

Calculated for $C_{25}H_{21}N_4OClSn$: C = 54.84; H = 3.83; N = 10.23 and Sn = 21.66 per cent.

39. Diparatolyl chlorotin diphenyl carbazonate:

0.78g of diparatolyl tin bis-diphenyl carbazonate and 0.37g of diparatolyltin dichloride was dissolved just in benzene. The solution on standing did not give any crystal. The solution was then concentrated by vacuum pump to one-fourth its original volume. The concentrated solution on standing gave beautiful shining reddish crystals of m.p. 140°C. This on recrystallisation

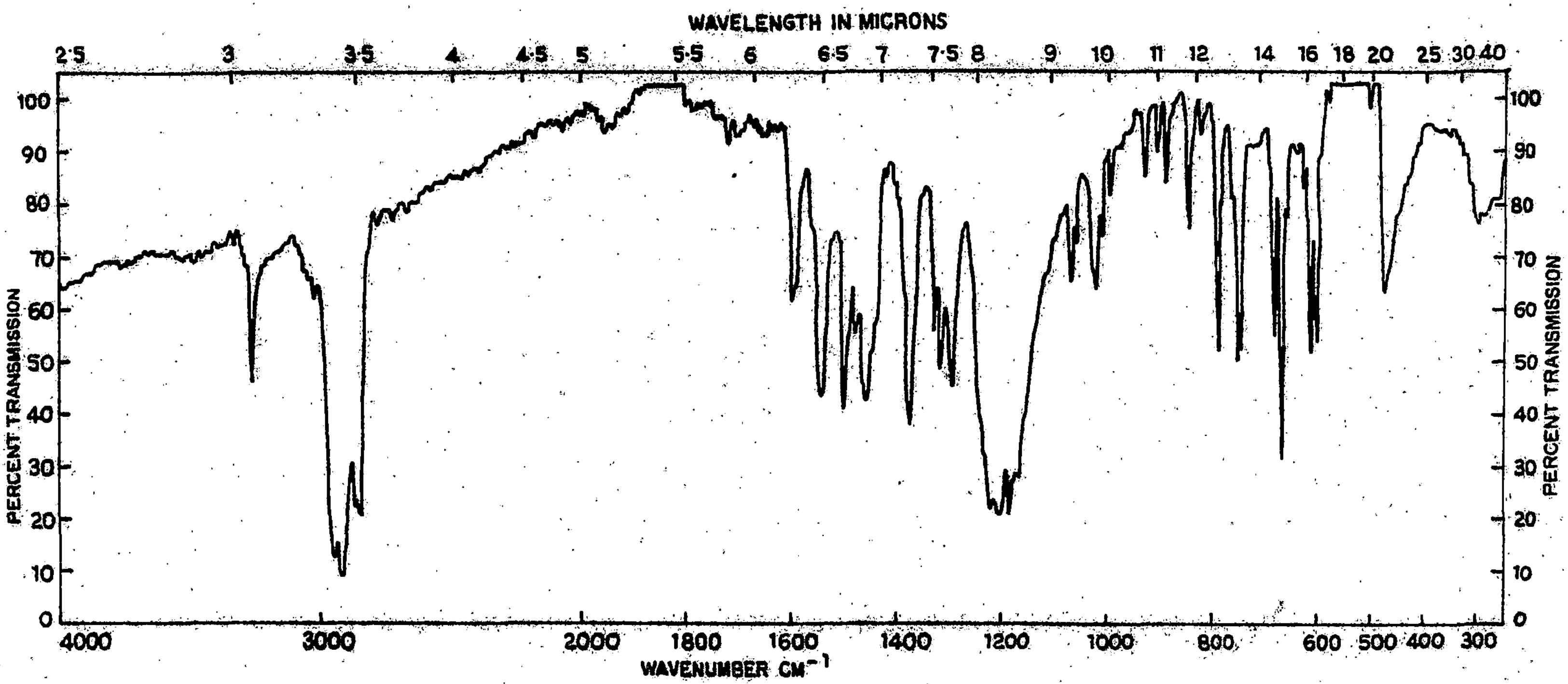


Fig.-29 I.R. Spectrum of diparatolyl chlorotin diphenyl carbazonate.

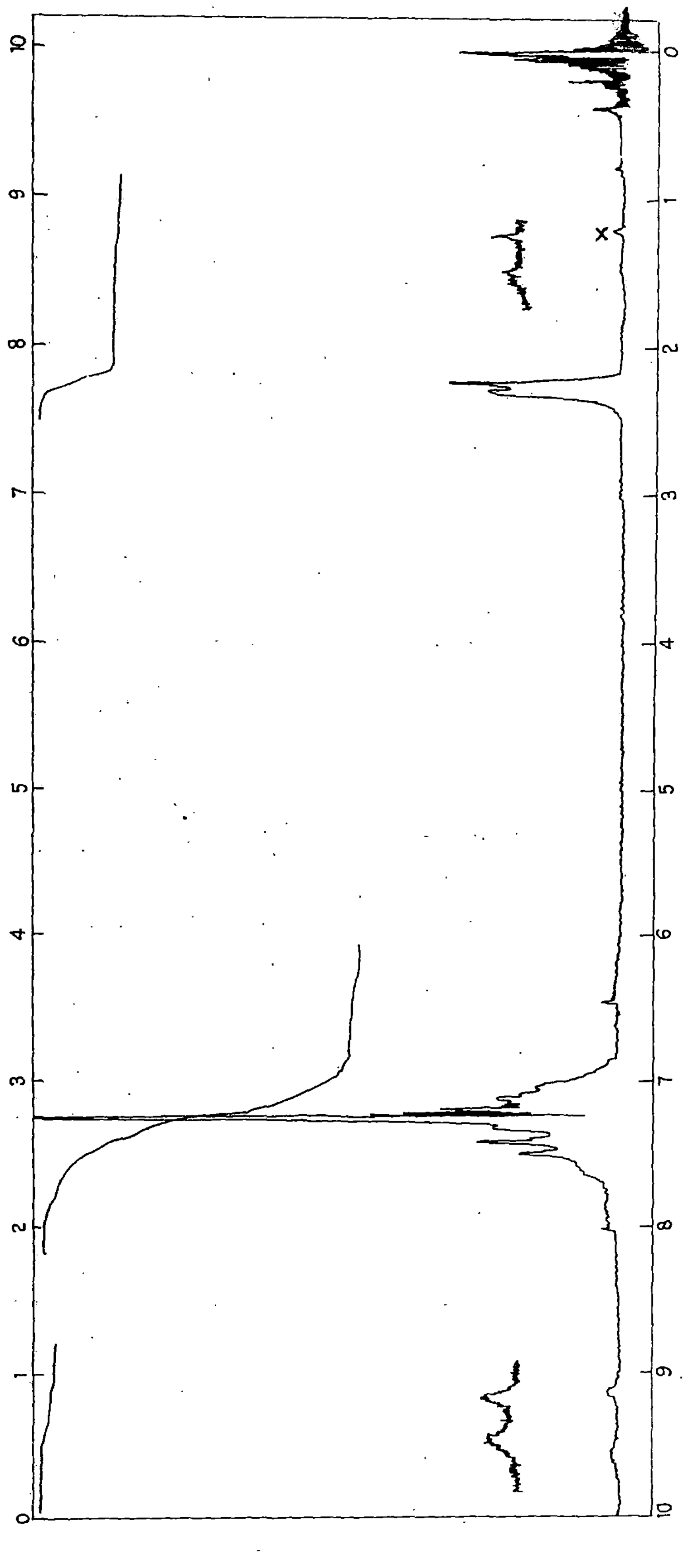


Fig. -30

PMR Spectrum of diparatolyl chloro tin diphenyl carbazonate from benzene afforded crystals of m.p. 142°C (with decomposition).

Found:	C = 55.87; H = 4.3; N = 9.46 and Sn = 20.42 per cent
Calculated for $C_{27}H_{25}N_4OClSn$:	C = 56.35; H = 4.35; N = 9.74 and Sn = 20.61 per cent.

40. <u>Monophenyl tin tris-diphenyl carbazonate</u>:

0.34g of phenyl tin trichloride and 0.77g of diphenyl carbazone was separately dissolved in 100 ml benzene. The two solutions were then mixed when the colour of the solution became red. The mixture was then refluxed for four hours. A few drops of ammonia (17N) solution was added to the refluxed solution to neutralise the liberated hydrochloric acid. The precipitated ammonium chloride was filtered off. The filtrate was completely evaporated to a pasty mass. The mass was dissolved in 10 cc chloroform. To it 20 ml methanol was added. The solution on cooling gave beautiful reddish crystals of m.p. 145-46°C. This on recrystallisation from chloroform-methanol mixture afforded crystals of 147°C. The yield was 0.40g.

Found:	C = 58.68; H = 4.05; N = 18.20 and Sn = 12.75 per cent
Calculated for $C_{45}H_{38}N_{12}O_3Sn$:	C = 59.14; H = 4.16; N = 18.40 and Sn = 13.03 per cent.

Tin was estimated by conversion to stannic oxide and finally converting to volatile stannic iodide gravimetrically, essentially following the method of Van der Kerk and Luijten (128).

Analysis of the compounds for carbon, hydrogen, nitrogen and some visible spectral data were carried out at the Central Drug Research Laboratories, Govt. of India, at Lucknow, India.

The infrared spectral data were taken for all the compounds using Beckman IR - 20 Infrared Spectrophotometer equipped with KBr optics and mulling the compounds in Nujol in all cases. The following abbreviations have been used: s = strong, m = medium, w = weak, v = very, b = broad, sh = shoulder. Nujol had peaks at 3000-2800 cm^{-1}(s), 1460 cm^{-1}(s), 1376 cm^{-1}(m).

Diphenyl carbazone: 3410sh, 3345m, 3280sh, 3250s, 3040sh, 1707s, 1650s, 1600s, 1490s, 1455s, 1373m, 1310w, 1280m, 1245w, 1195w, 1170w, 1145w, 1115w, 1075w, 1018w, 985m, 900w, 880w, 740s, 685s, 675sh, 655sh, 600w, 560w, 500m.

Tripropyl tin diphenyl carbazonate: 3380vw, 3322vw, 3292m, 1596m, 1543m, 1496m, 1455s, 1373s, 1322w, 1298m, 1221m, 1197s, 1161s, 1148s, 1069w, 1012m, 968vw, 768m, 756m, 741m, 719w, 688m, 670w, 605w, 553w, 526w.

Tricyclohexyl tin diphenyl carbazonate: 3530w,br, 3210w,br, 3050w, 1598s, 1549s, 1500s, 1479w, 1455s, 1370s, 1310m, 1297s, 1265w, 1250m, 1220s, 1185s, 1160s, 1145s, 1085w, 1070m, 1022m, 988m, 849w, 838sh, 760m, 741s, 712w, 689m, 665sh, 660w, 610m, 602m, 595w, 555sh, 550sh, 529w, 512w.

Triphenyl tin diphenyl carbazonate: 3298s, 3059w, 1598s, 1543s, 1500s, 1482m, 1460s, 1376s, 1326m, 1308s, 1222s, 1190s, 1182s, 1172s, 1076s, 1039s, 1022m, 1000m, 975w, 960w, 932w, 920w, 890w, 850m, 770s, 750s, 739s, 730m, 725sh, 696s, 679m, 668w, 604s, 589m, 532m, 520w.

Triparatolyl tin diphenyl carbazonate: 3300s, 3058w, 1599s, 1548s, 1500s, 1459s, 1438m, 1375s, 1322m, 1303s, 1218s, 1201s, 1185s, 1165s, 1156s, 1110s, 1072s, 1029s, 1014m, 998w, 930m, 920w, 905sh, 892w, 848m, 800w, 790m, 768s, 749s, 690s, 672m, 630w, 610m, 600s, 580m, 523m, 510m, 488m.

Dimethyl tin bis-diphenyl carbazonate: 3560m, 3490w, 3130w,br, 3055w, 1595s, 1590s, 1545s, 1512s, 1480m, 1458s, 1375s, 1332w, 1320m, 1300s, 1200s,br, 1165s, 1155s, 1100w, 1070m, 1030s, 938w, 895m, 855m, 825w, 780m, 750s, 685m, 665s, 620s, 610s, 580m, 535sh, 520m, 495w,br.

Dibutyl tin bis-diphenyl carbazonate : 3540w,br, 3470w, 3410sh, 3230m, 3060w, 1600s, 1545s, 1500s, 1480m, 1458s, 1370s, 1325m, 1300s, 1230sh, 1200s, 1165s, 1150s, 1095w, 1070m, 1020s,br, 930w, 885w, 850m, 742s, 685m,br, 662m, 627w, 600s, 520sh, 510m, 495sh.

Dicyclohexyl tin bis-diphenyl carbazonate: 3300w, 1600s, 1550m, 1500s, 1480m, 1460m, 1445sh, 1375s, 1328m, 1300s, 1255sh, 1223s, 1185s, 1162s, 1149s, 1090w, 1072m, 1020m, 990w, 930w, 905w, 885w,br, 850m, 762m, 748m, 689m, 673w, 661w, 610w, 600m, 596w, 529w, 515w, 490w, 370w, 335w, 314m, 300m.

Diphenyl tin bis-diphenyl carbazonate: 3440m,br, 1580w, 1540m, 1442s, 1365s, 1316m, 1292s, 1212s, 1182m, 1162m, 1122s, 1065s, 1029s, 990m, 922sh, 912m, 880w, 839w, 790w,br, 765sh, 760m, 745s, 730m, 687m, 669m, 575m,br.

Diparatolyl tin bis-diphenyl carbazonate: 3285m, 1595m, 1540s, 1500s, 1455s, 1435m, 1375s, 1325m, 1305s, 1200s, 1185s, 1110m, 1070m, 1028m, 1015w, 930w, 920w, 890w, 845w, 790w, 765s, 750s, 690m, 670m, 600m, 595w, 520w, 510w, 485w.

Dimethyl chlorotin diphenyl carbazonate: 3565s, 3498m, 3150m,br, 3070m, 3030m, 1598m, 1590m, 1548s, 1512s, 1495m, 1485m, 1460s, 1378s, 1335m, 1320s, 1301s, 1210s,br, 1165s, 1155s, 1101w, 1075m, 1030s, 962w, 938w, 909w, 892m, 853m, 825w, 782s, 748s, 681m, 662s, 640w, 615s, 603s, 565m,br, 512m, 489m.

Dimethyl thiocyanato tin diphenyl carbazonate: 3300s, 3050w, 2000vs, 1598m, 1590m, 1535s, 1500s, 1480m, 1459m, 1438m, 1375s, 1329m, 1318m, 1298m, 1230s, 1199s, 1169s, 1160m, 1148m, 1128m, 1100m, 1088m, 1072s, 1028s, 998w, 938w, 908w, 888w, 858w, 800m, 759s, 740s, 725sh, 682s, 670s, 620s, 609m, 582m, 525m, 508m, 485w.

Dibutyl chlorotin diphenyl carbazonate: 3300s, 3060w, 1598s, 1590m, 1575w, 1500s, 1470m, 1450s, 1432m, 1410w, 1375s, 1320s, 1300s, 1215s,br, 1190s, 1165s, 1155s, 1130w,br, 1100m, 1080m, 1070s, 1020s, 1015s, 990m, 955vw, 929w, 918w, 882m, 875w, 860w, 849m, 809w, 770s, 745s, 705w, 688s, 680s, 670m, 610s, 600s, 585m, 530m, 510m, 485m.

Dibutyl bromotin diphenyl carbazonate: 3298s, 3050w, 1598s, 1578w, 1544s, 1500s, 1488m, 1480m, 1456s, 1435m, 1372s, 1320m, 1300s, 1210s, 1190s, 1160m, 1130s, 1100m, 1082m, 1015m, 990w, 930w, 918w, 885w, 875w, 848w, 770s, 748s, 708w, 690s, 682m, 670w, 660w, 640vw,br, 530w, 510w, 490w.

Diparatolyl chlorotin diphenyl carbazonate: 3260m, 3020vw, 1598m, 1540s, 1500s, 1478m, 1456s, 1372s, 1329m, 1318m, 1292s, 1201s, 1182s, 1165s, 1070m, 1060w, 1025sh, 1022vw, 1010w, 995w, 930w, 905w, 890w, 848m, 820w, 790s, 750s, 745s, 682s, 670s, 660w, 615s, 600s, 480m.

Results and discussions

Diphenyl carbazone has two imino protons but it acts as a monobasic acid towards metals. The second hydrogen is not replaced under normal conditions. In case of dithizone, the second hydrogen atom could be replaced in some cases of metallic derivatives but in the formation of organotin derivatives, it was possible to replace only one hydrogen of dithizone (106). Similarly, we could replace only one imino hydrogen of diphenyl carbazone by organotin moieties.

Triorganotin diphenyl carbazonates and diorganotin bis-diphenyl carbazonates have been prepared by following methods:

a) By refluxing a mixture of organotin oxide and diphenyl carbazone in appropriate molar ratio in benzene or chloroform.

$$(R_3Sn)_2O + 2Ph.NH.NH.CO.N : N.Ph \longrightarrow 2R_3Sn\ (Ph.NH.NCO.N : N.Ph) + H_2O$$

$$R_2SnO + 2Ph.NH.NH.CO.N : N.Ph \longrightarrow R_2Sn(Ph.NH.N.CO.N : N.Ph)_2 + H_2O\ .$$

The water formed was separated by azeotropic distillation.

b) By the reaction of one mole of organotin chloride with one or two moles of diphenyl carbazone.

$$R_3SnCl + Ph.NH.NH.CO.N : N.Ph$$

$$\longrightarrow R_3Sn(Ph.NH.N.CO.N : N.Ph) + HCl$$

$$R_2SnCl_2 + 2Ph.NH.NH.CO.N : N.Ph$$

$$\longrightarrow R_2Sn(Ph.NH.N.CO.N : N.Ph)_2 + 2HCl.$$

The hydrochloric acid liberated was neutralised with concentrated ammonia solution and precipitated ammonium chloride was removed by filtration.

Diorganotin halo- or thiocyanato diphenyl carbazonates R_2SnX (HDPC) (where R = Ph, Bu, Me, p-tolyl; X = Cl, Br, SCN and H_2DPC = diphenyl carbazone) were prepared by the following reaction:

$$R_2Sn(HDPC)_2 + R_2SnX_2 = 2.\ R_2SnX\ (HDPC)$$

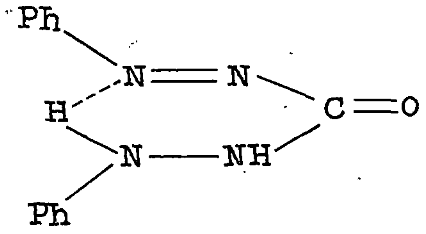
~~$R_2SnCl(HDPC) + KSCN = R_2SnSCN(HDPC) + KCl$~~

~~Potassium chloride was removed by filtration.~~ The monophenyltin tris-diphenyl carbazonate was prepared by the following method:

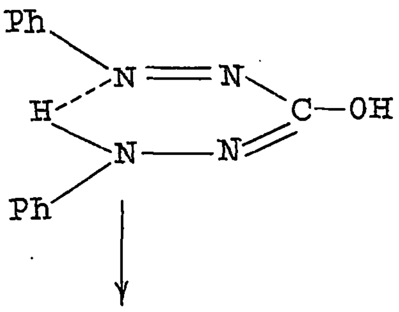
$$PhSnCl_3 + 3(Ph.NH.NH.CO.N : N.Ph)$$

$$\longrightarrow PhSn(Ph.NH.N.CO.N : N.Ph)_3 + 3\ HCl.$$

The visible spectrum of diphenyl carbazone in a polar solvent gave two absorption maxima (129). The more intense one at about 455nm and the other with much lower intensity at 565nm. In 1966 Kemula and Janowski suggested the 565 nm band due to the following pseudo six-ring form of diphenyl carbazone.

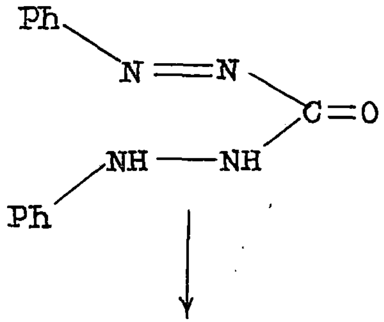


But Willems and Zeeger-Huyskens (130) attributed 565 nm band to the 'enol' form present in low concentration. The 455 nm absorption band is generally attributed to the free 'keto' form as shown below



'enol' form

$\lambda_{max} = 565$ nm

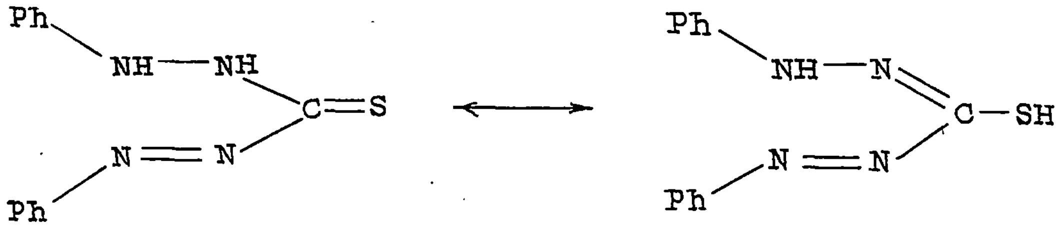


'keto' form

$\lambda_{max} = 455$ nm

They concluded that the golden yellow colour of diphenyl carbazone is associated with the 'Keto' form.

The visible absorption spectrum of dithizone (sulphur analogue of diphenyl carbazone) in an organic solvent also exhibits two well defined bands at 450 nm and 620 nm respectively for thione-thiol tautomerism.



But the organotin dithizonates possess a single absorption band in the region of 450-510 nm. Since, there is commonly a bathochromic shift when chelating agents such as acetyl acetonate, 8-hydroxy quinoline, and N-phenyl benzohydroxamic acid etc form their organotin chelate complexes and since there is also a bathochromic shift of the absorption band at 450 nm in free dithizone to 450-510 nm in organotin dithizonates, all the organotin - dithizonates are supposed to be chelated complexes (106).

The visible spectra of some organotin diphenyl carbazonates in $CHCl_3$ were taken. In all these compounds there is a single absorption band in the region 530-550 nm.

Compound	λ_{max} (nm)
$Ph_3Sn(HDPC)$	548
$Ph_2Sn(HDPC)_2$	550
$Ph_2SnCl(HDPC)$	550
Bu_2SnCl (HDPC)	530
Bu_2SnBr (HDPC)	530
Me_2SnCl (HDPC)	530

By analogy with organotin dithizonates, it may be concluded that the 455 nm band of diphenyl carbazone is due to 'keto' form, which has suffered a bathochromic shift due to chelate formation.

The IR spectral data of organotin diphenyl carbazonates gave some interesting observations. The IR spectrum of pure diphenyl carbazone in $CHCl_3$ or CCl_4 are reported (129) to show two absorption bands in 3000-4000 cm^{-1}, at 3410 and 3350 cm^{-1}. The intensity of the two bands decreases and three new bands appear at 3275, 3195 and 3075 cm^{-1} when the concentration of diphenyl carbazone increases. Kemula and Janowski ascribed the 3410 cm^{-1} band to free N-H stretching vibration of the N-H group in the β-position to the $>C = O$ group. They assigned 3350 cm^{-1} band to free N-H stretching vibration of the N-H group in the α-position and the three new bands at 3275, 3195 and 3075 cm^{-1} to intermolecular bonded N-H stretching vibrations. But Willems and Zeegers - Huyskens (loc. cit) assigned the 3410 cm^{-1} band to free N-H vibration and 3350 cm^{-1} band to intramolecular bonded N-H vibrations.

From the IR measurements on diphenyl carbazone powder (KBr pellets), Blaton et al (129) concluded that solid diphenyl carbazone is present only as the keto form. The ν_{OH} stretching band is absent and the $\nu_{>C=O}$ stretching band is strong (1707 cm^{-1}). They observed four absorption bands in the region 3000-4000 cm^{-1}. The 3375 cm^{-1} band was attributed by them for intramolecular bonded ν_{N-H} vibration and the bands at 3275, 3195 and 3075 cm^{-1} to intermolecular bonded ν_{N-H} vibrations. But from X-ray crystal structure determination, they concluded that in the solid state, the diphenyl carbazone exists only in the 'keto' form and that no intramolecular but only intermolecular N-H .... O bonds are present.

The infrared spectrum of a sample of pure diphenyl carbazone (recrystallised from a G.R./E. Merck sample) was taken in a nujol mull. The spectra showed a number of bands at 3410, 3345, 3280 (sh), 3250 and 3040 cm^{-1} (may be also due to aromatic C-H) and three strong bands at 1707 cm^{-1}, 1650 cm^{-1} and 1600 cm^{-1}

apart from other bands. The bands between 3040-3410 cm^{-1} is probably due to N-H stretching vibrations as reported above. We also believe that 1707 cm^{-1} band is due to $\nu_{C=O}$ stretching mode but Blaton et al (129) did not mention about any other band beyond 1707 cm^{-1}, though other bands were surely present in their spectra. The strong band at 1650 cm^{-1} has not been mentioned by them for reasons not known to us. Such a band is not present in dithizone. The origin of this band is not definite to us. This band could be possibly due to N-H bending vibrations or it could be an additional band for carbonyl group present in the vicinity of N-H band. The 1600 cm^{-1} band is most probably due to ring stretching vibrations of the aromatic groups present in the ligands. The N-Ph frequencies at $\sim$1375 cm^{-1} in organotin diphenyl carbazonate could not conclusively be assigned due to interference of Nujol peaks though there are clear evidences of these bands in most of the compounds and 740 cm^{-1} and 690 cm^{-1} bands are also due to aromatic groups present. In all organotin diphenyl carbazonates no band was found in the region 1600-1800 cm^{-1}, but a strong and new band at $\sim$ 1540 cm^{-1} appeared in all cases. We believe that this band is most probably due to chelated C = O group in the organotin compounds. Thus considerable shifting of C = O group has been observed in organotin diphenyl carbazonates indicating their strong chelated nature.

In case of metallic dithizonates, δNH bend vibrations are reported at ~ 1520 cm^{-1} by Irving (137). He also suggested that two secondary dithizonates Ag_2Dz and $PdDz, 2H_2O$ have δNH bend vibrations at 1530 and 1528 cm^{-1} respectively, which however, apparently have no such NH bond. In case of organotin dithizonates, strong absorption around 1500 cm^{-1} have been observed. Similarly we also obtained strong absorptions at ~ 1500 cm^{-1} for organotin diphenylcarbazonate. It is rather difficult to assign unequivocally the ~ 1500 cm^{-1} band due to δNH bend vibrations, since the aromatic part of the ligand should also contribute $C = C$ ring vibrations in the same region. Therefore, the best we can assign the ~ 1500 cm^{-1} band is probably due to coupled δ NH bend and $C = C$ ring vibration.

Except some methyl and butyl organotin diphenyl carbazonates, most organotin diphenyl carbazonates gave a sharp absorption around 3300 cm^{-1}. This is probably due to intra molecular hydrogen bonding of NH stretching vibration.

All the organotin compounds of diphenyl carbazone showed a very characteristic nature in the region 1150-1220 cm^{-1}. Here, we observe either a number of stong absorptions or large broad band. This is probably due to coupled C-N and C = O vibrations involved in co-ordination with organotin moieties. A similar type of absorptions were also noticed incase of organotin dithizonates, which has been assigned as NCS coupled vibrations.

In the spectrum of diphenyl carbazone, there are three bands in the region 480-620 cm^{-1} but in organotin diphenyl carbazonates, some more bands appeared in this region. A new band around 520 cm^{-1} may be reasonably assigned due to Sn-O vibrations and others may be due to Sn-C bands.

The IR spectra of organotin diphenyl carbazonates are extremely complicated in nature, since both the organotin and ligand moieties have large number of bands of different intensities. Hence it was not found feasible to interpret many other bands present in organotin diphenyl carbazonates.

The IR spectrum of dimethyl thiocyanato diphenyl carbazonate had a strong absorption at 2000 cm^{-1}. The ambident ligand —SCN - can co-ordinate to metal either through sulphur or through nitrogen or it can act as a bridge. Sabatini and Bertini (131) have suggested the following criteria to distinguish the nature of co-ordination of -SCN- group.

	$M-N\equiv CS$	$M-S-C\equiv N$
$\nu(C\equiv N)$	below 2100 cm^{-1}	2100 cm^{-1}
$\nu(C=S)$	860-760 cm^{-1}	690-720 cm^{-1}
$\nu(NCS)$	490-450 cm^{-1}	440-400 cm^{-1}.

Due to experimental inadequency, the reliability of spectra below 450 cm^{-1} in our case was not so much and the uncertainity of C-S stretching band in appropriate region due to interferences of other bands, forced us to suggest that the SCN group in dimethyl thiocyanato diphenyl carbazonate is probably linked to tin atom through the nitrogen atom. For the reasons stated above Sn-N and Sn-halogen bands were not ~~be~~ assigned in any compounds.

The PMR spectra of organotin diphenyl carbazonates were recorded mostly in 90 MHz N.M.R. Spectrophotometer at the Central Drug Research Institute, Govt. of India, Lucknow, India, as an analytical service rendered by that Institute. Some spectra were also recorded at Bose Institute, Calcutta-700009. The solvent used was $CDCl_3$. In some cases, impurities in the solvent used have some signals particularly around 7.2 ppm. As a result of which, integration curves in some cases did not precisely correspond to the composition of the complexes.

All chemical shift values have been given here in δ ppm scale against TMS as internal standard.

<u>Table - 1</u>

P.M.R. data (δ ppm) against TMS as internal standard

Sl. No.	Compound	Aromatic protons	Alkyl protons	NH protons
1.	Diphenyl carbazone	6.7-6.96(t)	-	5.72 (s)
2.	Dimethyl tin bis-(diphenyl carbazonate)	7.1-7.83	0.80	9.05-9.40 6.7-6.9
3.	Dimethyl chlorotin diphenyl carbazonate	7.2-7.9	0.85-1.0	6.8-7.0
4.	Dimethyl thiocyanato tin diphenyl carbazonate	7.18-7.82	0.82(t)	6.7-6.96
5.	Dibutyl tin bis-diphenyl carbazonate	6.9-8.0	0.6-1.9	9.5

Contd..

Table - 1 (Contd..)

Sl. No.	Compound	Aromatic protons	Alkyl protons	NH protons
6.	Dibutyl chlorotin diphenyl carbazonate	6.8-7.9	0.7-2.2	6.4-6.8 9.4
7.	Dibutyl Bromotin diphenyl carbazonate	6.7-8.0	0.6-2.1	6.2-6.4
8.	Triphenyl tin diphenyl carbazonate	7.0-8.0	-	9.33
9.	Diphenyl tin bis-diphenyl carbazonate	7.0-8.0	-	9.35
10.	Di-p-tolyl tin bis-diphenyl carbazonate	6.9-7.7	2.1,2.3	6.3-6.7 9.1
11.	Di-p-tolyl chlorotin diphenyl carbazonate	6.9-7.7	2.25(d)	9.15,9.6
12.	Tricyclohexyl tin diphenyl carbazonate	6.6-7.8	0.7-2.3	5.63,9.3

In the pmr spectra of diphenyl carbazone, the N-H protons give a sharp singlet at 5.72 ppm and the aromatic protons appear as triplet in the region 6.7-6.96 ppm. The signals over 7.0 ppm is probably due to some impurities ($CHCl_3$) in the solvent. In dimethyl tin bis-diphenyl carbazonate, the methyl protons appear at 0.80 ppm as sharp singlet indicating trans methyl structure (132).

The aromatic protons of dimethyl tin bis-diphenyl carbazonate suffer deshielding (7.1-7.83 ppm) compared to the ligand aromatic protons (6.7-6.96 ppm) owing to the drainage of electron density from the ligand moiety. The N-H protons appear in two different regions (9.05-9.40; 6.7-6.9).

The methyl protons of the dimethyl tin bis-diphenyl carbazonate are shielded (0.8 ppm) compared to the methyl protons of Me_2SnCl_2 (1.22 ppm). This shielding of the methyl protons in dimethyl tin bis-diphenyl carbazonate is probably due to increased electron density on tin atom via ligand donation (133). When a strongly electron withdrawing chlorine atom is bonded to tin, we can expect an electron pull from the methyl groups through tin and in consequence, the methyl protons of dimethyl chlorotin diphenyl carbazonate will suffer deshielding (0.85-1 ppm) compared to the methyl protons of dimethyl tin bis-diphenyl carbazonate.

The splitting of the methyl protons in dimethyl chlorotin diphenyl carbazonate and dimethyl thiocyanato tin diphenyl carbazonate may be due to restricted rotation of the methyl groups (134).

The alkyl protons of dibutyl tin bis-(diphenyl carbazonate) (0.6-1.9 ppm) and dibutyl bromotin diphenyl carbazonate (0.6-2.1 ppm) are found in the similar region. In comparison with these two compounds, the alkyl protons of dibutyl chlorotin diphenyl carbazonate (0.7-2.2 ppm), are slightly deshielded. This may be due to the electron pull of the chlorine as was explained in the case of dimethyl tin derivatives of diphenyl carbazonate previously.

In the diphenyl and triphenyl tin derivatives of diphenyl carbazone, the NH signal, have been observed 9.34 ppm and the aromatic protons appear in the region 7.0-8.0 ppm. The aromatic protons suffer considerable deshielding compared to the ligand aromatic protons (6.7-6.96 ppm). This is due to drainage of electron density from the ligand moiety as is usually observed.

For di-p-tolyl tin bis-diphenyl carbazonate, the tolyl methyl protons appear at 2.1 and 2.3 ppm whereas in di-p-tolyl chlorotin diphenyl carbazonate, the tolyl methyl protons appear at 2.25 ppm as doublet. In the former compound, the NH protons have been observed in two different regions 6.3-6.7 ppm and 9.1 ppm and in later compound the NH protons appear at 6.45, 9.15 and 9.6 ppm. The aromatic protons in both these compounds are shielded (6.9-7.7 ppm) compared to the aromatic protons of diphenyl tin bis-diphenyl carbazonate owing to the presence of electron repelling methyl group.

In case of tricyclohexyl tin diphenyl carbazonate the aromatic protons are deshielded to 6.6-7.8 ppm and cyclohexyl ring protons appeared in the region 0.7-2.3 ppm. The NH protons could be obtained in 6.63 and 9.3 ppm. The positions of alkyl and aromatic protons are expected due to the chelated nature of the complex.

In the p.m.r. spectra of organotin derivatives of diphenyl carbazone, the position of NH protons are variable.

In diphenyl carbazone, we have noticed the NH protons to appear at 5.72 ppm. But in organotin diphenyl carbazonates, the NH protons appear in the region of 6.2-9.6 ppm. Such variation in position may be due to the nature and extent of hydrogen bonding present in such molecules. Apart from it, the position of NH is also dependent of concentration. In this connection we can cite a comparable situation in case of p.m.r. spectra of dithizone (135). "Coleman et al only observed 1.6 non aromatic protons at τ-2.03 in place of the total of 2.0 protons to 8.0 aromatic protons. Recent measurements in Leeds, using an instrument of higher resolving power (90 MHz Bruker HFX) ~~showed~~ showed that the p.m.r. spectrum of dithizone in $CDCl_3$ present two signals, at τ-2.61 and τ9.03, of integrated area 3:1, and completely accounting for the two non-aromatic protons. The signal at τ9.03 occurs in the characteristic region for the SH group in the absence of significant hydrogen bonding . Carlin(R) had previously noted that the infrared vibration at 2590 cm^{-1} in the solid corresponded to the stretching frequency for a non-hydrogen bonded SH group. The lack of infrared absorption in region (3100-3500 cm^{-1}) indicates the absence of a free : NH group and implies its participation in strong hydrogen bonding".

The presence of NH signals at more than one position is rather intricating . We can not at present offer any definite explanation unless more detailed p.m.r. studies are carried out.

The crystal structure determination by X-ray clearly indicates the structural differences between dithizone and diphenyl carbazone. Laing (136) has established the crystal structure of dithizone by X-ray method with a good single crystal. He has found that the molecule is nearly planar, with the C-S bond lying on the intersection of two minor planes, although phenyl groups are twisted slightly out of the mean plane in opposite sense. It is evident from the measured bond length that the electrons in the N-N-C-N-N chains are delocalised in all cases and that there are no localised single or double bonds. The two imino hydrogen atoms are located as shown in the following figure, which are equivalent.

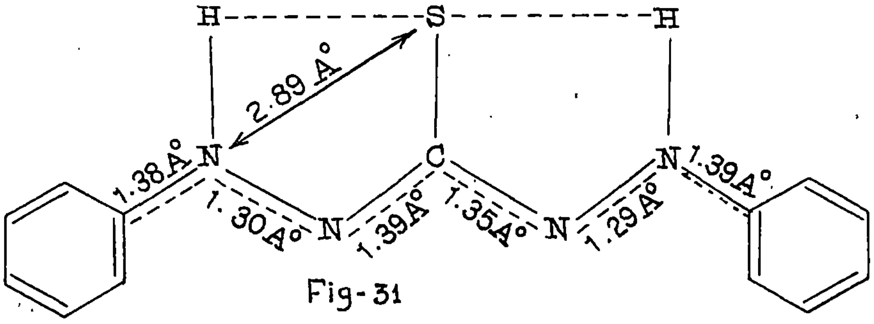


Fig-31

Thus it is clear that dithizone in the solid state may not contain $>C=S$ group.

On the other hand crystal structure determination of diphenyl carbazone by X-ray analysis (129) clearly indicate that the molecule is not planar. It was found that the phenyl group attached to the azo-chain is nearly co-planar while the phenyl group attached to the hydrazo chain is almost perpendicular. They have also observed that there is no intramolecular hydrogen bond but only intermolecular N-H .....O bonds are present. From the measurement of carbon-oxygen distance, they concluded that diphenyl carbazone exists only in the keto form and they could get evidence about delocalisation of bonds in the hydrazo chain.

The crystal structure of diphenyl carbazone and the packing pattern of the crystals are indicated in figs.32 & 33.

In view of the presence of sharp N-H stretching vibrations around 3250 cm^{-1} - 3300 cm^{-1} in most organotin diphenyl carbazonates, it can be assumed that only one imino hydrogen atom of the ligand is displaced by organotin moieties. The remaining imino protons are probably intramolecularly hydrogen bonded with nitrogen though the possibility of intermolecular hydrogen bonding can not be completely excluded. The hydrogen atom of N-3 (as indicated in the figs.32,33) possibly is not replaced.

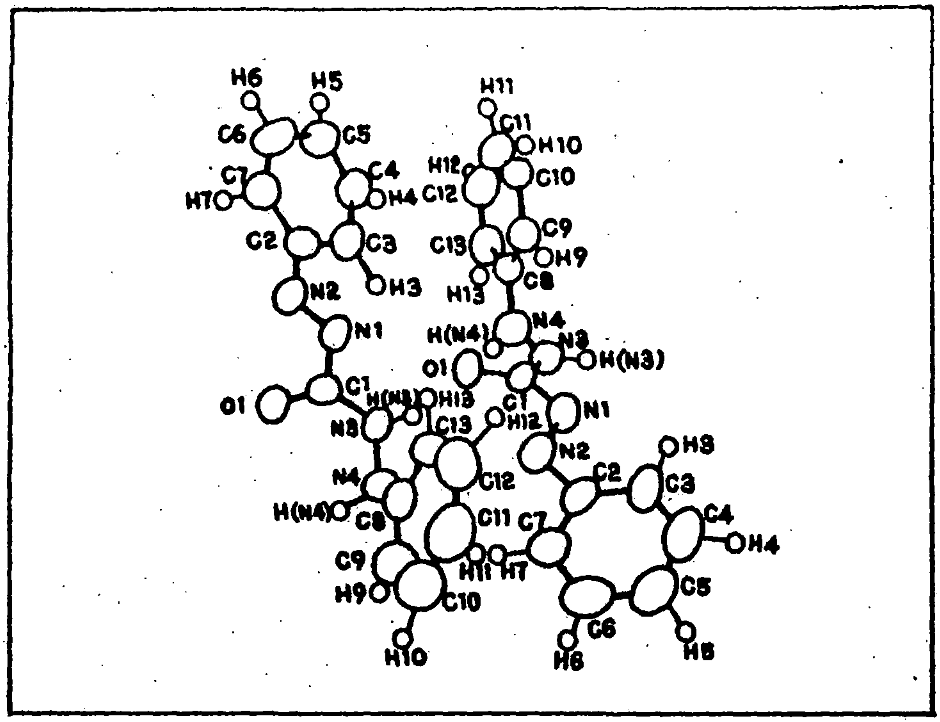


Fig.-32 X-ray crystal structure of diphenyl carbazone molecule in the asymmetric unit.

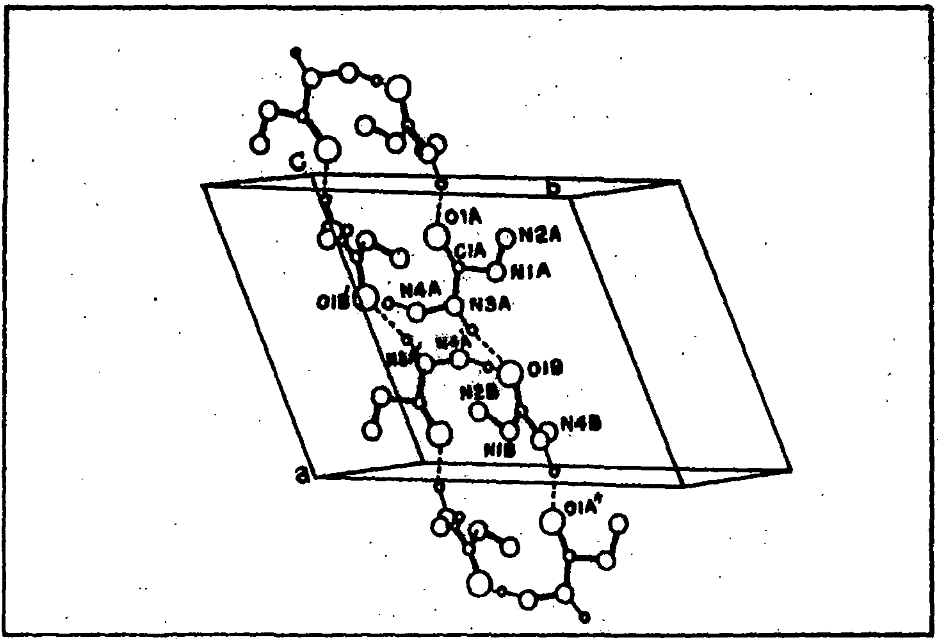
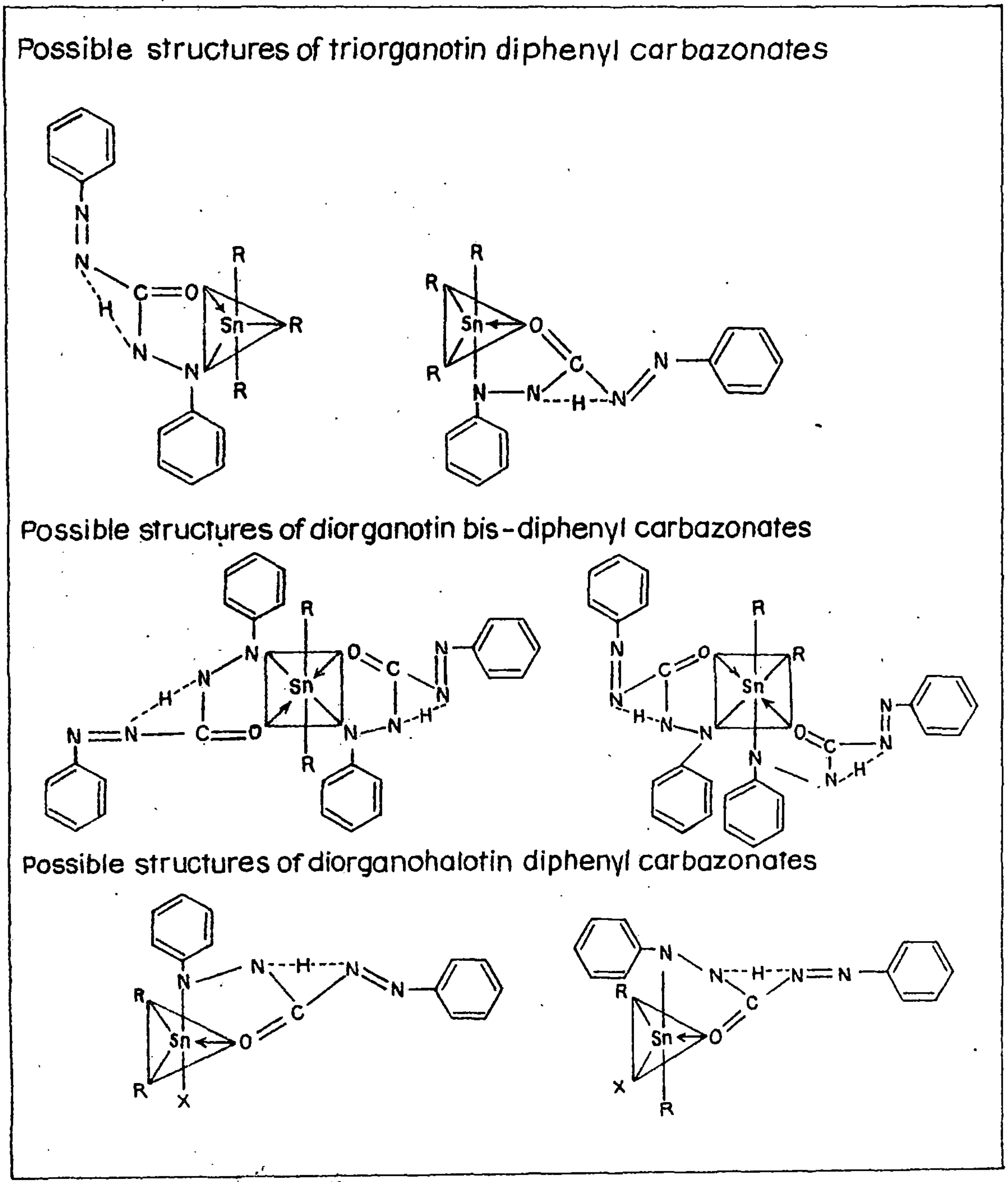


Fig.-33 Packing of diphenyl carbazone molecules (hydrogen bonds are shown in dotted line and phenyl rings are omitted for clarity).

PMR spectra of many organotin diphenyl carbazonate also confirm the presence of one imino proton in organotin complexes. The IR and visible spectra of organotin diphenyl carbazonates clearly indicate the presence of carbonyl group in the complexes as indicated by shifting of absorption bands both in visible and IR spectra.

Considering the crystal structure of diphenyl carbazone and different spectra data, we can tentatively propose the few structures of organotin diphenyl-carbazonates as follows(Figs 34A & 34B.).

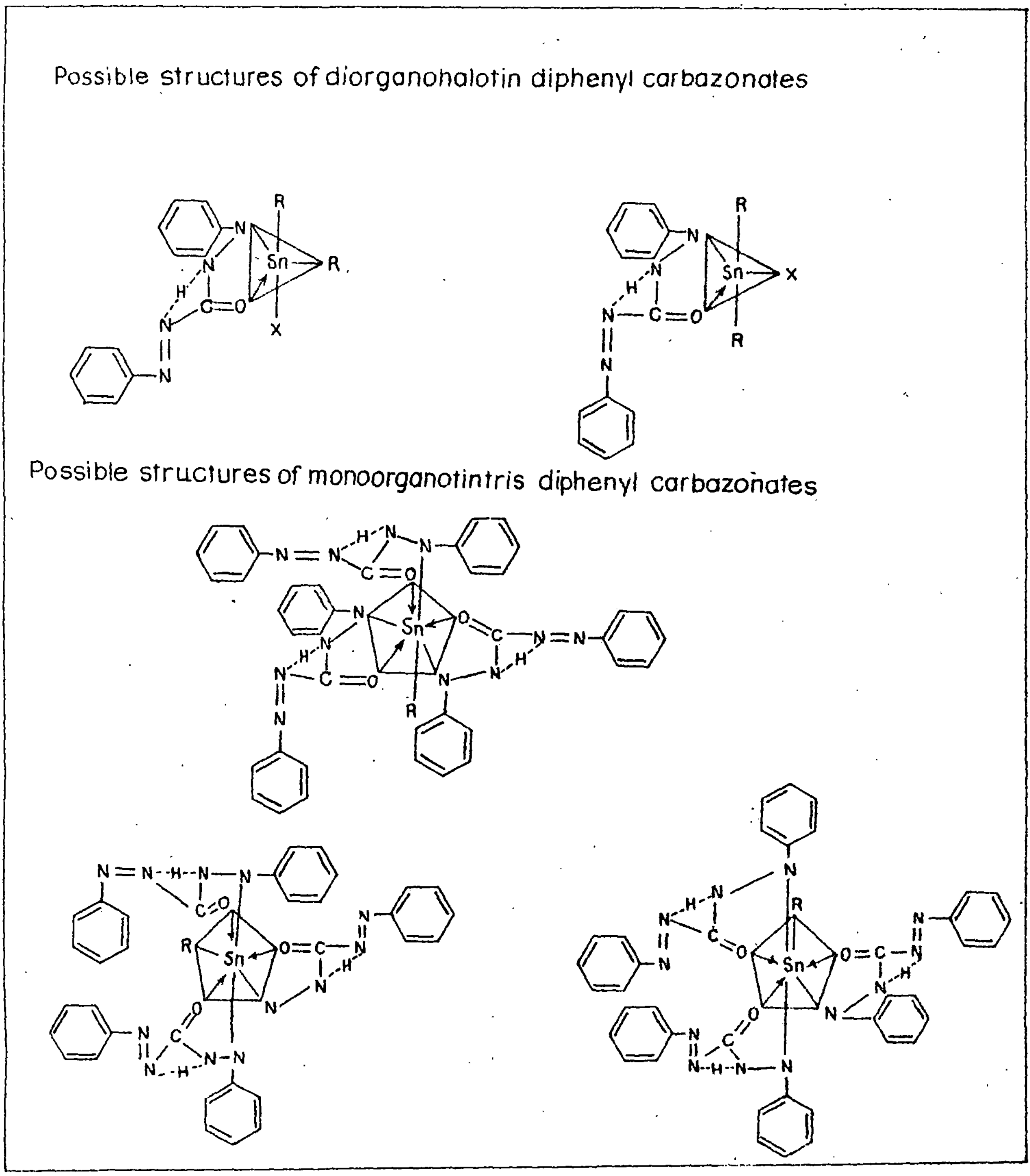


Possible structures of triorganotin diphenyl carbazonates

Possible structures of diorganotin bis-diphenyl carbazonates

Possible structures of diorganohalotin diphenyl carbazonates

Fig-34A



Possible structures of diorganohalotin diphenyl carbazonates

Possible structures of monoorganotintris diphenyl carbazonates

Fig-34B.

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PART - II

LIGAND EXCHANGE STUDIES

Introduction

The generality of Lewis definition of acids and bases has made it specially useful in discussing and predicting the course of many chemical reactions. All chemical reactions can be classified as either acid base or oxidation-reduction types. Luder and Zuffanti (1) classified all reactions into three categories: acid-base, oxidation-reduction and free radical. More recently Pearson (2) reduced these types to simply generalised acid-base and oxidation-reduction by treating free radicals as a form of oxidation reduction. Pearson considered oxidation-reduction reactions to be of two types : (i) Electron transfer and (ii) Atom or group transfer. A free radical reaction might be considered as of the second type and can be expressed as

$$A\cdot + B\cdot \rightleftharpoons \overset{+}{A} : B^{-}$$

The correlation of Lewis acid-base definition had a serious limitation that it can not give a consistent ordering of acid and base strengths. To approach this problem, we might consider the relative strengths in terms of the reactions.

$$A' + A : B \longrightarrow A' : B + A$$

and

$$B' + A{:}B \longrightarrow A{:}B' + B$$

As indicated above, if the reactions proceed to right, we can assume for these systems A' is a stronger acid than A and B' is a stronger base than B. The relative stabilities of acid-base complexes can then be guessed from such relative strengths.

It has been recognised for a long time that a strong acid forms a strong bond with a strong base, i.e., the equilibrium constant of the reaction

$$A + :B \rightleftharpoons A : B$$

is determined by the strength factor S. However, a simple correlation is not always adequate and Pearson proposed a four parameter equation for the minimum requirement for such an equilibrium

$$\text{Log } K = S_A S_B + \sigma_A \sigma_B$$

where S_A and S_B are quantities related to the relative acid and base strengths and σ_A σ_B are called 'softness' factors corresponding to acid and base which are different from strength.

A similar equation was also proposed by Edwards (3)

$$\log (K/K_0) = \alpha E_n + \beta H$$

where K/K_0 = relative (to water) rate or equilibrium constant
α = substrate constant
β = substrate constant
E_n = A nucleophilic constant characteristic of an electron donor

H = Relative basicity of the donor to protons.

For Lewis acids with a high positive charge and small size, is large, whereas Lewis acids with low charge and large size have small values. It follows that corresponds to Pearson's S_A and therefore $\beta H = S_A \cdot S_B$ and $\alpha E_n = \sigma_A \sigma_B$. The softness parameters are correlated with the oxidation potential and hence, the polarizability of acids and bases. Inspite of these equations, it was not possible to define an unequivocal acid-base scale, though certain qualitative correlations have been observed. Ahrland, Chatt and Davies (4) classified the metal ions into two general categories : Class (A) acceptors and class (B) acceptors.

The class (A) metal ions form their most stable complexes with the first member of each of the non-metal groups in the periodic table, whereas class (B) metal ions form their most stable complexes with the heavier members of the given group. Thus we find the distinction

Class (A)	$N \gg P > As > Sb > Bi$
Class (B)	$N \ll P > As > Sb > Bi$
Class (A)	$O \gg S > Se > Te$
Class (B)	$O \ll S \sim Se \sim Te$
Class (A)	$F > Cl > Br > I$
Class (B)	$F < Cl < Br < I$

According to this classification the class (A) metal ions are small and not very easily polarized whereas the class (B) metal, ions turn out to be essentially opposite in character. Class (A) metals combine with non metals of similar character and so also class (B) metals.

These ideas have been expanded and generalised by R.G. Pearson (2) along with a change in terminology to hard and soft acids and bases. Pearson defined a soft base as one in which the donor atom is of high polarizability and low electronegativity and is easily oxidised or is associated with empty, low lying orbitals. A hard base is of low polarizability and high electronegativity, is hard to reduce and is associated with empty orbitals of high energy. The acceptor atom of a soft acid is defined to be one which has one or more of the following properties: low or zero positive charge, large size and several easily excited outer electrons. On the other hand, a hard acid is associated with small size, high positive oxidation state and the absence of any outer electrons which are easily excited to higher state.

Pearson observed that the correlating principle on acid-base reaction is based on the assumption that hard acids prefer to co-ordinate with hard bases and soft acids prefer to co-ordinate with soft bases. The following reaction can be stated on the above basis,

$$A_H : B_1 + A_S : B_2 \rightleftharpoons A_H : B_2 + A_S : B_1$$

B_1 is softer than B_2 if $K > 1$

Pearson suggested a list of hard and soft acids and bases as follows:

Classification of Lewis acids

Hard	Soft
H^+, Li^+, Na^+, K^+ (Rb^+, Cs^+), Be^{2+}, $Be(CH_3)_2$, Mg^{2+} Ca^{2+}, (Ba^{2+}), Sr^{2+} Mn^{2+}, Al^{3+}, Sc^{3+}, Ga^{3+} In^{3+} La^{3+} Gd^{3+}, Lu^{3+}, Th^{4+} U^{4+} UO_2^{2+}, Pu^{4+} Ti^{4+} Zr^{4+} Hf^{4+} VO_2^{2+}, Cr^{3+}, Cr^{6+} MoO^{3+}, WO^{4+} Mn^{2+} Mn^{7+} Fe^{3+} Co^{3+}, BF_3, BCl_3, $B(OR)_3$, Al^{3+}, $Al(CH_3)_3$, $AlCl_3$, AlH_3, CO_2, RCO^+, NC^+ Si^{4+} Sn^{4+} CH_3Sn^+ $(CH_3)_2Sn^{2+}$ N^{3+} RPO_2^+, $ROPO_2^+$ As^{3+} SO_3, RSO_2^+, $ROSO_2^+$, Cl^{3+}, Cl^{7+} I^{5+} I^{7+} HX (hydrogen bonding molecules)	$Co(CN)_5^{3-}$, Pd^{2+} Pt^{2+} Pt^{4+} Cu^+, Ag^+ Au^+, Cd^{2+} Hg^+ Hg^{2+} CH_3Hg^+, BH_3, $Ga(CH_3)_3$, $GaCl_3$, $GaBr_3$, GaI_3, Tl^+, $Tl(CH_3)_3$, CH_2, Carbenes. π-acceptors, Trinitrobenzene, chloranil, quinones, tetracyanoethylene etc. Ho^+, RO^+, RS^+, RSe^+ Te^{4+} RTe^+, Br_2, Br^+, I_2, I^+ ICN etc. O, Cl, Br, I, N, RO, RO_2 M^0 (metal atoms) and bulk metals.

Borderline acids

Fe^{2+} Co^{2+} Ni^{2+} Cu^{2+} Zn^{2+} Rh^{3+}

Ir^{3+} Ru^{3+} OS^{2+} $B(CH_3)_3$, GaH_3,

R_3C^+, $C_6H_5^+$, Sn^{2+}, Pb^{2+}, No^{2+},
Sb^{3+}, Bi^{3+}, SO_2

Classification of Lewis bases

Hard bases	Borderline bases	Soft bases
NH_3, RNH_2, N_2H_4,	$C_6H_5NH_2$, C_5H_5, N_3^-,	H^-
H_2O, OH^-, O^{2-},	N_2, NO_2^-, SO_3^{2-}, Br^-	R^-, C_2H_4, C_6H_6,
ROH, RO^-, R_2O,		CN^-, RNC, CO, SCN^-,
CH_3COO^-, CO_3^{2-},		R_3P, $(RO)_3P$, R_3AS,
NO_3^-, PO_4^{3-},		R_2S, RSH, RS^-,
SO_4^{2-}, ClO_4^-, F^-,		$S_2O_3^-$, I^-.
Cl^-		

In an alternative approach, Gutmann and his co-workers (5) have characterized the donor properties of a great number of solvents in a quantitative manner. They have suggested that the enthalpy of complex formation between a ligand and antimony pentachloride should be a measure of the ligand donor strength, i.e.

$$\text{DN (donor number)} = -\Delta H \ (D.\ SbCl_5)$$

Gutmann et al (6) have obtained the following ligand-donor property series which also includes data for halide and pseudo halide ligand ions.

$N_3^- > NCS > Py > HMTAP > Ph_3PO > DMSO$

$Cl^- \sim DMF > TMF > Br^- > I^-$

In view of the diversity in the types of acids and bases, Gutmann's concept has not been accepted widely.

The extent of a given co-ordination equilibrium in solution is also strongly affected by the solvent, which can not be considered as an inert medium and often acts as a ligand competing with the nucleophile. It was found (7) that not only is solvent-ligand competition important but ligand solvation must also be taken into account. This effect is strongly dependent on the nature of the solvent.

The stability of organometallic complexes may be estimated qualitatively on the basis of Gutmann donor numbers of Pearson hard-soft (HSAB) concept. These two approaches, however, permit only preliminary estimates to be made of such stabilities and to obtain a quantitative estimate, a particular complex should be examined experimentally in an appropriate medium.

For an understanding of many problems of structure and reactivity of organotin co-ordination complexes, the concept of organotin compounds as Lewis acids is of primary importance. Tin has d-orbitals of sufficiently low energy, which can be frequently used in bonding so that tin can expand its co-ordination number above four. As a result of which, many organotin compounds form stable adducts and chelate compounds. When the chlorine atoms of stannic chloride are replaced by relatively electropositive organic groups, the acceptor strength of tin, declines as indicated by the sequences

$$SnCl_4 > RSnCl_3 > R_2SnCl_2 > R_3SnCl \quad (8)$$

$$Ph_3SnCl > Bu_3SnCl \quad \text{and} \quad PhSnCl_3 > MeSnCl_3 > BuSnCl_3 \; .$$

These sequences according to the nature of the donor molecules can exhibit some minor variations. It is widely accepted that Sn(IV) as a class A acceptor or using the HSAB concept, it is a hard acid. A general consensus is that hardness increases (or softness decreases) with increasing positive oxidation state. For example, Ni(0) is soft, Ni(II) is borderline and Ni(IV) is hard. The sulphur atom in RS^+ is soft, medium soft in RSO^+ and it is hard in RSO_2^+, S^{2-} is softer than SO_3^{2-} . There are a few exceptions to the rule, however. For instance, Tl(III), Sn(IV) and Pb(IV) are softer than their respective lower valent ions. Because Tl(I), Sn(II) and Pb(II) ions have d^{10} s^2 electrons in their outermost shells, the shielding of the d-electrons decreases the softness of the lower valent species. Factual demonstration of this reverse hardness/valence relationship is considerably highly stability of organo-thalliums only at 3 state and organotins at 4 state.

Many workers accept organotins as hard acids (Class A acceptor) (9). Bolles and Drago (10) from the evaluation of the enthalpy of interaction of Ph_3P, Et_2S, HMPA, DMSO, DMA, Pyridine, Acetone, DMTA, CH_3CN with Me_3SnCl concluded that Me_3SnCl interacts more strongly with nitrogen or oxygen donors than with phosphorous or sulphur donors and classified Me_3SnCl as a class A acceptor or relatively hard acid. They in a subsequent publication measured the tin-proton coupling constants of Me_3SnCl and showed these values are linearly related to enthalpy of formation of the complexes.

Donor	$J_{Sn^{119}-CH_3}$ (cps)
HMPA	71.6
DMSO	69.2
DMA	68.8
Py	67.0
$(C_2H_5)_2O$	60.6
$(C_2H_5)_2S$	60.4

M. Yasuda and R.S. Tobias (11) also reported the hard nature of R_2Sn^{2+} complexes.

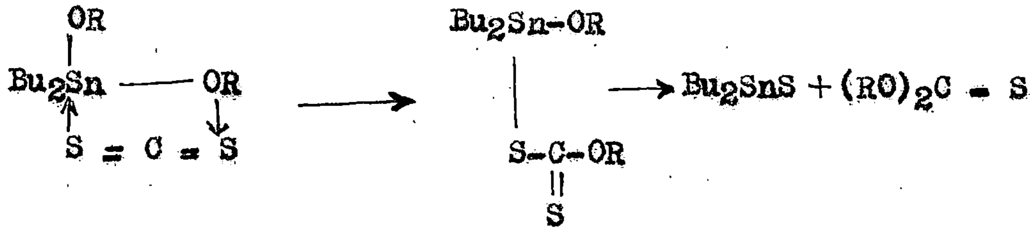
But several workers have shown the soft nature of organotin compounds. Saville (12) considered the presence of organic groups on tin would confer softness. There are reports that organotin compounds show characteristics of class B acceptors (soft acid) towards certain ligands (13). Luijten et al (14a) during a viscocity study observed the relative ability of a Lewis Base B to cause depolymerisation of polymeric Trialkyl imidazone according to the following reaction

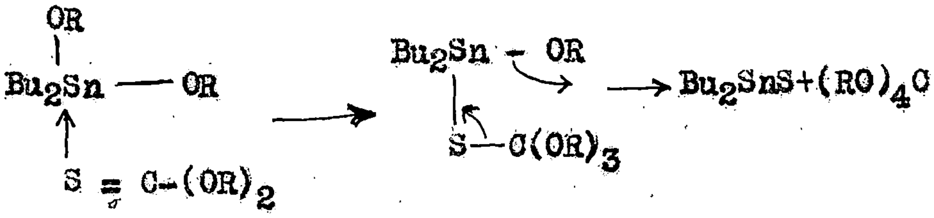
$$[X - Sn\ (R)_3]_n + nB \longrightarrow n\,[X - SnR_3 - B]$$

This was interpreted to indicate that this Lewis acid exhibits definite B character.

Organotin hydride are synthesised by the reduction of the halides or oxides with lithium aluminium hydrides. The tin atom of these halides and oxides is softened to a large extent by the organic ligands; therefore, it is a better partner for the hydride ion than aluminium (14b).

The soft character of organotin compounds is also supported by the synthesis of orthocarbonates by the reaction of carbon disulphide with dialkoxy stannes, each successive stage is aided by symbiosis (14b).





In view of above evidences, the hard or soft nature of organotin compounds can not be determined with any certainity. Moreover, the relative stability of organotin complexes with bidentate chelating ligands have not been extensively studied so far. In the present investigation, we attempted to find the relative donor strengths of Diphenyl thiocarbazone (H_2DZ), 8-hydroxy quinoline (HOX), Diphenyl carbazone (H_2DPC) and substituted hydroxamic (HPBHA) acids by reacting an organotin complex of one such ligand with another ligand, in the expectation that stronger donor ligand will displace comparatively weaker ligand according to the following scheme

$$R_3SnL + L' \longrightarrow R_3SnL' + L$$

$$R_2SnL_2 + 2L' \longrightarrow R_2SnL'_2 + 2L$$

$$R_2SnLX + L' \longrightarrow R_2SnL'X + L$$

where $R = CH_3$, C_6H_5 and

$L, L' = H_2DZ$, HOX, H_2DPC, PBHA etc.

All these reactions were carried out in $CHCl_3$ /benzene/CCl_4 medium to keep solvent effects minimum in such displacement reactions.

It has been found during the present investigation that in many cases, such displacement of ligands can proceed in a very facile manner.

EXPERIMENTAL

Materials and methods

All the solvents used were purified and dried before use. Pet ether used had the boiling range 60°-80°.

Diphenyl carbazone, G.R. E. Merck; dithizone, G.R. E. Merck and Oxine (8-hydroxy quinoline) A.R. B.D.H. were used. All the melting points were uncorrected. Known compounds were checked by mixed melting point determination with authentic samples.

Triphenyl tin dithizonate was prepared according to the method of Ghosh and Ghosh (15) by refluxing a mixture of triphenyl tin oxide (2.0g) and dithizone (1.43g) in chloroform (150 ml) for one hour. The deep coloured solution was filtered. The filtrate was concentrated, methanol was added in excess when after some time fine brick red crystals of triphenyl tin dithizonate (m.p. 144-45°) was obtained. On recrystallisation from chloroform-methanol mixture it afforded crystals of m.p. 146° ⌈lit (15) m.p. 145-46°C⌋.

Diphenyl tin bis-dithizonate was prepared according to the method of Ghosh and Ghosh (15). A mixture of 0.88g of diphenyl tin dichloride and 1.28g of dithizone in 100 ml chloroform was heated on a water bath for 10 minutes. 7-8 drops of ammonia solution (17N) was added to neutralise the liberated hydrochloric acid and the precipitated ammonium chloride was filtered off. The filtrate was concentrated and methanol was added when 1.15g of shining reddish crystals of diphenyl tin bis-dithizonate was obtained. This on recrystallisation from chloroform methanol mixture afforded crystals of m.p. 181-83° [lit (15) m.p. 181-83°C].

Triphenyl tin N-phenyl benzohydroxamate was prepared by the method of Pradhan and Ghosh (16) by refluxing for four hours a mixture of 2.15g of bis-triphenyl tin oxide and 1.25g of N-phenyl benzohydroxamic acid (PBHA) in 50 ml benzene using a Dean-Stark Water Separator. The light yellow solution was filtered and evaporated to a pasty mass on a water bath which was crystallised from methanol. Yield was 2.50g and m.p. was 133°C [lit (16) m.p. 133°C].

Diphenyl tin bis-N-phenyl benzohydroxamate was prepared according to the method of Pradhan and Ghosh (16). This was crystallised from benzene and methanol. This was dried in vacuum and had a m.p. of 160° [lit (16) m.p. 160°].

Dimethyl tin bis-(N-phenyl-p-nitrobenzohydroxamate) was prepared according to the method of Chaudhuri (17) by refluxing a mixture of 1g of dimethyl tin oxide and 3g of N-phenyl p-nitro benzohydroxamic acid (nitro PBHA) in 150 ml benzene for two hours using a Dean and Stark Water Separator. The yellow coloured solution was filtered and concentrated to a pasty mass. Shining yellow crystals (3g) appeared after the addition of methanol. The compound on recrystallisation from methanol afforded crystals of m.p. 237°C [lit (17) m.p. 237°C].

N-phenyl-p-nitro benzohydroxamic acid was prepared by the reaction of p-nitrobenzoyl chloride with phenyl hydroxylamine (18). The compound was crystallised from rectified spirit and dried by heating in vacuum. M.P. was noted to be 159°C [lit (19) m.p. 159°C].

Triphenyl tin oxinate was prepared by reacting bis-triphenyl tin oxide with oxine. The compound had m.p. of 145°C [lit (20) m.p. 145-46°C].

Diphenyl tin dioxinate was prepared by reacting diphenyl tin dichloride and oxine. The liberated hydrogen chloride was neutralised by ammonia. M.P. was found to be 249-51°C [lit (20) m.p. 251°C].

All the organotin diphenyl carbazonates, namely, triphenyl tin diphenyl carbazonate, diphenyl tin bis-diphenyl carbazonate, dimethyl tin bis-diphenyl carbazonate, dibutyltin bis-diphenyl carbazonate and dimethyl chlorotin diphenyl carbazonate have been described before.

1. <u>Reaction of Triphenyl tin oxinate with Dithizone</u>

1.98g of triphenyl tin oxinate and 1.02g of dithizone were separately dissolved in 100 ml chloroform. These two solution were mixed together and the mixture was refluxed for 2 hours on a water bath. The refluxed solution on cooling did not give any crystal but on concentration of the reaction mixture over a water bath to one-fourth of the original volume and cooling, a fine deep brown coloured crystals of melting point 140-41°C appeared. The yield was 2.20g. This compound on recrystallisation twice from chloroform-methanol mixture afforded crystals of m.p. 143-44°C. This compound showed no depression of melting point with an authentic sample of triphenyl tin dithizonate.

The mother liquor, after separation of triphenyl tin dithizonate, was further concentrated and kept for some time when fine shining yellowish crystals of m.p. 69-72°C appeared. This was collected and on recrystallisation from chloroform-methanol mixture it afforded crystals of m.p. 75°C. This compound was confirmed as oxine as it showed no depression of melting point with an authentic sample of oxine. The yield was 0.50g.

On the basis of the products obtained we infer that the following reaction has taken place:

$$Ph_3SnOx + H_2DZ \longrightarrow Ph_3SnHDZ + HOx$$

The conversion in this case was about 90% on the basis of isolation of triphenyl tin dithizonate (Ph_3SnHDZ).

2. Reaction of Diphenyl tin dioxinate with Dithizone

0.56g of diphenyl tin dioxinate and 0.51g of dithizone were separately dissolved in 100 ml chloroform, in each case. Both these solutions were mixed when the colour of the mixture became yellowish-red. This mixture was then refluxed for one hour on a water bath. The refluxed solution on cooling did not give any crystal. This was concentrated to one-fourth its original volume and kept for some time when a beautiful yellowish-black crystals of m.p. 72°C appeared and was collected. The yield was 0.27g. The compound on recrystallisation thrice from chloroform-methanol mixture afforded shining yellow crystals of m.p. 75°C and showed no depression of melting point with an authentic sample of oxine.

The mother liquor was further concentrated and kept in the refrigerator for two days when beautiful pink coloured crystals of melting point 177-79°C were formed. This on further recrystallisation from chloroform methanol mixture afforded crystals of m.p. 181-82°C. This compound was identified as diphenyl tin bis-dithizonate since it showed no depression of melting point with an authentic sample of diphenyl tin bis-dithizonate. The yield was approximately 0.70g.

On the basis of the products obtained we infer that the following reaction has taken place.

$$Ph_2Sn(Ox)_2 + 2H_2DZ \longrightarrow Ph_2Sn(HDZ)_2 + 2HOX.$$

The conversion was almost 89%.

3. Reaction between diphenyl tin bis-diphenyl carbazonate and dithizone

0.75g of diphenyl tin bis-diphenyl carbazonate and 0.51g of dithizone were separately dissolved in chloroform and then mixed together. The mixture after being refluxed on a water bath for about 2 hours did not give any crystal on cooling. It was then concentrated to one-fourth its original volume and cooled, but no crystals appeared. To it slight excess of methanol was added and the solution was kept for some time when beautiful red shiny crystals of m.p. 180-82°C appeared and was collected. This on recrystallisation twice from chloroform-methanol mixture afforded crystals of melting point 181-82°C. The yield was 0.74g. This compound was characterised as diphenyl tin bis-dithizonate since it gave no depression in melting point with an authentic sample of diphenyl tin bis-dithizonate.

After separating the shining red crystals, the mother liquor was concentrated almost to evaporation when after cooling this highly concentrated solution produced shining orange crystals of m.p. 153-156°C. The yield was 0.40g. This on recrystallisation from chloroform-methanol mixture afforded crystals of m.p. 155-57°C. This was diphenyl carbazone as was confirmed by mixed melting point checking with an authentic sample of diphenyl carbazone.

Thus, the following reaction has taken place here:

$$Ph_2Sn(HDPC)_2 + 2H_2DZ \longrightarrow Ph_2Sn(HDZ)_2 + 2H_2DPC$$

The percentage of conversion in this case was 94% .

4. <u>Reaction of dimethyl chlorotin diphenyl carbazonate with dithizone</u>

0.42g of dimethyl chlorotin diphenyl carbazonate and 0.26g of dithizone were mixed and dissolved in 100 ml chloroform. The mixture was then refluxed on a water bath for about 3 hours. The refluxed solution on colling did not give any crystal. It was then concentrated to one-fourth its original volume and cooled but no crystals appeared. To it slight excess of methanol was added and the mixture was kept for some time when fine shining reddish crystals of m.p. 180-81°C were formed and collected. This on recrystallisation from chloroform-methanol mixture afforded crystals of m.p. 183-84°C. This was found to be dimethyl chlorotin dithizonate since no depression of melting point of it with an authentic sample of dimethyl chlorotin dithizonate [lit (15a) m.p. 184°C] was noted. The yield was 0.40g.

After separating these crystals, the mother liquor was highly concentrated and allowed to stand for some time when beautiful shining orange crystals of m.p. 148-50°C appeared. This was collected. On recrystallisation from highly concentrated chloroform-methanol mixture it afforded orange coloured crystals of m.p. 154-55°C. The yield was 0.22g. This compound was confirmed as diphenyl carbazone by mixed melting point checking with an authentic sample.

A small amount of dimethyl chlorotin diphenyl carbazonate and dithizone could not be recovered.

Thus the following reaction has taken place in the above case:

$$Me_2SnCl\ HDPC + H_2DZ \longrightarrow Me_2SnClHDZ + H_2DPC$$

In this reaction percent conversion = 91% [on the basis of dimethyl chlorotin diphenyl carbazonate]

and percent recovery of diphenyl carbazone = 92%.

5. Reaction between diphenyl tin bis-(N-phenyl benzohydroxamate) and dithizone.

0.70g of diphenyl tin bis-(N-phenyl benzohydroxamate) and 0.50g of dithizone were mixed. To it added 100 ml benzene and refluxed for two hours on a water bath. The refluxed solution on cooling did not give any crystal. It was then concentrated and kept for some time when a gummy mass was found to be appeared. This gummy mass was extracted with methanol for several times when after some time a deep violet coloured crystal of m.p. 180-81°C was formed. This on recrystallisation from chloroform-methanol mixture afforded crystals of m.p. 180°C which showed no depression in melting point with an authentic sample of diphenyl tin bis-dithizonate. The yield was 0.65g.

After separating these crystals the mother liquor was further concentrated and cooled when again a gummy mass appeared. This was dissolved in carbon tetrachloride. Upon concentration and cooling the filtrate produced pale yellow crystals of m.p.

120-21°C. The yield was 0.38g. This on recrystallisation from carbon tetrachloride produced yellow crystals of m.p. 121-22°C. This was N-phenyl benzohydroxamic acid as it showed no depression in melting point with an authentic sample of N-phenyl benzohydroxamic acid.

So, in this reaction percent conversion = 83%

and percent recovery of N-phenyl benzohydroxamic acid = 89%. Thus it is evident that the following reaction has taken place.

$$Ph_2Sn(PBHA)_2 + 2H_2DZ \longrightarrow Ph_2Sn(HDZ)_2 + 2HPBHA$$

6. <u>Reaction of triphenyl tin N-phenyl benzohydroxamate and dithizone:</u>

0.56g of triphenyl tin N-phenyl benzohydroxamate and 0.26g of dithizone were dissolved separately in carbon tetrachloride. These were then mixed and the mixture was refluxed on a water bath for about three hours. The refluxed solution on cooling gave no crystal. It was then concentrated and kept for sometime when snuff coloured crystals of m.p. 186-87°C were formed. The yield was 0.10g. Mixed melting point of this compound showed it as unreacted triphenyl tin N-phenyl benzohydroxamate.

After separating this product the mother liquor was further concentrated and allowed to stand for sometime when a violet coloured crystal (0.45g) of m.p. 146° was formed and collected. This compound was confirmed as triphenyl tin dithizonate by mixed melting point determination with an authentic sample.

This product was separated and the mother liquor was highly concentrated and kept for sometime when yellow crystals of m.p. 119-20°C. were formed and collected. On recrystallisation from carbon tetrachloride solution it afforded crystals of m.p. 122°C. This compound, N-phenyl benzo hydroxamic acid was separated and confirmed by noting no depression in melting point with an authentic sample of N-phenyl benzohydroxamic acid. The yield was 0.18g.

So, percent conversion on the basis of $Ph_3SnPBHA = 75\%$ Therefore, on the basis of the products obtained in the reaction, we infer that the following exchange reaction has taken place.

$$Ph_3Sn(PBHA) + H_2DZ \longrightarrow Ph_3SnHDZ + HPBHA$$

7. Reaction between triphenyl tin dithizonate and diphenyl carbazone:

0.61g of triphenyl tin dithizonate and 0.24g of diphenyl carbazone were separately dissolved in 100 ml chloroform. These were mixed and the mixture was refluxed on a water bath for two hours. The refluxed solution on cooling gave no crystal. It was then concentrated to one-sixth its original volume and kept for sometime when fine orange coloured crystals of m.p. 150°C were formed and collected. The yield was 0.22g. This on recrystallisation from chloroform methanol mixture afforded crystals of m.p. 155°C. This compound was found to be diphenyl carbazone.

After separating these orange coloured crystals the mother liquor was highly concentrated but did not give any crystal on cooling. To it a slight excess of methanol was added and kept for some time when fine reddish crystals of m.p. 140-41°C appeared. These were collected. The yield was 0.57g. On recrystallisation from chloroform-methanol mixture it afforded crystals of m.p. 145-46°C. This compound was triphenyl tin dithizonate.

Thus no reaction has taken place.

$$Ph_3SnHDZ + H_2DPC \longrightarrow \text{no reaction.}$$

8. Reaction between diphenyl tin bis-dithizonate and diphenyl carbazone:

0.78 gms of diphenyl tin bis-dithizonate and 0.48 gms of diphenyl carbazone were weighed and dissolved separately in 100 ml chloroform. These were mixed together and the mixture was refluxed for four hours. On cooling it did not give any crystal. The refluxed solution was then concentrated to one-third its original volume and kept for some time when orange-coloured crystals of melting point 151-52°C separated out. This on recrystallisation from chloroform-methanol mixture afforded orange coloured crystals of melting point 155-56°C. The yield of this compound was 0.47 gms. It gave no depression in melting point with an authentic sample of diphenyl carbazone.

After the separation of the orange crystals the mother liquor was further concentrated to a small volume. The concentrated mother liquor on cooling did not give any crystal. To this concentrated mother liquor, excess methanol was added and this mixture was kept for some time when fine shiny red crystals appeared and was collected. Melting point of this crystal was found to be 180-81°C. This on further recrystallisation from chloroform-methanol mixture afforded crystals of melting point 181-82°C. The crystals gave no depression in melting point with an authentic sample of diphenyl tin bis-dithizonate. The yield was 0.78g.

On the basis of the observations it seems that no reaction has taken place in the above case.

$$Ph_2Sn(HDZ)_2 + 2H_2DPC \longrightarrow \text{no reaction.}$$

9. Reaction between diphenyl tin bis-diphenyl carbazonate and oxine:

0.75g of diphenyl tin bis-diphenyl carbazonate and 0.29g of oxine were separately dissolved in chloroform and mixed together. The mixture was refluxed on a water bath for about two hours. The solution on cooling did not give any crystal. The reaction mixture was then concentrated to one-fourth its original volume which on cooling gave no crystal. To it a slight excess of methanol was added and the mixture was kept for one day when crystals appeared on recrystallisation twice from chloroform-methanol mixture it afforded shining yellowish crystals of m.p. 250°C. These crystals were confirmed as diphenyl tin bis-oxinate by noting the mixed melting point. The yield was 0.52g.

After separating the yellowish crystals the mother liquor was further concentrated but no crystals appeared on cooling. The mother liquor was then evaporated to dryness and the solid mass was dissolved in chloroform. This was kept for some time when beautiful shining orange crystals of m.p. 148-50°C appeared. The yield was 0.40g. This on recrystallisation from chloroform-methanol mixture afforded crystals of m.p. 154-55°C and was found to be diphenyl carbazone.

In the above reaction

percent conversion = 92.3%

and percent recovery of diphenyl carbazone = 84%.

So the following reaction has taken place.

$$Ph_2Sn(HDPC)_2 + 2HOx \longrightarrow Ph_2Sn(Ox)_2 + 2H_2DPC$$

10. Reaction of dibutyl tin bis-diphenyl carbazonate with oxine:

0.62g of dibutyl tin bis-diphenyl carbazonate and 0.25g of oxine were mixed. To it added 100 ml chloroform and the mixture was refluxed for one hour on a water bath. The refluxed solution on cooling did not give any crystal. On concentration of the mixture over a water bath to one-fourth its original volume, no crystals appeared. To it a slight excess of methanol was added and kept for sometime when beautiful shining yellowish-red crystals were formed and collected. These on further crystallisation from chloroform-methanol mixture afforded shining yellowish crystals of m.p. 150°C. This was dibutyl tin bis-oxinate as was confirmed by mixed melting point checking with an authentic sample [lit (20a) m.p. 150-52°C]. The yield was 0.45g. After separating it the mother liquor was further concentrated to a small volume, when orange coloured crystals appeared. The yield was 0.42g. These crystals melted at 151°C. On recrystallisation from chloroform-methanol mixture it afforded crystals of m.p. 154-55°C. The crystals were confirmed as diphenyl carbazone by mixed melting point checking with an authentic sample of diphenyl carbazone.

So, the following reaction has taken place.

$$Bu_2Sn(HDPC)_2 + 2HOX \longrightarrow Bu_2Sn(OX)_2 + 2H_2DPC$$

The conversion was practically quantitative in nature.

11. Reaction between triphenyl tin oxinate and diphenyl carbazone:

0.49g of triphenyl tin oxinate and 0.24g of diphenyl carbazone were separately dissolved in chloroform, mixed together and the mixture after being refluxed on a water bath for four hours did not give any crystal on cooling. The refluxed solution was then concentrated to one-fourth its original volume and kept for some time, but no crystals appeared. To this solution added a slight excess of methanol. This solution, upon concentration, produced yellowish orange crystals. This was collected and recrystallised from chloroform-methanol mixture when beautiful shining yellowish crystals of m.p. 144°C was obtained. The yield was 0.47g. By mixed melting point checking the compound was confirmed as triphenyl tin oxinate.

After separating these yellow crystals the mother liquor was further concentrated and kept for some time when fine orange coloured crystals of m.p. 152-53°C appeared. This was collected. The yield was 0.20g. On recrystallisation from highly concentrated chloroform/methanol mixture it afforded crystals of m.p. 155°C. This was confirmed as diphenyl carbazone by observing the mixed melting point. Thus, here, no reaction has taken place.

$$Ph_3Sn(OX) + H_2DPC \longrightarrow \text{no reaction}$$

12. Reaction between dimethyl tin bis-(N-phenyl p-nitrobenzohydroxamate) and oxine:

0.33g of dimethyl tin bis-(N-phenyl p-nitrobenzohydroxamate) and 0.14g of oxine, i.e. 8-hydroxy quinoline were mixed. To it added 100 ml benzene and the mixture was refluxed for one hour on a water bath. The refluxed solution on cooling did not give any crystal. The solution was then concentrated to about one-fourth its original volume and the concentrated solution was kept for sometime when fine pale yellow crystals of melting point 155-58°C appeared. This on recrystallisation from concentrated benzene solution afforded crystals of m.p. 159°C. This was confirmed as N-phenyl p-nitrobenzohydroxamic acid by mixed melting point checking with an authentic sample. The yield was 0.21g. After separating this product the mother liquor was evaporated to an oily liquid, this was then dissolved in methanol and the solution was kept for sometime when a fine yellow crystals of m.p. 230°C appeared. This was collected. On recrystallisation from methanol it gave crystals of melting point 231°C. This was dimethyl tin dioxinate as it showed no depression in melting point with an authentic sample [Lit (20a) m.p. 231-33°C]. The yield was 0.20g.

Thus the following reaction has taken place here.

$$\mathrm{Me_2SnL_2 + 2HOX \longrightarrow Me_2Sn(OX)_2 + 2LH}$$

(LH = N-phenyl p-nitrobenzohydroxamic acid)

50, percent conversion in this case ≈ 84%.

13. Reaction between dimethyl tin bis-(N-phenyl p-nitro benzohydroxamate) and diphenyl carbazonate:

0.33g of dimethyl tin bis-(N-phenyl p-nitro benzohydroxamate) and 0.24g of diphenyl carbazone were separately dissolved in benzene. The two solutions were mixed and the mixture was refluxed for one hour on a water bath. The refluxed solution on cooling gave orange-coloured crystals of m.p. 150-52°C. The yield was approximately 0.20g. This on recrystallisation from benzene-methanol mixture afforded orange-coloured crystals of m.p. 155-56°C. This compound was diphenyl carbazone as it showed no depression in melting point with an authentic sample of diphenyl carbazone. After separating these crystals the mother liquor was concentrated to about one-fourth its original volume. This solution, on cooling, gave no crystal. To it slight excess of methanol was added and after some time this mixture produced a beautiful shining reddish crystals of melting point 192-93°C. The yield was 0.10g. After separating these crystals the mother liquor was concentrated to about one-fourth its original volume. On cooling, this solution gave beautiful shining reddish crystals of m.p. 131°C. This compound was found to be dimethyl tin bis-diphenyl carbazonate which showed no depression in melting point with an authentic sample. The yield was 0.05g. This product was separated and the mother liquor was concentrated almost to evaporation when yellow crystals of m.p. 236°C appeared. The yield was approximately 0.25g. This compound was unreacted dimethyl tin bis-(N-phenyl p-nitrobenzohydroxamate) as it showed no depression in melting point with an authentic sample.

On recrystallisation from chloroform-methanol mixture the crystals of m.p. 192-93°C gave two types of yellow crystals. One was obtained from moderately concentrated solution, the m.p. of which was 157°C . The yield was 0.05g. This was confirmed as N-phenyl p-nitrobenzohydroxamic acid by mixed melting point checking with an authentic sample. The other yellow crystals (0.04g) was unreacted dimethyl tin bis-(N-phenyl p-nitro benzohydroxamate) as it showed no depression in melting point with an authentic sample. This product was obtained from highly concentrated solution.

The following reaction has taken place:

$$Me_2SnL_2 + 2H_2DPC \longrightarrow Me_2Sn(HDPC)_2 + 2LH$$

where LH = N-phenyl p-nitrobenzohydroxamic acid.

Percent of conversion in this case $\approx 8\%$.

14. Reaction between dimethyl tin bis-diphenyl carbazonate and N-phenyl p-nitrobenzohydroxamic acid:

0.62g of dimethyl tin bis-diphenyl carbazonate and 0.51g of N-phenyl p-nitrobenzohydroxamic acid were mixed. To it added 50 ml chloroform and the mixture was refluxed for two hours. The refluxed solution on cooling did not give any crystal. The solution was then concentrated to one-third its original volume and a slight excess of methanol was added. The solution was kept for some time when beautiful shining reddish crystals of m.p. 130-32°C were formed. This product was collected and on recrystallisation from chloroform-methanol mixture it afforded shining reddish crystals of m.p. 130-31°C. The yield was 0.60g. This product was dimethyl tin bis-diphenyl carbazonate as it showed no depression in melting point with an authentic sample.

After separating this product, the mother liquor was completely evaporated to a pasty mass on a water bath, which was dissolved in 20 ml benzene. This solution, upon concentration, gave pale yellow crystals of m.p. 155-57°C. The yield was approximately 0.5g. This on recrystallisation from benzene afforded crystals of m.p. 158-59°C. This was confirmed as N-phenyl p-nitro benzohydroxamic acid by mixed melting point checking.

From the observations of the products obtained we infer that no reaction has taken place in the above case.

$$Me_2Sn(HDPC)_2 + 2LH \longrightarrow \text{no reaction.}$$

where LH = N-phenyl p-nitro benzohydroxamic acid.

The following table shows the percentage of ligand displacement obtained during the present investigation.

Table - 1

Reaction	Products	% of conversion
1. $Ph_3SnOX + H_2DZ$	$\longrightarrow Ph_3Sn(HDZ) + H.OX$	90.0
2. $Ph_2Sn(OX)_2 + 2H_2DZ$	$\longrightarrow Ph_2Sn(HDZ)_2 + 2HOX$	89.0
3. $Ph_2Sn(HDPC)_2 + 2H_2DZ$	$\longrightarrow Ph_2Sn(HDZ)_2 + 2H_2DPC$	94.0
4. $Me_2SnCl(HDPC) + H_2DZ$	$\longrightarrow Me_2SnCl(HDZ) + H_2DPC$	91.0
5. $Ph_2Sn(PBHA)_2 + 2H_2DZ$	$\longrightarrow Ph_2Sn(HDZ)_2 + 2HPBHA$	83.0
6. $Ph_3Sn(PBHA) + H_2DZ$	$\longrightarrow Ph_3Sn(HDZ) + HPBHA$	75.0
7. $Ph_3Sn(HDZ) + H_2DPC$	$\longrightarrow$ no reaction	-
8. $Ph_2Sn(HDZ)_2 + 2H_2DPC$	$\longrightarrow$ no reaction	-
9. $Ph_2Sn(HDPC)_2 + 2HOX$	$\longrightarrow Ph_2Sn(OX)_2 + 2H_2DPC$	92.3
10. $Bu_2Sn(HDPC)_2 + 2HOX$	$\longrightarrow Bu_2Sn(OX)_2 + 2H_2DPC$	~100.0
11. $Ph_3SnOX + H_2DPC$	$\longrightarrow$ no reaction	-
12. Me_2Sn(nitro PBHA)$_2$ + 2HOX	$\longrightarrow Me_2Sn(OX)_2$ + 2nitro PBHA	84.0
13. Me_2Sn(nitro PBHA)$_2$ + $2H_2DPC$	$\longrightarrow Me_2Sn(HDPC)_2$ + 2nitro PBHA	8.0
14. $Me_2Sn(HDPC)_2$ + 2 nitro PBHA	$\longrightarrow$ no reaction	-

Here the following abbreviations have been used:

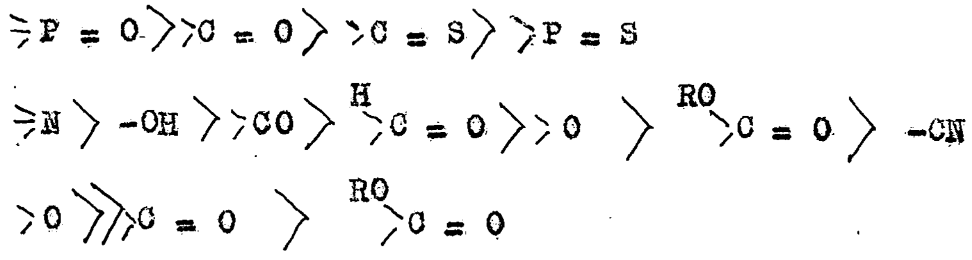
HOX = oxine or 8-hydroxy quinoline; H_2DZ = Dithizone; H_2DPC = diphenyl carbazone; HPBHA = N-phenyl benzohydroxamic acid and nitro PBHA = N-phenyl-p-nitro benzohydroxamic acid.

From the above table it is apparent that of the bidentate chelate ligands diphenyl thiocarbazone has highest donor strength for different organotin moieties. The order of donor abilities of these ligands used in the following study are as follows:

Diphenyl thiocarbazone Oxine Diphenyl carbazone

Hydroxamic acid.

This order of reactivity can be expected if we consider the organotin moieties as relatively soft acid according to HSAB concept. T.L.Ho (21) has observed that it is now established that thiols, thioethers and phosphines (soft donors) form much weaker complexes with the metal ions in reagents which happen to be hard Lewis acids than do ethers and amines (hard donors) by co-ordination with the magnitude of proton resonance shifts in the proximal methylene or methyl groups. The relative abilities of various groups for hard acids are listed as follows:



$$\geqq P = O \gg\ >C = O >\ >C = S >\ \geqq P = S$$

$$\geqq N > -OH \gg\ >CO > \overset{H}{>}C = O \gg\ >O > \overset{RO}{>}C = O > -CN$$

$$>O \ggg\ >C = O > \overset{RO}{>}C = O$$

Thus, though it is expected that the proximal methyl groups in Me_2SnCh_2 (Ch = chelate) should undergo considerable shielding compared to Me_2SnCl_2 and consequently might have different ^{119}Sn-C-H coupling constant values. $Me_2Sn(OX)_2$ have very similar coupling constant values to Me_2SnCl_2. The close similarity of these values has been ascribed due to structural features of the complex. We also observed anomaly in the shielding of $Me_2Sn(HDZ)_2$ and $Bu_2Sn(HDZ)_2$. In $Me_2Sn(HDZ)_2$ the methyl group absorbs at δ 1.28 ppm where as the triplets (δ -0.58, 0.66, 0.74 ppm) associated with the methyl groups have been observed for $Bu_2Sn(HDZ)_2$, possibly for structure features of these compounds. The position of the methyl groups in p.m.r. spectra is given in the following table.

Table - 2

Compound	Position of CH_3 proton (in δ-ppm)
$Me_2Sn(HDZ)_2$	1.28 (15)
$Me_2Sn(OX)_2$	0.44 (20)
$Me_2Sn(HDPC)_2$	0.80
$Me_2Sn(nitro\ PBHA)_2$	0.80 (17)
Me_2SnCl_2	1.22 (20)

In $Me_2Sn(HDZ)_2$, the methyl group suffers deshielding instead of usual shielding expected for such co-ordination compounds. Apart from this compound, the nature of displacement of ligands observed during the present investigation closely resemble the shielding observed in these compounds. Thus oxine can replace both diphenyl carbazone and nitro PBHA quite easily, whereas the diphenyl carbazone can only marginally displace nitro PBHA from its complexes. The diphenyl thiocarbazone can replace all these ligands from their complexes quite easily. Hence we may assume where the structural features do not affect the p position of CH_3 protons, the magnitude of shielding can possibley give some idea about the relative donor strength of the ligands.

Drago and Wayland (22) observed that every acid and base has both class A and B character but generally one type of behaviour predominates. The rates of bimolecular nucleophilic substitution reactions are determined by several factors relative to the nature of substrate and reagent and to the conditions (solvent, temperature, etc.) (23). By measuring under the same experimental conditions the rate of displacement of the ligand from a substrate M - X by various reagents Y, a quantitative sequence of relative reactivity can be obtained.

In view of the number of variables that can affect the nucleophilicity, it is desirable to limit the range of the nucleophiles studied in order to eliminate certain structural factors such as steric hindrance etc. Following Pearson's classification of soft and hard acids and bases, it appears that in substitution reactions at soft reaction centres, the micropolarizability or softness of Y is most important factor in determining nucleophilicity, whereas the basicity of Y play only a minor role.

Unfortunately, from a practical point of view, Drago et al observed that, "softness is not a property that can be quantitatively measured by a direct physical experiment. It should be borne in mind that the HSAB concept represents an empirical approach which is often invalidated by the fact that there is no clear boundary between the two different types of acids and bases. The exact softness scale is neither available nor advisable empirical systematization of various acids and bases is essential for correlating experimental observations. The best compromise would be to establish guide lines for the rough estimation of softness in a comparative sense" (24).

It is interesting to note that of the two ligands viz. oxine and diphenyl carbazone, the former produces complexes with organotin moieties displacing diphenyl carbazone. In oxine complexes, the formation of co-ordination bond is effected through nitrogen, whereas in diphenyl carbazone, it is through oxygen. Since, nitrogen is a better donor than oxygen, the stability of oxine compound is expected to be higher than diphenyl carbazone.

The assumption of organotin compounds as a hard acid is, therefore, should be under some scrutiny, since the experimental observations obtained during the present investigation clearly show the opposite character, i.e., these are at least borderline between hard and soft acid, if not definitely soft acids, since N-S donor apparently forming strongest complex, followed by N-O donors and the O-O donors form weakest complexes.

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PART - III

FUNGITOXIC PROPERTIES

Introduction

The unique role of metal ions in the regulation of various life processes is now well established. The function of cobalt in cobalamin (Vitamin B_{12}), magnesium in chlorophyll and the role of iron and copper in oxygen carrying systems need not be emphasised. Like other living systems, fungi also require metals like iron, copper, zinc and a few other metals for proper growth and development. But when some of these metals especially zinc and copper when supplied to fungi in more than optimal amounts, these act as fungicides. Apart from these metals some other such as silver, mercury, cadmium, nickel, lead etc. can also create fungitoxicity. Though stannous or stannic tin can cause very little fungitoxicity, some organotin compounds have unusually high fungitoxicities. Organometallic compounds of mercury and some group IV or V of the periodic table exhibit pronounced fungitoxicity.

Organomercurials are still being used as one of the most effective biocidal agents due to their high effectivenss in extremely minute doses. But recently their high mammalian and phytotoxic properties have placed these compounds under scrutiny for future use. It is quite possible that within a few years, these organomercurials may be replaced ~~[illegible]~~ by highly effective but relatively non toxic organotin preparation (1).

Organometallic compounds of group IV and V of the periodic table, such as those of germanium, tin, lead, arsenic, antimony and bismuth show considerable biological activities (2). It has been found that of all these metals, tin shows maximum promise as fungicide due to their high activity and low toxicity.

The systematic investigation of organotin compounds was first carried out by the T.N.O. group (Institute for Organic Chemistry, Utrecht, Netherlands), under the guidance of Van der Kerk, Luijten and others. The pioneering works of the TNO group have established the profound importance of organotin compounds as biocidal agents and consequently for their commercial uses.

In a systematic study of organotin compounds of the following types, R_4Sn, R_3SnX, R_2SnX_2 and $RSnX_3$ (R = alkyl/aryl group, X = anions), they observed that R_3SnX compounds are exceptionally fungitoxic.

Table - 1

Minimum Inhibitory concentrations of organotin compounds to Aspergillus niger (3)

Type of compound	R = Ethyl	R = Butyl	R = phenyl
R_4Sn	> 500	> 500	> 500
R_3SnX	2	1	0.5
R_2SnX_2	> 500	> 500	> 500
$RSnX_3$	> 500	> 500	> 500

Concentration in μg/ml

They also observed that the variation of anion had only a minor influence on triorganotin compounds. From subsequent examinations of a series of tri-n alkyltin acetates, they showed the profound influence of the length of alkyl chains against a number of fungi. The most active compound in the series of tri-n-alkyl tin acetates was tri-n-propyl and tri-n-butyl tin acetates. These inhibited the growth of A. niger at concentrations of 1 μg/l or even less(3).

Experiments by TNO group with unsymmetrical trialkyl tin acetates i.e. compounds in which tin has different alkyl groups reveal that the activity depend on the nature of individual group but on the total number of carbon atoms in the three groups. Vander Kerk and Luijten (4) showed that diethyl butyl-, dimethyl hexyl-, diethyl octyl-, dimethyl octyl and dimethyl decyl tin acetate as well as ethyl dipentyl tin acetate all exhibited the same order of activity as triethyl tin acetate but less active than tributyl tin acetate. They concluded from their investigations that the maximum activity among the trialkyl tin acetate is associated with a total number of 9 to 12 carbon atoms regardless the nature of individual groups. But a similar rule does not apply in case of mixed aliphatic - aromatic compounds (5).

The antifungal activity in most cases diminished by the introduction of functional groups into organotin compounds (6). Thus $[(CH_3)_2ClCH_2]SnCl$ has the same antifungal activity as trimethyl tin chloride but $(n\text{-}C_3H_7)_2\ (CN.CH_2CH_2CH_2)SnO.CO.CH_3$ and

$(nC_3H_7)_2(CH_3OCOCH_2CH_2)SnBr$ are far less active than tri-n-propyl tin acetate; $(NaOCOCH_2CH_2)_3SnOH$ is inactive even at 100 μg/ml. Thus the introduction of hydrophilic groups appears to diminish the activity (7).

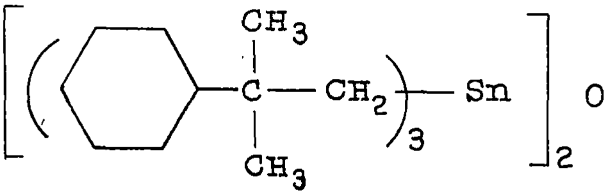
In spite of careful screening, no active compound was ever found among the types R_4Sn, R_2SnX_2 and $RSnX_3$ except the activity of diphenyl tin dichloride (8), although there are some unsubstantiated claims (9-11). The so called activity of R_4Sn type of compounds is due to some R_3Sn type impurities or due to cleavage of one R group from R_4Sn type compound under experimental conditions (6).

Klotzer in an East German Patent (10) claimed that monobutyl tin tri-acetate at 0.01% concentration is as effective as 0.1% tributyl tin oxide fungicides. He also claimed in another patent (11) that mono butyl tin triformate or monophenyl tin triformate have no phytotoxicity and monobutyl tin compounds are effective against phytopthora infestans etc.

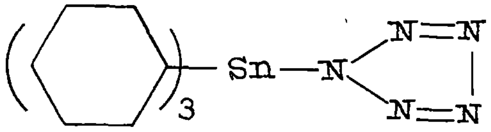
In spite of such claims, it is generally accepted that mono organotin compounds do not have any appreciable fungicidal properties. Very recently, however, it has been found by the TNO group that a stannatrane $PhSn(OCH_2CH_2)_3N$ have some remarkable and unusual antifungal activity (12). Besides the TNO group, Baumann (13) and Hartel (14) have carried out independent research on simple alkyl and aryl tin compounds with practical aim. These works cultiminated into the development of the first organotin fungicide for agricultural purposes based on triphenyl tin acetate ('Brestan' - A.G. Hoechst). Other workers extended these results varying the anionic part of R_3SnX compounds (15,16,17). Shortly after the introduction of 'Brestan', Philips Duphar introduced fentin hydroxide (called also Du - Ter) with active ingredient of triphenyl tin hydroxide having similar spectrum of disease control (18). 'Brestan' and 'Du - Ter' were recommended for the control of phytophthora infestans (late blight) on potatoes and cercospora beticola on sugar beets at the rate of few grams per acre.

At present in U.S.A., 'Du-Ter' is registered for controlling fungi on potatoes, sugar beets, peanuts, pecans etc (18). These compounds are highly effective protectant fungicides against almost the same range of fungi as copper fungicides but less than one-tenth the dosage (19). Organotin compounds can also be used for the control of leaf spot on celery, blast and algal control on rice. Recently organotin fungicides are being used to control coffee leaf rust and also as antifeedant for the giant looper caterpillar in Kenya. It is expected that the use of organotin fungicides will be greatly extended in the control of more fungal diseases in near future (20).

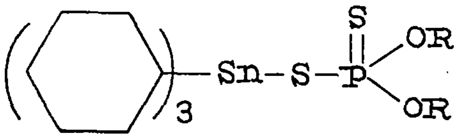
Next important breakthrough in the field of pesticides, came through the discovery of tricyclohexyl tin hydroxide in 1963 as a joint research effort of M.T. Chemicals and Dow Chemical Co. of U.S.A. Tricyclohexyl tin hydroxide has been introduced in the market under the trade name of Plictran for controlling the phytophagous (plant feeding) mites on apples and pears, citrus, stone fruit, hop, tea, vegetable etc (21). Organotin miticides have little toxicity towards honey bees and it also shows the antifeedant activity against some insects larvae (22). There are now three other organotin miticides of following types.



I. VENDEX (SHELL)



II. PEROPAL (BAYER, CHEMAGRO)



III. R-28627 (STAUFFER)

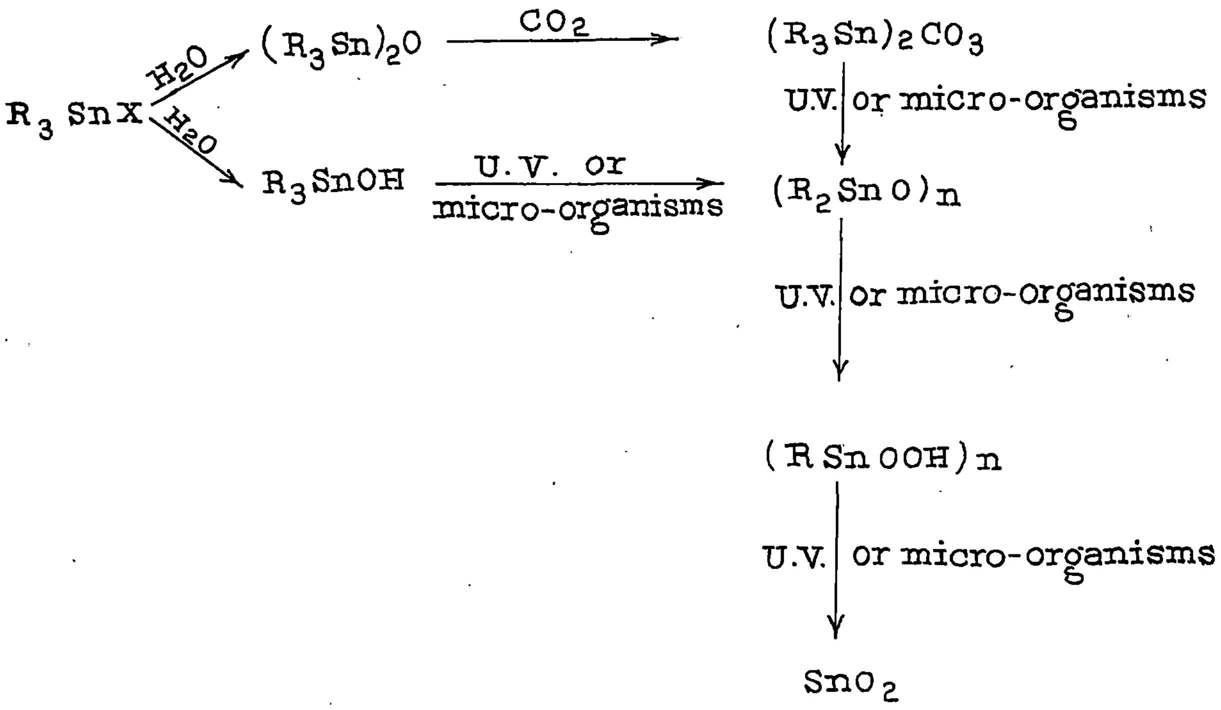
Regarding the phytotoxicity, these miticides are well tolerated by crops which normally require an acaricide to protect them except the hop plant. Apples, grape, tomato, bean, cabbage and cotton plants all showed good tolerance to 'Peropal' (23).

Chemicals are important tools in modern crop protection and the search of suitable compounds has been primarily directed towards finding those which can rapidly eliminate most of the pest population on the crop. Since late 1940, organo chlorines and subsequently organophosphorus compounds were being used. Recently however, these pesticides, particularly organochlorines have come under severe criticism on the following grounds (24). These compounds have a broad spectrum of activity, which means that beneficial and non target pests may also be adversely affected. It has been found that spraying a crop with such compounds have resulted in a subsequent outbreak of target pest far worse than before because the pest's natural enemies have also been killed. An added problem with such pesticides is that many of those are persistent in environment and can remain toxic for a long time before being degraded to less harmful products. More over, excessive uses of pesticides has resulted in many pest populations building up resistance to such compounds.

Problem of toxic residues from sprays of organotin compounds has been extensively investigated. Organotin compounds have a relatively short half life (3-4 days) on plant leaves in the field (25-27). The amount of organotin residues in potato tubers has been found to be less than 0.1 mg of tin per kg after the foliage were repeatedly sprayed with Brestan (28). When the cows are fed with sugar beet leaves, which were extensively sprayed with Brestan, very little amount of triphenyl tin acetate ingested is found in the milk (about 4 $\mu g/ml$) (29).

Organotin pesticides, that are in current use do not considerably accumulate in the soil with successive applications. They are metabolised readily in animals and soils to inorganic tin compounds which are not taken up by the plants (27). It was also found that 'Plictran' was sprayed in three different locations during a period of three years, building up of its residue in the upper six inches of the soil was negligible (19).

In view of the very large number of growing industrial and agricultural applications, the knowledge of environmental breakdown pattern of organotin compounds, has been investigated to ensure their continued safe use. A generalised degradation scheme for the tributyl and triphenyl tin derivatives, which is probably applicable to other organotins is proposed by Sheldon (30).



Fish and his co-workers (31-32) have shown that tributyltins are metabolised under *in vitro* and *in vivo* conditions in mammals to di-and mono butyl tins via carbon hydroxylated intermediates. Fungal degradation of T.B.T.O. to di-and mono butyl tins by

Coniophora Cerebella and *Polystictus Varsicolor* has also been reported recently (33).

Unlike mercury compounds, there is no evidence of methylation of organotins under environmental conditions (34) . From the above discussions it may be concluded that organotin pesticides can probably answer different problems posed by organo chlorine and organophosphorus compounds about environmental hazards. More over, organotins have remarkable anti feedant activities (24) and have also chemosterillant activity (29) and no major field resistances of pests have so far been reported (18). Evidently for such reasons, some triorganotin compounds have been cleared by World Health Organisation as safe agricultural pesticides.

The lower trialkyltin compounds are able to inhibit mitochondrial oxidative phosphorylation (34) and it has been suggested by Zuckerman (34) that their remarkable biological activity pattern may be dependent upon the effectiveness of their interaction at an active site or sites which involves co-ordination to certain amino acids. Smith (34) considering available data on most probable binding sites for the organotins on proteins, concluded that binding is effected via the HS and imidazole NH groups of the proteins.

$$R_3SnX + \left\{ \begin{matrix} HS \\ HN \end{matrix} \right. \longrightarrow \left\{ \begin{matrix} R_3SnS- \\ R_3SnN- \end{matrix} \right. + \quad HX$$

The published reports generally confirm the initial observation of relative non importance on the nature of the anionic part of triorganotins. Poller (35) has reported that once the R_3Sn^+ group gets to the site of biochemical reaction i.e. at cell mitochondria, it may not matter what the anionic part is but the latter can significantly influence the transporation of the biocide to the reaction site. He prepared a few sucrose derivatives which show better fungicidal activities against some paint destroying fungi, although their tin content is much smaller than the commercial fungicides. Several workers have found considerably lower activity of some organotin chelated compounds (36-37). Therefore, it appears that the activity of trisubstituted organotin compounds (R_3SnX) may be somewhat dependent on the nature of X group, particularly when the X group is a ligand which can form intramolecularly chelated complex.

Srivastava reported that diphenyl tin dichloride is the most active fungitoxic agent against colletotrichum falcatum among diaryltin dichlorides and their activities on complexation with 2,2'-bipyridyl and 1:10 phenanthroline are slightly increased (38).

Recently Smith et al (39) reported that organotin pyridine-2-carboxylates and substituted riazine derivatives (100 ppm/ml) can control coffee leaf rust and coffee bacterial blight diseases in vitro. But so far not much work has been done about the fungitoxic activities of organotin co-ordination compounds.

In order to study the effect of co-ordination on Ph_3Sn^+ moieties by ligands like diphenyl carbazone, we studied some preliminary fungicidal properties of Triphenyl tin diphenyl carbazonate against some selected fungi under the present investigation.

EXPERIMENTAL

Materials and methods

1. Compounds: Diphenyl carbazone, bis-triphenyl tin oxide and triphenyl tin diphenyl carbazonates, used for the present investigation have already been described.

2. Organisms:

   a) *Helminthosporium oryzae* Breeda de Haan-Causal organism of brown leaf spot disease of rice.

   b) *Verticillium albo-atrum* Reinke and Berthhold - Causal organism of stalk rot disease of banana.

   c) *Aspergillus niger* Van Teigh - Store fungus of rice grains.

   d) *Penicillium jenseni* - Žaleski-Store fungus of rice grains.

3. Culture media - Liquid medium (malt solution) was prepared by the following method. 40g of malt extract (Difco) was boiled in water till dissolution took place. The volume of the solution was then made up to 1 litre by addition of water. pH of the solution was adjusted with sodium hydroxide to 6.5. Malt solution was then sterilized at 15 p.s.i. pressure for 20 minutes in an autoclave.

4. Antifungal activities of compounds:
   (*in vitro*)

Antifungal activities of the compounds were tested following the conidial germination inhibition studies described as follows by using slide germination technique (40). Acetone solution of the compound was diluted by sterile water in order to get the required amount of compound in water suspension. Conidial suspension of the fungus was prepared by flooding the surface of 12 to 15 days old culture with 10 ml sterile water, for *A. niger* and *P. jenseni* sterile 0.01% agar solution was used as wetting agent in place of sterile water. Density of the conidial suspension was determined in a haemocytometer and the concentration was adjusted to 5 x 10^5/ml. Slides having conidia in compound suspension and malt solution were incubated at $30 \pm 1^{o}C$ and observation of the conidial germination were made after 24 and 48 hours. Three replications of each concentration of the compound were maintained. A total number of 300 conidia from three replications were counted and percent inhibition of conidial germination was calculated against appropriate control.

5. Determination of ED$_{50}$ and ED$_{95}$

The ED$_{50}$ [effective dose for 50% inhibition] and ED$_{95}$ values (μg/ml) were calculated by least square regression analysis using a computor (D.C.M. - Spectra m-1). Regression analysis was done only when there were at least three relevant values.

Table - 2

Effect of diphenyl carbazone on conidial germination of *Helminthosporium oryzae*

Concentration ($\mu g/ml$)	Percentage of inhibition over control after 24 hours	48 hours
500.00	0.00	0.00
250.00	0.00	0.00
125.00	0.00	0.00
100.00	0.00	0.00
50.00	0.00	0.00
25.00	0.00	0.00

Table - 3

Effect of bis-(triphenyltin) oxide on conidial germination of *Helminthosporium oryzae*

Concentration µg/ml	Percentage of inhibition over control after	
	24 hours	48 hours
12.50	100.00	100.00
6.25	100.00	100.00
5.00	100.00	94.00
2.50	80.00*	69.00*
1.25	61.00*	47.00*
0.50	41.00*	20.00*
0.25	30.00*	07.00
0.13	01.00	00.00
ED_{50}	0.69 µg/ml	1.35 µg/ml
ED_{95}	5.46 µg/ml	5.95 "
Regression constant	$Y = mx + c$	
m	50.0	40.8
c	58.1	69.0
γ	0.994	0.999

* Data have been used for regression analysis.

Table -4

Effect of triphenyl tin diphenyl carbazonate on conidial germination of *Helminthosporium oryzae*

Concentration (μg/ml)	Percentage of inhibition over control after 24 hours	48 hours
12.50	100.00	100.00
6.25	81.00*	77.00*
5.00	76.00*	66.00*
2.50	51.00*	40.00*
1.25	24.00*	16.00*
0.50	03.00	00.00
0.25	00.00	00.00
0.13	00.00	00.00
ED_{50}	2.52 μg/ml	3.23 μg/ml
ED_{95}	8.81 μg/ml	10.74 μg/ml
Regression constants $Y = mx + c$		
m	82.60	86.31
c	16.87	6.01
γ	0.998	0.998

* Data have been used for regression analysis.

Table - 5

Effect of diphenyl carbazone on conidial germination of *Verticillium albo-atrum*.

Concentration (µg/ml)	Percentage of inhibition over control after	
	24 hours	48 hours
500.00	07.00	00.00
250.00	01.00	00.00
125.00	00.00	00.00
50.00	00.00	00.00
25.00	00.00	00.00

Table - 6

Effect of bis-(triphenyltin) oxide on conidial germination of *Verticillium albo-atrum*

Concentration ($\mu g/ml$)	Percentage of inhibition over control after	
	24 hours	48 hours
5.0	100.00	100.00
2.5	100.00	96.00
1.25	98.00	69.00*
0.50	77.00*	47.00*
0.25	56.00*	30.00*
0.13	40.00*	13.00*
ED_{50}	0.19 $\mu g/ml$	0.57 $\mu g/ml$
ED_{95}	1.01 $\mu g/ml$	3.62 $\mu g/ml$
Regression constant $Y = mx + c$		
m	61.45	56.01
c	94.66	63.68
γ	0.996	0.999

* Data have been used for regression analysis.

Table - 7

Effect of triphenyl tin diphenyl carbazonate on conidial germination of *Verticillium albo-atrum*

Concentration (μg/ml)	Percentage of inhibition over control after	
	24 hours	48 hours
12.50	100.00	100.00
6.25	100.00	98.00
5.00	100.00	93.00
2.50	97.00	80.00*
1.25	80.00*	55.00*
0.50	55.00*	31.00*
0.25	41.00*	13.00*
0.13	19.00*	3.00
ED_{50}	0.39 μg/ml	0.95 μg/ml
ED_{95}	2.22 μg/ml	4.55 μg/ml
Regression constant	$y = mx + c$	
m	59.68	66.09
c	74.25	51.50
γ	0.997	0.996

* Data have been used for regression analysis.

Table - 8

Effect of diphenyl carbazone on conidial germination of *Aspergillus niger*.

Concentration (μg/ml)	Percentage of inhibition over control after	
	24 hours	48 hours
500.00	3.00	0.00
250.00	0.00	0.00
125.00	0.00	0.00
100.00	0.00	0.00
50.00	0.00	0.00
25.00	0.00	0.00

Table - 9

Effect of bis-(triphenyl tin) oxide on conidial germination of *Aspergillus niger*

Concentration (µg/ml)	Percentage of inhibition over control after	
	24 hours	48 hours
6.25	100.00	100.00
5.00	100.00	97.00
2.50	100.00	78.00*
1.25	100.00	60.00*
0.50	99.00	30.00*
0.13	08.00	00.00
ED_{50}	$<$ 0.50 µg/ml	0.94 µg/ml
ED_{95}	$<$ 0.50 µg/ml	4.32 µg/ml
Regression constant $Y = mx + c$		
m		68.14
c		51.71
γ		0.999

* Data have been used for regression analysis.

Table - 10

Effect of triphenyl tin diphenyl carbazonate on conidial germination of *Aspergillus niger*.

Concentration (µg/ml)	Percentage of inhibition over control after	
	24 hours	48 hours
12.50	100.00	100.00
6.25	100.00	95.00*
5.00	97.00	85.00*
2.50	89.00*	62.00*
1.25	63.00*	38.00*
0.50	33.00*	16.00*
0.25	15.00*	7.00
ED_{50}	0.79 µg/ml	1.62 µg/ml
ED_{95}	3.19 µg/ml	6.80 µg/ml
Regression constant	$Y = mx + c$	
m	74.15	72.27
c	57.58	34.80
γ	0.997	0.996

* Data have been used for regression analysis.

Table - 11

Effect of diphenyl carbazone on conidial germination of penicillium jenseni

Concentration (µg/ml)	Percentage of inhibition over control after	
	24 hours	48 hours
500.00	7.00	0.00
250.00	0.00	0.00
125.00	0.00	0.00
100.00	0.00	0.00
50.00	0.00	0.00
25.00	0.00	0.00

Table - 12

Effect of bis-(triphenyl tin) oxide on conidial germination of *Penicillium jenseni*

Concentration (μg/ml)	Percentage of inhibition over control after	
	24 hours	48 hours
2.5	100.00	100.00
1.25	100.00	94.00
0.50	74.00	51.00
0.25	42.00	24.00
0.13	08.00	04.00
ED_{50}	$<$ 0.50 μg/ml	$<$ 0.50 μg/ml
ED_{95}	$<$ 1.25 μg/ml	$<$ 2.5 μg/ml

Table - 13

Effect of triphenyl tin diphenyl carbazonate on conidial germination of *Penicillium jenseni*

Concentration (μg/ml)	Percentage of inhibition over control after	
	24 hours	48 hours
6.25	100.00	100.00
5.00	100.00	98.00
2.50	98.00	87.00*
1.25	69.00*	61.00*
0.50	38.00*	29.00*
0.25	19.00*	09.00
0.13	04.00	00.00
ED_{50}	0.70 μg/ml	0.88 μg/ml
ED_{95}	2.94 μg/ml	3.29 μg/ml
Regression constant	$y = mx + c$	
m	71.86	78.33
c	61.31	54.30
γ	0.998	0.998

* Data have been used for regression analysis.

Results

H. Oryzae

Results from 1-3 show that diphenyl carbazone is totally ineffective to inhibit the conidial germination of *H. oryzae* even at a concentration of 500 μg/ml. Bis-triphenyl tin oxide is more effective than triphenyl tin diphenyl carbazonate. The ED$_{95}$ values for bis-triphenyl oxide was 5.95 μg/ml whereas the ED$_{95}$ values for triphenyl tin diphenyl carbazonate was 10.74 μg/ml for 48 hours of incubation.

V. albo-atrum

From the results obtained in tables 4-6, it was found that diphenyl carbazone has no antifungal properties against *V. albo-atrum* even at a concentration of 500 μg/ml after 48 hours. At this concentration only 8% inhibition was observed after 24 hours. Bis-triphenyl tin oxide was found to be highly effective for inhibition of conidial germination of *V. alob-atrum* [ED$_{95}$ = 3.62 μg/ml], whereas the corresponding ED$_{95}$ value for triphenyl tin diphenyl carbazonate was found to be 4.55 μg/ml (48 hours incubation).

A. niger

Tables 7-9 indicate that diphenyl carbazone has no activity against *A. niger* even at a concentration of 500 μg/ml after 48 hours. For 48 hours, $(Ph_3Sn)_2O$ has ED$_{95}$ of 4.32 μg/ml.

The corresponding ED_{95} value for triphenyl tin diphenyl carbazonate is 6.808 μg/ml.

P. jenseni

Table 10-12 show that diphenyl carbazone even at a concentration of 500 μg/ml has no antifungal activity after 48 hours incubation of conidial germination of P. jenseni. But bis triphenyl tin oxide is highly active and the ED_{95} value is just little over 1.25 μg/ml. The corresponding ED_{95} value for triphenyl tin diphenyl carbazonate was found to be 3.289 μg/ml.

Discussion

Examining the data obtained from conidial germination inhibition studies, the triorganotin diphenyl carbazonate has comparable fungicidal properties with corresponding bis-triphenyl tin oxide. The ED_{95} values show that the activity of triorganotin diphenyl carbazonates has been reduced some what. But it should be borne in mind that the percentage of tin in bis-triphenyl tin oxide is approximately 33% whereas the percentage of tin in triphenyl tin diphenyl carbazonate is approximately 22%. Hence on basis of total tin content of the above organotins, we may conclude that triphenyl tin diphenyl carbazonate has not very reduced activity as compared to bis-triphenyltin oxide. The co-ordinating ligand diphenyl carbazone has practically no fungitoxic properties even at a concentration of 500 μg/ml. It has been reported (34) by some workers, that some intramolecularly chelated compounds is approximately 8 times less toxic in their biologically activity. The lesser activity of such compound may be due to a reduced tendency to attack the active sites of the protein because of its internally co-ordinating nature, since the activity of triorganotin compounds depend on the formation of co-ordinated complexes with proteins of the cell mitochondria. As the triphenyl tin diphenyl carbazonate is already strongly chelated entity, it might have much reduced tendency to co-ordinate with the protein sites of the mitochondria, unless rapid exchanges of ligands take place with the facile formation of triphenyl tin amino acid complexes. At the present stage of our knowledge, the idea of ligand exchange may be purely a conjecture though we cannot possibly over ride such a possibility. Alternatively, we may assume that at the dilution used for such fungitoxicity tests, triphenyl tin diphenyl carbazonate may be converted to bis-triphenyl tin oxide, which will then possibly react with proteins of cell mitochondria of the fungi. The ED_{95} values obtained for the bis-triphenyl tin oxide and triphenyl tin diphenyl carbazonate are quite satisfactory for such a possibility. But it may be mentioned here that investigations carried out in our laboratory have shown the following ED_{95} values of certain organotins for inhibition of conidial germination of V. albo-atrum and certain other fungi.

Table -14

Compounds	ED$_{95}$ values 9 µg/ml)
Bis-(triphenyl tin) oxalyl bis-N-P-tolyl hydroxamate	3.44
Triphenyl tin dithizonate	4.20
Bis-(triphenyl tin) oxide	3.62
Tributyl tin diphenyl carbazonate	5.65
Tributyl tin acetate	6.21
Tripropyl tin diphenyl carbazonate	107.15

From the above data, we can observe that the activities of tributyl tin diphenyl carbazonate and tripropyl tin diphenyl carbazonate are widely different. If we consider that the organo-tin co-ordination compounds suffer hydrolysis prior to their reaction with cell mitochondria, then we would expect that tripropyl and tributyl tin diphenyl carbazonates should have at least equivalent fungitoxicities. Since the tripropyl tin compounds have equivalent if not better fungitoxic properties than tributyl tin compounds. Moreover from the above data tributyl tin diphenyl carbazonate has better activity than tributyl tin acetate showing clearly that the co-ordination has not only reduced the activity of organotins but in fact it has enhanced the activity marginally. Considering above data, we may suggest that the marginally better fungitoxicities of organotin co-ordination compound may be due to some synergetic effect of the ligand moiety as diphenyl carbazone has practically no fungitoxic properties. Hence, under the present stage of our knowledge, we are at present not in a position to conclude any definite conclusion, whether co-ordination of ligand would definitely enhance or reduce the activity of organotins.

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