A BRIEF DISCUSSION ON THE NATURE OF BONDING IN ORGANOTIN COMPOUNDS.

Introduction:

According to the definition of Gilman et al (1) an organotin compound must contain a carbon-tin bond. Assuming that there are no naturally occuring organotin compounds, the first such compound was reported by Lewig (2) in 1852, the product being formed by the action of a sodium-tin alloy upon ethyl iodide. Frankland (3) in 1853 revealed his work going back to 1849 on the reaction between tin and ethyl iodide and characterised as diethyltin diiodide. Many significant contributions were made in this field during the next few decades.

A number of reviews on this area have been published. One such thorough review work covering the literature upto about 1935 is that of Krause and Von Grosse (4). Ingham, Rosenberg and Gilman(1) extended the literature through 1959. An exhaustive list of organotin compounds was compiled by Weiss (5) covering the literature from 1937 to 1964. From 1964, the literature of organotin chemistry is being published in annual surveys (6-15). The tin-annual survey covering the year 1974 had been published (16). Another review of organo derivatives of tin and lead with 464 references has been published by Harrison (17). Apart from these review articles several valuable books have recently been published (18-21).

Bonding in Organotin Compounds:

The electronic configuration (22) of tin ($[Kr]4d^{10}5s^{2}5p^{2}$) in the ground state is a ^{3}P state with two unpaired electrons in the

p sub-shell available for bonding resulting in a two covalent tin. The tin (II) chemistry has been reviewed by Donaldson (23). The common four-covalent state of tin is derived from the sp^3 hybridization for the element and the great majority of organotin compounds possess a tetravalent tin atom. The marked increase in stabilities of R_4Sn compounds over R_2Sn types demonstrate the effect of increased hybridization.

It is expected that the presence of the lone pair ($5p^2$) in the low oxidation state [Sn(II)] would result in lower coordination numbers compared to the higher oxidation state of the element [Sn(IV)]. But there is no definite correlation between valency state and the maximum co-ordination number. Tin (IV) can show co-ordination number greater than four and Okawara et al (25-26) have reviewed the structures of organotin compounds that display a co-ordination number greater than four. In the present discussions, only the organic compounds of tetravalent tin would be considered.

The covalent radius of tin atom is 1.40Å and is independent of the nature of the ligands. Only when there is an accumulation of strongly negative ligands around the tin atom there is some decrease in bond lengths. Thus, the bonding of tin appears to be almost entirely covalent in these compounds at least in crystalline solids, in non-polar media and in the vapour state. However, the electronegativity of tin is less than that of the most common ligands, e.g. carbon, nitrogen, oxygen, halogen and even hydrogen and hence the bonds are expected to be sufficiently polar. Closely connected with

this is the inductive effect which tin atoms or stannyl groups exert on their surroundings. The bond polarization $C^{\delta-} \rightarrow Sn^{\delta+}$, which is there in principle, may be changed by substitution at carbon as well as at tin. N.M.R. data on organotin compounds (27-29) also emphasise this. According to Eaborn et al (29) polarization is increased by electron donor substituents in the para-position of a phenyl group bonded to tin.

There are many controversies (30-40) about the existence of the π-character of the bond formed between tin and other elements. According to West (30) and Drago et al (31) there may be some π-character in a bond between tin and an element possessing p electrons. Thus in a Sn - X bond where X is $C(sp^2)$, N, O, S or halogens, it is possible that, opposing the inductive electron drift in Sn-X, there may be some overlap between a filled p-orbital on X and an empty 5d orbital on tin causing a transfer of electron density in the opposite direction. NMR (32-33), infrared (34), ultraviolet (35) and dipole moment data (33) of phenyltin compounds and the acid strengths of the substituted benzoic acids, $p\text{-}Me_3M\text{-}C_6H_4COOH$ (M = C, Si, Ge, Sn), give some evidence of interaction between the electrons of the phenyl groups and the 5d orbitals of tin in these compounds. Anderson et al (36) have shown that there is no $d\pi - p\pi$ bonding in the tin-pyridine linkage. Evidences of $d\pi - p\pi$ interaction between tin and certain transition metals are also available (37-38). That $d\pi - p\pi$ bonding is operative in

evidenced for the higher values of Sn-Cl stretching frequency in certain tin compounds (39) and Sn-O frequency in $(Ph_3Sn)_2O$ (40).

Comparison of the catenation properties among the group IVA elements has revealed that there is a decrease in the tendency to catenation in the order C $\ggg$ Si $>$ Ge $\approx$ Sn $\ggg$ Pb. This general, if not smooth, decrease in the tendency to catenation may be ascribed to diminished strength of the C-C, Si-Si, Ge-Ge, Sn-Sn and Pb-Pb bonds, which are approximately 83, 42, 40 and 37 K.Cal./mole for C-C, Si-Si, Ge-Ge and Sn-Sn bonds respectively (34).

A SHORT REVIEW ON THE METHODS OF PREPARATION, PROPERTIES AND SOME STRUCTURAL ASPECTS OF ORGANOTIN COMPLEX COMPOUNDS.

Prior to the discussion on scopes, objectives and experimental results of the present investigations, it will certainly be most appropriate to have a brief review of the methods of preparations, properties and some structural aspects of organotin (IV) Complex Compounds.

Organotin Adducts:

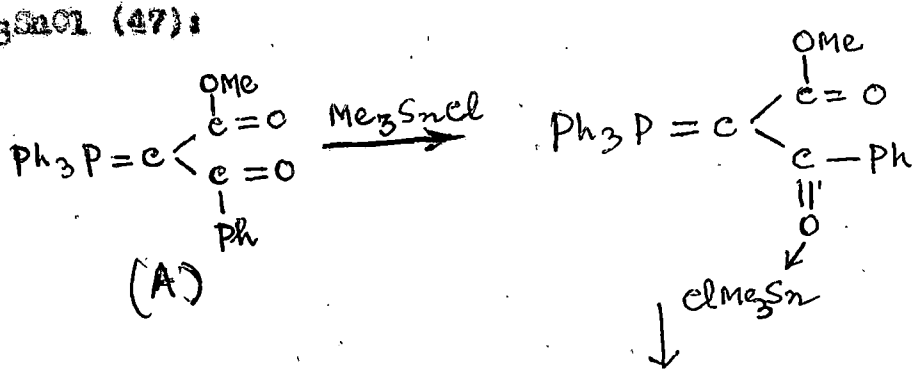
Organotin compounds which can act as Lewis acids react with certain electron-pair donors i.e. Lewis bases to form addition compounds. In many cases unstable and less-defined organotin compounds have been characterized through the formation of their stable crystalline adducts. All the three types of organo (mono-, di-, and tri-) tin compounds can form adducts with mono-, di- and polydentate ligands, of which halides have been extensively studied. And, as expected, the ability of the organotin halides to form adducts increases in the series $R_3SnX < R_2SnX_2 < RSnX_3$. Generally, the adducts with a monodentate ligand have compositions $R_3SnX.L$, $R_2SnX_2.L_2$ and $RSnX_3.2L$.

1:1 Complexes of hexamethylphosphoric triamide (HMPA) with Ph_3SnX (X = Cl, Br, I, NO_3, CN) have been prepared (41-42), the general reaction being

$$Ph_3SnX + HMPA \xrightarrow[\text{or pet-ether}]{\text{in } CHCl_3} Ph_3SnX.HMPA$$

Kumar Rao (43) has prepared complexes of the type $R_3SnX.L$ (where R = Me, Ph; X = Cl, NO_3 and L = HMPA, OPO, OAsO, DMSO, Phen). However he was not able to prepare the 1:2 adduct of Ph_3SnNO_3 with DMSO as reported earlier (44).

$Me_3SnCl.Py$ (Py = pyridine) was precipitated when Me_3SnCl and pyridine were mixed in pet-ether (40-60°) (45). Similarly with bipyridyl, $Me_3SnX.bipy$ (where X = Cl, Br, I) adducts were obtained (46). The complex $Me_3SnCl.OPPh_3$ was reported to be formed during an attempted complex formation between the disubstituted ylid (A) and Me_3SnCl (47):



$$Me_3SnCl.OPPh_3 + PhC\equiv CCO_2Me$$

The complexations of trimethyltin halides in donor solvents e.g. acetone, dioxan, DMF, pyridine, DMF, DMSO, HMPT and tetramethylethylenediamine have been studied by means of ^1H N.M.R. spectroscopy and equilibrium constants evaluated for the $Me_3SnX.L_n$ complexes (43). Reaction of the $Ph_3SnCl.HMPA$ complex with I^- and N_3^- gives the corresponding $Ph_3SnX.HMPA$ (X = I, N_3) complexes (41). The $Ph_3SnNO_3.L$ (L = HMPA, DMSO and Phen) complexes appear to be relatively good electrolytes in absolute alcohol, suggesting the nitrate moiety to be only weakly coordinated to tin. Evidence for

coordinated nitrate groups in these complexes comes from I.R. data and these three complexes have been suggested to be penta-coordinated from the Mossbauer spectra (43). The $Me_3SnX.bipy$ complexes are very unstable, loosing the tin halide quantitatively on exposure to air. These are easily soluble in organic solvents (46).

Smith and Liengme (49) reported the formation of 1:1 complexes of triorganotin chlorides and thiocyanates with tridentate chelating agents 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 complexes isolated were: $(CH_3)_3SnCl.L$; $(C_6H_5)_3SnCl.L$ (L = I and II) and $(C_6H_5)_3Sn(NCS).L$ (L = I). These complexes are stable crystalline solids which behave as non-electrolytes in nitrobenzene.

With diorganotin dihalides pyridine, bipyridyl, phenanthroline and terpyridyl form adducts which vary in composition. Thus, the isolated complexes have the compositions: $Me_2SnCl_2.2Py$ and $Me_2SnCl_2.Phen$ (45,56), $Me_2SnX_2.bipy$ (45-46) (X = Cl, Br, I), $2R_2SnX_2.$ Terpy (46) (R = Me, Ph; X = Cl, Br, I). These complexes were precipitated quantitatively from pet-ether or benzene by mixing the required reactants. $R_2SnCl_2.2$ (p-Tolyl)$_2SO$ (where R = Me or Ph) and $R_2SnX_2.L$ (L = $Bipy O_2$, OPO, $diphos O_2$, OAsO, R = Me, Ph) complexes have also been reported (43). With dimethyl formamide (DMF), Ar_2SnX_2 formed complexes of the type $Ar_2SnX_2.2DMF$ (Ar = Ph, o-, p-tolyl, benzyl and X = Cl, Br, I). These were prepared by mixing the reactants

in any molar ratios (51). The interaction of the $2Ar_2SnCl_2.2DMF$ with other Lewis bases stronger than DMF such as 1,10-phenanthroline, 2,2'-bipyridine, DMSO and N, N-dimethylacetamide resulted in complete substitution of the ligand verifying the weak donor ability of the DMF compared to the ligands examined (51). Mention may also be made of the adducts: $Me_2SnCl_2.(Ph_3PO)_2$(54) and $Bu_2SnX_2.Phen$ (55).

By the direct interaction of diarylthn dichlorides in acetonitrile with mono-, di-and tri-ethanolamines adducts of the general formula $ArSnCl_2.nL$ (where Ar = Ph, O-, m-, p-tolyl; n = 1 for MEA and DEA, and n = 2 for TEA) have been isolated by Srivastava et al (50). All these complexes are white crystalline solids with thermal stability and inert to atmosphere. A Cis-aryl-trans-halogen arrangement about octahedral tin has been suggested. Both MEA and DEA function as bidentate ligands, bonding through both oxygen and nitrogen atoms while TEA acts as a unidentate ligand via the oxygen atom. Jeura et al (57) have prepared compounds of the type $R_2SnCl_2.L$ (where R = Me, Et, n-Pr, n-Bu, benzyl and L = bipyridyl and phenanthroline) by precipitating the bipyridyl adducts in pet-ether and phenanthroline adducts in the carbon disulfide. These adducts were non-electrolytes in nitrobenzene. An octahedral arrangement with Cis- chlorine atoms around tin has been indicated.

A number of butyltin trichloride adducts with different Lewis bases have been prepared by Davies et al (53). These complexes were

$BuSnCl_3.2L$ (L = Ph_3PO, DMA, Py, DMSO, DyO). Bipyridyl (59) and phenanthroline (60) complexes e.g. $BuSnCl_3$.bipy and $BuSnCl_3$.Phen have also been reported. Adducts (1:1) have also been reported(46) to be formed from $MeSnX_3$ (X = Br, I) and bipyridyl. But terpyridyl complexes reported (46) are of variable compositions e.g. $3BuSnCl_3$. 2 Terpy, $MeSnBr_3$.Terpy, $MeSnI_3$.Terpy. Clark et al (61) have reported some 1:1 adducts of $RSnX_3$ (R = Me, Et, Bu, and X = Br, I) with phenanthroline and bipyridyl. These were prepared by mixing approximately equimolecular benzene solutions of the reactants whereas $MeSnCl_3$. 2 Py, $MeSnCl_3$.bipy and $MeSnCl_3$.Phen have been precipitated by mixing the reactants in CCl_4 (for Py and bipy) and CO_2 (for Phen) (43). In some cases these compounds have been suggested to be octa-coordinated.

Organotin Oxinates:

Organotin derivatives of 8-hydroxyquinoline (oxine) have extensively been studied. They are stable, well defined compounds which have given a great impetus in the studies of organotin complex compounds. These organotin oxinates are principally of the types $R_3Sn(Ox)$, $R_2Sn(Ox)_2$, $R_2Sn(Ox)X$, $RSn(Ox)_2X$ and $RSn(Ox)_3$, where R = organic group, OxH = 8-hydroxyquinoline and X = halogen or isothiocyanate.

The simple organotin oxinates viz., $R_3Sn(Ox)$, $R_2Sn(Ox)_2$ and $RSn(Ox)_3$ have been generally prepared by the reaction of corresponding organotin halides with oxine (39,62-63).

$$Me_2SnCl_2 + 4HOx \longrightarrow Me_2Sn(Ox)_2 + 2HOx.HCl,$$

organotin halides with sodium oxinate (26,64)

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

and organotin oxides with oxine (64-65)

$$(Ph_3Sn)_2O + 2HOx \longrightarrow 2Ph_3SnOx + H_2O.$$

Diorganotin bis oxinates can also be prepared by the condensation of Tl(I)- Oxinate and diorganotin dichloride (39):

$$2Tl(Ox) + R_2SnCl_2 \longrightarrow R_2Sn(Ox)_2 + 2TlCl.$$

Bis(pentafluorophenyl)tin bis oxinate has been prepared from a mixture of tetrakis (pentafluorophenyl)tin or tris(pentafluorophenyl)tin chloride and an excess of oxine in ethanol under reflux (72). Triorganotin oxinates have also been prepared by reacting triorganotin chloride with a mixture of oxine and sodium methoxide(70)

$$R_3SnCl + NaOMe + OxH \longrightarrow R_3Sn(Ox) + NaCl + MeOH$$

Diorganotin halide oxinates, $R_2Sn(Ox)X$, have been prepared by the reaction of diorganotin dihalide with oxine (67-68) or by the reaction of diorganotin dihalide and diorganotin dioxinates in benzene or absolute ethanol (68-70). Di-n-butyltin isothiocyanate oxinate has been prepared by the reaction of di-n-butyltin diisothiocyanate and di-n-butyltin dioxinate whereas diphenyltin isothiocyanate oxinate has been prepared by the displacement of chlorine from diphenyltin chloride oxinate with KCNS (71).

McGrady et al (73) have prepared dimethyltin chloride oxinate through the disproportionation of $(CH_3)_2SnCl_2$ and $(CH_3)_2Sn(Ox)_2$ in

refluxing benzene. Dialkyltin isothiocyanate oxinate and acetate oxinate have similarly been prepared (68).

Organotin halide bis-oxinates, $RSnX(Ox)_2$ (R = CH_3, n-Bu, Ph; X = Cl, Br) have been prepared by reacting organotin trihalides with oxine (1:2 mole) in ethanol followed by neutralization with aqueous ammonia or sodium acetate (70,74):

$$RSnX_3 + 2OxH \longrightarrow RSnX(Ox)_2 + 2HX$$

Roy (83) has shown that the polymer $Sn(OH)_4$ on treatment with oxine produces $PhSnCl(Ox)_2$ and $(OH)_3Sn_2(Ox)_3$. He also has prepared $PhSn(OCOCH_3)(Ox)_2$, $PhSn(OCOC_2H_5)(Ox)_2$, $PhSn(OCOCH_2Cl)(Ox)_2$ and $PhSn(OCOCF_3)(Ox)_2$ complexes.

A novel compound, $[n\text{-}C_4H_9Sn(Ox)_2]_2O$, has been prepared from n-butyltin sesquisulfide and oxine in boiling toluene (75). Okawara et al (75) have reported the preparation of methyltin trisoxinate by reacting methyltin sesquisulfide with oxine in a 1:2 molar ratio in boiling toluene for 20-30 hrs.

Butyltin isopropoxy oxinates of the formula $BuSn(OPr^i)_{3-n}(Ox)_n$ have been obtained by Mehrotra et al (80) by reacting butyltin triisopropoxide with oxine and removing isopropanol by azeotropic fractionation with refluxing benzene; the products depend upon the mole ratio of the reactants used. Thus $BuSn(Ox)_3$ has been obtained by the reaction of $BuSn(OPr^i)_3$ with oxine in 1:3 mole ratio.

Organotin derivatives of substituted oxines have also been reported. Srivastava et al (76) have prepared some diaryltin bis-oxinates/2-methyl-oxinates and diaryltin chloride oxinate/2-methyl-oxinates. The bis-oxinates have been prepared by mixing an ethanolic solution of Ar_2SnCl_2 (Ar = Ph, Bz, o-, m-, p-tolyl) with an ethanol solution of oxine in 1:2 mole ratio followed by NaOAc and aqueous ammonia. The haloxinates have been prepared by adding an ethanol solution of Ar_2SnCl_2 to an warm solution of 2-methyl-oxine (1:1 mole ratio) in ethanol. Di-O-tolyltin chloride oxinate was prepared by the method described for the corresponding phenyl compounds (39,67). Son et al (77-78) have synthesised and characterised several diorganotin bis (mono- and di-substituted-oxinates). These compounds have been prepared by the reaction of diorganotin dichloride with ligand in 1:2 molar ratio in DMF or alcohol.

Action of oxine on SnX_4 produces compounds of the type $Sn(Ox)_2X_2$. In fact, $Sn(Ox)_2Cl_2$ forms the first example of oxinate derivatives of tin (79), though it is not an organotin derivative.

Of the three types of oxinates, the dioxinato derivatives appear to be significantly more stable than the mono and trioxinate derivatives. For example (26), n-BuSn(Ox)$_3$ is easily hydrolysed to n-BuSn(Ox)$_2$OH which is resistant to further hydrolysis. Similarly, the solvolysis of $Ph_3Sn(Ox)$ has been shown to be quite facile. In the halotin oxinates, $R_2SnX(Ox)$, the halide group is found to be readily exchangable with groups such as butyl, alkoxy or even by

chelates such as acetylacetonate (67). Thus,

$$R_2Sn(Ox)Cl + Tl\text{-}OC_2H_5 \longrightarrow R_2Sn(Ox)(OC_2H_5)$$

$$R_2Sn(Ox)Cl + NaI \longrightarrow R_2Sn(Ox)I$$

$$R_2Sn(Ox)Cl + n\text{-}BuLi \longrightarrow R_2Sn(Ox)(n\text{-}Bu) \longrightarrow R_2Sn(Ox)_2 + (n\text{-}Bu)_2SnR_2$$

$$R_2Sn(Ox)Cl + Tl\text{-}acac \longrightarrow R_2Sn(Ox)(acac) \longrightarrow R_2Sn(Ox)_2 + R_2Sn(acac)_2 .$$

Ghosh and his co-workers (81) have examined the action of mercuric halides on organotin oximates and probable mechanisms of these reactions have been given. Whereas the penta-coordinated compound triphenyltin oximate has been shown to react readily with HgX_2 (X = Cl, Br, I) at room temperature, the hexa-coordinated compound diphenyltin dioximate is attacked by HgX_2 only when refluxed in benzene or ether. In both the cases quantitative amount of $Ph_2Sn(Ox)_2$ is obtained. It has also been shown by them that $Ph_2Sn(Ox)_2Cl$ can react with $HgCl_2$ with the complete cleavage of the tin-phenyl bond producing $Sn(Ox)_2Cl_2$, $PhHgCl$ and Ph_2SnCl_2.

Organotin oximates can react with silver salts (63):

$$R_2Sn(Ox)_2 + AgIO_3 \xrightarrow{CH_3OH} R_2Sn(IO_3)(Ox) + Ag(Ox)$$

$$2R_2SnCl(Ox) + Ag_2SO_4 \xrightarrow{CH_3OH} [R_2Sn(Ox)]_2 \cdot SO_4 + 2AgCl.$$

N.M.R. and U.V. data indicate that coordinating solvents such as pyridine, trimethylphosphate, DMSO or HMPA do not interact with the substituted dimethyltin bis (oximates), $Me_2Sn(Ox\text{-}Y)_2$ (Y = Me, Et) (82).

Organotin Tropolonates, Kojates and Dithio-Carbamates:

A number of organotin tropolonate complexes are known such as Ph_3SnT, Me_2SnXT, R_2SnT_2, $RSnXT_2$ (R = alkyl or Ph; X = Cl, Br, I; TH = tropolone) where the tropolone acts as bidentate chelating agent bonding through both oxygen atoms. Diorganotin bis-tropolonates have been prepared by the following reactions (84-85).

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

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

Phenyltin tristropolonate and phenyltin chloride bistropolonate have been prepared by reacting phenyltin trichloride with a solution of tropolone in benzene or ether (86).

Kojic acid can form complexes with organotin compounds. Thus $(CH_3)_2SnCl_2$ and kojic acid (1:2 mole) were reacted in aqueous solution followed by aqueous ammonia yielding dimethyltin bickojate(87). Methyltin chloride and methyltin bromide bis-kojates have been prepared upon addition of kojic acid to a solution of methyltin oxide and either aqueous hydrochloric acid or hydrobromic acid (87).

Organotin dithiocarbamates are frequently prepared by reacting sodium dithiocarbamate and an organotin chloride (88-89):

$$R_3SnCl + R'_2NCSSNa \longrightarrow R_3SnSCSNR'_2 + NaCl$$

$$R_2SnCl_2 + 2R'_2NCSSNa \longrightarrow R_2Sn(SCSNR'_2)_2 + 2NaCl.$$

They can also be prepared by the following reactions (88-89):

$$(R_3Sn)_2O + 2R'_2NH + 2CS_2 \longrightarrow 2R_3SnSCSNR'_2 + H_2O$$

$$R_2SnO + 2R'_2NH + 2CS_2 \longrightarrow R_2Sn(SCSNR'_2)_2 + H_2O$$

When $PhSnCl_3$ and NaS_2CNEt_2 (1:3 mole) were reacted in methanol, colourless crystals of $PhSnCl(S_2CNEt_2)_2$ were obtained (90). When $Ph_2Sn(S_2CNPh_2)_2$ was heated in air one of the products was diphenyltin oxide (89).

Organotin Acetylacetonates and other β-diketonates:

One of the most important class of bidentate oxygen donors are the β-diketones. The ability of organotin moieties to react with β-diketones to form stable organotin complexes of high co-ordination is well established. The organotin acetylacetonates and other β-diketonates can be classified e.g. for acetylacetonates $R_3Sn(acac)$, $R_2Sn(acac)_2$, $RSn(acac)_3$, $RSnX(acac)_2$, $RSnX(OR')(acac)$ and $RSn(acac)_n(OR')_{3-n}$.

R_3SnL [R = Me, Ph; LH = acetylacetone (acac), benzoylacetone (bzac), dibenzoylmethane (bz_2bz)] compounds have been prepared and

characterized by I.R, N.M.R and Mossbauer spectroscopy (100). They have been prepared by use of the Tl(I) salt method (33,66,100) e.g.

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

$R_3Sn(p\text{-}BrC_6H_4COCHCOCH_3)$ (where R = Me, Et, Pr, Bu, Ph) have been prepared by refluxing a mixture of equimolecular quantities of triorganotin chloride and sodium salt of the p-bromobenzoylacetone in dry methanol (99).

Diorganotin bisacetylacetonates, $R_2Sn(acac)_2$, have been obtained by adding acetylacetone to a mixture of diorganotin dichloride and sodium methoxide in methanol (91).

$$R_2SnCl_2 + 2CH_3ONa \longrightarrow R_2Sn(OCH_3)_2 + 2NaCl$$

$$R_2Sn(OCH_3)_2 + 2acacH \longrightarrow R_2Sn(acac)_2 + 2CH_3OH$$

McGrady and Tobias (73) have prepared dimethyltin bisacetylacetonate by refluxing dimethyltin oxide in acetylacetone for several hours. Other dialkyltin acetylacetonates and substituted β-diketonates have similarly been obtained (33-100).

$$R_2SnO + 2HacAc \longrightarrow R_2Sn(acac)_2 + H_2O$$

These diorganotin bis(β-diketonates) can also be obtained by direct reaction of the reactants in the presence of a base (30).

$$R_2SnCl_2 + 2ChH \longrightarrow R_2SnCh_2 + 2HCl$$

(where ChH = acetylacetone, benzoylacetone) or, by the condensation

of thallium (I) chelate and diorganotindichloride (39,100):

$$R_2SnCl_2 + 2TlCh \longrightarrow R_2SnCh_2 + 2TlCl.$$

Srivastava and Saxena (93) have synthesised some diorganotin bis(acetylacetonates), $R_2Sn(acac)_2$ (R = Ph, o-, m-, p-Tolyl) by the method reported by Allred and Thompson (103). Diorganotin bis(acetylacetonates) have also been obtained by reacting diorganotin dichloride and sodium acetylacetonate in dichloromethane (98,104-106).

Organotin halide bisacetylacetonates, $RSnX(acac)_2$ (X = Cl, Br) have been prepared by the reaction of organotin trihalides with acetylacetone in water (91):

$$RSnX_3 + 2HacacH \longrightarrow RSnX(acac)_2 + 2HX.$$

These can also be obtained by the reaction of organotin trihalides with sodium acetylacetonate in dichloromethane or chloroform (91,105):

$$RSnX_3 + 2Nacacla \longrightarrow RSnX(acac)_2 + 2NaX$$

Oxidative-addition reactions of tin(II) bis(β-diketonate) with organic halides have been applied to obtain organotin halide bis(β-diketonates) (95-97) e.g. for acetylacetone:

$$Sn(acac)_2 + RX \longrightarrow RSnX(acac)_2$$

(where RX = MeI, $BrCH_2CH = CH_2$, $PhCH_2Br$).

Compounds of the type $RSn(R'COCHCOR'')_n(OPr^i)_{3-n}$ (where R = Et, R' = CH_3, R'' = C_6H_5 and n = 2; R = Bu, R' = R'' = CH_3, R' = CH_3, R'' = C_6H_5, R' = R'' = C_6H_5 and n = 1 and 2) have been synthesised by Mehrotra et al (80) by refluxing a mixture of alkyltin triisopropoxide with β-diketones in benzene; for 1:1 and 1:2 molar ratios, respectively the mono-and bis-β-diketonates were resulted. Under similar conditions, ethyl and butyltin tris-acetylacetonates were obtained when alkyltin tris-isopropoxides react with acetylacetone in 1:3 molar ratio. Kawasaki et al (102) have synthesized alkyltin halide methoxy acetylacetonates, $RSnX(OMe)(acac)$, and suggested the compound to be dimeric through methoxy bridges.

Alkyltin mono-, bis-, and tris-β-diketonates studied by Mehrotra et al (80) are all brown viscous liquids. All these derivatives are decomposed on attempted distillation under reduced pressure. Their molecular weights suggest that $BuSn(OPr^i)_2(acac)$ and $BuSn(OPr^i)_2(bzac)$ in the neat form are probably dimeric. The tri- and diorganotin derivatives are all monomeric in benzene solution and are non-ionic in nitrobenzene (93, 99). A mixture of $Bu_2Sn(acac)_2$ and $Bu_2Sn(OMe)_2$ disproportionates in hexane forming a dimer (94):

$$Bu_2Sn(acac)_2 + Bu_2Sn(OMe)_2 \longrightarrow [Bu_2Sn(acac)(OMe)]_2 .$$

Serpone and his co-workers (98) have investigated the mechanism of

intermolecular ligand exchange and configurational rearrangements in organotin acetylacetonates. Acetylacetonate exchange between $Ph_2Sn(acac)_2$ and $Me_2Sn(acac)_2$ is first order in $Ph_2Sn(acac)_2$ but zero order in $Me_2Sn(acac)_2$ concentration.

Sachlas and Jain (101) have prepared tri- and diorganotin complexes of 2-thenoyltrifluoroacetone of the types $R_3Sn(TTA)$ (where R = CH_3, C_2H_5, C_3H_7, C_4H_9 and C_6H_5) and $R_2Sn(TTA)_2$ (where R = CH_3, C_2H_5, C_4H_9 and HTTA = 2-thenoyltrifluoroacetone). These compounds have been prepared by the following reactions:

$$CH_3ONa + HTTA \longrightarrow Na^+(TTA^-) + CH_3OH$$

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

$$(R_2SnO)_x + 2x\ HTTA \longrightarrow xR_2Sn(TTA)_2 + xH_2O.$$

These compounds are monomeric in benzene solution and non-ionic in nitrobenzene.

Organotin oximates and hydroxamates:

Mehrotra and his co-workers (107) have reviewed the oximes and hydroxylamine derivatives of organotin compounds. The general preparative methods for the organotin oximates are: the action of sodium or lithium salts with organotin halides (108-110):

$$R_{4-n}SnCl_n + nNa(Li)ON = CR'R'' \longrightarrow$$
$$R_{4-n}Sn(ON = CR'R'')_n + n\ NaCl(LiCl)$$

Azeotropic distillation of water from a mixture of organotin oxide or hydroxide with oxime in benzene or toluene (63,107-109, 111,113-116):

$$(R_3Sn)_2O + 2HON = CR'R'' \longrightarrow 2R_3SnON = CR'R'' + H_2O$$

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

Reaction of alkyltin alkoxides with oximes (63,107-108, 111,118):

$$R_{4-n}Sn(OR')_n + nHON = CR''R''' \longrightarrow nR'OH + R_{4-n}Sn(ON = CR''R''')_n$$

Koehler et al (119) have prepared diorganotin derivatives of a dicyano formaldehyde oxime by reacting diorganotin dichloride with the silver salt of the oxime. Various types of butyltin derivatives of alkanolamines have been obtained by Mehrotra et al (121) during the investigation of the reaction of butyltin tris(isopropoxide) with alkanolamines in different molar ratios.

Organotin derivatives of oxime are generally volatile and readily hydrolysed by water to give parent oxime (107-108):

$$R_{4-n}Sn(ON = CR'R'')_n + nH_2O \longrightarrow R_{4-n}Sn(OH)_n + nR'R''C = NOH.$$

They also react with acyl or benzoyl halides forming organotin halides and O-acyl or O-benzoyl oxime (107):

$$R_{4-n}Sn(ON=CR'R'')_n + nR'''COX \longrightarrow R_{4-n}SnX_n + nR'R''C=NO.COR'''.$$

The organotin hydroxylamine derivatives have been synthesized by Harrison (117, 122) by the azeotropic removal of water from the mixture of appropriate hydroxylamine and the organotin oxide or hydroxide:

$$\tfrac{1}{2}(R_3Sn)_2O \text{ or } R_3SnOH + HONR'R'' \xrightarrow{-H_2O} R_3SnONR'R''$$

(where R = Me, R' = R'' = Et; R = Me, R' = Ph, R'' = CO.Ph; R = n-Pr, R' = Ph, R'' = CO.Ph; R = n-Bu, R = Ph, R' = Ph, R'' = CO.Ph; R = Me, R' = H, R'' = CO.Ph; R = n-Pr, R' = H, R'' = CO.Ph). However, attempts to prepare $Ph_3SnONHCOPh$ by the same method only resulted in the formation of tetraphenyltin in high yield, presumably by a disproportionation reaction, although no pure diphenyltin 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-hydroxylamines are extremely stable to moisture. The $Ph_3SnONPHCOPh$ is monomeric in both the crystal and solution phases, whereas the trimethyltin derivatives are associated in the solid. Ho and Zuckerman (120) have prepared compounds of the type R_3SnAA, where AA is the anion of amino acids (e.g. glycine,

β-alanine, etc.) by azeotropic distillation of water from benzene solutions of the corresponding stannol or bis (trialkyltin) oxide and the acids.

Organotin Alkoxides:

Since the present work includes some methoxyl derivatives of organotin N-substituted benzohydroxamates, a short review on the more important organotin alkoxides seems to be reasonable. A review on organotin alkoxides has been made by Bloodworth and Davies (20e).

Organotin alkoxides can be prepared in a number of ways.

1. Preparation by nucleophilic substitution at tin . The basis of the method is generalized by the equation:

$$Y \leftarrow OR' + R_3Sn - X \longrightarrow Y^+ + R_3SnOR' + X^-$$

Where alkoxide displaces some other substituent X (halide, alkoxide, oxide, amino, etc.) by nucleophilic attack at tin. Examples are (63, 123):

$$Na\ OMe + Bu_3SnCl \longrightarrow Bu_3Sn.OMe + NaCl$$

$$2NaOBu + Et_2SnCl_2 \longrightarrow Et_2Sn(OBu)_2 + 2NaCl$$

The alkoxides themselves can be used (124-125):

$$R_2Sn(OMe)_2 + R_2SnX_2 \longrightarrow 2R_2Sn(OMe)\ X$$

Organotin alkoxides can very conveniently be prepared by the exchange of alkoxy groups between a tin alkoxide derived from a low boiling alcohol, e.g., methoxide and a higher boiling alcohol (126-127):

$$Et_3Sn(OMe) + HO.CHMe.C:CH \longrightarrow MeOH + Et_3SnO.CHMe.C:CH$$

Trialkyltin alkoxides can readily be prepared by azeotropic dehydration of a mixture of oxide and alcohol in benzene or toluene (123):

$$(Bu_3Sn)_2O + 2HO.CHMeCH \xrightarrow{-H_2O} 2Bu_3Sn.O.CHMeCH.$$

Organotin amines are highly susceptible to protolysis (129) and their reaction with alcohols provides a route to organotin alkoxides (62,130) e.g. :

$$PhSn(NEt_2)_3 + 3EtOH \longrightarrow PhSn(OEt)_3 + 3HNEt_2$$

The only disadvantage of this method is that it requires the initial preparation and purification of highly reactive organotin amines. Lutsenko and his co-workers have shown that α-stannyl-ketones, -esters and -amides react with alcohols or enols by cleaving the Sn-C bond (131-134):

$$Et_3Sn.CH_2.CO.Me + MeOH \longrightarrow Et_3Sn.OMe + Me_2CO$$

$$Et_2Sn(CH_2.CO.OMe)_2 + 2MeOH \longrightarrow Et_2Sn(OMe)_2 + 2Me.CO.OMe$$

etc.

2. Preparation by addition of tin hydrides, alkoxides, amines, etc. to carbonyl compounds.

An organotin alkoxide is formed when any Sn-X bond adds to a carbonyl compound:

$$R_3Sn-X + R'R''.C = O \longrightarrow R_3Sn.OCR'R''.X$$

And this forms the basis of a very versatile preparative route to these compounds. Addition usually proceed under mild conditions, indeed they are frequently exothermic and by variation of the group X, a wide section of simple and substituted alkoxides is made available. A few among the many examples are (135-137):

$$Et_3SnH + Pr^i.CHO \longrightarrow Et_3Sn.OBu^i$$

$$Bu_2Sn(OMe)_2 + Me.CHO \longrightarrow Bu_2Sn(OMe)O.CHMe.OMe$$

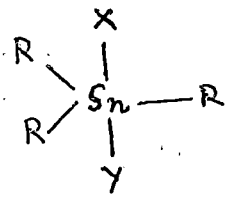
$$\xrightarrow{Me.CHO} Bu_2Sn(O.CHMe.OMe)_2$$

$$R_3Sn.R' + R''.CO.R''' \longrightarrow R_3Sn.OCR'R''R'''.$$

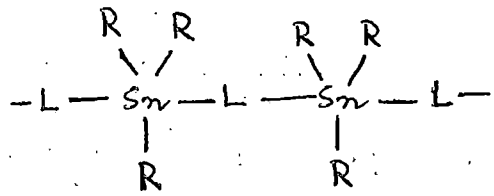
Some structural Aspects of Organotin Complexes:

The availability of d-orbitals makes the organotin moities to form various types of complexes with ligands. The structures of these organotin complexes have been reviewed by Okawara and Wada (25), Bokii et al (138), Ingham et al (1), Poller (139), Gielen and Sprecher (140). Ho and Zuckerman (141) have critically reviewed the organotin compounds studied by microwave and diffraction techniques covering the literature upto middle of 1972. Harrison (14-16) has reviewed some structural aspects of organotin compounds covering the years 1972-1974.

Co-ordination numbers greater than four (in most cases penta and hexa-coordination) are usually displayed by organotin (IV) compounds. Compounds of the type R_3SnX (X = Cl, Br, I) are generally tetrahedral but when X = F^-, NO_3^-, AsF_6^-, BF_4^-, ClO_4^-, CO_3^{-2}, $OCOR^-$, the compounds are penta coordinated around tin where the anions are probably either bridging or chelate types (142-143). The R_3SnX type compounds can form various types of adducts with Lewis bases (1) and the resulting adducts are generally penta-coordinated (144-145). Thus the complex formed from trimethyltin chloride and pyridine provided one of the first conclusive structural evidences for five coordination at tin in 1962 (146). The trigonal bipyramidal structure with equatorial methyl groups is ~~di~~epi~~s~~oted in figure (1a).



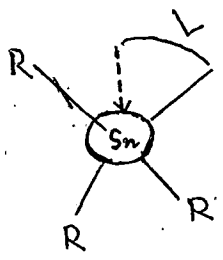
(1a)



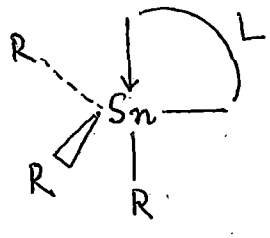
(1b)

The most general feature of the R_3SnL type compounds which are penta-coordinated about tin is the polymeric nature which is an approximate trigonal bipyramidal structure with planer equatorial

organic groups; the more electronegative groups forming bridge in the apical position as shown in figure (1b). Examples are provided by trimethyltin nitrate monohydrate (147), trimethyltin hydroxide (148), trimethyltin cyanide (49), trimethyltin isothiocyanate (150-151), trimethyltin dicyanamide (152), tribenzyltin acetate (153). The flattened tetrahedron structure (Fig. 1c) with an open angle to accept a potential donor is a feature for the triorganotin compounds containing a bidentate chelating ligand and which in favourable conditions can assume a more nearly trigonal bipyramidal shape (Fig. 1d). Thus, the flattened tetrahedron structure which approximates to a trigonal bipyramidal one, with intramolecular carbonyltin coordination have been proposed (122) for N-acyl substituted hydroxylamine derivatives of triorganotin moiety. Full details of crystal structure of $Ph_3SnONPh.CO.Ph$ have been published (155) in which tin atom has been shown to be five-coordinated with a distorted cis - Ph_3SnI_2 configuration with two phenyl groups occupying equatorial sites and the third an axial site at a longer distance.

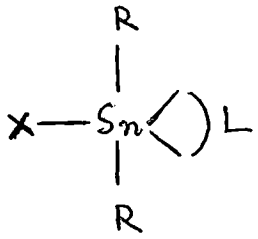


(1c)

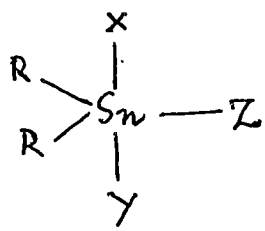


(1d)

Ruddick and Sams (154) have shown from magnetically perturbed Mossbauer spectroscopy that triphenyltin oxinate and trimethyltin acetate possess intramolecular five-coordination stereochemistries. They have also shown that $R_2SnCl(Ox)$ (R = Me, Ph, HOx = oxine) and the $Me_2Sn($ Sal - N-2OC$_6H_4$) have penta-coordinated structures. NMR, IR and UV studies of R_2SnX (Ox) type compounds have been interpreted (67-68, 70) as indicating monomer in solution containing a penta-coordinated tin atom having a probable trigonal bipyramidal configuration with the R groups in trans-positions (Fig. 1e). On the other hand, $Ph_2SnX(Ox)$ (X = Cl, SCN) have been suggested to have a trigonal



(1e)



(1f)

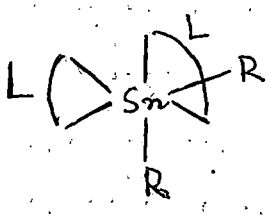
bipyramidal structure (168) with cis-arrangement of the phenyl groups (71) as revealed by dipole moment data on the thiocyanate compound in benzene solution . The all-cis-structure has been confirmed for $Ph_3Sn(bzbz)$ (bzbz = dibenzoyl methane anion) by a single crystal X-ray diffraction study; the co-ordination about the tin

atom being essentially a distorted trigonal bipyramid. The phenyl groups occupy one axial and two equatorial co-ordination sites with the chelating ligand bonded to one equatorial and one axial site (106). Lorberth and Lange (156) from IR, Raman and Mossbauer data have indicated the presence of trigonal pyramidally co-ordinated tin with bridging ligands for the type of the compounds $R_3SnOSnR'R''$.

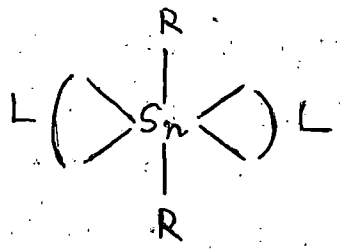
The dimeric tetraalkyl distannoxanes $(XR_2SnOSnR_2X)_2$ and $(XR_2SnOSnR_2OH)_2$ are unique in that they are believed to contain both tetra-coordinated and penta-coordinated tin atoms (136). Another interesting example is the terpyridyl adduct of dimethyltin dichloride which crystallises as a double salt, $[(CH_3)_2SnCl.terpy]^+[(CH_3)_2SnCl_3]^-$. This compound contains a five-coordinated, axially most electronegative trigonal bipyramidal anion (Fig. 1f) and a six-coordinated octahedral cation (157-158). Organotin complexes of strong π-acids e.g. $Me_3Sn.TCNQ$ (TCNQ = Tetracyano p-quinodimethane) exhibits a single band at 555 cm^{-1} in the tin carbon stretching region in the IR spectrum, which is assigned to the antisymmetric mode of a planar Me_3Sn moiety, with bridging TCNQ residue resulting in a trigonal bipyramidal configuration at the tin atom (176). The intense colouration of the compound is indicative of the formation of $(TCNQ)^-$ radical anion on complexation. The complex is therefore best represented by the canonical form $(Me_3Sn)^+.(TCNQ)^-$ and thus provides the first example of an isolable paramagnetic organotin complex.

A number of diorganotin bis-chelates have been isolated (62-63, 73, 92-93, 150-152,167) and found to contain hexa-coordinated tin atom. Some representative compounds are acetyl acetonates, oxinates

and carboxylates. Thus, the dimethyltin bis-oxinate assumes a distorted octahedral structure with a cis-dimethyl group (Fig. 2a) in which the oxygen atoms are trans-and the nitrogen atoms are cis (165). Dimethyltin dinitrate (164-165) is an octahedral complex with trans methyl groups and unsymmetrical bidentate chelating nitrate groups (Fig. 2b) . Very closely resembled with this structure



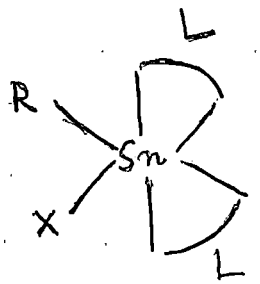
(2a)



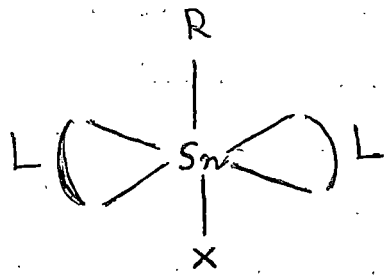
(2b)

in dimethyltin bis-(dimethyldithiocarbamate) (181). The X-ray crystal structure of $Me_2Sn(O.NMe.CSMe)_2$ has been determined by Harrison et al (166). The geometry at tin is distorted octahedral as for $(CH_3)_2Sn(NO_3)_2$. The two N-acylhydroxylamino residues function as bidentate ligands forming one short and one long co-ordinate bond to tin whilst the Me-Sn-Me group is not linear, the C-Sn-C bond angle being 145.8°. The distortion from regular octahedral coordination results from the steric demands of the ligands.

Dimethyltin dichloride forms 1:2 complexes with dimethylsulfoxide (DMSO) (169-170) and pyridine N-oxide (171). In both structures the methyl groups are trans with $SnCl_2$ and SnO_2 units in cis in the first, but trans in the second compound. The crystal structure of Ph_2SnCl_2.bipy shows that the tin atoms are octahedrally co-ordinated with trans-phenyl groups and cis-chlorine atoms (52). The complex Ph_2SnCl_2 . 2DMSO has an almost identical structure (53). The two-dimensional lattice of dimethyltin bisfluorosulfate crystals contain polymeric sheets with fluorosulfate groups acting as bridges between linear (trans) dimethyltin units so that the tin atoms are coordinated octahedrally (182). The dimethyldicyano compounds of group IVb are all associated in the solid state (172). In the tin compound stronger bridging gives rise to planar sheets in which the molecules are distorted to a nearly octahedral arrangement with trans-dimethyltin groups perpendicular to the sheets.Mossbauer spectra of $Bu_2Sn(CNS)Ox$ is consistent with the structure of a hexa-coordinated tin (168). The dipolemoment indicates a cis-arrangement of the hydrocarbon groups for the compound in benzene solution (71). The crystal and molecular structure of $PhSnCl(S_2CNEt_2)_2$ has been determined (185) The tin atoms are six-coordinated in a distorted octahedral fashion by the phenyl groups, chlorine atoms, and two chelating diethyldithiocarbamato residues, the phenyl group and the chlorine atom occupying mutually cis-positions (Fig. 2c). The NMR spectra of $PhSnX(acac)_2$ (X = Cl,Br) compounds indicated an octahedral configuration at tin with phenyl and halogen above and below the plane of the acetylacetonato rings (Fig. 2d) (187).

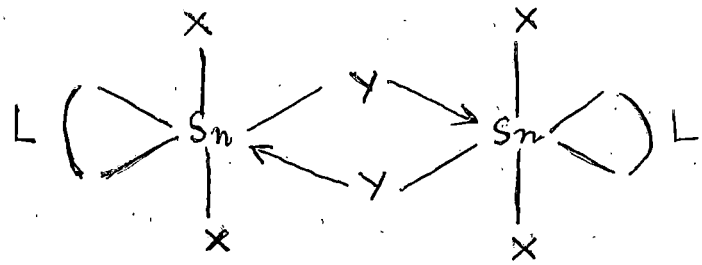


(2c)



(2d)

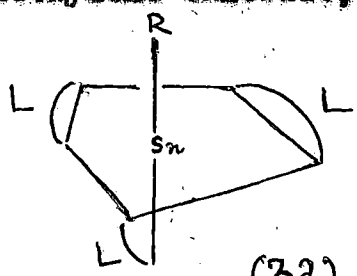
The novel type of compounds methoxy (acetylacetonate) tin dihalides were shown to be dimeric and their configurations have been interpreted (173) from IR studies in which each tin atom is hexa-coordinated (Fig. 2e). Dibutyltin bismethoxide and dibutyltin



(2e)

bisacetylacetonates disproportionate in hexane and forms a dimer (34), which is believed to have a configuration analogous to $Bu_2Sn(SCN)(Ox)$ dimer (Fig. 2e) with hexa-coordinated tin atom. Ruddick and Sams (154) have suggested from Mossbauer spectra for $RSnCl(Ox)_2$ (R = Bu, Ph) compounds a cis-$RSnX_4$ octahedral structure which had been assumed by Faraglia et al (74). Similar hexa-coordinated tin has been assumed for mono-organotin halide bisacetylacetonates (31) and for addition compounds of the type $R_2SnI_2 \cdot 2L$ (48). Bis (pentane-2, 4-dionato) dimethyltin is a regular octahedron with linear O-Sn-O groupings, which consists of discrete monomeric units (103).

Not many organotin compounds have been found to possess hepta-coordinated tin, the geometry of which would be pentagonal bipyramidal one (Fig. 3a). Phenyltin tristropolonate has been reported (86) to be monomeric in methylene chloride, which suggested a seven



(3a)

coordination around tin. Kawakami et al (86) have concluded from UV, NMR and IR data that n-butyltin trisoxinate may have a hepta-coordinated tin atom. Ruddick and Sams (154) from Mossbauer spectroscopy determined the coordination number around tin in $BuSn(Ox)_3$ which is consistent with a seven coordination with three equivalent bidentate oxine groups. Anhydrous methyltin trinitrate crystallizes with three chelating nitrate groups forming a pentagonal bipyramid about tin (177). Tris(dimethylsulfoxide) nitratodiphenyltin nitrate has

been characterised as a hepta-coordinated organotin complex from IR and X-ray crystal structure of the compound (173). The structure consists of monomeric hepta-coordinated cations $[Sn(C_6H_5)_2NO_3\{(CH_3)_2SO\}_3]^+$ and NO_3^- anions. Coordination around tin is pentagonal bypyramidal with the bidentate nitrate group and the three dimethyl sulfoxide molecules in the equatorial positions and the two phenyl rings at the apices.

Cleavage of Tin-Carbon Bonds:

The present work justifiably demands some discussions on the cleavage of the tin-carbon bonds in organotin compounds. The cleavage of tin-carbon bond in organotin compounds may be represented by the reaction:

$$\rightarrow Sn - C \leftarrow + A - B \longrightarrow \rightarrow Sn - A + \rightarrow C - B$$

Where A-B may be halogen, mineral acid, carboxylic acid, thiol, phenol, alcohol, metallic or non-metallic halide, alkali, alkali metal and co/n on. But whether or not and how the Sn-C bond will be cleaved i.e. the reactivity of the Sn-C bond will depend definitely on the molecular environment of it. The mechanism of the cleavage reactions can be realised by electrophiles; A-B may be electrophiles or radicals.

Reactions of the electrophiles e.g. I_2, Br_2, HgX_2 with tetraalkyltins have been shown to proceed by a complex mechanism (182-185) which involves a predetermining equilibrium between the

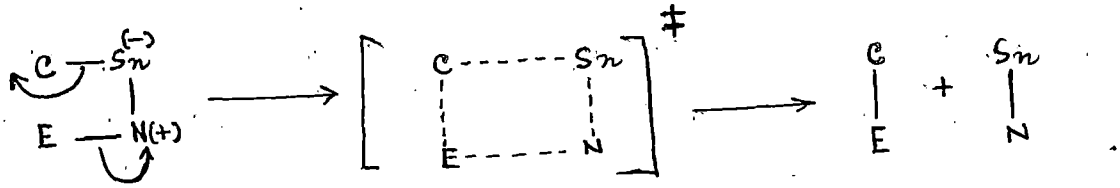
organotin substrate and a nucleophile. This step is then followed by the reaction of an electrophile with the activated carbon-tin bond. Thus, depending upon the solvent polarity, two different cases may arise:

(1) Reactions in "non polar" solvents: S_E2 .

The most nucleophilic species available in non polar solvents is the electrophile, E-X, itself e.g. X-X, H-Cl (The available species in solution depends upon the relative nucleophilicity of the electrophiles, E-X, the solvent and any dissolved species present in the solution):

$$C\text{-}Sn + E\text{-}X \rightleftharpoons C\text{-}\overset{(-)}{Sn}\text{-}\overset{(+)}{X}\text{-}E$$

The complex formed in this equilibrium contains activated carbon atoms (bound to a negatively charged tin atom) and an enhanced electrophilic species (E bound to a positively charged atom). Now, there might be three possibilities.(i) Both the activated carbon atom and the enhanced electrophilic species might react reasonably intramolecularly to give a cyclic four-membered activated complex (four centre mechanism S_E2) which leads to the products:



or, (ii) The complex which now contains a rather nucleophilic carbon atom might also react with another electrophile E-N, leading to tin-carbon cleavage products:

$$N\text{-}E + C - \overset{(-)}{Sn} - \overset{(+)}{N} - E \longrightarrow C\text{-}E + N\text{-}\overset{(-)}{Sn} - \overset{(+)}{N} - E.$$

or, (iii) Another organotin molecule might be involved to react with the complex:

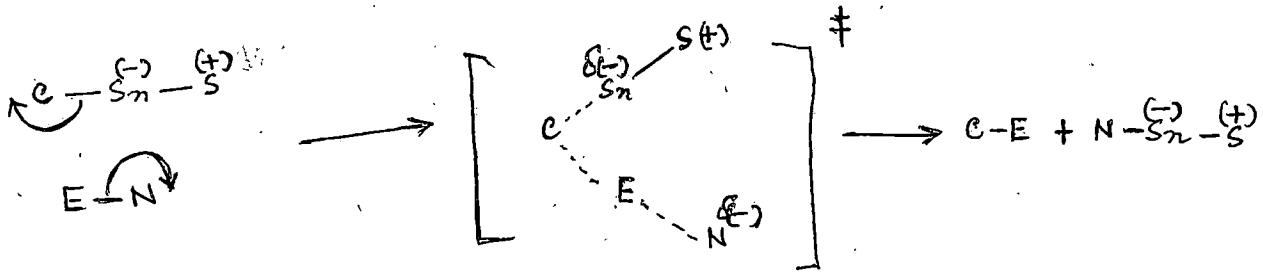
$$C\text{-}\overset{(-)}{Sn}\text{-}\overset{(+)}{N}\text{-}E + C' - Sn' \longrightarrow C' - E + Sn' - N + C\text{-}Sn.$$

(2) Reactions in "polar" solvents: S_E2.

In polar solvents, the most nucleophilic species available in solution is the solvent itself and not the electrophile, which can react with the organotin molecule forming a "Collision Complex":

$$C\text{-}Sn + S \rightleftharpoons C - \overset{(-)}{Sn} - \overset{(+)}{S}$$

This "Collision Complex" like the equilibrium complex in nonpolar solvents possess rather nucleophilic carbon atoms to be attacked by an electrophile in an S_E2 mechanism yielding an open activated complex, the existence of which has been fairly well established by Abraham and Spalding (191):



The nucleophilic solvent has not yet become electrophilic enough through the coordination with the metal to compete with the electrophilic E-N and to react either intramolecularly or intermolecularly with a tin-carbon bond. These two steps seem thus the only reasonably possible reactions in nucleophilic solvents, such as methanol. What has been said has been derived from the study of symmetrical tetraalkyltins. Now a few specific reactions of tin-carbon bond cleavage involving symmetrical or unsymmetrical aromatic derivatives can be mentioned.

The main reaction of aryltins is the electrophilic substitution at the aromatic carbon atom and the corresponding C_{Ar} - Sn bond is usually the first one to be broken when a competition is possible between alkyl and aryl cleavage (1). This feature has been used to synthesize tetraorganotins with four different groups attached to the metal, starting with tetraphenyltin or an alkyltriphenyltin (196). Tetraorganotins have been cleaved under a variety of conditions and kinetic results are available for I_2 in CCl_4 (29), in methanol, in

chloroform, benzene and cyclohexene (198-202), for ICl and Br_2 in methanol (203), for $HgCl_2$ in THF and alcohol (193-195,204), for the solvolysis in acetic acid (205) and for $HgCl_2$ and I_2 (206).

Substituted phenyltrimethyltins react with NaOMe in methanol to yield trimethyltin methoxide or compounds derived from it and the corresponding substituted benzenes. The kinetics of this surprisingly smooth reaction have been examined by Eaborn et al (207-209). A special case of tin-carbon bond cleavage by acids is presented by the reaction of diphenyltin compounds with chelating agents in DMSO at elevated temperatures in which benzene was formed as the cleaved product (39, 162, 209-210). Thus diphenyltin bis(oxinate) reacts with oxine at 300° to give tin tetrakis (oxinate), an eight-coordinate tin compound (211). Similarly, Ph_2SnCl_2 at temperatures between 170 and 200° reacts with bidentate, monoprotic chelating agents (HCh) and quadridentate diprotic ligands (H_2Ch') to give compounds of the types $SnCl_2(Ch)_2$ and $SnCl_2(Ch')$ respectively, e.g. :

$$Ph_2Sn(Ox)_2 + 2HOx \longrightarrow Sn(Ox)_4 + 2PhH$$

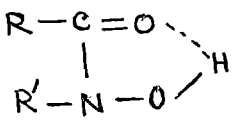
$$Ph_2SnCl_2 + 2HOx \longrightarrow Cl_2Sn(Ox)_2 + 2PhH$$

Reaction of Ph_3SnCH_2CN with Br_2 (1:1) in CCl_4 gave $Ph_2Sn(Br)CH_2CN$ whereas with I_2 (1:1 and 1:2) it gave Ph_3SnI and Ph_2SnI_2 respectively. Similarly, Ph_3SnCH_2CN with ICl (1:1 and 1:2) gave $Ph_2Sn(Cl)CH_2CN$ and $PhSn(Cl_2)CH_2CN$ respectively and with IBr (1:1) $Ph_2Sn(Br)CH_2CN$ was formed (197).

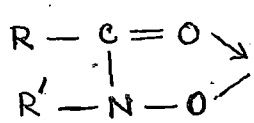
The Nature of the Ligand:

Finally, it would not be irrelevant to mention a few words on the present ligand, the N-substituted benzohydroxamic acids, which are enormous in number and which have been proved to be versatile bidentate chelating agents for metal ions.

The class of organic compounds containing the reactive group $-\overset{O}{\overset{\|}{C}}-\overset{OH}{\overset{|}{N}}-H$, is known as hydroxamic acid and has been widely studied by organic chemists. Unsubstituted hydroxamic acids can exist in two forms, (the keto-enol forms) the keto-form being predominated in the acid medium. But N-substituted hydroxamic acids can exist only in the keto form (211). I.R. analysis of various hydroxamic acids have been done by Mathis (212) and suggested intramolecular hydrogen bonding(Fig. 4a). Both the N-substituted and unsubstituted hydroxamic acids are potential chelating agents and form chelates (Fig. 4b) with metal ions with the loss of protons (213).



(4a)



(4b)

(M^{2+} = metal ion)

The vast number of hydroxamic acids are used as colorimetric reagents and in the gravimetric estimation of metals and separation of metals from a mixture by extracting the metal chelates in suitable solvents. The preferential formation of a colour or precipitate depends on pH, the solvent and reagent concentration and is not a function of the presence or absence of a substituent on the nitrogen atom (214).

All the hydroxamic acids gave characteristic colour test of Vanadium (V) in strong HCl medium (2-10M) and reaction products on extraction with $CHCl_3$ give characteristic violet extract (215). The most interesting and promising hydroxamic acid is the N-phenyl-benzohydroxamic acid (PBHA; R = R' = C_6H_5 in fig. 6). This compound was first prepared by Bamberger (216) and latter the procedure was modified by Shome (217). This compound and its analogues are moderately stable in air, light and temperature and in HCl, $HClO_4$ and H_2SO_4. They have little solubility in water but they are all readily soluble in organic solvents.

A few aromatic hydroxamic acids of various acidities have been examined for their reactions towards copper and tin (218). Tin (II) was originally presumed to combine with PBHA with the formation of the complex $(C_{13}H_{11}O_2N)_2SnCl_2$, m.p. 171°. However, the precipitation titrations of Sn(II) and Sn(IV) with PBHA give tin to reagent mole ratios of 1 to 4 and 1 to 2, respectively. As both the products are the same $[Sn(PBHA)_2Cl_2]$, it is suggested that PBHA acts as an oxidising agent and not as a reducing agent. Thus two moles of PBHA are consumed in oxidising tin (II) to tin (IV) before complexation (219). The IR spectral analysis shows (220) the tin complex to contain

tin(IV). The compound is an inner complex and not an addition compound, since from the spectra, the tin compound appears to contain no hydroxyl hydrogen of PBHA and tin is combined with carbonyl oxygen.

SCOPE, OBJECT AND METHODS OF THE PRESENT INVESTIGATIONS.

During the last few years, extensive work has been observed in the field of organotin complex compounds of bidentate chelating agents. Among them special mention may be made about the oximates and acetylacetonates. These compounds are principally of the following types: R_3SnL, R_2SnL_2, $RSnL_3$, R_2SnLX, $RSnL_2X$ which are either penta-, hexa- or hepta-coordinated. The proceeding discussions give a short review of their preparations, properties and of structural elucidations based on UV, IR, NMR, Mossbauer, X-ray and other physicochemical methods.

A number of hydroxamic acids and their substituted derivatives have been successfully used in analytical chemistry of different elements for a long time. The first reported tin compound of hydroxamic acid dates back to 1953, when Ryan and Lutwick (loc.cit.) precipitated tin in hydrochloric acid solution with N-phenylbenzohydroxamic acid and estimated tin gravimetrically assuming the composition of the complex to be $(C_{13}H_{10}O_2N)_2SnCl_2$.

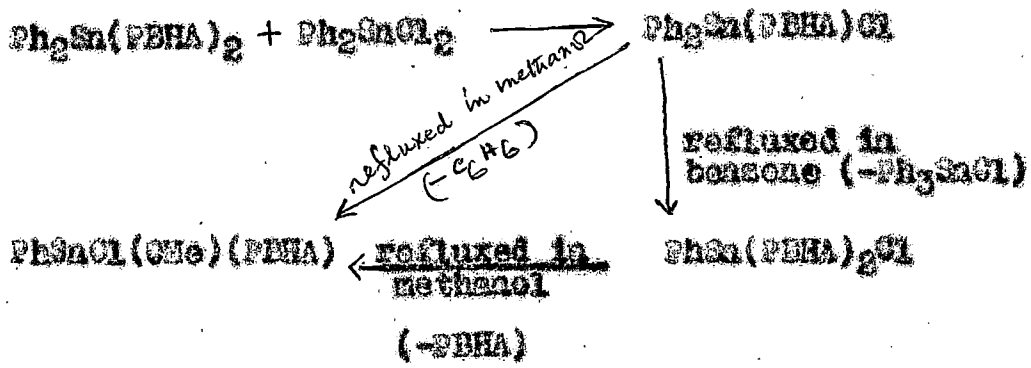
Keeping in mind, particularly the works in the field of organotin derivatives of oximes and β-ketoesters and the exciting possibilities of the hydroxamic acids as novel bidentate chelating agents, which have acidic and at the same time oxidising properties, we began our investigations on different types of organotin derivatives of N-substituted benzohydroxamic acids. The hydroxamic acids chosen were: N-phenylbenzohydroxamic acid, N-phenylparachlorobenzohydroxamic acid, N-phenylparanitrobenzohydroxamic acid, N-ethylparachlorobenzohydroxamic acid, N-paratolylbenzohydroxamic acid, N-orthotolylbenzohydroxamic acid, N-parachlorophenylbenzohydroxamic

acid. Our expectations have amply been fulfilled in isolation of the following classes of new organotin N-substituted benzohydroxamates. (a) R_3SnL, (b) R_2SnL_2, (c) $RSnL_3$, (d) R_2SnXL and (e) $RSnX(OR')L$. These compounds have been characterized by analytical as well as by UV and IR spectral data available to us and where possible tentative structures have been suggested.

In this connection we like to mention that Harrison in 1972 (117) reported few triorganotin derivatives of N-substituted and unsubstituted benzohydroxamic acids as a part of their structural studies in the main group chemistry. Though a little unfortunate, we inadvertently missed this first publication on organotin hydroxamates during the early part of our investigations. But the triphenyltin N-phenylbenzohydroxamate reported by Harrison had a m.p. of 16-17° lower than that prepared by us, though the analytical data of both the compounds are the same.

Action of mercuric halides on triphenyltin oximates have been studied by Ghosh and his co-workers (81), which yielded $Ph_2Sn(Ox)_2$ besides $PhHgX$ and Ph_3SnX. Triphenyltin derivatives of N-substituted benzohydroxamic acids being identical with that of the oximate have been expected to undergo similar reactions with mercuric halides. In fact, all the $RSnL_2$ type compounds, prepared here, have been obtained by this method along with $PhHgX$ and Ph_3SnX. The compounds of the type R_2SnXL have been prepared by mixing R_2SnL_2 and R_2SnX_2; the thiocyanate complex being prepared by the displacement of the chlorine from the corresponding chloride complex. Both R_2SnXL and $RSnXL_2$

types of compounds produced the same type of compound $R_2Sn(OCH_3)_2$ when both the compounds were reacted with methanol. Also R_2SnX_2 compounds have been found to undergo disproportionation to give $RSnX_3$ type compounds. These simple but interesting interconversions, as in the case of PBHA, can be summarized as



EXPERIMENTS AND DISCUSSIONS OF THE PRESENT INVESTIGATION.

All the solvents used in the experiments were purified and dried as described in Vogel's practical organic chemistry (221). The petroleum-ether used throughout the investigation was of boiling range 60°-80°. Mercuric chloride (B.D.H), mercuric bromide (B.D.H. and mercuric iodide (B.D.H.) were dried in an air oven at 110° for about 12 hours and stored in a vacuum desiccator. Dibutyltin dichloride (Fluka) was recrystallised from benzene and had a m.p. of 43°. All melting points were uncorrected.

1. Preparation of Tetraphenyltin:

Tetraphenyltin was prepared following the method of Harris (222). It was recrystallised from benzene and dried in vacuum m.p. 226° (lit. (223) m.p. 225°). Found C = 67.75, H = 4.70%; calculated for $C_{24}H_{20}Sn$: C = 67.51, H = 4.72%.

2. Preparation of Triphenyltin chloride:

Tetraphenyltin prepared as mentioned above was converted to triphenyltin chloride according to the method of Gilman et al (224). Triphenyltin chloride was finally crystallized from pet-ether and dried in vacuum, m.p. 106° (lit. (223) m.p. 106°). Found C = 56.36, H = 3.80, Cl = 9.10% and calculated for $C_{18}H_{15}ClSn$: C = 56.10, H = 3.92, Cl = 9.23% .

3. Preparation of Bis(triphenyltin) oxide:

Bis(triphenyltin) oxide was prepared by the reaction of triphenyltin chloride with 50% excess of sodium hydroxide as described by

McKeen et al (41). It was dried in air and finally in vacuum at room temperature for 12 hours and had m.p. of 122° (lit. (30a) 124°). Found : C = 61.21, H = 4.40%; calculated for $C_{36}H_{30}Sn_2O$: C = 60.41, H = 4.42% .

4. Preparation of Diphenyltin dichloride:

Diphenyltin dichloride was prepared by the method of Gilman et al (224) and was crystallised from pet-ether. It was air-dried and had a m.p. of 42-44° (lit. (224) m.p. 42-44°). Found : C = 41.65, H = 2.83%; calculated for $C_{12}H_{10}Cl_2Sn$: C = 41.9, H = 2.91% .

5. Preparation of Diphenyltin oxide:

Polymeric diphenyltin oxide was prepared by the reaction of diphenyltin dichloride with 50% excess of sodium hydroxide as described by Siegbede and McKeen (41). This was dried in air and finally in vacuum at room temperature for 12 hours. Found : Sn = 40.91% and calculated for $C_{12}H_{10}SnO$: Sn = 41.11% .

6. Preparation of Dibutyltin oxide:

Dibutyltin oxide was prepared from dibutyltin dichloride with 50% excess of sodium hydroxide. This was dried in vacuum at room temperature for 12 hours. Found : Sn = 47.30% and calculated for $C_8H_{18}SnO$: Sn = 47.79% .

7. Preparation of Triphenyltin thiocyanate:

Bis(triphenyltin) oxide was dissolved in benzene and to it was added an excess of ammonium thiocyanate and the mixture was refluxed for one hour. This was then filtered, concentrated to a small volume and treated with pet-ether. Fine white needle shaped crystals came, which was finally crystallized from a mixture of benzene and pet-ether and had a m.p. of 167°. Analysis gave : C = 55.61, H = 3.58, Sn = 28.96% and calculated for $C_{19}H_{15}NSSn$: C = 55.88, H = 3.65, Sn = 29.16% .

8. Preparation of Dibutyltin dithiocyanate:

Dibutyltin dithiocyanate was prepared by the method of Seyferth et al (225). Thus 3.04 gm of dibutyltin dichloride was taken in hot ethanol and to it was added a hot ethanol solution of 1.94 gm of potassium thiocyanate. Filtered; ethanol solution was evaporated to dryness and the solid was crystallised from benzene. Fine white crystals of m.p. 141-42° came (lit. (225) m.p. 144-45°). Analysis gave : C = 34.6, H = 5.0 , Sn = 33.81% and calculated for $C_{10}H_{18}N_2S_2Sn$: C = 34.4, H = 5.16, Sn = 34.1% .

9. Preparation of Diphenyltin diiodide:

Diphenyltin diiodide was prepared by the method of Ballard et al (226), which consists of reacting tetraphenyltin and iodine in 1:2 mole ratio in the absence of a solvent. This was recrystallized

from pet-ether and had a m.p. of 71° (lit. (226) m.p. 71°). Found: Sn = 22.40% and calculated for $C_{12}H_{10}SnI_2$: Sn = 22.53% .

10. Preparation of Diphenyltin dihydride:

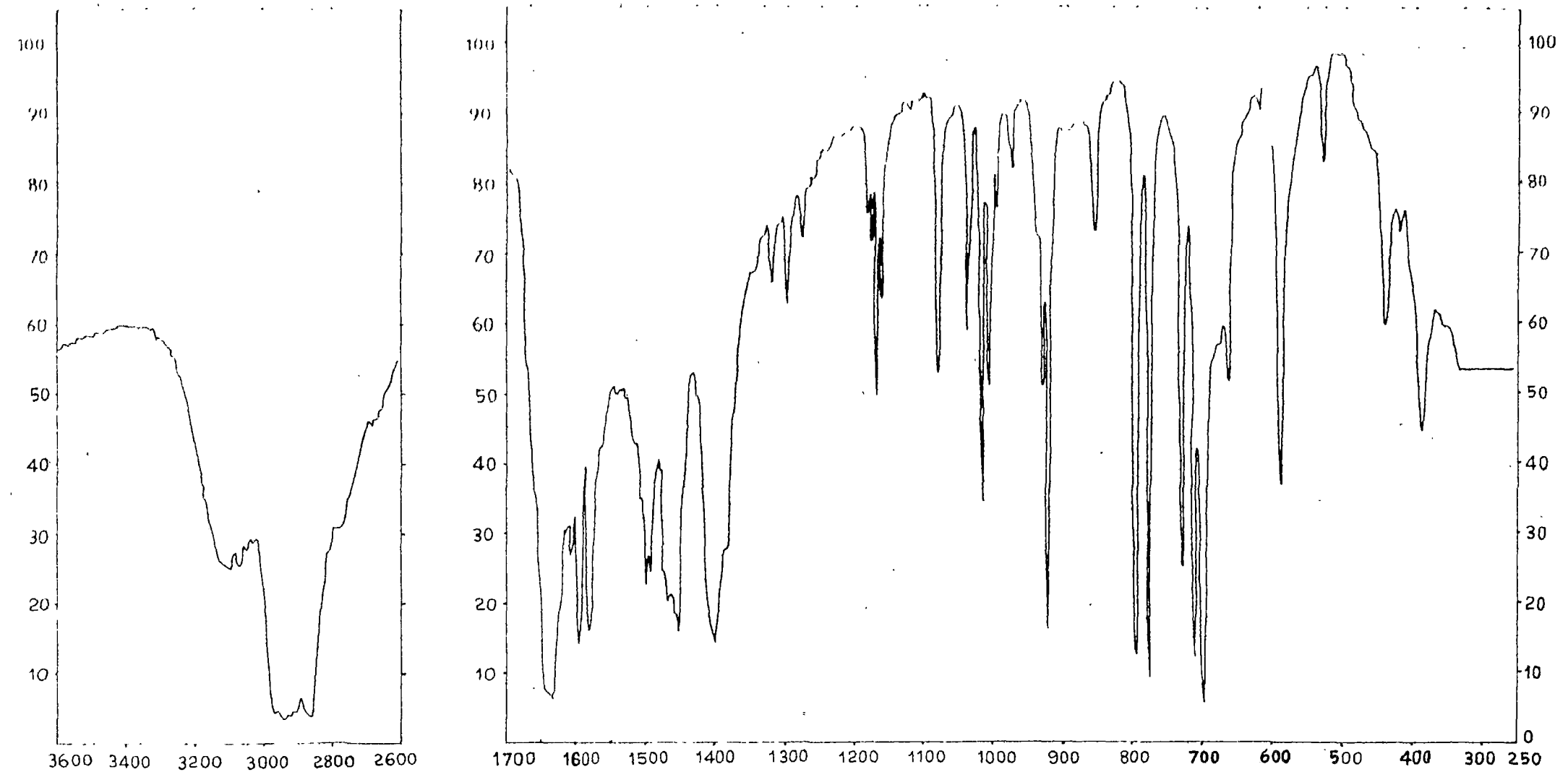
Diphenyltin dihydride was prepared essentially by following the method of Kuivila et al (227) where diphenyltin dichloride was reduced by lithium aluminium hydride in diethylether under nitrogen atmosphere. The diphenyltin dihydride solution was washed thrice with ice-cold water, dried over calcium chloride under nitrogen medium.

11. Preparation of Tetraphenylditin 1,2-diacetate:

Tetraphenylditin 1,2-diacetate was prepared by the method of Sawyer et al (228). Thus, to the dried ether solution of diphenyltin dihydride prepared by the above method was added glacial acetic acid and the mixture was kept under nitrogen medium for one day. White crystals came, which was crystallized from chloroform and showed a m.p. of 152° (lit. (228) m.p. 152°).

12. Preparation of N-phenylbenzohydroxamic acid:

N-phenylbenzohydroxamic acid was prepared by the benzoylation of phenylhydroxylamine with benzoylchloride following the method of Shome (217). It was crystallized from benzene and dried in vacuum and had a m.p. of 123° (lit. (229) 121-22°). Analysis gave : C = 73.7, H = 5.0% and calculated for $C_{13}H_{11}O_2N$: C = 73.4, H = 5.1% .



I.R. Spectrum of N-Phenylbenzohydroxamic Acid

FIG - 5a

13. Preparation of N-phenylparachlorobenzohydroxamic acid:

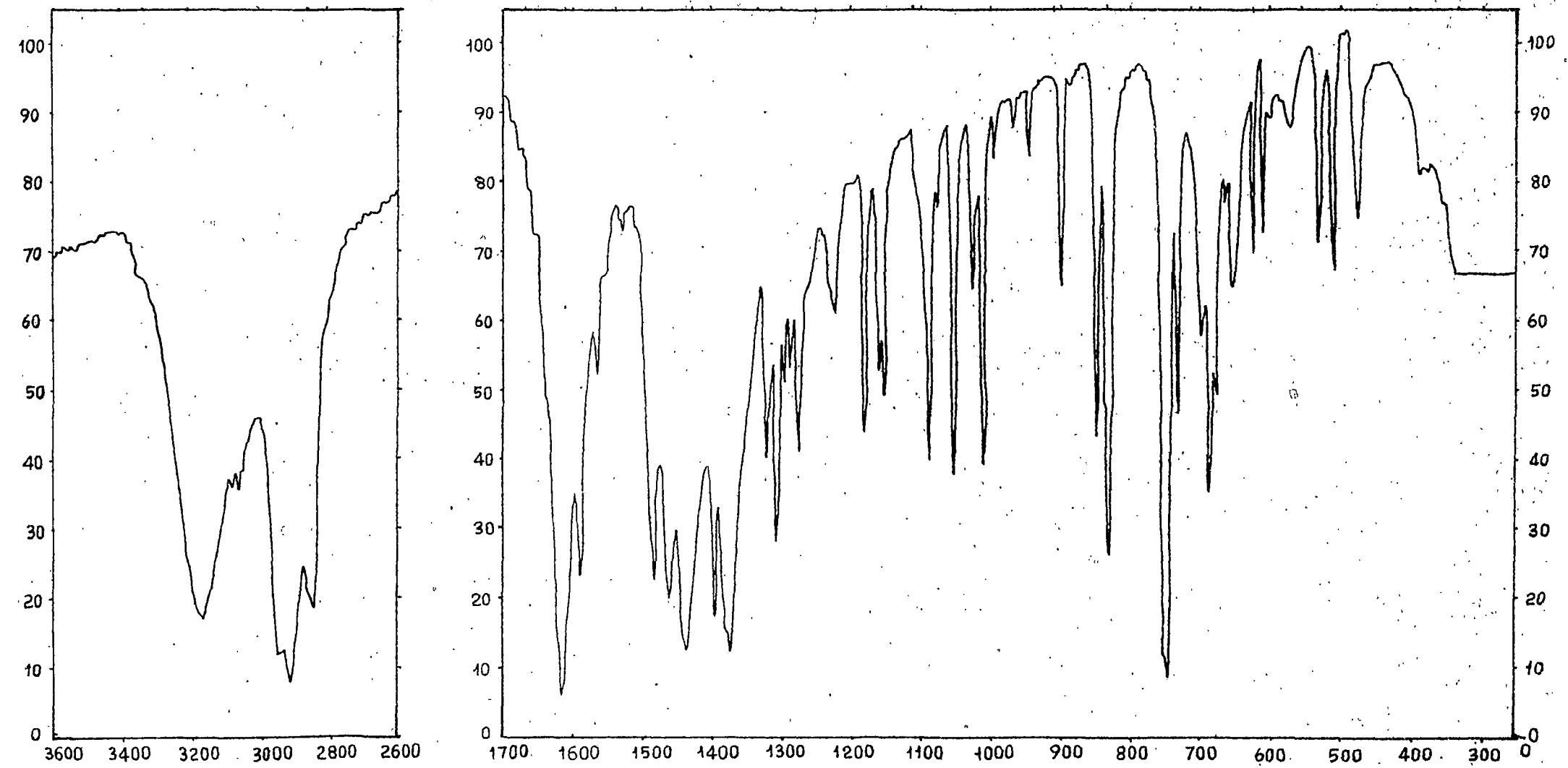
N-phenylparachlorobenzohydroxamic acid was prepared by the reaction of parachlorobenzoylchloride with phenylhydroxylamine following a typical procedure of Tandon et al (230). It was crystallised from rectified spirit, dried in vacuum and had a m.p. of 162°. Analysis gave : C = 62.31, H = 4.10% and calculated for $C_{13}H_{10}O_2NCl$: C = 63.03, H = 4.04% .

14. Preparation of N-phenylparanitrobenzohydroxamic acid:

This was prepared by the reaction of paranitrobenzoyl chloride with phenylhydroxylamine (230). It was crystallised from rectified spirit and dried by heating in vacuum and had a m.p. of 159° (lit. (231) m.p. 159°). Analysis gave : C = 59.62, H = 4.04, N = 11.47% and calculated for $C_{13}H_{10}O_4N_2$: C = 60.49, H = 3.88, N = 10.85% .

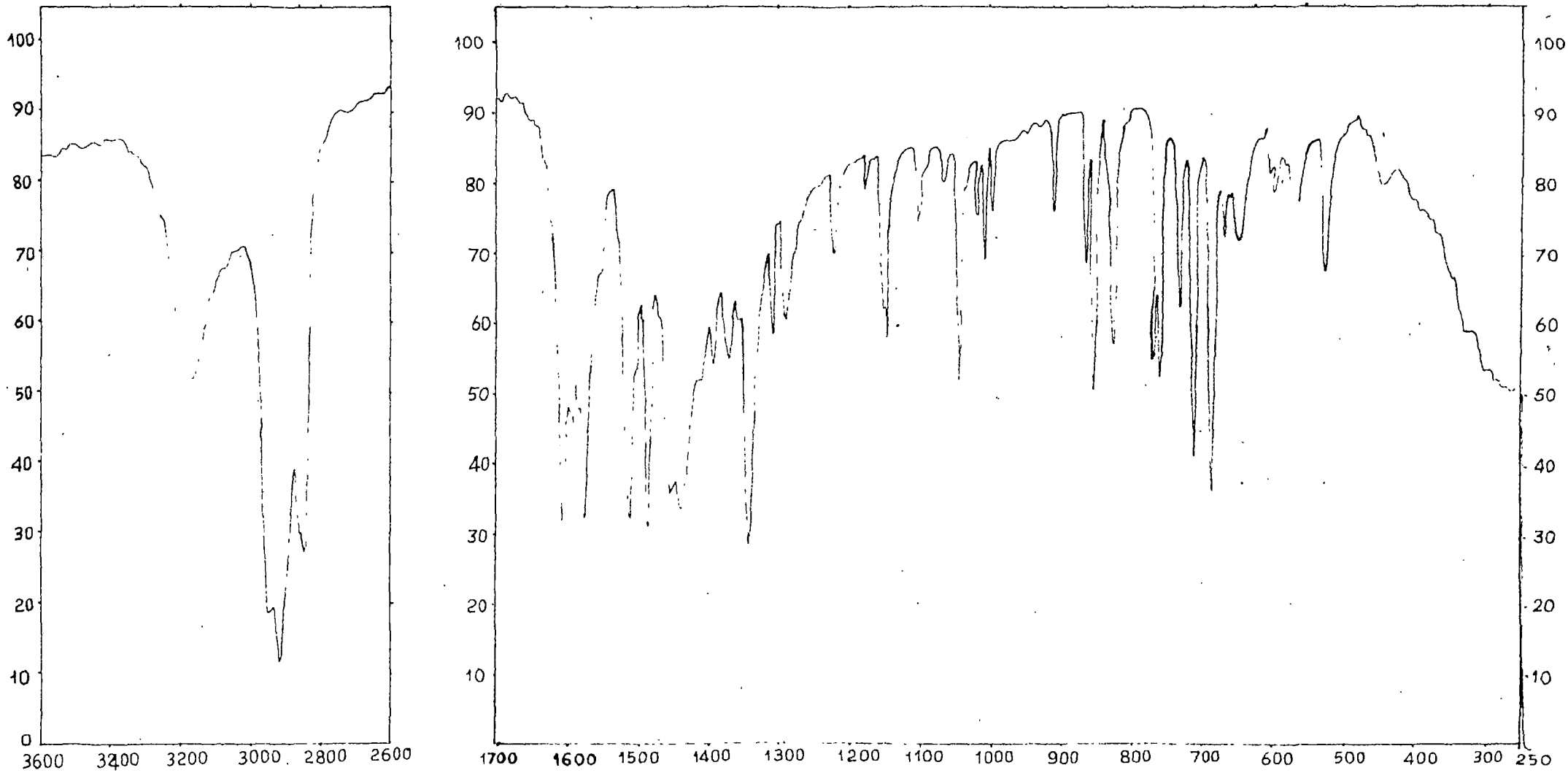
15. Preparation of N-parachlorophenylbenzohydroxamic acid:

N-parachlorophenylbenzohydroxamic acid was prepared according to the method of Majumdar (229) by benzoylating parachlorophenylhydroxylamine. It was recrystallised from rectified spirit and dried in vacuum and had a m.p. of 155° (lit. (229) m.p. 155°). Analysis gave : C = 63.23, H = 3.90% and calculated for $C_{13}H_{10}O_2NCl$: C = 63.03, H = 4.04% .



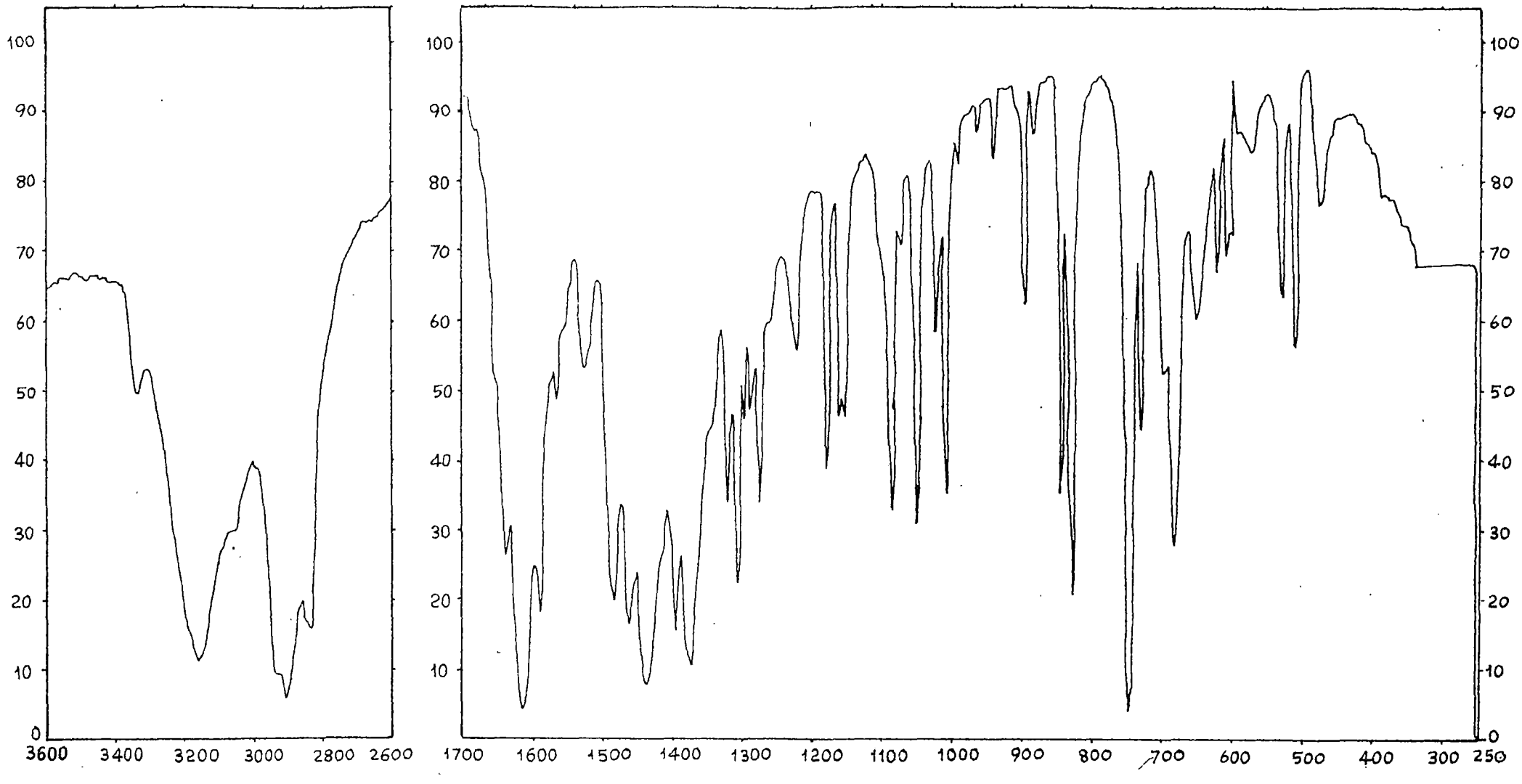
I.R. Spectrum of N-Phenyl parachlorobenzohydroxamic Acid.

FIG - 5b



I.R. Spectrum of N-Phenylparanitrobenzohydroxamic Acid .

FIG- 5e



I.R. Spectrum of N-Parachlorophenylbenzohydroxamic Acid

FIG - 5d

16. Preparation of N-Paratolylbenzohydroxamic acid:

N-Paratolylbenzohydroxamic acid was prepared by benzoylating paratolylhydroxylamine with benzoylchloride according to the method of Majumder et al (232). This was crystallised from a mixture of benzene and pet-ether and showed a m.p. of 103° (lit. (232) m.p. 103°). Analysis gave : C = 74.42, H = 5.61% and calculated for $C_{14}H_{13}O_2N$: C = 74.03, H = 5.72% .

17. Preparation of N-Orthotolylbenzohydroxamic acid:

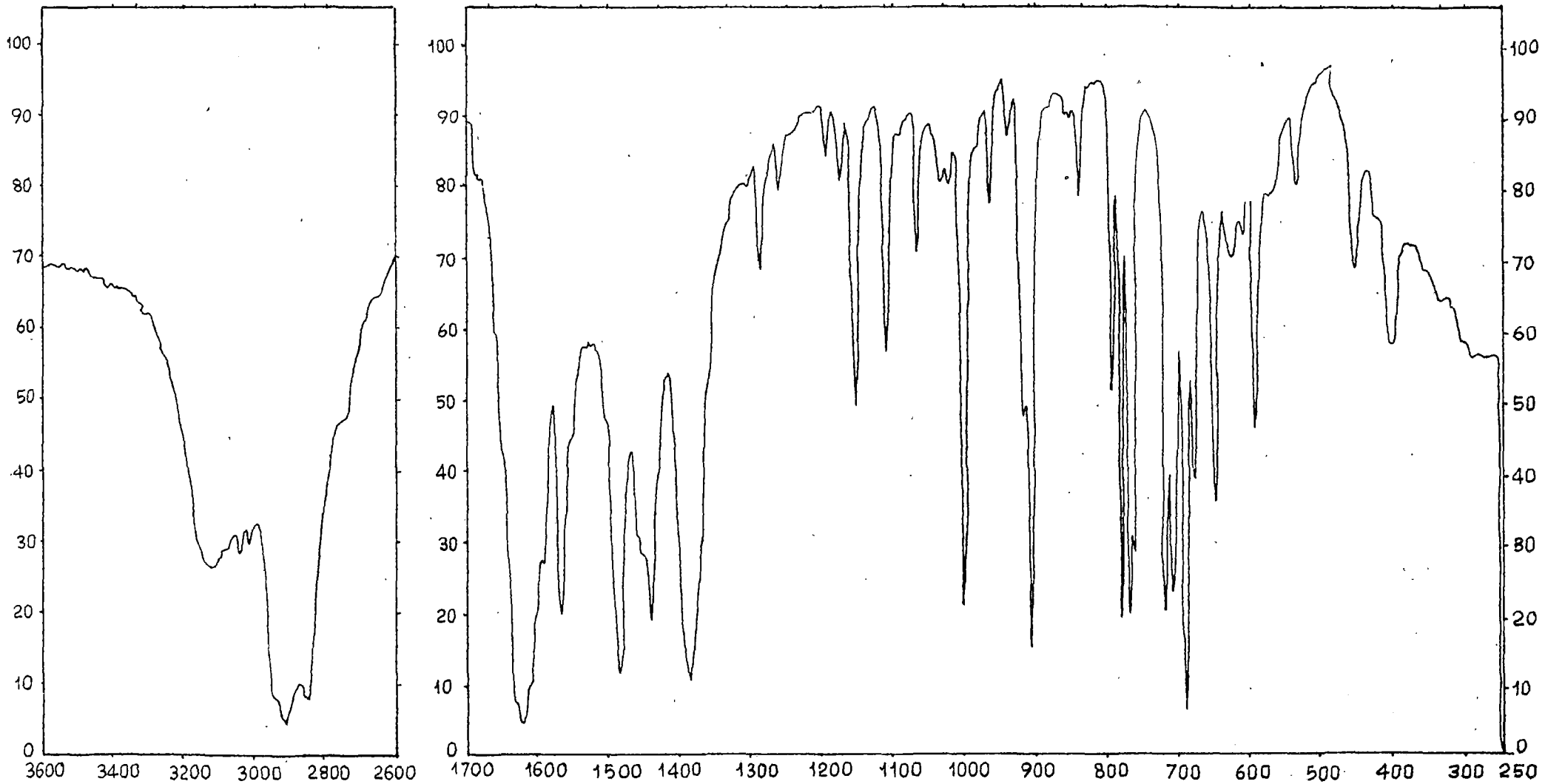
This was prepared similarly as for N-paratolylbenzohydroxamic acid and crystallised from rectified spirit. This was dried in vacuum and it showed a m.p. of 104° (lit. (232) m.p. 104°). Analysis gave : C = 74.21, H = 5.73% and calculated for $C_{14}H_{13}O_2N$: C = 74.03, H = 5.72% .

18. Preparation of N-Ethylparachlorobenzohydroxamic acid:

N-Ethylparachlorobenzohydroxamic acid was prepared by reacting parachlorobenzoyl chloride with ethylhydroxylamine following the procedure adopted for N-phenylparachlorobenzohydroxamic acid. It was crystallised from benzene and dried in vacuum. The compound showed a m.p. of 99°, analysis of which gave: C = 54.62, H = 5.14% and calculated for $C_9H_{10}O_2NCl$: C = 54.05, H = 5.0% .

19. Preparation of Triphenyltin N-phenylbenzohydroxamate:

a) 2.15 gm of bis-triphenyltin oxide was taken in 50 ml of benzene and to it was added 1.25 gm of N-phenylbenzohydroxamic acid and the



I.R. Spectrum of N-Orthotolylbenzohydroxamic Acid

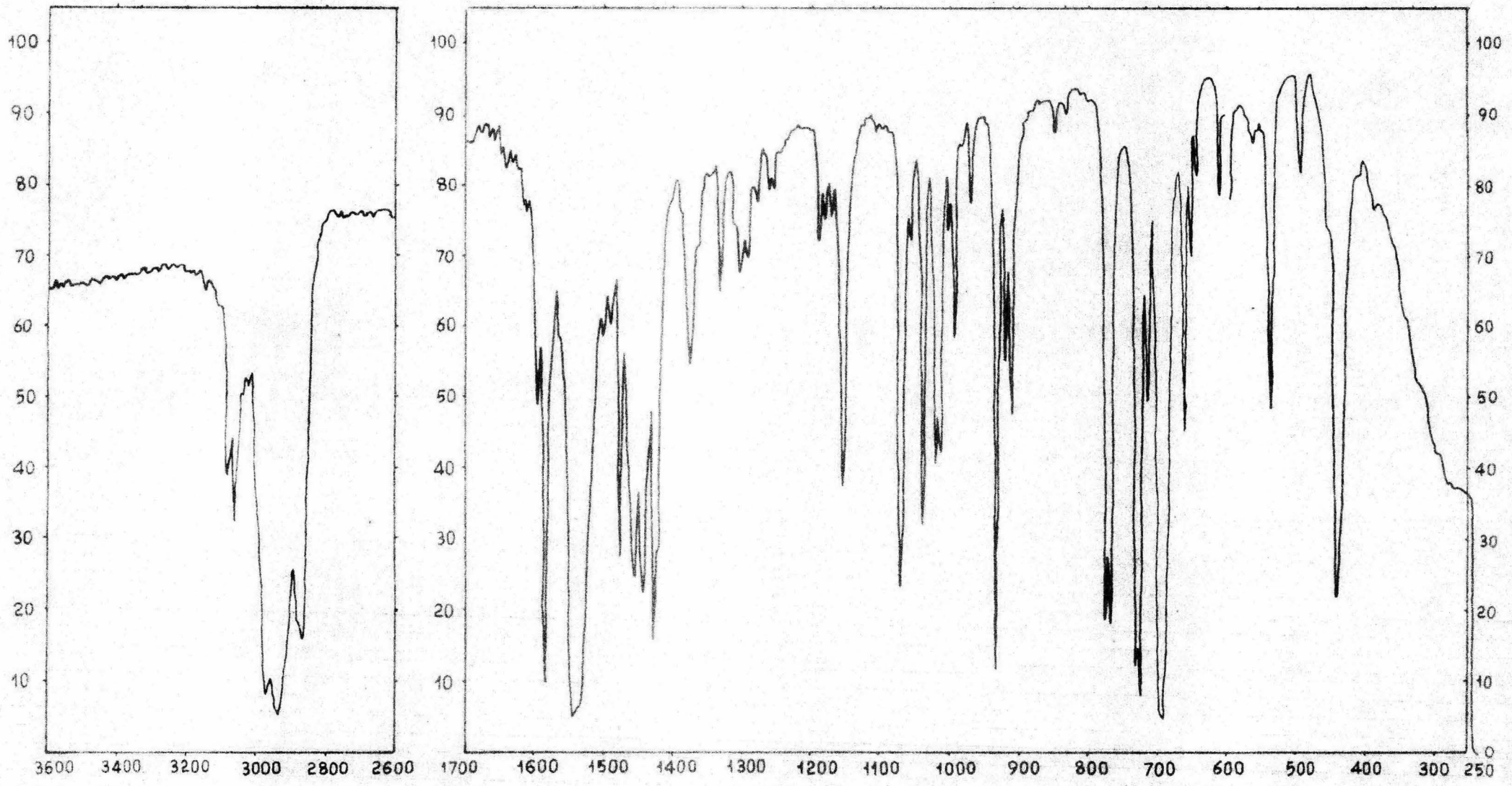
Fig- 5e

mixture was refluxed for four hours using water-separator. After the reaction the light yellow solution was evaporated on a water-bath to a pasty mass which was then boiled with methanol. Fine white crystals appeared, which was filtered and washed with methanol. Crystals weighing 2.5 gm had a m.p. of 130-31°, which after several crystallisation from methanol showed m.p. of 133°. Analysis gave: C = 65.98, H = 4.73, Sn = 20.73% and calculated for $C_{31}H_{29}NO_2Sn$: C = 66.2, H = 4.5 and Sn = 21.1% . This compound has also been crystallized from benzene and was found to have the same melting point of 133° [lit. (122) m.p. 115.5 - 116.5° (crystallised from benzene)].

b) The same compound was prepared directly from the chloride. Thus 2.13 gm of N-phenylbenzohydroxamic acid was taken in 30 ml of benzene and dissolved by heating. To this hot solution was added 3.85 gm of triphenyltin chloride with shaking. The mixture was cooled and to it was added 25% ammonia solution to neutralise the acid liberated in the reaction. This was then filtered and the light yellow solution was evaporated on a water bath and boiled with methanol. Fine white crystals of m.p. 132° came weighing 5 gm. This was then crystallized twice from benzene and gave colourless crystals of m.p. 133° and found to be undepressed when mixed with the above analysed sample.

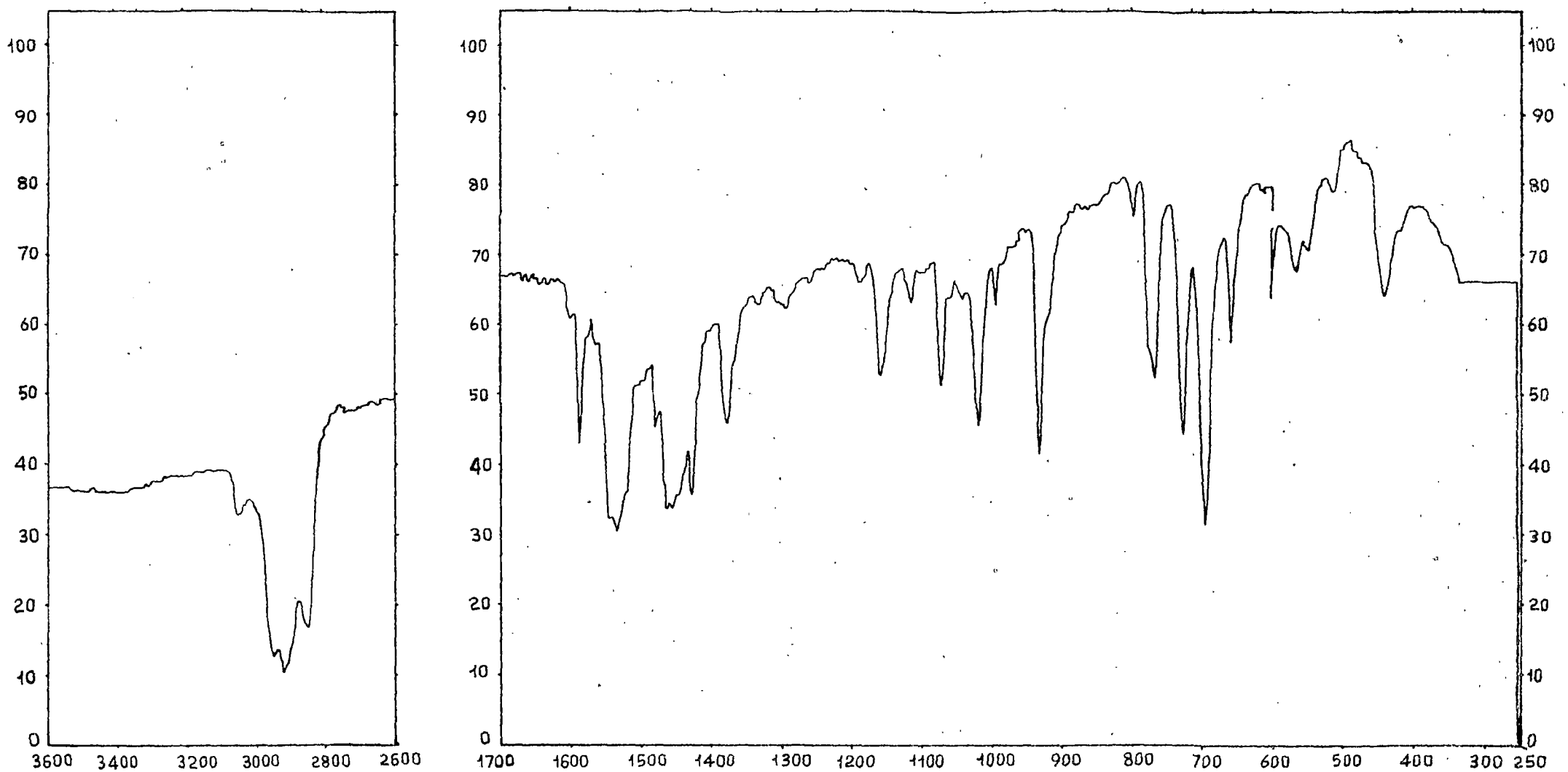
20. <u>Preparation of Triphenyltin N-orthotolylbenzohydroxamate:</u>

3.75 gm of triphenyltin hydroxide was taken in 50 ml of benzene and to it was added 1.75 gm of N-orthotolylbenzohydroxamic



I.R. Spectrum of Triphenyltin N-Phenylbenzohydroxamate.

Fig- 6a



I.R. Spectrum of Triphenyltin N-Orthotolylbenzohydroxamate.

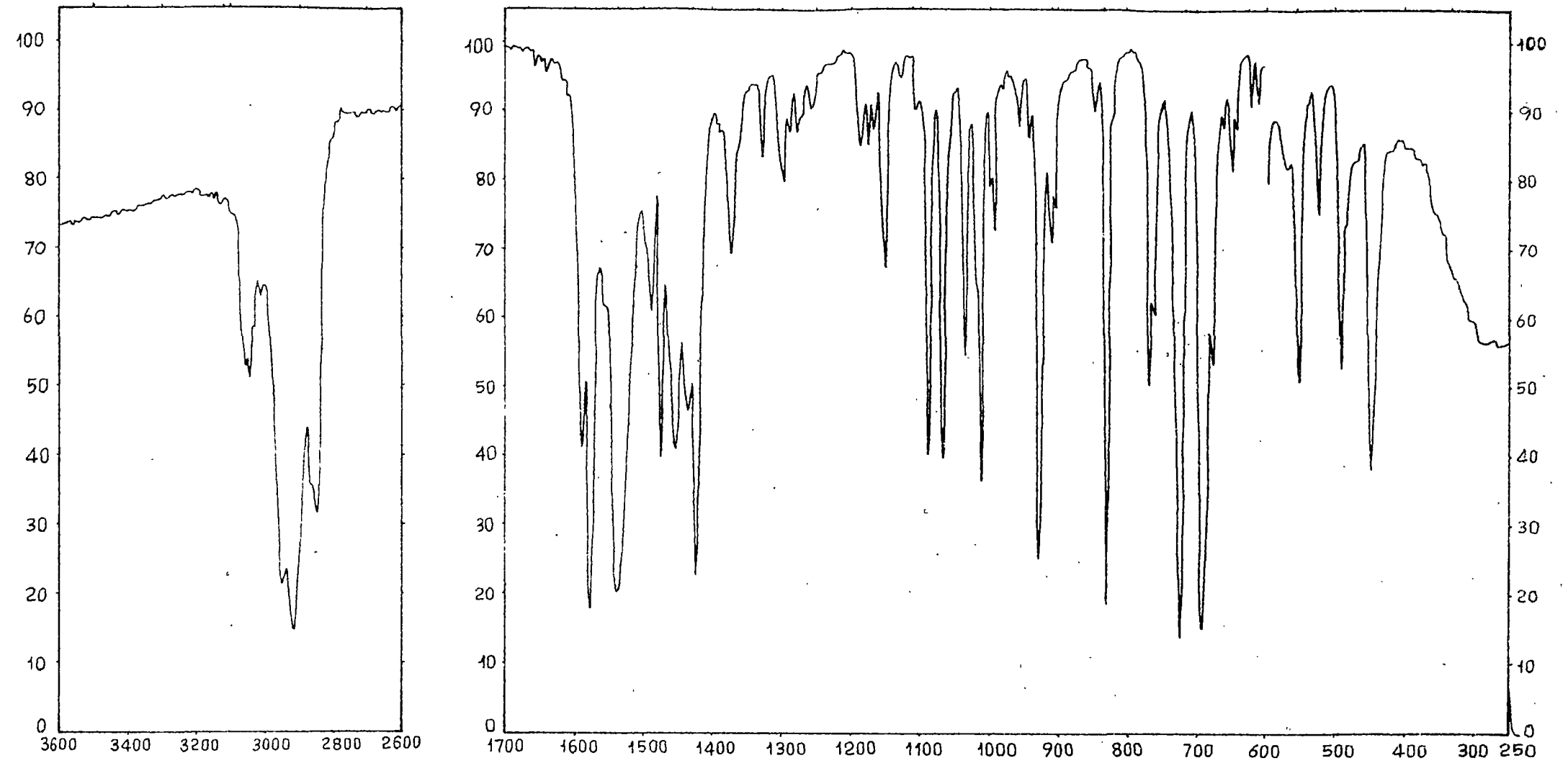
Fig - 6b

acid and the mixture was refluxed for five hours removing water azeotropically. After the reaction, the light yellow solution was evaporated to a pasty mass on a water bath. The yellow mass was then boiled with ethanol whereupon white precipitate came, m.p. 53°, yield being 3.8 gm. This was reprecipitated six times from the same solvent, which gave a m.p. of 55°. The analysis of this compound showed: C = 67.03, H = 4.90, Sn = 20.1% and calculated for $C_{32}H_{27}NO_2Sn$: C = 66.67, H = 4.70, Sn = 20.58% .

21. Preparation of Triphenyltin N-phenylparachlorobenzohydroxamate:

a) 3 gm of bis-triphenyltin oxide was taken in 50 ml of benzene and to it was added 2 gm of N-phenylparachlorobenzohydroxamic acid and the mixture was refluxed for two hours using water separator. The light yellow solution was then evaporated on a water bath to a pasty yellow mass which was crystallised from a mixture of benzene and pet-ether. White crystals (1.9 gm) of m.p. 134-35° came. This was again dissolved in benzene and concentrated to a pasty mass and then boiled with methanol. Fine white crystals of m.p. 133-40° came, which was crystallised twice in the same way and had a m.p. of 139-40°. Analysis gave : C = 62.66, H = 4.24, Sn = 19.90% and calculated for $C_{31}H_{24}O_2NClSn$: C = 62.37, H = 4.02, Sn = 19.96% .

b) The same compound was prepared directly from the triphenyltin chloride. Thus 1.24 gm of N-phenylparachlorobenzohydroxamic acid was dissolved in 50 ml of benzene by heating and to this hot solution was



I.R. Spectrum of Triphenyltin N-Phenylparachlorobenzohydroxamate.

Fig- 6C

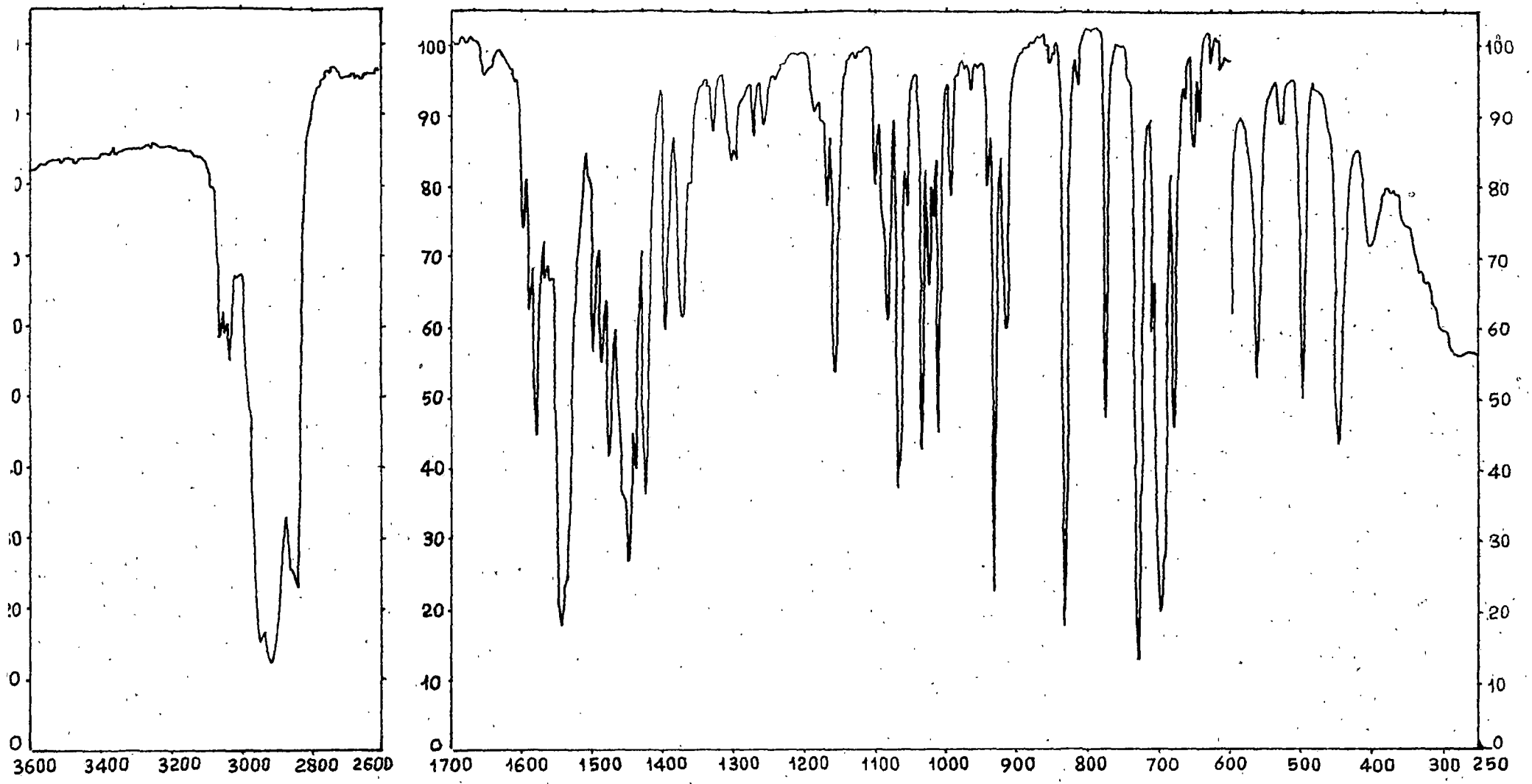
added 1.92 gm of triphenyltin chloride. To this mixture was then added 25% ammonia solution just to neutralise the liberated hydrochloric acid. The precipitated ammonium chloride was then filtered off. The light yellow filtrate was evaporated to dryness and boiled with methanol. 2.1 gm of white crystals of m.p. 137-39° came, which was similarly crystallised twice and the final product had a m.p. of 139-40° and found to be identical with the compound prepared by method (a) by mixed melting point determination.

22. Preparation of Triphenyltin N-parachlorophenylbenzohydroxamate:

3 gm of bis-triphenyltin oxide was taken in 50 ml of benzene and to it was added 1 gm of N-parachlorophenylbenzohydroxamic acid and the mixture was refluxed for three hours using water separator. After the reaction, the light yellow solution was evaporated on a water bath and the pasty mass was boiled with methanol. Fine white needle shaped crystals of m.p. 127-29° came weighing 3.6 gm. This was crystallised twice from methanol and had a m.p. of 129°. Analysis gave : C = 62.11, H = 3.99, Sn = 19.85% and calculated for $C_{31}H_{24}O_2NClSn$: C = 62.37, H = 4.02 and Sn = 19.93% .

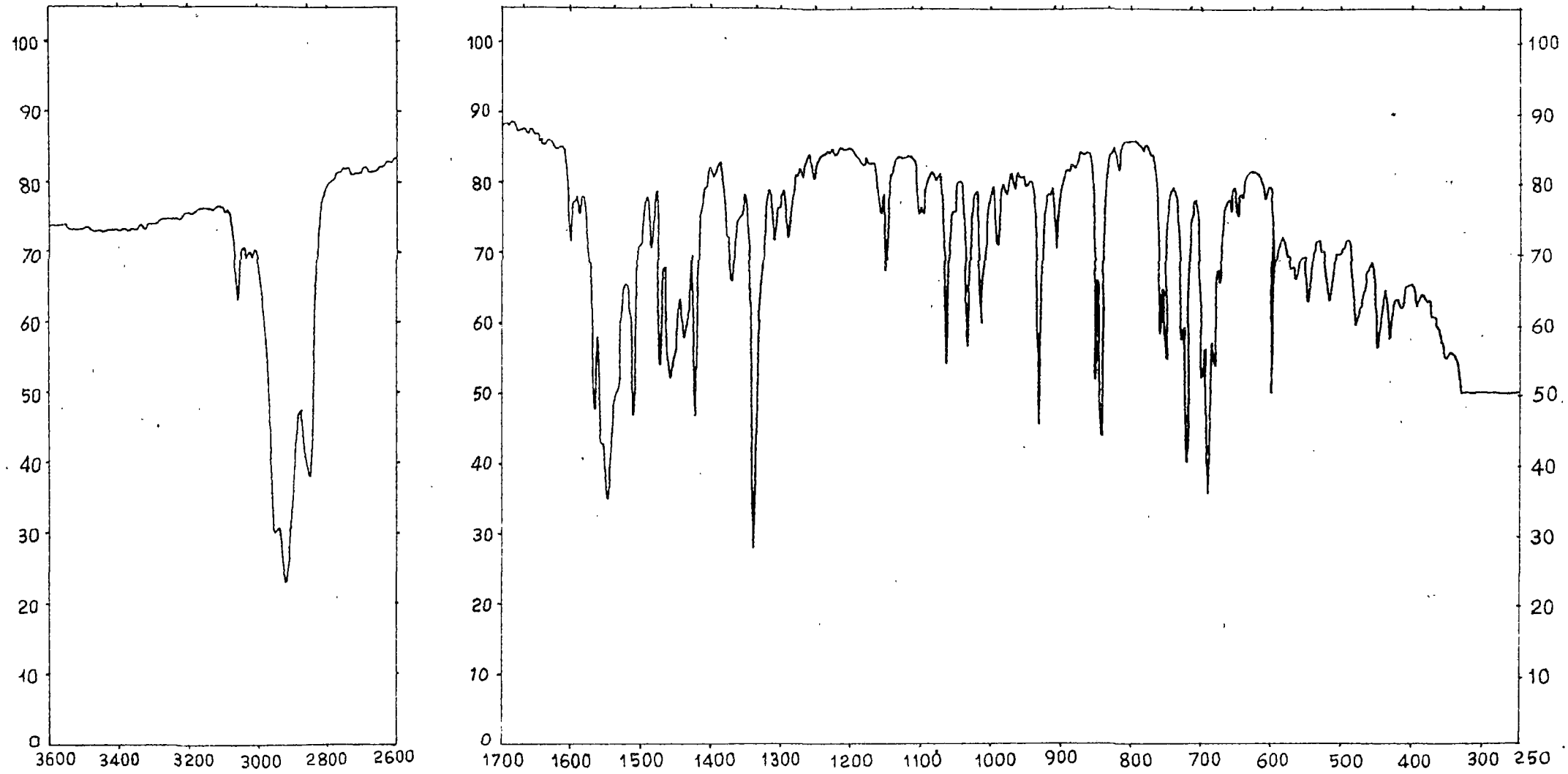
23. Preparation of Triphenyltin N-phenylparanitrobenzohydroxamate:

a) 2.86 gm of bis-triphenyltin oxide was taken in 50 ml of benzene and to it was added 2.1 gm of N-phenylparanitrobenzohydroxamic acid. The mixture was refluxed for four hours using water separator. After the reaction, the bright yellow solution was concentrated to a small volume and treated with methanol. Yellow crystals of m.p.



I. R. Spectrum of Triphenyltin N-P-Chlorophenylbenzohydroxamate.

Fig-6d



I.R. Spectrum of triphenyltin N-Phenylparanitrobenzohydroxamate

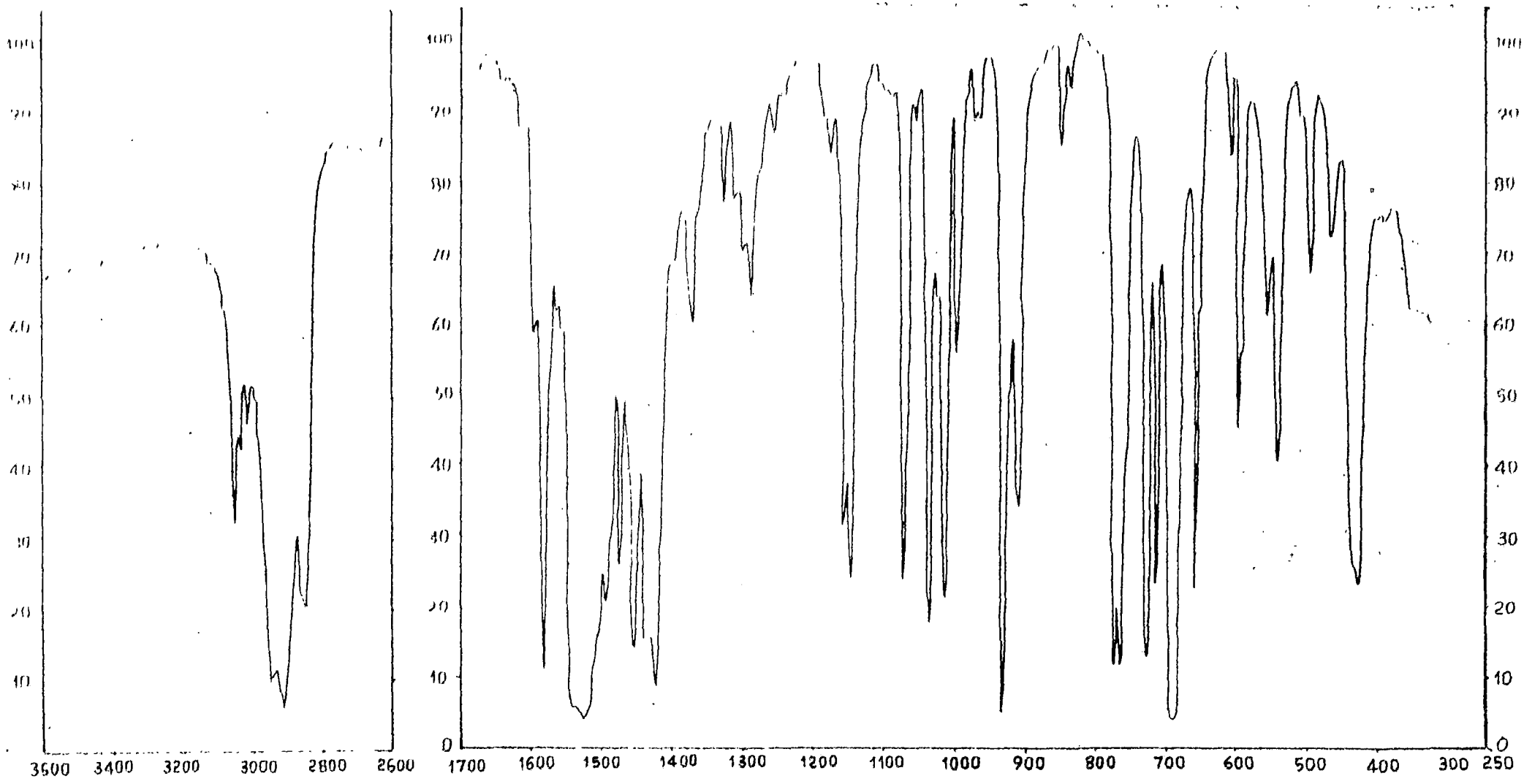
FIG - 6e

184-85° came, weighing only 2.6 gm. This was crystallised thrice from a mixture of benzene and methanol. Fine bright yellow crystals of m.p. 188° came, which on analysis gave: C = 61.21, H = 4.00, Sn = 19.45% and calculated for $C_{31}H_{24}O_4N_2Sn$: C = 61.33, H = 3.95, Sn = 19.60% .

b) The same compound was prepared by taking 2.58 gm of N-phenylparanitrobenzohydroxamic acid and 3.85 gm of triphenyltin chloride in 50 ml of benzene and refluxing the mixture for half an hour. This was cooled and added 25% aqueous ammonia just to neutralise the acid. The precipitated ammonium chloride was filtered off and the yellow solution was concentrated to a small volume and added methanol. 2.6 gm of yellow crystals came melting at 180-87°. This was crystallised thrice from the same solvent mixture and the fine bright yellow crystals of m.p. 188° came, which was found to be the same compound as obtained in (a) as shown by the mixed melting point determination.

24. Preparation of Diphenyltin bis-(N-phenylbenzohydroxamate)

a) 11.56 gm (0.04 mole) of diphenyltin oxide was taken in 150 ml of benzene and to it was added 17.04 gm (0.08 mole) of N-phenylbenzohydroxamic acid. This mixture was refluxed for four hours using water separator. The light yellow coloured solution was filtered and the filtrate was evaporated on a water bath to a pasty mass. This was then crystallised from a mixture of benzene and pet-ether or benzene and methanol. Crystallisation from the latter solvent



I.R. Spectrum of Diphenyltin bis-(N-Phenylbenzohydroxamate)

Fig- 7a

mixture yielded 26.5 gm of fine white crystals which melted at 160°. Analysis gave : C = 65.03, H = 4.53, Sn = 16.98% and calculated for $C_{38}H_{30}N_2O_4Sn$: C = 65.42, H = 4.30, Sn = 17.07%; molecular weight in chloroform (vapour pressure osmometry) = 688 and calculated for the above formula = 697.

b) The same compound was also prepared by dissolving 2.13 gm (0.01 mole) of N-phenylbenzohydroxamic acid in 25 ml of benzene and adding to this solution 1.72 gm (0.005 mole) of diphenyltin dichloride with shaking. To this clear mixture was added 2 ml of 25% aqueous ammonia. This was filtered and the benzene layer was separated from the aqueous layer. The filtrate was concentrated to a pasty mass on a water bath and boiled with methanol, when fine white crystals weighing 2.4 gm came. The crystals showed a melting point of 160° and was identified as diphenyltin bis-N-phenylbenzohydroxamate by mixed melting point determination.

25. <u>Preparation of Diphenyltin bis(N-paratolylbenzohydroxamate).</u>

Diphenyltin oxide (1.45 gm) was taken in benzene (50 ml) and to it was added N-paratolylbenzohydroxamic acid (2.27 gm) and the mixture was refluxed using water separator for three hours. The yellow coloured solution was concentrated on a water bath to a pasty mass and precipitated with pet-ether or methanol. Repeated precipitation from either of the solvents gave 2 gm of white solid of m.p. 166-67°. Analysis gave : C = 66.26, H = 4.76, Sn = 16.30% and calculated for $C_{40}H_{34}O_4N_2Sn$: C = 66.20%, H = 4.68, Sn = 16.41%.

26. Preparation of Diphenyltin bis(N-orthotolylbenzohydroxamate)

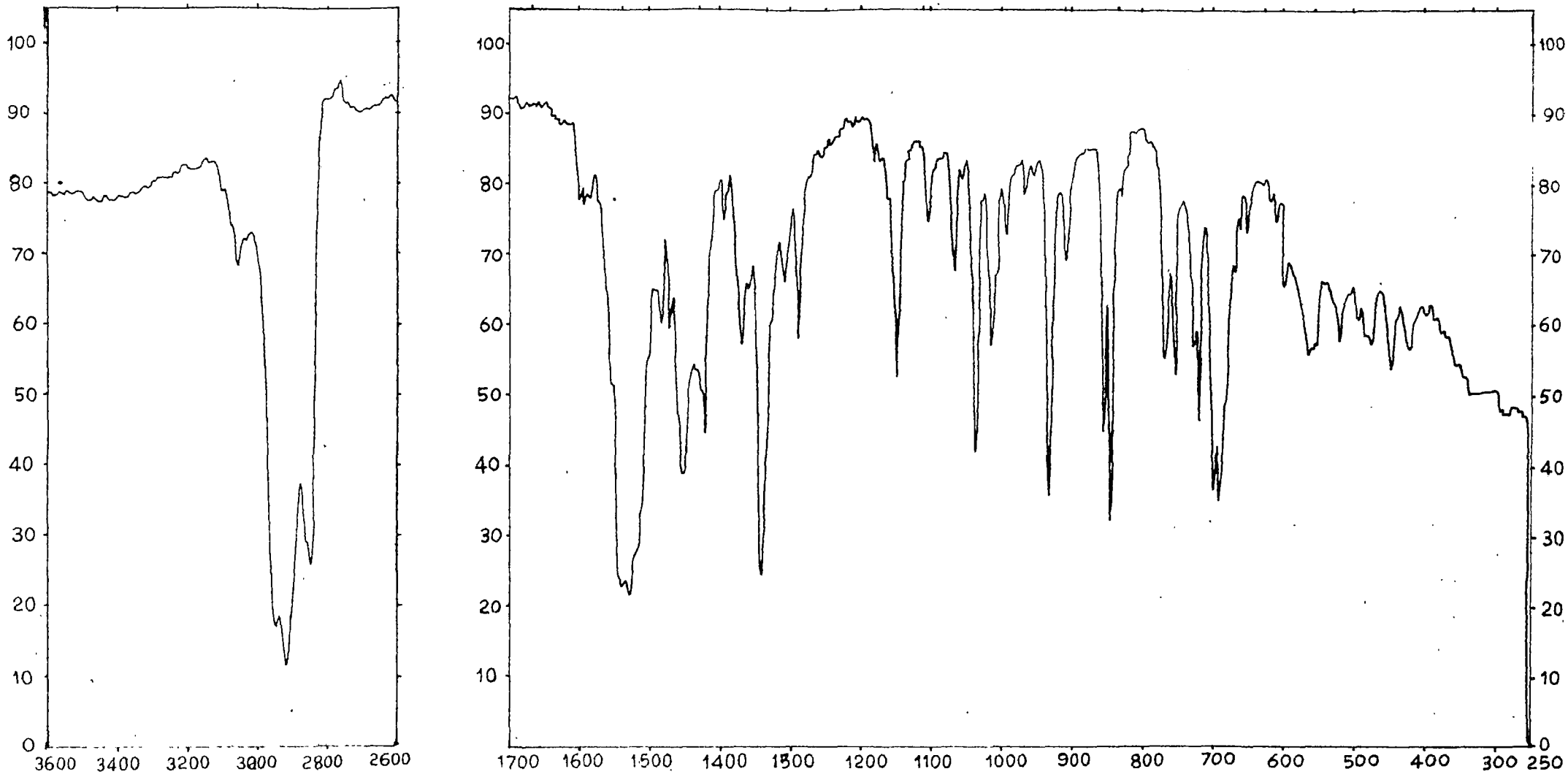
A mixture of 1.33 gm of diphenyltin oxide and 2.27 gm of N-orthotolylbenzohydroxamic acid taken in 50 ml of benzene was refluxed for five hours using water separator. The light yellow solution was concentrated on a water bath to a pasty mass which when boiled with methanol gave 3.1 gm of a white solid. This solid was repeatedly treated with methanol and had a m.p. of 197°. Analysis of this compound gave : C = 66.30, H = 4.61, Sn = 16.22% and calculated for $C_{40}H_{34}O_4N_2Sn$: C = 66.20, H = 4.68, Sn = 16.41% .

27. Preparation of Diphenyltin bis(N-phenylparachlorobenzohydroxamate)

1.43 gm of diphenyltin oxide and 2.47 gm of N-phenylparachlorobenzohydroxamic acid were taken in 50 ml of benzene. The mixture was refluxed using water separator for three hours. The light yellow coloured solution was evaporated on a water bath and treated with methanol. Fine white crystals of m.p. 135-36° came, weighing 2.5 gm. This was crystallised similarly four times and crystals of m.p. 139° were obtained, analysis of which gave : C = 59.73, H = 3.97, Sn = 15.41% and calculated for $C_{38}H_{28}O_4N_2Cl_2Sn$: C = 59.53, H = 3.67, Sn = 15.53% .

28. Preparation of Diphenyltin bis(N-phenylparanitrobenzohydroxamate)

Diphenyltin oxide (2.60 gm) and N-phenylparanitrobenzohydroxamic acid (5.16 gm) were taken in 50 ml of benzene and the mixture was refluxed for three hours using water separator. The yellow solution was then evaporated on a water bath to a very small volume and treated



I.R. Spectrum of Diphenyltin bis (N-Phenylparanitrobenzohydroxamate).

FIG- 7b

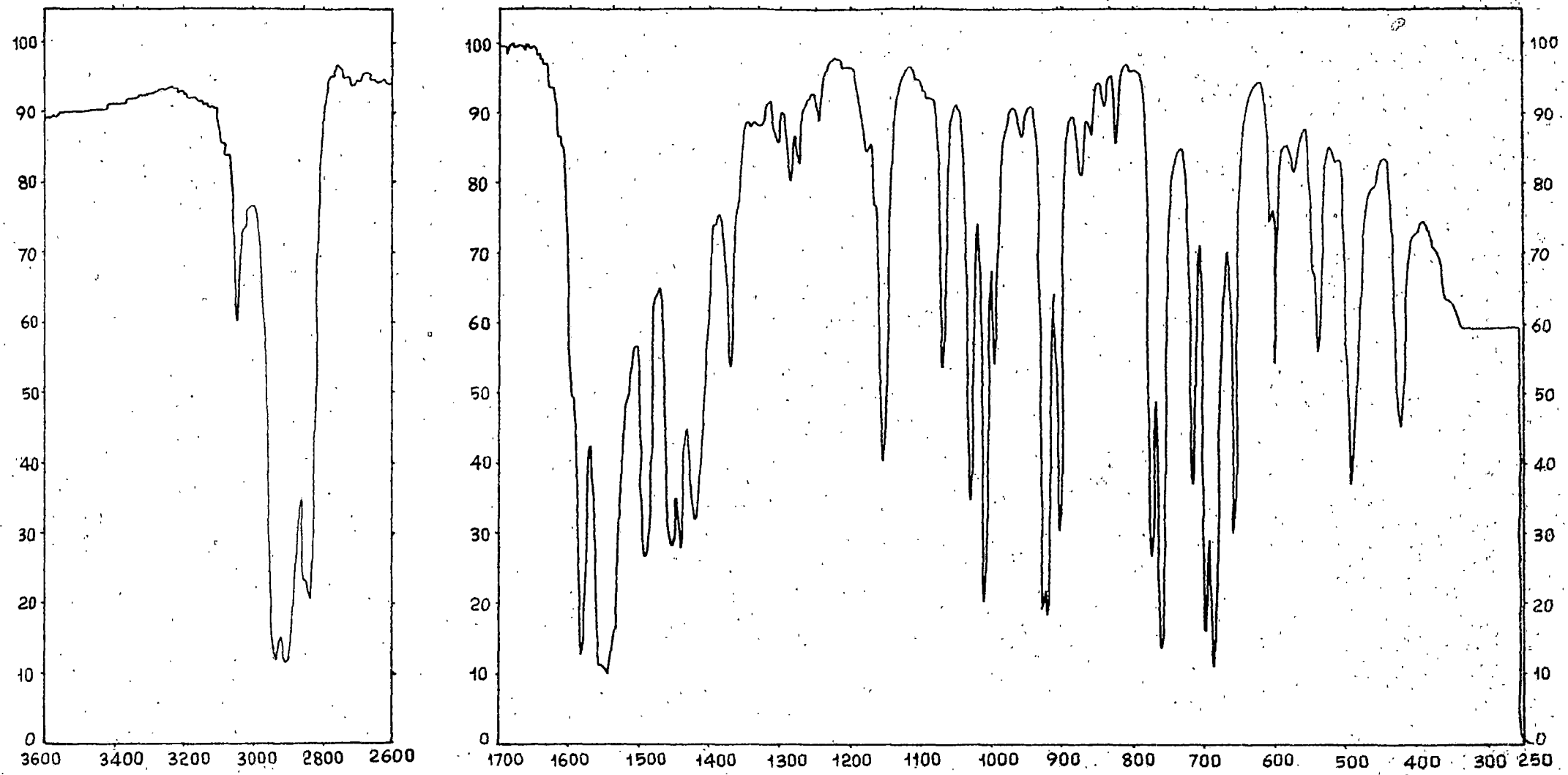
with methanol when yellow crystals of m.p. 190-92° were obtained. After repeated crystallisation from a mixture of benzene and methanol fine light yellow crystals of m.p. 196° came. Analysis gave : C = 58.00, H = 3.66, Sn = 16.02% and calculated for $C_{39}H_{29}O_8N_4Sn$: C = 57.94, H = 3.81, Sn = 16.12%; molecular weight in chloroform (vapour pressure osmometry) = 812 and calculated for the above formula = 737.

29. Preparation of Diphenyltin bis(N-ethylparachlorobenzohydroxamate):

A mixture of 1.16 gm of diphenyltin oxide and 1.6 gm of N-ethylparachlorobenzohydroxamic acid taken in 50 ml of benzene was refluxed using water separator for two hours. This was then evaporated on a water-bath to a pasty mass and crystallised from a mixture of benzene and ethylacetate. 2.3 gm of fine white crystals of melting point 222.5° came. Analysis gave : C = 53.93, H = 4.39, Sn = 17.45% and calculated for $C_{30}H_{28}O_4N_2Cl_2Sn$: C = 53.98, H = 4.18, Sn = 17.46%.

30. Preparation of Dibutyltin bis(N-phenylbenzohydroxamate):

2.5 gm of dibutyltin oxide and 4.2 gm of N-phenylbenzohydroxamic acid taken together in 50 ml of benzene was refluxed using water separator for one hour. The solution was concentrated on a water bath to a small volume and treated with pet-ether. 3.5 gm of white crystals of melting point 105° came. This was crystallised from rectified spirit thrice and had a m.p. of 106-07°. Analysis gave : C = 62.42, H = 5.84, Sn = 17.73% and calculated for $C_{34}H_{38}O_4N_2Sn$: C = 62.11, H = 5.78, Sn = 18.11% .



I.R. Spectrum of Dibutyltin bis(N-Phenylbenzohydroxamate)

Fig- 7c

31. Preparation of Dibutyltin bis(N-phenylparachlorobenzohydroxamate)

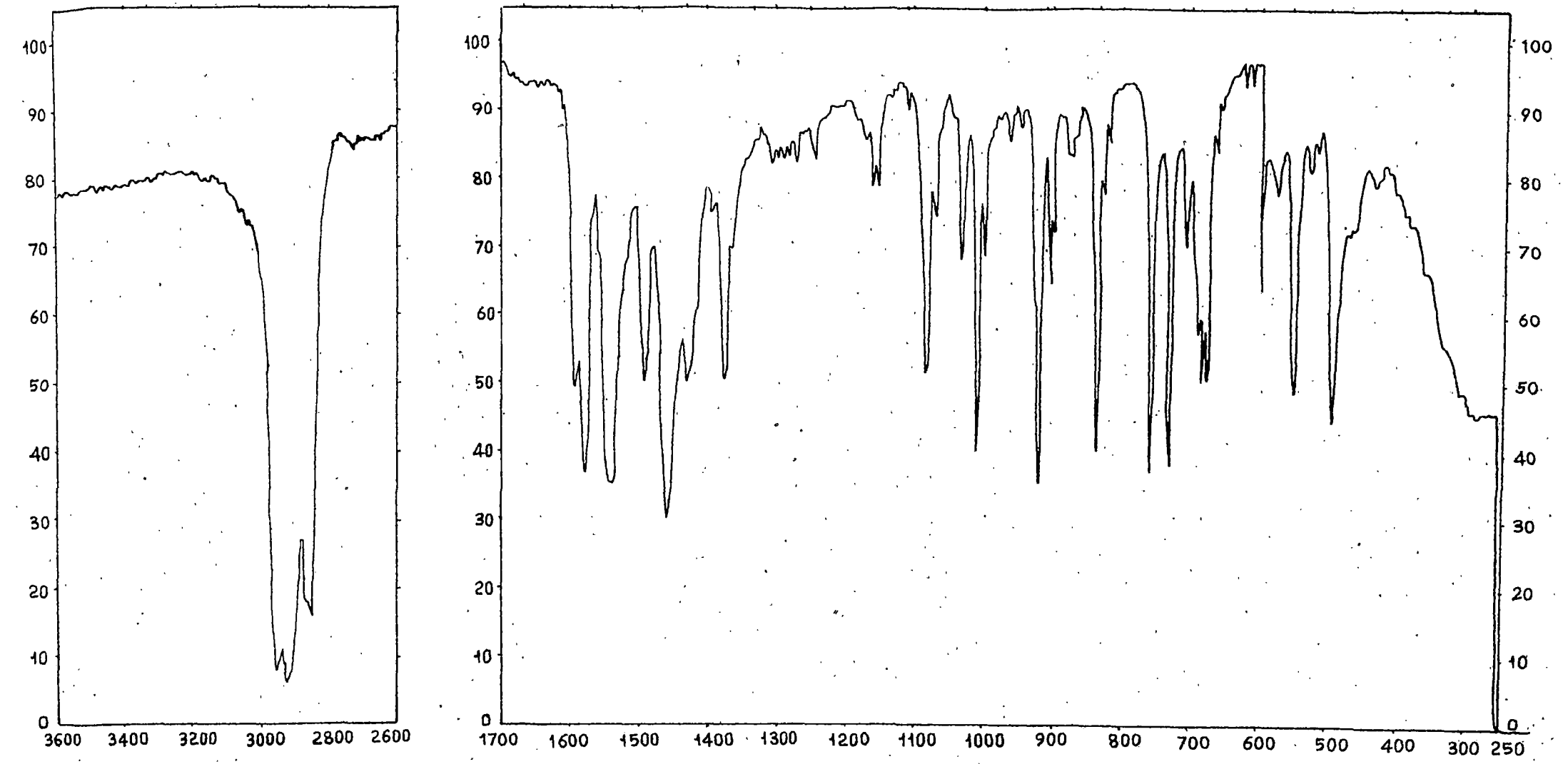
1.25 gm of dibutyltin oxide was taken in 50 ml of benzene and to it was added 2.50 gm of N-phenylparachlorobenzohydroxamic acid and the mixture was refluxed for two hours - using water separator. The volume of the light yellow coloured solution was concentrated on a water bath and treated with pet-ether. 3.5 gm of crystals melting at 85° came, which on several crystallisations from methanol gave fine white crystals of m.p. 93-100°. Analysis gave: C = 56.71, H = 4.95, Sn = 15.67% and calculated for $C_{34}H_{36}O_4N_2Cl_2Sn$: C = 56.20, H = 4.96, Sn = 16.36% .

32. Preparation of Dibutyltin bis(N-parachlorophenylbenzohydroxamate)

Dibutyltin oxide (1.25 gm) was taken in 50 ml of benzene and to it was added 2.50 gm of N-parachlorophenylbenzohydroxamic acid. The mixture after refluxing for two hours using water separator was concentrated and treated with ethanol. 2.1 gm of light yellow crystals melting at 75-77° came. This on crystallisation four times from ethanol afforded fine white crystals of melting point 102-3°. Analysis gave : C = 55.73, H = 5.15, Sn = 15.40% and calculated for $C_{34}H_{36}O_4N_2Cl_2Sn$: C = 56.20, H = 4.96, Sn = 16.36% .

33. Preparation of Dibutyltin bis(N-ethylparachlorobenzohydroxamate)

A mixture of 1.25 gm of dibutyltin oxide and 2.0 gm of N-ethylparachlorobenzohydroxamic acid taken in 50 ml of benzene was refluxed using water separator for three hours. The volume of the



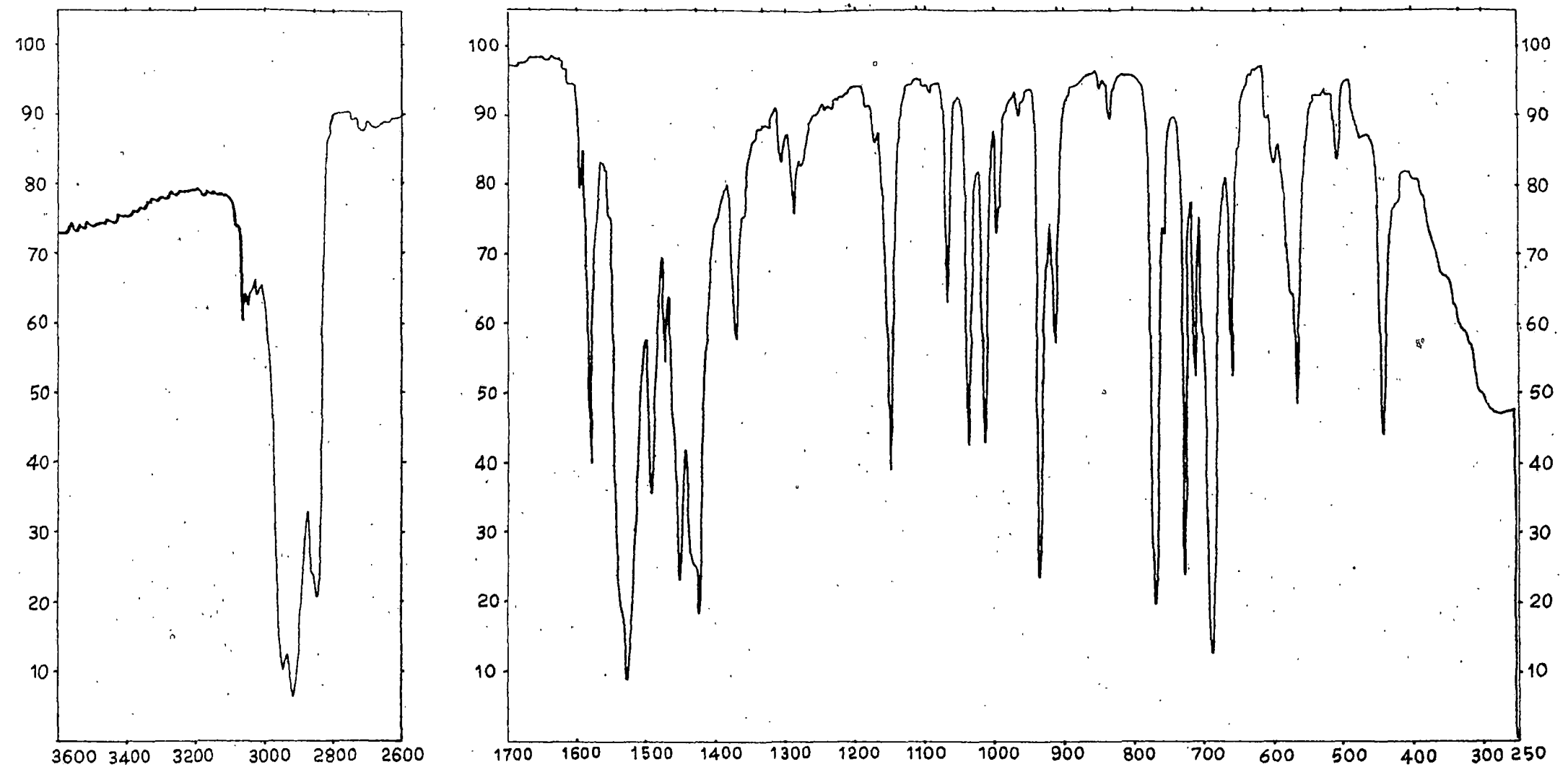
I.R. Spectrum of Dibutyltin bis(N-Phenyl p-chlorobenzohydroxamate)

Fig- 7d

solution was concentrated and treated with methanol when 2.9 gm of white crystals melting at 95-100° was obtained. This on repeated crystallisation from methanol afforded fine white leafy crystals of m.p. 100°. Analysis gave : C = 49.84, H = 5.52, Sn = 18.67% and calculated for $C_{26}H_{36}O_4N_2Cl_2Sn$: C = 49.52, H = 5.71, Sn = 18.83% .

34. Preparation of Phenyltin Chloride bis-(N-phenylbenzohydroxamate):

2.55 gm of triphenyltin N-phenylbenzohydroxamate was taken in 50 ml of benzene and 1.25 gm of mercuric chloride was added to it. The mixture was refluxed for 2 hours. The clear solution was cooled and the glassy white leafy crystals weighing 1.2 gm that had a m.p. of 243-9° was separated on cooling. This on recrystallisation from benzene afforded crystals of m.p. 251°, which showed no depression in m.p. when mixed with an authentic sample of phenyl mercuric chloride. The filtrate after the separation of phenyl mercuric chloride was concentrated to a very small volume and cooled. 0.2 gm of phenyl mercuric chloride was again separated. The filtrate was then completely evaporated to dryness, cooled and washed several times with hot pet-ether. The pasty mass which remained was a white solid of m.p. 150-165° (A). The pet-ether washings were taken together, concentrated and cooled. 0.4 gm of crystals of m.p. 104-05° came, which on further crystallisation from pet-ether gave crystals of m.p. 106° and found to be identical with that of triphenyltin chloride (by mixed m.p.). (A) on crystallisation several times from benzene afforded 1.1 gm of fine white crystals of m.p. 196°. Analysis of (A)



I.R. Spectrum of Phenyltin Chloride bis(N-Phenylbenzohydroxamate).

FIG - 8a

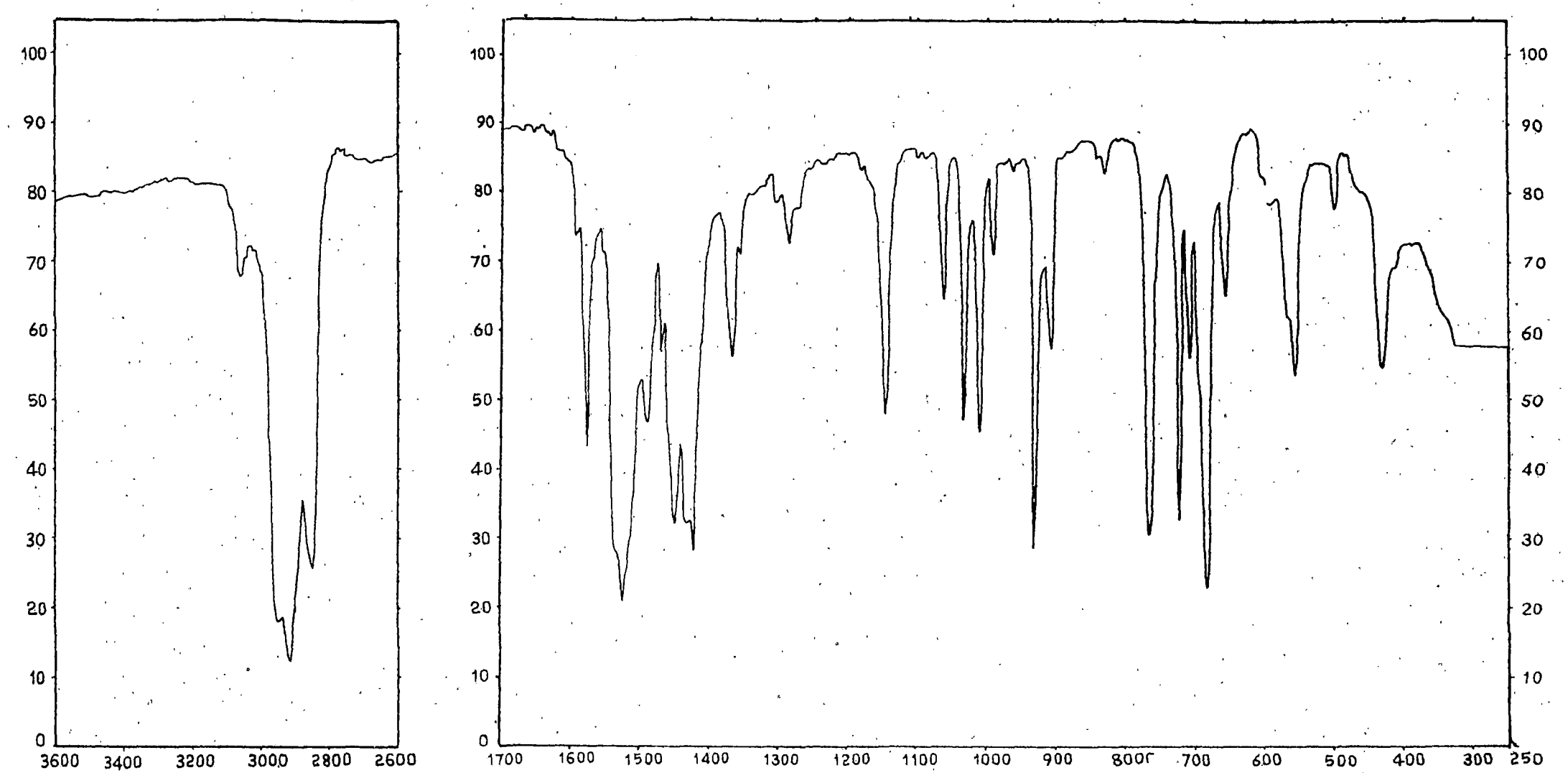
gave : C = 58.53, H = 3.09, Sn = 18.11% and calculated for $C_{32}H_{25}O_4N_2ClSn$: C = 58.53, H = 3.8, Sn = 18.15%; molecular weight in chloroform (vapour pressure osmometry) = 658 and calculated for the above formula = 656.

35. Preparation of Phenyltin bromide bis(N-phenylbenzohydroxamate):

1.69 gm of triphenyltin N-phenylbenzohydroxamate and 1.03 gm of mercuric bromide were taken in 50 ml of benzene and the mixture was refluxed for 2 hours with occasional shaking. The reaction mixture was then concentrated to a small volume and cooled. After the separation of the leafy crystals (which on repeated crystallization from benzene was found to have a m.p. of 270°, identical with that of phenyl mercuric bromide) the residual volume was concentrated to a pasty mass. This pasty mass was washed several times with pet-ether, which afforded crystals of m.p. 117° and on recrystallization twice from pet-ether gave triphenyltin bromide of m.p. 122°. The residual mass was then crystallized several times from a mixture of benzene and pet-ether and gave granular crystals of m.p. 133°. Analysis of this compound gave : C = 54.75, H = 3.76, Sn = 16.70% and calculated for $C_{32}H_{25}O_4N_2BrSn$: C = 54.35, H = 3.57, Sn = 17.00%.

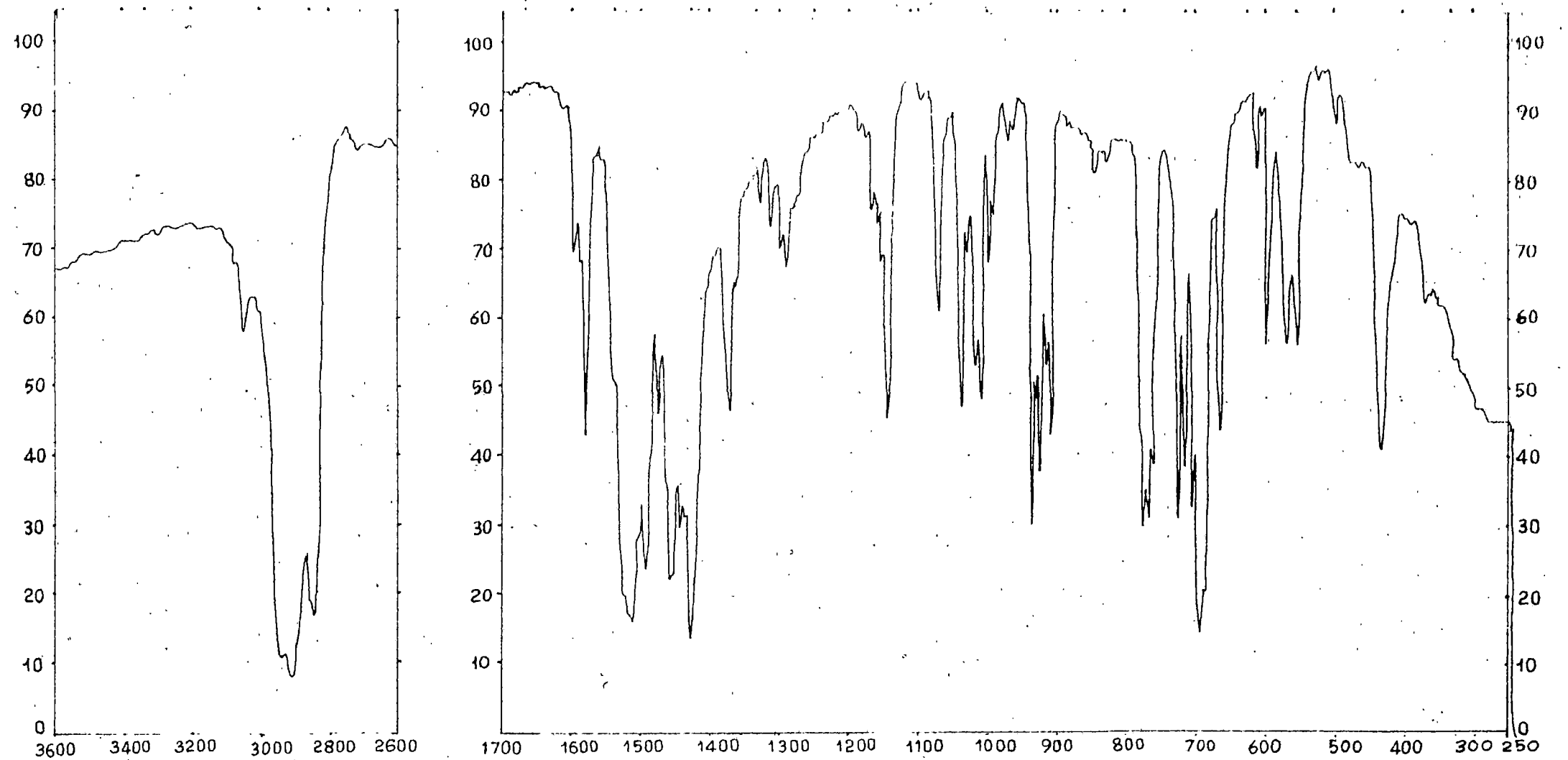
36. Preparation of Phenyltin iodide bis(N-phenylbenzohydroxamate):

Triphenyltin N-phenylbenzohydroxamate (2.81 gm) and mercuric iodide (2.27 gm) were taken in 100 ml of benzene and the mixture was refluxed with occasional shaking for 2 hours. The reaction mixture was then concentrated to a small volume and cooled. After the separation of the leafy crystals of phenyl mercuric iodide (m.p. 268°) the residual solution was concentrated to a pasty mass. This pasty mass



I.R. Spectrum of Phenyltin bromide bis (N-Phenylbenzohydroxamate)

Fig- 8b



I.R. Spectrum of Phenyltin Iodide bis (N-Phenylbenzohydroxamate)

FIG- 8C

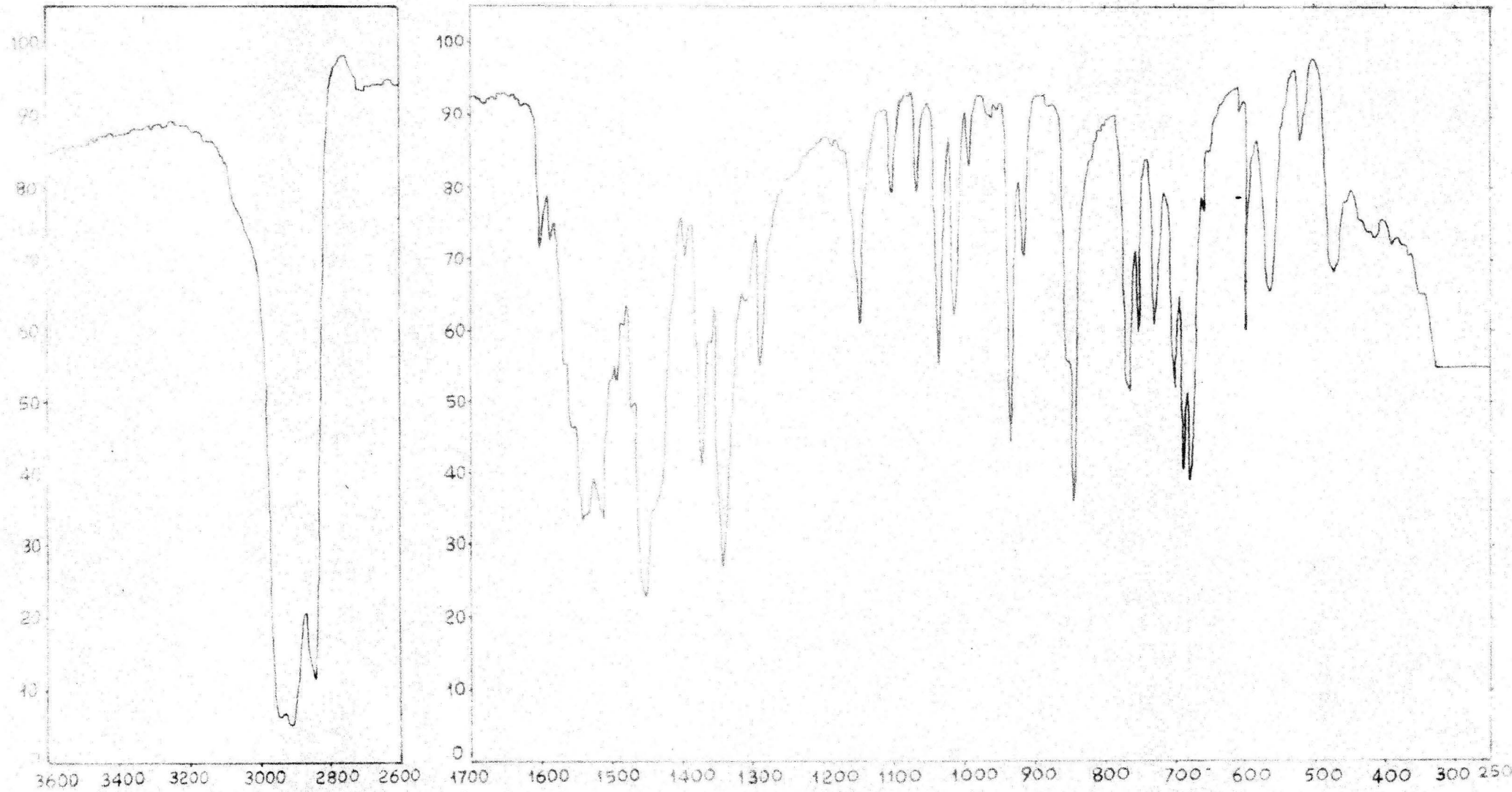
was then washed several times with pet-ether. Pet-ether soluble fractions yielded triphenyltin iodide of m.p. 121° (crystallised from pet-ether thrice). The residue from pet-ether treatment was dissolved in benzene, filtered, concentrated to a small volume, cooled and added ethanol while white crystals of m.p. 175-77° came, which on similar treatment for five times gave crystals of m.p. 177-79°. Analysis gave : C = 51.28, H = 3.51, Sn = 15.38% and calculated for $C_{32}H_{25}O_4NSn$: C = 51.40, H = 3.35, Sn = 15.93% .

37. Preparation of Phenyltin thiocyanate bis(N-phenylbenzohydroxamate):

Phenyltin chloride bis(N-phenylbenzohydroxamate) (1 gm) was dissolved in 30 ml of benzene and to this solution was added 0.3 gm of potassium thiocyanate. The mixture was then stirred magnetically for 3 hrs. Heavy white precipitate (A) came, which was filtered. (A) was found to have a m.p. of 75-90° weighing 1.1 gm. This was then crystallized from benzene when needle-shaped crystals of m.p. 93-95° came. Analysis of this compound gave : C = 59.34, H = 3.91, Sn = 17.23% and calculated for $C_{33}H_{25}N_3O_4SSn$: C = 59.70, H = 3.69, Sn = 17.55% .

38. Preparation of Phenyltin chloride bis(N-phenylparanitrobenzohydroxamate):

1.82 gm of triphenyltin N-phenylparanitrobenzohydroxamate was taken in 30 ml of benzene and to it was added 0.81 gm of mercuric chloride. This was then refluxed for 2 hrs. The clear hot solution



I.R. Spectrum of Phenyltin Chloride Bis(N-Phenylparanitrobenzohydroxamate)

Fig. 8d

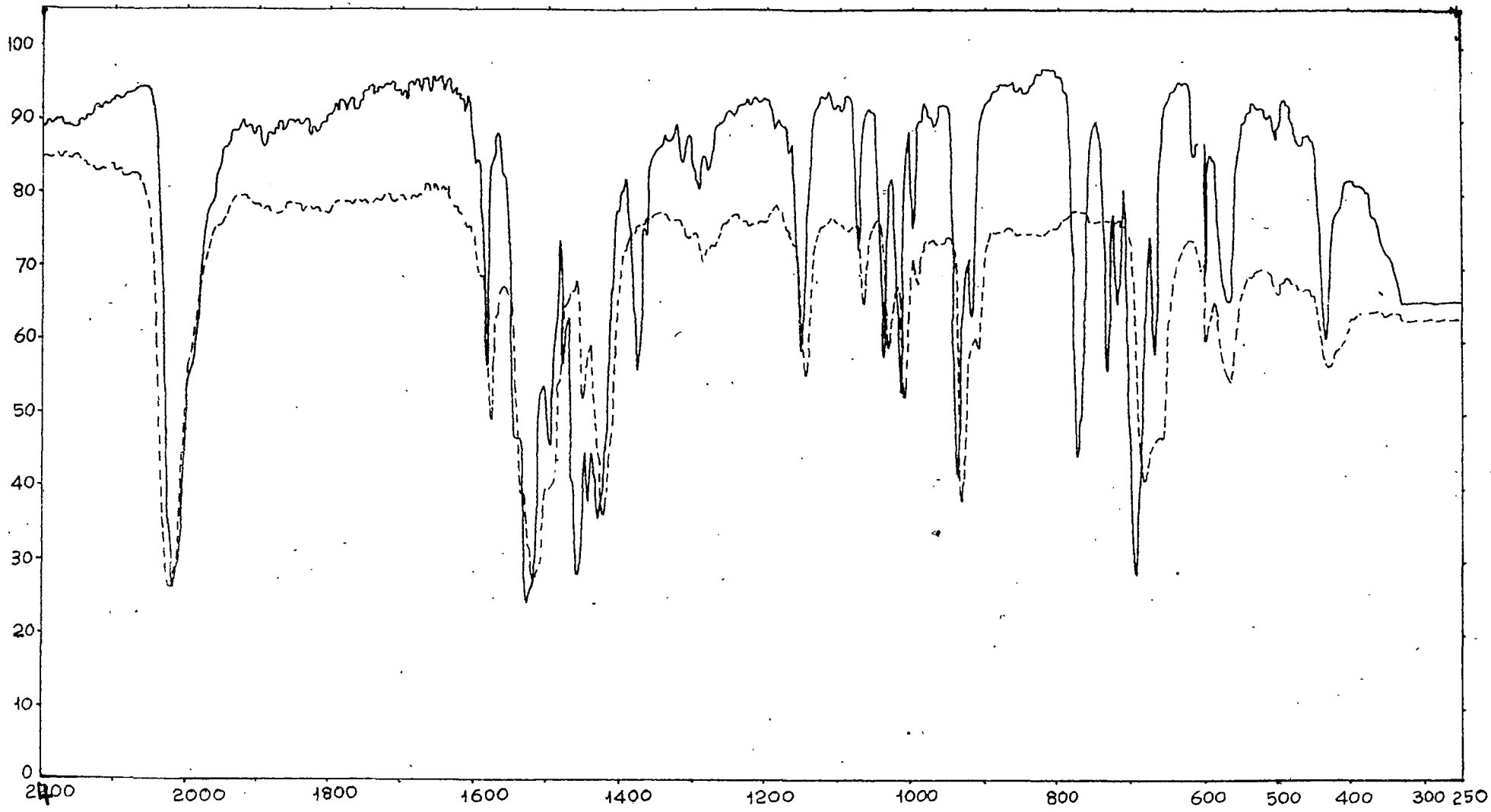


Fig:- 8e. IR Spectrum of Phenyltin thiocyanate bis(N-Phenylbenzohydroxamate)

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---- in $CHCl_3$ Solution.

was cooled and filtered while the leafy crystals of phenylmercuric chloride m.p. 248-49° was separated. The filtrate was concentrated further and cooled. A second crop of phenyl mercuric chloride was filtered out. The mother liquor from this was evaporated to dryness and washed with pet-ether several times. The washed solid was then crystallised from benzene when 1.3 gm of light yellow granulated crystals (A) of m.p. 110° was obtained. (A) on further crystallisation from benzene had a m.p. of 113°. The pet-ether washings yielded triphenyltin chloride. Analysis of the compound (A) gave : Sn = 16.32% and calculated for $C_{38}H_{28}O_3N_4ClSn$: Sn = 15.96% .

39. Preparation of Phenyltin bromide bis(N-phenylparanitrobenzohydroxamate):

A mixture of 1.08 gm of triphenyltin N-phenylparanitrobenzohydroxamate and 1.08 gm of mercuric bromide in 30 ml of benzene was refluxed for 8 hrs. After removing the phenyl mercuric bromide and triphenyltin bromide as in the case for chloride, the solid was crystallised from a mixture of benzene and pet-ether. 1.4 gm of a light yellow crystalline solid of m.p. 95-97° came, which was further crystallised several times from the same solvent mixture to have a compound of m.p. 97-9°. Analysis of this compound gave : C = 49.31, H = 3.97, N = 6.97, Sn = 15.28% and calculated for $C_{38}H_{28}O_3N_4BrSn$: C = 48.61, H = 3.15, N = 7.09, Sn = 15.06%; molecular weight in chloroform (vapour pressure osmometry) = 794 and calculated for the above formula = 799.

40. Preparation of Phenyltin iodide bis(N-phenylparanitrobenzohydroxamate) :

A mixture of 1.82 gm of triphenyltin N-phenylparanitrobenzohydroxamate and 1.36 gm of mercuric iodide was taken in 50 ml of benzene and the mixture was refluxed for 3 hrs. Proceeding as in the case of chloride, phenyl mercuric iodide and triphenyltin iodide were separated out and a yellow solid (A) was obtained . (A) was dissolved in benzene and precipitated in the cold by adding pet-ether. Precipitation for several times yielded yellow solid of m.p. 90°. Analysis gave : C = 46.08, H = 3.06, N = 6.03, Sn = 14.87% and calculated for $C_{32}H_{23}O_6N_4ISn$: C = 45.83, H = 3.28, N = 6.69, Sn = 14.22% .

41. Preparation of Phenyltin bromide bis (N-phenylparachlorobenzohydroxamate) :

A mixture of 1.79 gm of triphenyltin N-phenylparachlorobenzohydroxamate and 1.08 gm of mercuric bromide was taken in 50 ml of benzene and the mixture was refluxed for 3 hrs. Proceeding as for other such reactions phenyl mercuric bromide and triphenyltin bromide which were formed in the reaction were separated out. The white solid (A) remained after the separation was dissolved in benzene and added an excess of pet-ether when crystals of m.p. 170-72° came. Final crystallisation of this compound from a mixture benzene and pet-ether yielded crystals of m.p. 175-6°, analysis of which gave: C = 50.16, H = 3.21, N = 4.46% and calculated for $C_{32}H_{23}O_6N_2Cl_2BrSn$:

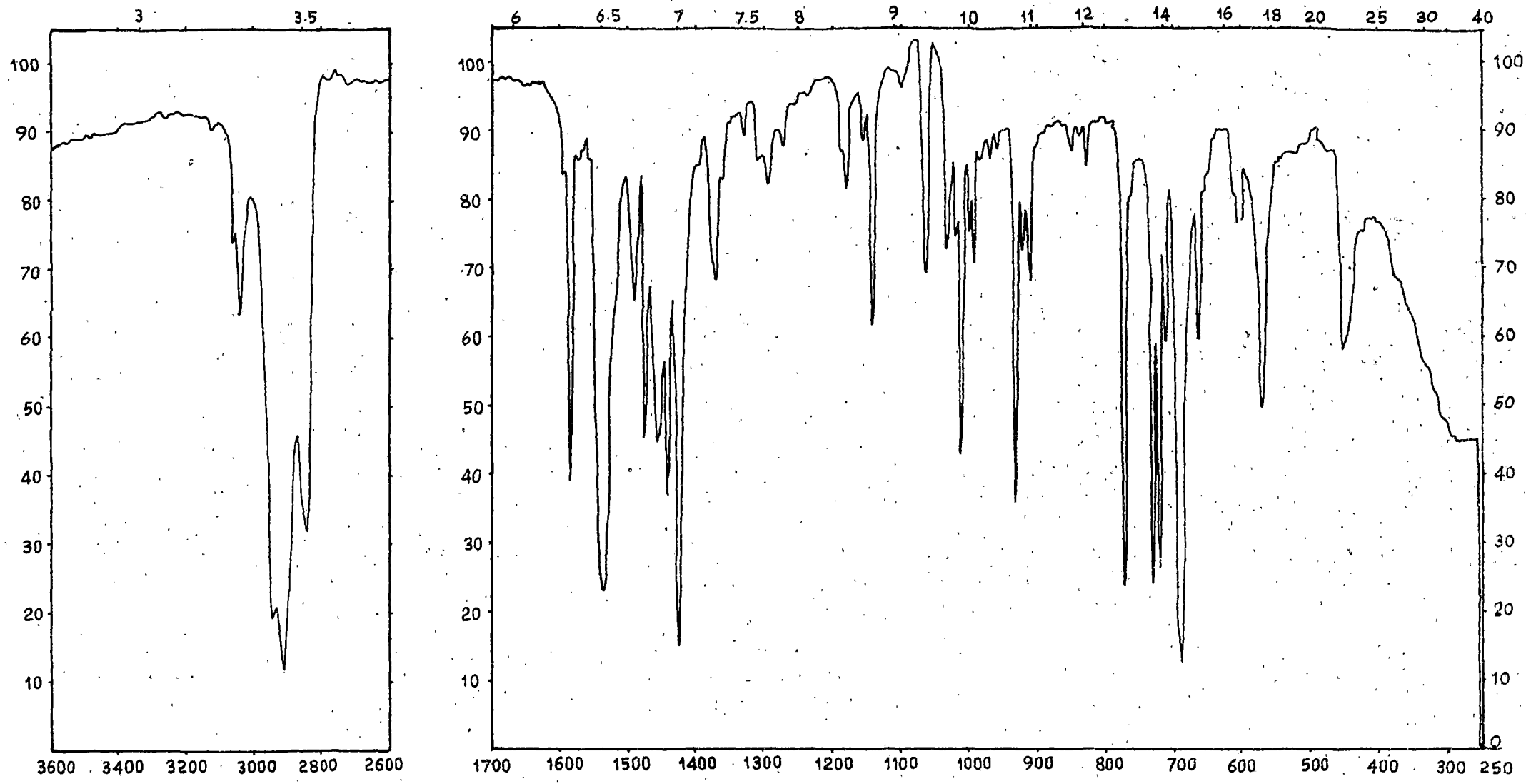
C = 50.0%, H = 3.99, N = 3.64% .

42. Preparation of Phenyltin iodide bis (N-phenylparachlorobenzohydroxamate) :

1.70 gm of triphenyltin N-phenylparachlorobenzohydroxamate was dissolved in boiling benzene and to it was added 1.36 gm of mercuric iodide with shaking. This was heated and shaken for 15 minutes more, while the red mercuric iodide almost disappeared and the solution became turbid. This mixture was then stirred magnetically for 3 hrs. to ensure complete reaction and proceeded as for the preparation of phenyltin iodide bis (N-phenylparanitrobenzohydroxamate). After the separation of phenyl mercuric iodide and triphenyltin iodide the white solid was crystallized from a mixture of benzene and pet-ether. Fine white crystals of m.p. 196° was obtained, which on analysis gave : C = 47.36, H = 3.24, N = 3.83% and calculated for $C_{32}H_{23}O_4N_2Cl_2ISn$: C = 47.05, H = 2.82, N = 3.43% .

43. Preparation of Diphenyltin chloride N-phenylbenzohydroxamate:

20 gm of diphenyltin bis-N-phenylbenzohydroxamate was dissolved in 15 ml of hot benzene and to it was added 9.9 gm of diphenyltin dichloride slowly with shaking at 25°. Heat was generated and the yellow colour of the solution disappeared. This mixture was then shaken for another 5 minutes and benzene was evaporated completely under vacuum to a white pasty mass which was washed with cold pet-ether. After pet-washings, the pasty residue was dissolved



I.R. Spectrum of Diphenyltin Chloride N-Phenylbenzohydroxamate.

FIG-9a

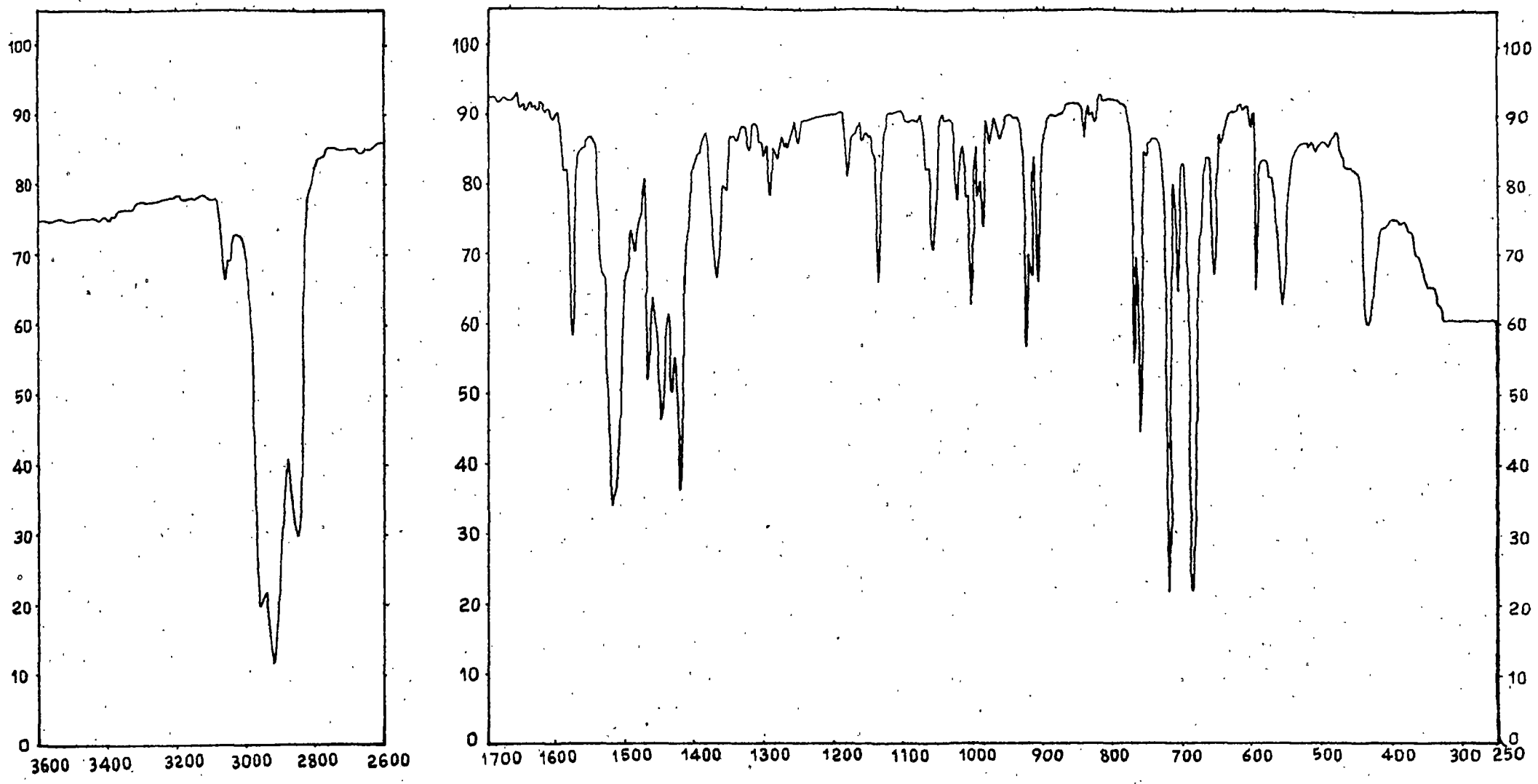
in cold methanol by shaking. Excess methanol was removed in the pump in cold and the solution was kept in the refrigerator. 24 gm of fine white crystals of m.p. 110-12° was separated, which was similarly treated and final crystallised product had a m.p. of 113°. Analysis of this compound gave : C = 57.78, H = 3.81, Sn = 22.75% and calculated for $C_{25}H_{20}O_2NClSn$: C = 57.64, H = 3.84, Sn = 22.86%; molecular weight in chloroform (vapour pressure osmometry) = 523 and calculated for the above formula = 521.

44. Preparation of Diphenyltin iodide N-phenylbenzohydroxamate:

1.39 gm of diphenyltin bis(N-phenylbenzohydroxamate) was dissolved in 15 ml of hot benzene and to this hot solution was added with shaking 1.05 gm of diphenyltin diiodide. This mixture was cooled and added pet-ether and kept in the refrigerator overnight. 2.1 gm of fine white crystals came, which showed a m.p. of 127-29°, the crystals being gradually changed to amorphous white solid. This was similarly crystallised from a mixture of benzene and pet-ether twice and the crystals had a m.p. of 132°. Analysis of this compound gave C = 43.82, H = 3.27, Sn = 19.30% and calculated for $C_{25}H_{20}O_2NISn$: C = 49.02, H = 3.27, Sn = 19.44% .

45. Preparation of Diphenyltin thiocyanate N-phenylbenzohydroxamate:

2.1 gm of diphenyltin chloride N-phenylbenzohydroxamate was taken in 15 ml of benzene and to it was added an ethanol solution of excess of potassium thiocyanate. Turbidity came, shaken for 5 minutes, filtered. The filtrate was cooled, while colourless square



I.R. Spectrum of Diphenyltin Iodide N-Phenylbenzohydroxamate.

Fig- 9b

crystals weighing only 1.2 gm came, which on further crystallization gave crystals of m.p. 158-59°. Analysis of this compound gave : C = 57.65, H = 3.75, Sn = 21.70% and calculated for $C_{28}H_{20}O_2N_2Sn$: C = 57.45, H = 3.71, Sn = 21.91% .

46. Preparation of Dibutyltin thiocyanate N-phenylbenzohydroxamate:

2.19 gm of dibutyltin bis-N-phenylbenzohydroxamate was taken in 30 ml of benzene and to it was added 1.16 gm of dibutyltin dithiocyanate. The mixture was then refluxed on a water bath for one hour. The clear solution was concentrated on a water bath to a very small volume and treated with pet-ether. 2.21 gm of colourless square crystals of m.p. 77-78° came. This was crystallised twice from the same solvent mixture and crystals had a m.p. of 79-80°. Analysis of this compound gave : C = 52.12, H = 5.94, Sn = 23.51% and calculated for $C_{23}H_{28}O_2N_2SSn$: C = 52.48, H = 5.61, Sn = 23.65% .

47. Preparation of diphenyltin chloride N-phenylparanitrobenzohydroxamate:

1.6 gm of diphenyltin bis(N-phenylparanitrobenzohydroxamate) was dissolved in 20 ml of benzene and to this solution was added with shaking 0.40 gm of diphenyltin dichloride. Immediate decolourization (yellow to colourless) took place with the precipitation of white solid. This was filtered and washed with benzene. The solid turned slowly to white amorphous powder, m.p. being 142-44°. This was again

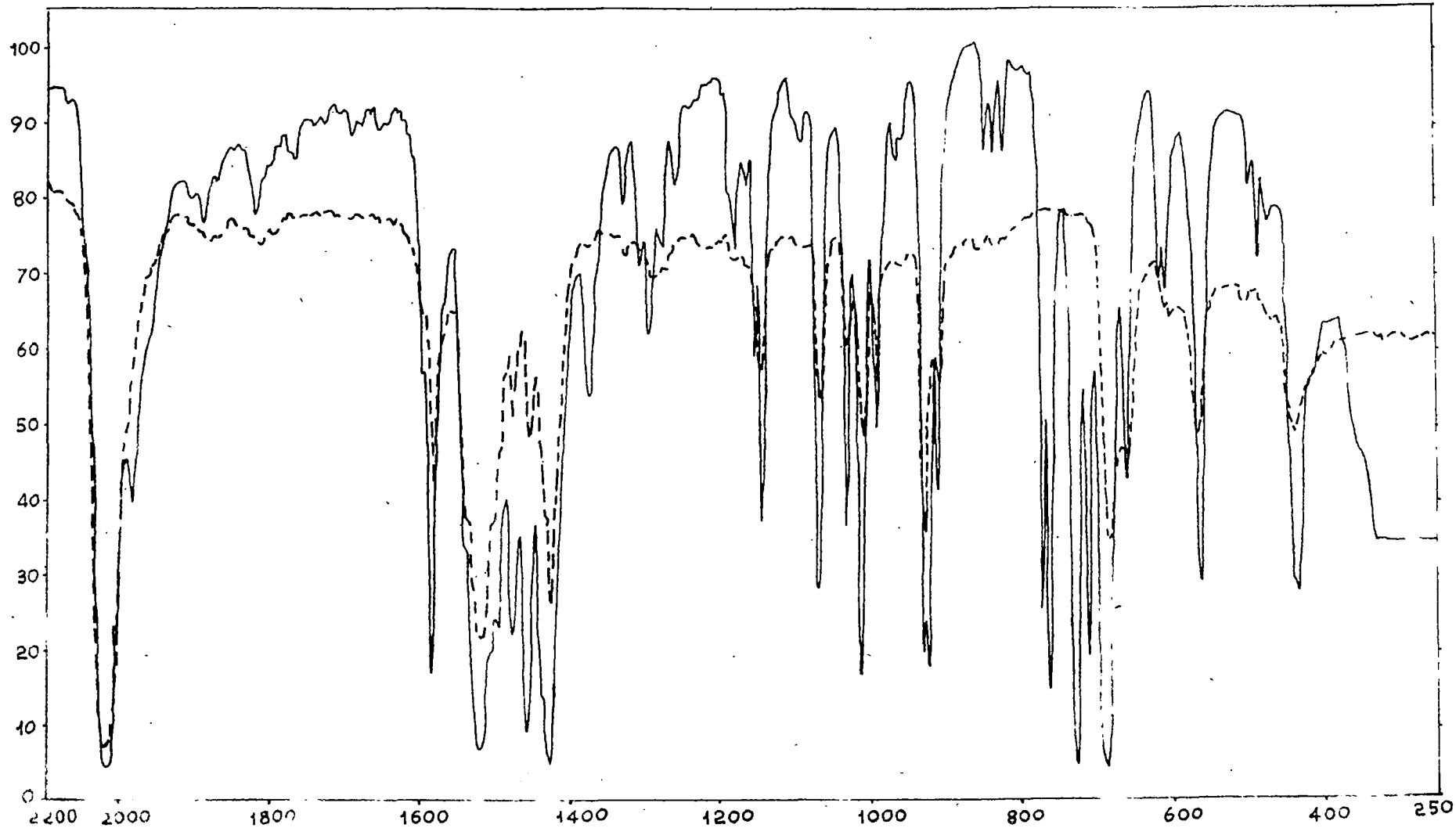


Fig 9c IR Spectrum of Diphenyltin thiocyanate N-Phenylbenzohydroxamate

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----- in $CHCl_3$ Solution

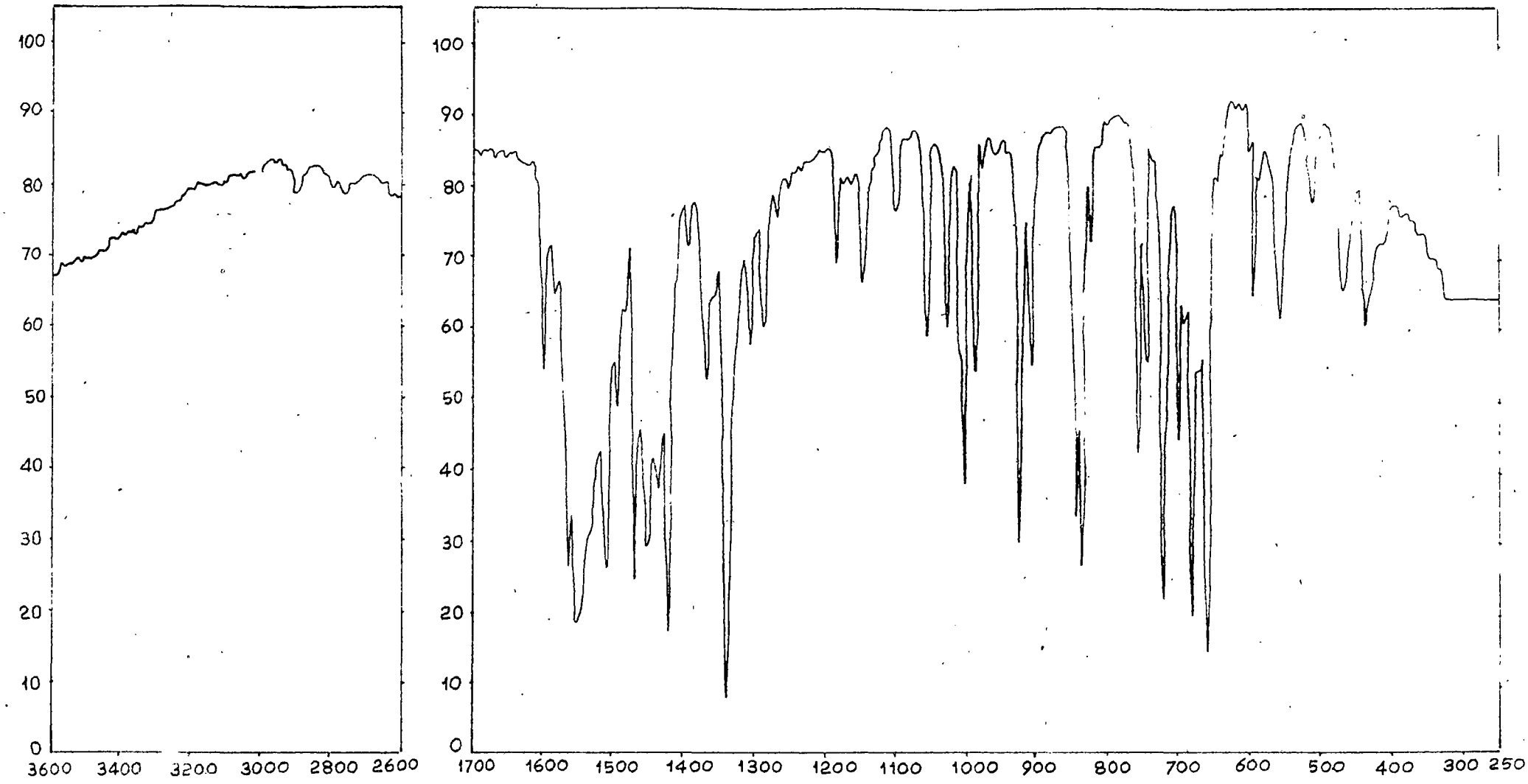
dissolved in comparatively excess of benzene and filtered. Filtrate was kept in the refrigerator overnight and the crystals of m.p. 143-45° was filtered out, which on further crystallization from benzene gave crystals of same m.p. 143-45°. Analysis of the compound gave: C = 57.40, H = 3.77, N = 4.24, Sn = 18.23% and calculated for $C_{25}H_{19}O_4N_2ClSn.C_6H_6$: C = 57.73, H = 3.83, N = 4.22, Sn = 18.48% .

48. Preparation of Diphenyltin iodide N-phenylparanitrobenzohydroxamate:

1.60 gm of diphenyltin bis(N-phenylparanitrobenzohydroxamate) was dissolved in benzene and to this solution was added with shaking 1.06 gm of diphenyltin diiodide. The clear mixture was kept in the refrigerator overnight when light yellow crystals weighing 2.1 gm came, which had a m.p. of 115-19°. This was similarly crystallised from benzene. The final light yellow crystals had a m.p. of 118-19°. Analysis of this compound gave : C = 50.03, H = 3.51, Sn = 16.02% and calculated for $C_{25}H_{19}O_4N_2ISn.C_6H_6$: C = 50.61, H = 3.40, Sn = 16.19% .

49. Disproportionation reaction of diphenyltin chloride N-phenylbenzohydroxamate:

Diphenyltin chloride N-phenylbenzohydroxamate (1 gm) was taken in 30 ml of benzene and this solution was refluxed for 11 hours. Then benzene was evaporated completely when a pasty mass came. This pasty mass was crystallised from a mixture of benzene and pet-ether



IR Spectrum of Diphenyltin iodide N-Phenylparanitrobenzohydroxamate.

Fig.....9d

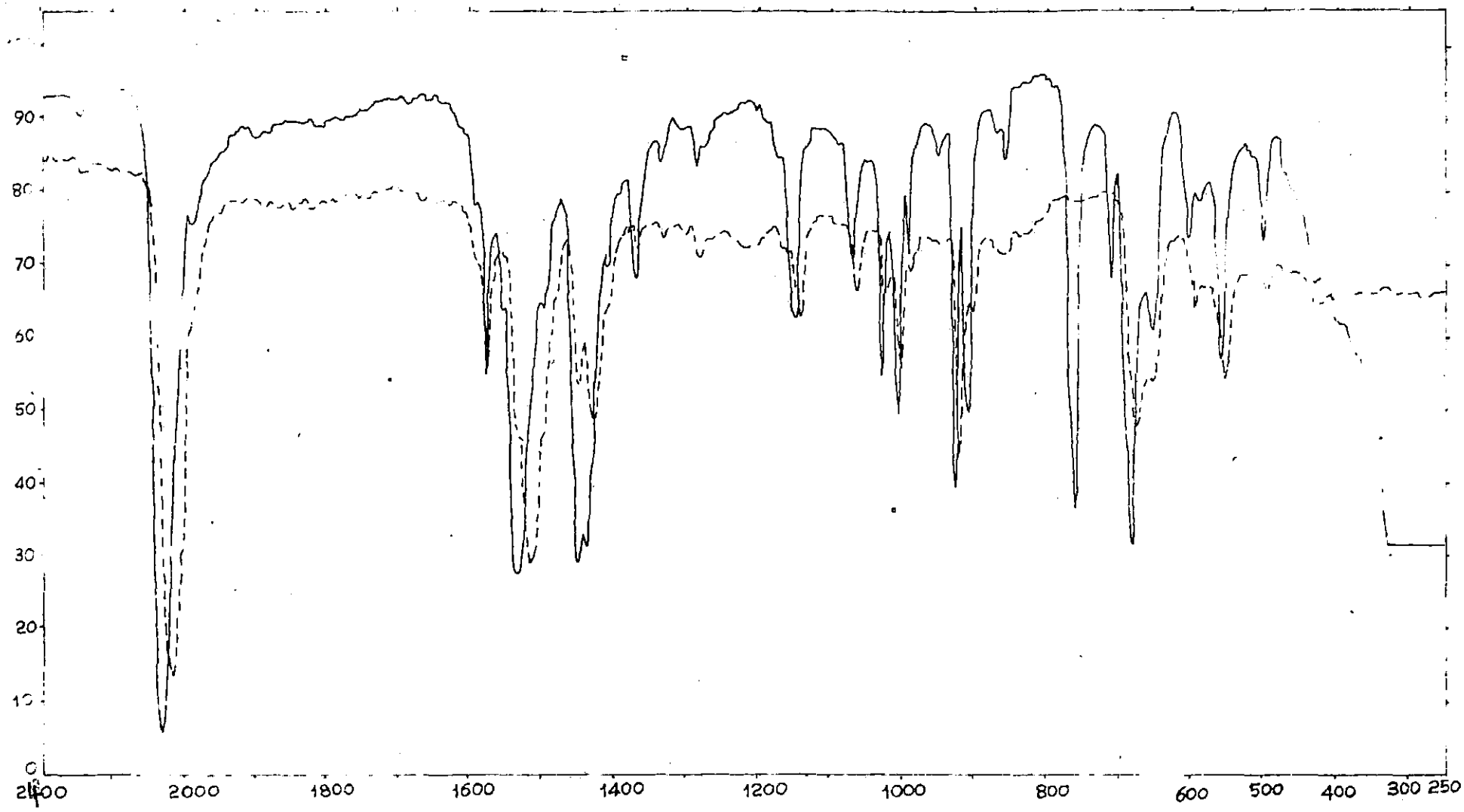


Fig:- 9e. IR Spectrum of Dibutyltin thiocyanate N-Phenylbenzohydroxamate.

—— in nujol mull

----- in $CHCl_3$ Solution

White crystals of m.p. 185-90° came (A), which on crystallisation thrice from the same solvent mixture gave 0.56 gm of a compound of m.p. 195°. This compound was found to be identical with phenyltin chloride bis (N-phenylbenzohydroxamate) (identified by mixed m.p.). Mother liquor from (A) was evaporated to a pasty mass which when crystallised from pet-ether gave 0.3 gm of a compound of m.p. 106° undepressed when mixed with an authentic sample of triphenyltin chloride.

50. Disproportionation reaction of diphenyltin thiocyanate N-Phenylbenzohydroxamate:

Diphenyltin thiocyanate N-phenylbenzohydroxamate (0.9 gm) was taken in 30 ml of benzene and the solution was refluxed for 10½ hours. This solution was then concentrated and cooled when glassy white amorphous solid (A) of m.p. 90-93° came, which on further crystallisation gave 0.4 gm of a compound of m.p. 93-98°. This was found to be identical with phenyltin thiocyanate bis(N-phenylbenzohydroxamate) (from mixed m.p.). Filtrate from (A) was evaporated to a pasty mass which was repeatedly washed with hot pet-ether. The pet-ether washings gave a white solid of m.p. 145-60° which when mixed with triphenyltin thiocyanate was found to be undepressed suggesting that this was probably a mixture of triphenyltin thiocyanate and the starting material [m.p. of $Ph_3Sn(SCN)$ = 107° and that of $Ph_2Sn(SCN)(PBHA)$ = 158°].

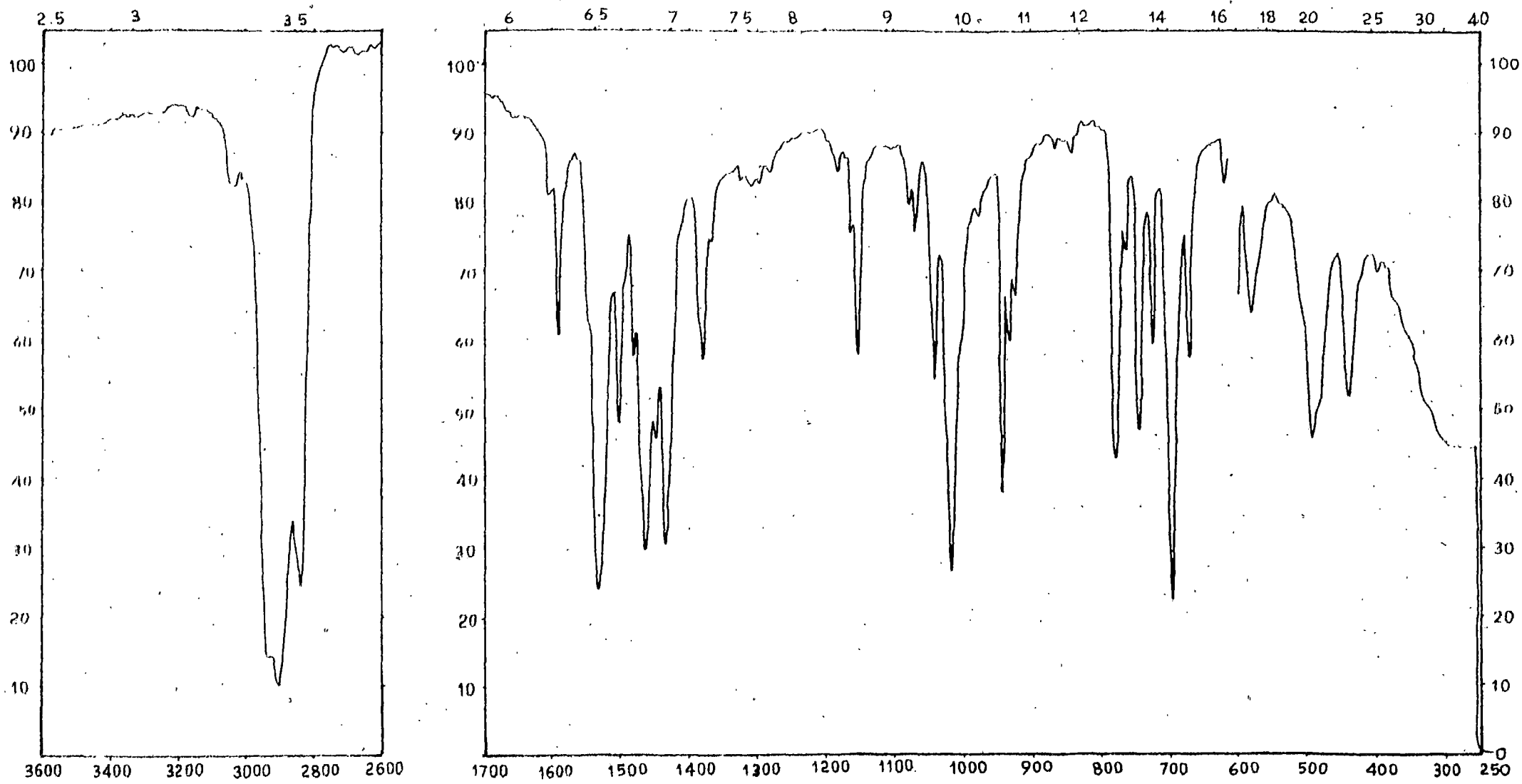
51. Preparation of Phenyltin Chloride methoxy N-phenylbenzohydroxamate:

a) Diphenyltin chloride N-phenylbenzohydroxamate was refluxed in methanol when fine white crystals appeared. Refluxing was continued for one hour and then it was filtered hot and washed several times with hot methanol. The crystals showed a m.p. of 223° (dec) in a preheated bath. Analysis gave : C = 50.57; H = 3.04; Sn = 25.18; Cl = 7.31; $-OCH_3$ = 6.59% and calculated for $C_{20}H_{18}ClNO_3Sn$, C = 50.42, H = 3.79, Sn = 25.03, Cl = 7.43, $-OCH_3$ = 6.53% .

b) The same methoxy compound was obtained when phenyltin chloride bis (N-phenylbenzohydroxamate) was refluxed in methanol. Thus 0.5 gm of phenyltin chloride bis (N-phenylbenzohydroxamate) was refluxed in methanol for 11 hrs. and filtered hot. 0.23 gm of a compound of m.p. 228° came, which was found to be phenyltin chloride methoxy N-phenylbenzohydroxamate (identified by the mixed m.p.) which showed no depression).

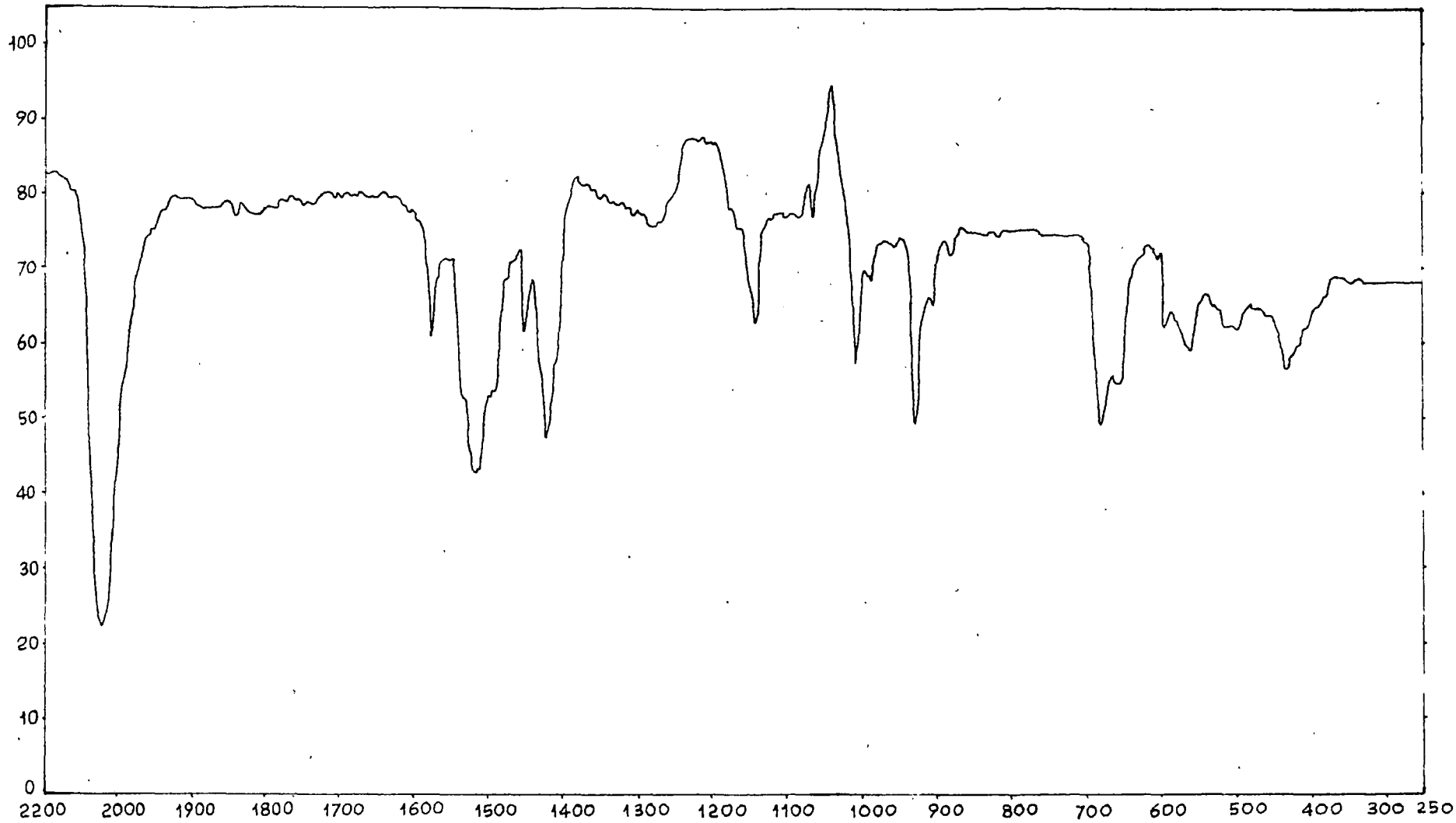
52. Preparation of Phenyltin thiocyanate methoxy N-phenylbenzohydroxamate:

This was prepared by refluxing diphenyltin thiocyanate N-phenylbenzohydroxamate in methanol for two hours. The white solid was filtered hot and washed with hot methanol, had a m.p. of 230-31° (dec.). Analysis gave : C = 50.94; H = 3.77, Sn = 23.71% and calculated for $C_{21}H_{18}SN_2O_3Sn$: C = 50.70, H = 3.62, Sn = 23.94% .



I.R. Spectrum of Phenylchlorotin methoxy N-Phenylbenzohydroxamate

FIG- 10a



IR Spectrum of Phenyltin thiocyanate methoxy N-Phenylbenzohydroxamate
(in $CHCl_3$ Solution)

Fig--10b

53. Preparation of Phenyltin bromide methoxy N-phenylbenzohydroxamate :

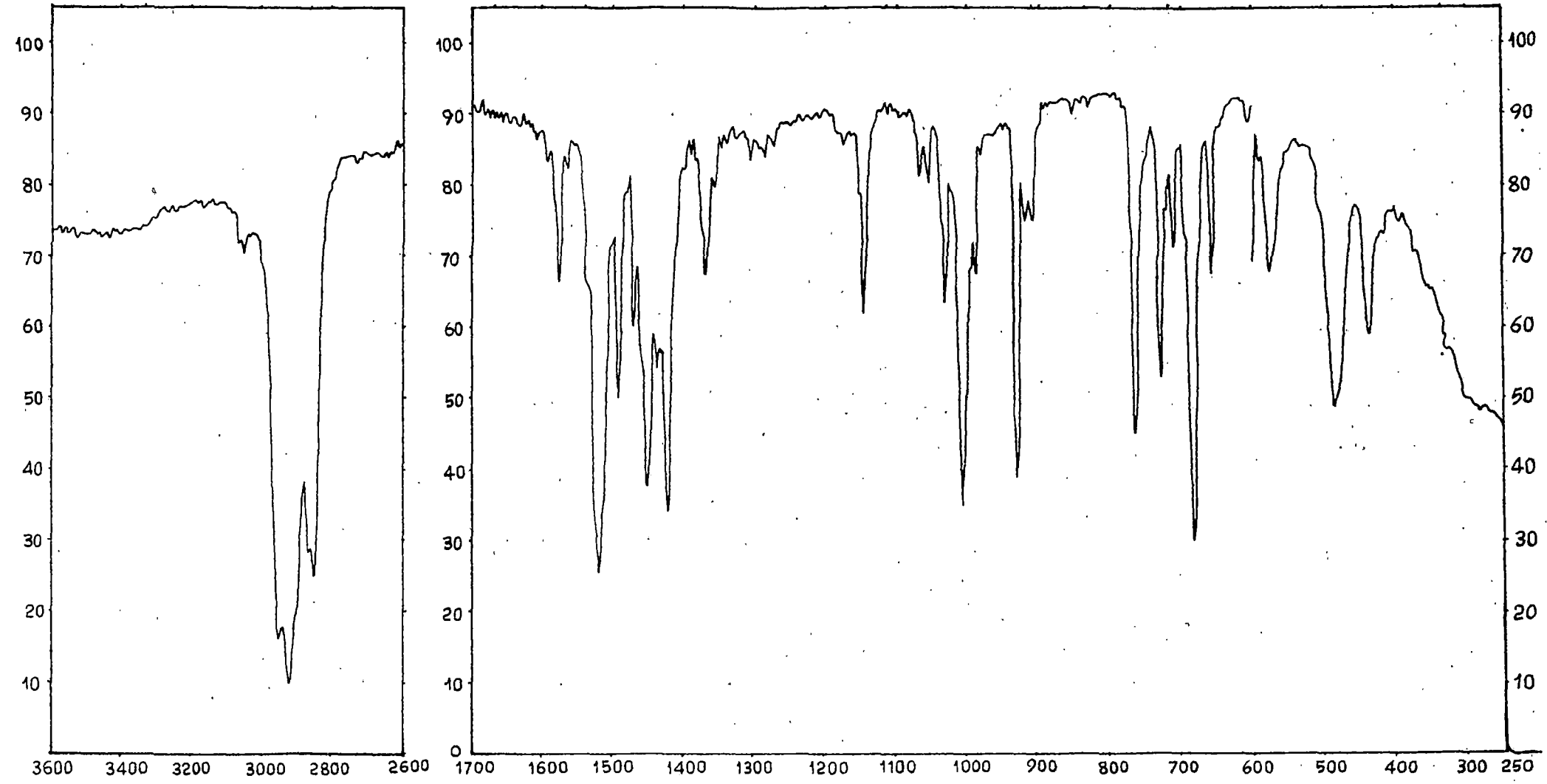
This was prepared by refluxing a methanol solution of phenyltin bromide bis(N-phenylbenzohydroxamate) for three hours and filtering the white solid in hot and washing with hot methanol. The solid had a m.p. of 235° (dec.). Analysis gave : C = 46.22, H = 3.59, Sn = 22.70% and calculated for $C_{20}H_{18}BrNO_3Sn$: C = 46.15, H = 3.46, Sn = 22.90% .

54. Preparation of Phenyltin iodide methoxy N-phenylbenzohydroxamate:

This compound was prepared by refluxing a methanol solution of diphenyltin iodide N-phenylbenzohydroxamate/phenyltin iodide bis (N-phenylbenzohydroxamate). Fine white crystals formed in the reaction was filtered hot and washed with hot methanol. This compound had a m.p. of 210-20° (dec.). Analysis gave : C = 42.52; H = 3.23; Sn = 20.90% and calculated for $C_{20}H_{18}INO_3Sn$: C = 42.40; H = 3.18; Sn = 21.02% .

55. Preparation of Phenyltin Chloride methoxy N-orthotolylbenzohydroxamate:

A methanol solution of diphenyltin chloride N-orthotolylbenzohydroxamate was refluxed for two hours. White solid came, which was filtered and washed with methanol. The solid had m.p. 207° (dec.) Analysis gave : C = 51.20; H = 4.10; Sn = 24.07% and calculated for



I.R. Spectrum of Phenylbromotin methoxy N-Phenylbenzohydroxamate

Fig--- 10c

$C_{21}H_{20}ClNO_3Sn$: C = 51.63; H = 4.09; Sn = 24.34% .

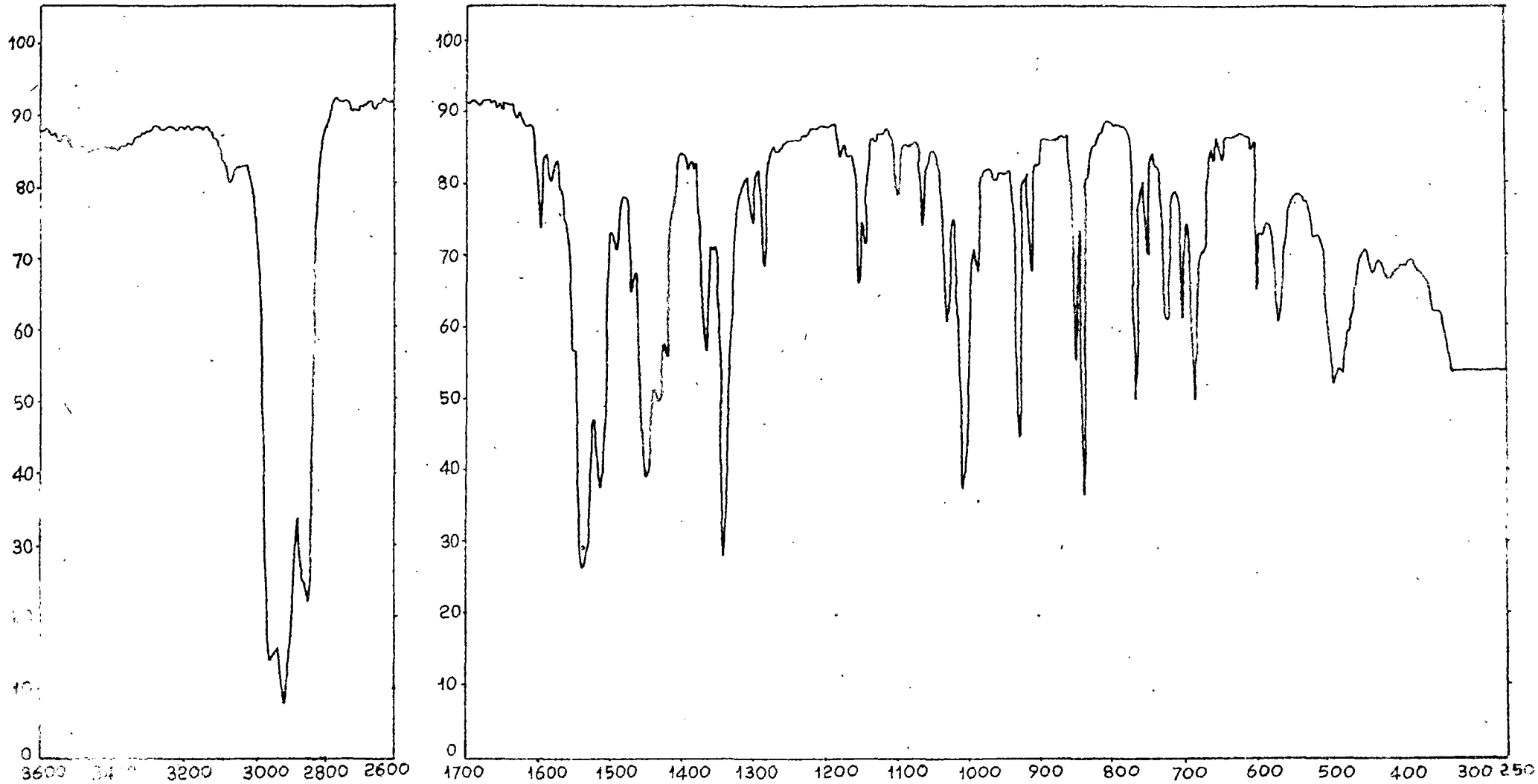
56. Preparation of Phenyltin Chloride hydroxy N-phenylparanitrobenzohydroxamate:

Attempts to prepare phenyltin chloride methoxy N-phenylparanitrobenzohydroxamate by refluxing phenyltin chloride bis(N-phenylparanitrobenzohydroxamate)/diphenyltin chloride N-phenylparanitrobenzohydroxamate in methanol yielded a compound, the analytical data of which corresponds more closely to the corresponding hydroxy compound and is supported by the presence of hydroxy peak in the IR spectrum. Thus the above compounds after refluxing for five hours in methanol gave light yellow precipitate which was filtered hot and washed with hot methanol. This precipitate had a m.p. of 238° (dec.), the analysis of which gave : C = 46.21, H = 3.21, N = 5.96, Sn = 24.2% and calculated for $C_{19}H_{15}O_5N_2ClSn$: C = 45.09, H = 2.97, N = 5.54, Sn = 23.56% .

57. Reaction of diphenyltin chloride N-phenylbenzohydroxamate with methanol:

All the apparatus was scrupulously cleaned, dried and washed with methanol before use so as to avoid the presence of any trace of benzene. Methanol used was of Uvasol grade.

Diphenyltin chloride N-phenylbenzohydroxamate prepared and crystallised as described previously was dried in the pump and washe with cold methanol. Methanol washings showed no characteristic



I.R Spectrum of Phenyltin Chloride methoxy N-Phenylparanitrobenzohydroxamate.

Fig---10d

absorptions for free benzene in the UV region of the spectrum. Then the washed crystals were taken in methanol and the solution was refluxed. White crystals started to come and the refluxing was continued for 2 hrs. Then the methanol was completely taken out of the compound (A) by distilling it. The distillate showed all the characteristic absorptions (234, 239, 243, 249, 254, 260 and 268 nm) of free benzene (Fig.11a) in the UV region of the spectrum. The liberated benzene was estimated by the following procedure.

Exactly 0.119 gm of diphenyltin chloride N-phenylbenzohydroxamate was taken in 125 ml of methanol. It was then refluxed for two hours and the methonol was completely taken out of the product by distillation in a closed system. The absorbance of the distillate was measured against a reference of methanol using 1 cm cells at the wavelength at 254 nm (the characteristic wavelength of maximum absorbance for free benzene in the UV region of the spectrum). The absorbance was found to be 0.450. The extinction of free benzene was estimated to be 210 at 254 nm in methanol. Benzene was found to obey the Beer's law in methanol at the wavelengths at 243, 254 and 260 nm in the concentration range of 0 - 1.0 gm litre^{-1} (Fig.11b) studied. Hence, the concentration of benzene in methanol distillate has been calculated by the use of Lambert - Beer's law.

$$A = \epsilon . C.l$$

where A = absorbance, ϵ = extinction coefficient, C = concentration

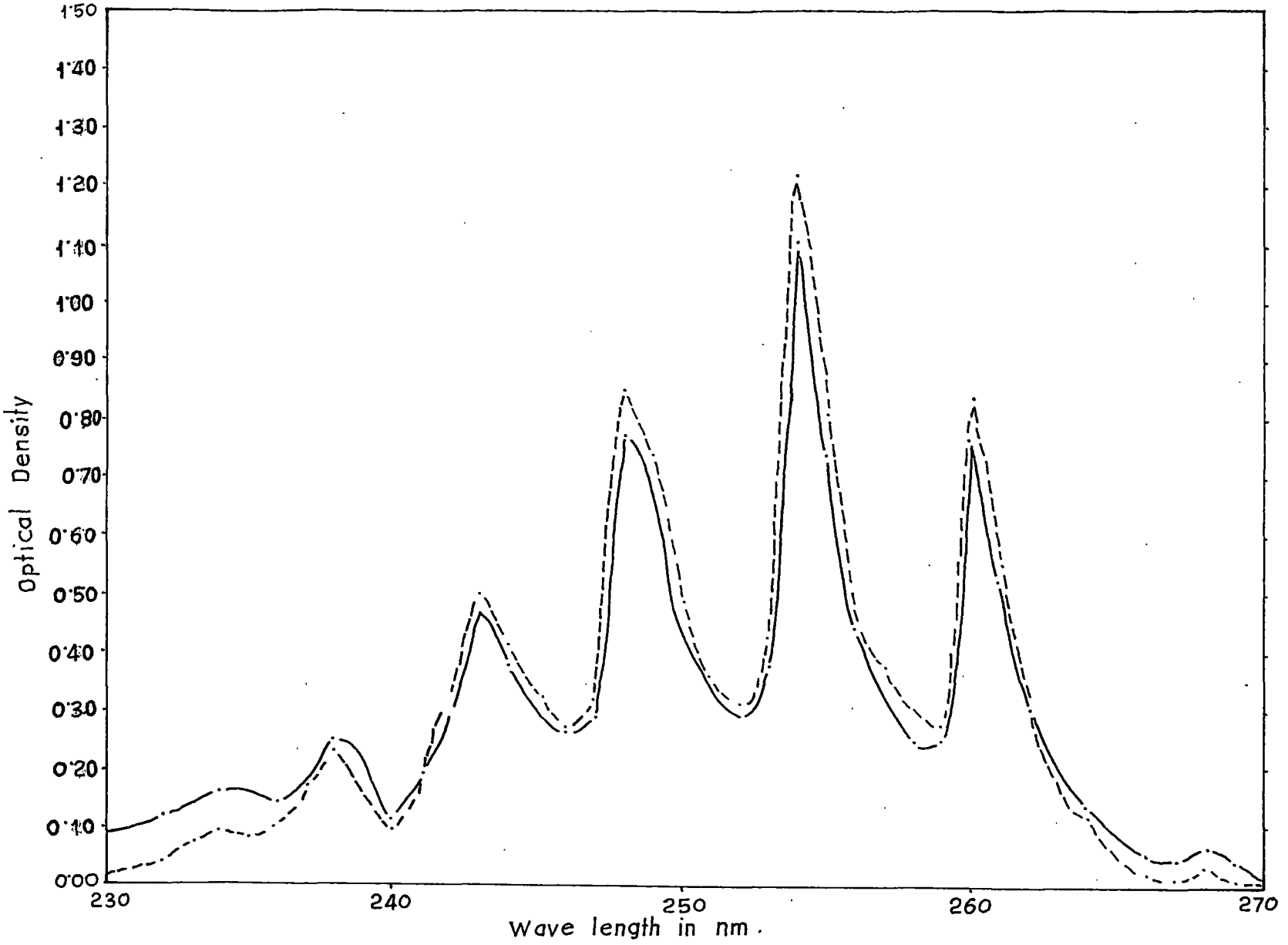


Fig:- 11a Absorption Spectrum of the Methanol distillate -----(dashed line)
Absorption Spectrum of the benzene in Methanol ——(Solid line)

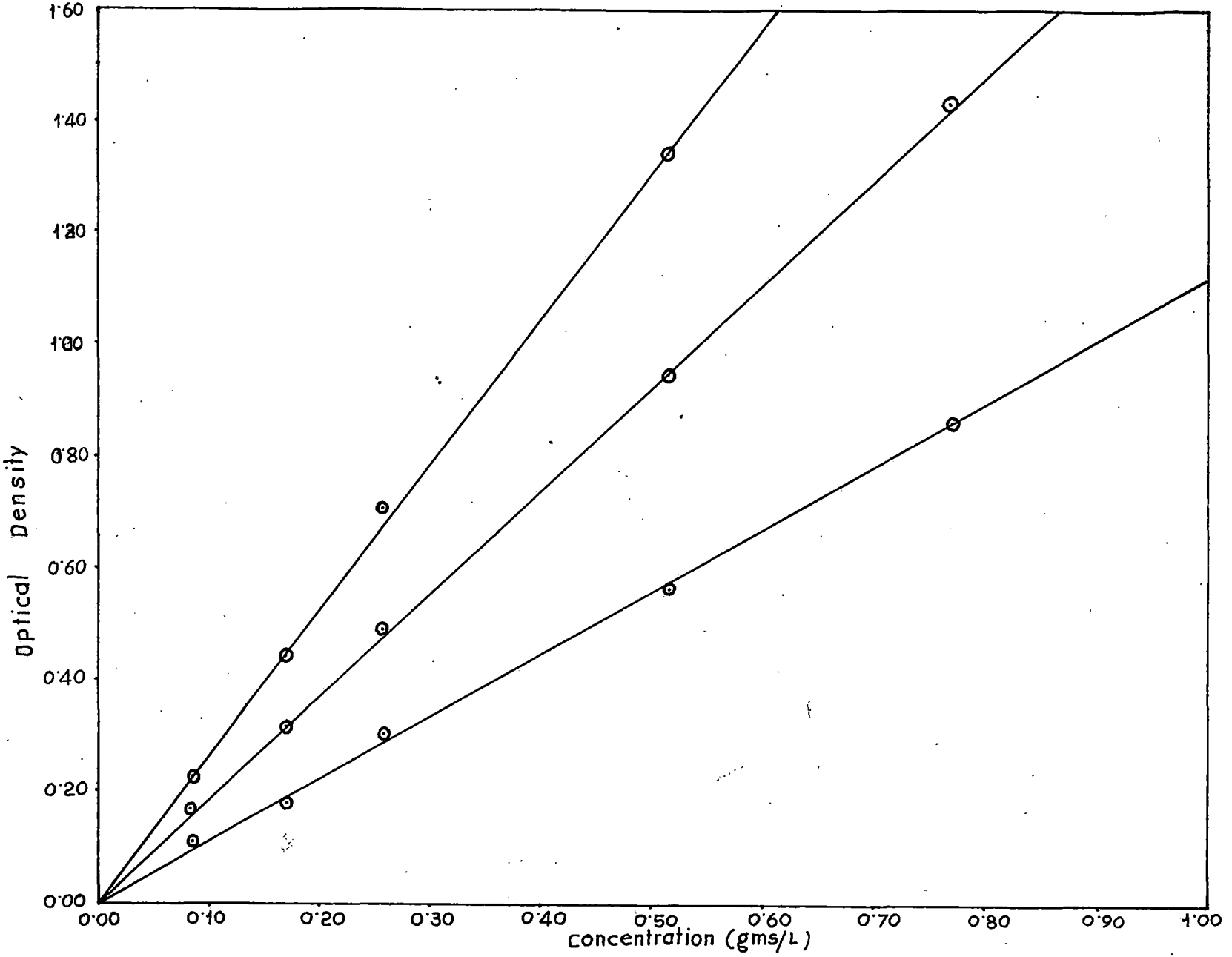


Fig:-11b Absorbance of Benzene in Methanol at (I) 243 nm, (II) 254 nm and (III) 260 nm at different concentrations.

and l = path length of the cells. Here, A = 0.450, ϵ = 210 at 254 nm, l = 1 cm, from which the amount of liberated benzene was estimated to be 0.0209 gm, i.e. this amount of benzene was obtained from 0.119 gm of the diphenyltin chloride N-phenylbenzohydroxamate, the ratio of which corresponded to 1:1 . In other words, one equivalent of the compound gave one equivalent of benzene. The white residue after distillation was found to be phenyltin chloride methoxy N-phenylbenzohydroxamate m.p. 223°(dec.) and weighed 0.1 gm.

30. Reaction of diphenyltin thiocyanate N-phenylbenzohydroxamate with methanol:

Diphenyltin thiocyanate N-phenylbenzohydroxamate was dried in the pump for 24 hours. This was washed thrice with methanol and each time the methanol washings was tested for free benzene in the UV region of the spectrum and was found absent. Then the washed diphenyltin thiocyanate N-phenylbenzohydroxamate was refluxed in methanol for 2 hours and the solvent was distilled out. The distillate after necessary dilution with methanol showed the presence of all the absorption peaks characteristic of free benzene. The white solid which was obtained in the reaction was filtered under suction in the hot, which had a m.p. of 230-31° (dec.) and identified as phenyltin thiocyanate methoxy N-phenylbenzohydroxamate.

59. Reaction of Phenyltin Chloride bis(N-phenylbenzohydroxamate) with methanol:

1.0 gm of phenyltin chloride bis(N-phenylbenzohydroxamate) was taken in excess of methanol and heated to dissolve. This solution was then refluxed for 11 hours, crystals came, which was filtered hot. The crystals had a m.p. of 238° (dec.) in a preheated bath, weighing 0.5 gm. This was found to be phenyltin chloride methoxy N-phenylbenzohydroxamate. The filtrate from this was concentrated and cooled when crystals of m.p. 160° weighing 0.30 gm came, which on further crystallisation was found to be unreacted phenyltin chloride bis (N-phenylbenzohydroxamate) (identified by mixed m.p.). The mother liquor from this was evaporated to dryness and the solid was crystallised from a mixture of benzene and pet-ether. The crystals had a m.p. of 122° (0.13 gm), which was found to be the ligand, the N-phenylbenzohydroxamic acid (identified by mixed m.p.).

60. Reaction of Phenyltin bromide bis(N-phenylbenzohydroxamate) with methanol :

A solution of 0.7 gm of phenyltin bromide bis(N-phenylbenzohydroxamate) in excess methanol (50 ml) was refluxed for 3 hours. White solid came, which was filtered hot and washed with hot methanol. The white solid (0.3 gm) had a m.p. of 238° (dec.). The filtrate from this was concentrated, cooled and filtered. This filtrate was then evaporated to a pasty mass which on repeated crystallisation

from a mixture of benzene and pet-ether afforded white crystals (0.1 gm) which had a m.p. of 122° and which showed no depression in m.p. when mixed with an authentic sample of N-phenylbenzohydroxamic acid.

61. Reaction of Phenyltin iodide bis(N-phenylbenzohydroxamate) with methanol :

A methanol solution of phenyltin iodide bis(N-phenylbenzohydroxamate) (0.75 gm in 50 ml methanol) was refluxed for four hours. Fine white crystals came, which was filtered hot and washed with hot methanol, had a m.p. of 219-20° (dec.) weighing only 0.25 gm. The crystals were found to be identical with phenyltin iodide methoxy N-phenylbenzohydroxamate. The filtrate from this was concentrated when 0.3 gm of a compound of m.p. 178-215° came. (This compound was found to be a mixture of the methoxy compound and the unreacted starting material). The mother liquor from this compound was evaporated to a pasty mass which on repeated crystallization from a mixture of benzene and pet-ether gave 0.1 gm of a white crystalline compound of m.p. 122°. This compound was found to be the ligand, the N-phenylbenzohydroxamic acid by mixed melting point determination.

62. Reaction of Phenyltin Chloride bis(N-phenylparanitrobenzohydroxamate) with methanol:

A solution of phenyltin chloride bis(N-phenylparanitrobenzohydroxamate) (0.4 gm) in methanol (30 ml) was refluxed for 5 hrs.

Light yellow precipitate came which was filtered hot and washed with hot methanol had a m.p. of 230° (dec.) weighing 0.2 gm (A). This was identified as phenyltin chloride hydroxy N-phenylparanitrobenzohydroxamate. Filtrate from (A) was concentrated and cooled, from which another crop of (A) weighing 0.05 gm came; the total yield of (A) being 0.25 gm. The mother liquor was then evaporated to a pasty mass which on crystallisation four times from a mixture of benzene and pet-ether gave white crystals (0.11 gm) of m.p. 150°, which was found to be undepressed when mixed with an authentic sample of N-phenyl-paranitrobenzohydroxamic acid.

Tin was estimated by conversion to stannic oxide and finally to volatile stannic iodide gravimetrically essentially by the method of Van der Kerk and Luijten (233).

The infrared spectral data have been taken in the range between 4000 - 300 cm^{-1} for all the compounds using Beckman IR-20. Infrared spectrophotometer equipped with KBr optics and mulling the compounds in Nujol in all cases otherwise mentioned. The following abbreviations have been used: s = strong, m = medium, w = weak, v = very, b = broad, sh = shoulder. Nujol has peaks at 3000-2900s, 1460s, 1376m.

N-phenylbenzohydroxamic acid: 3120s,b, 1645s,b, 1595m, 1530m, 1498m, 1450m, 1400s, sh, 1320w, 1300w, 1275w, 1170m,sh, 1080m, 1050m, 1015s, 1006m, 970w, 930m, 920s, 855w, 795s, 775s, 723s, 712s, 638s,

662m, 585s, 525w, 435s, 415vw, 385s.

N-phenylparachlorobenzohydroxamic acid: 3170s,b, 3060w,v, 1618s,b, 1500m, 1365w, 1480m, 1433s, 1393m, 1320w, 1307m, 1275m, 1224w, 1180m, 1150m, 1090s, 1050s, 1030m, 1010s, 940w, 900m, 860s, 830s, 750s,sh, 730m, 700m, 690m,sh, 654w, 624w, 610w, 574vw, 530m, 510m, 470m, 380vw.

N-phenylparanitrobenzohydroxamic acid: 3170s,b, 1609s, 1590w, 1575s, 1510s, 1485s, 1440s,b, 1385w, 1342s, 1310w, 1290m, 1220w, 1150, 1100w, 1070w,w, 1042m, 1020w,w, 1010w, 935w,w, 910w, 865w, 855m, 825m 765m,sh, 730m, 710s, 685s, 670w, 650w, 562w,b, 525m, 445w, b.

N-orthotolylbenzohydroxamic acid: 3120s,b, 1625s,b, 1570s, 1485s, 1440s, 1385s, 1295w, 1255vw, 1195vw, 1165vw, 1150m, 1110m, 1070w, 1030vw, 1020vw, 1000s, 965w, 940vw, 910s,sh, 840w, 790m, 760s, 770s,sh, 720s, 710s, 690s, 680m, 650m, 630w,b, 590m, 540w, 450m, 400m,b , 340vw.

N-paratolylbenzohydroxamic acid: 3100s,b, 1640s,b, 1600m, 1570m, 1510s, 1460s, 1410m, 1390s, 1318w,v, 1280w, 1272m, 1210w, 1180w, 1160m, 1110m, 1070w, 1040v,w, 1025m, 1010s, 970w, 950vw, 930m, 920s, 850w, 830s, 800m, 790s, 720s,sh, 693s, 680m, 560s, 522m, 442m, 392m,b.

N-parachlorophenylbenzohydroxamic acid: 3340w, 3160s,b, 1638s, 1615s,b, 1525w, 1480s, 1435s,b, 1395s, 1320m, 1305s, 1295w, 1285w, 1275m, 1220w, 1180m, 1160m,sh, 1085s, 1050s, 1022m, 1010s,

990vw, 965vw, 940w, 900m, 888vw, 845s, 830s, ^748s, ^730m, 694s,sh, 650w, 620w, 570w,b, 530m, 510m, 474w, 388vw.

N-ethylparachlorobenzohydroxamic acid: 3140s,b, 1600s,b, 1564s, 1493s, 1465s,b, 1430s,b, 1338m, 1300w, 1270s, 1183s, 1170s, 1100m, 1090s,sh, 1012s, 980m, 945w, 880m, 834s, 778w, 742s,sh, 708m, 680m, 664m, 620w, 570s, 510m, 475m, 378w,b.

Triphenyltin N-phenylbenzohydroxamate: 3080m, 3060m 1584s, 1543s,b, 1493vw, 1490vw, 1473m, 1442m, 1428s, 1330w, 1300w,sh, 1208vw, 1260vw, 1188w, 1160vw, 1170vw, 1152m, 1070s,sh, 1038s, 1020m,sh, 992m, 970w, 935s, 912m,sh, 850vw, 775s, 770s, 725s,sh, 715w, 690s,b, 660m, 650w, 610w, 570w, 545m, 498w, 445s, 390vw.

Triphenyltin N-phenylparachlorobenzohydroxamate: 3044m,sh, 1590m, 1580s, 1538s,b, 1490w, 1475m, 1435w, 1425s, 1330w, 1290w, 1280vw, 1260vw, 1190vw, 1175vw, 1155vw, 1150m, 1090s, 1068s, 1035m, 1010s, 900w, 958vw, 930s, 910w,sh, 850vw, 830s, 770m,sh, 725s, 690s,sh, 650w, 620vw, 610vw, 555m, 525w, 490m, 450s.

Triphenyltin N-phenylparanitrobenzohydroxamate: 3060m, 1600w, 1590vw, 1560m, 1545s,sh, 1512m, 1490w, 1475m, 1440w, 1430m, 1340s, 1310w, 1290w, 1256vw, 1150m,b, 1100w,sh, 1068m, 1035m, 1015m, 990w, 930s, 910w, 850s,sh, 820vw, 752m,sh, 720s,sh, 690s,sh, 650w, 600m, 565vw, 550w, 515w, 490w, 450w, 430w, 415vw, 390vw, 350vw.

Triphenyltin N-orthotolylbenzohydroxamate: 3060w, 1590m,

1540s,b, 1470w, 1430m, 1330vw, 1290w,b, 1260vw, 1190w,b, 1160m, 1115w, 1070m, 1020m, 995w, 930s, 900w, 770m, 730m, 695s, 660m, 600m, 565w,b, 550w, 515w,b, 440m,b.

Triphenyltin N-parachlorophenylbenzohydroxamate: 3060m, 3035m, 1590m, 1544s,b, 1500m, 1485m, 1480m, 1450s,sh, 1425s, 1400m, 1330vw, 1300w, 1270vw, 1260vw, 1170w, 1160m, 1100w, 1090m, 1070s, 1035m, 1025w, 1010m, 995w, 940w, 930s, 915m, 830s, 780m, 730s, 700s,sh, 690m, 652w, 600m, 560m, 530w, 500m, 450m, 400w,b.

Diphenyltin bis(N-phenylbenzohydroxamate): 3060s, 1600m, 1580s, 1522s,b, 1485m, 1450s, 1440s, 1422s, 1330w, 1310w, 1290m,sh, 1258w, 1174w, 1156s, 1140s, 1072s, 1034s, 1012s, 990m, 970w, 960w, 930s, 910s, 850w, 835vw, 770s, 760s,sh, 730s, 712s, 690s,b, 660s,sh, 610w, 600m, 555m, 540s, 498m, 463m, 430s,b, 330vw.

Diphenyltin bis(N-paratolylbenzohydroxamate): 3040m, 3000w, 1600m, 1580s, 1520s,b, 1475m, 1440s,sh, 1425m, 1400w, 1303w, 1290w, 1210w, 1170m, 1150s,sh, 1100w,sh, 1070s, 1034s,sh, 1010s, 990w, 930s,sh, 915m, 840m, 816s, 790m, 770m, 730s,sh, 710m, 695s,sh, 670m, 650w, 612m, 600m, 562m, 550m, 510m, 500m, 455m,sh, 450m, 434s.

Diphenyltin bis(N-orthotolylbenzohydroxamate): 3060m, 3034w, 3020w, 1600m, 1590s, 1580w, 1550s,b, 1500m, 1480m, 1445s, 1430s, 1300w, 1290w, 1260vw, 1200vw, 1160w, 1160s,sh, 1130w, 1120w, 1075m, 1062w, 1025s,sh, 1000vw, 980vw, 933s, 870w, 800m, 780s, 765m, 740m,

730s, 700s,sh, 660s, 620w, 570m, 560m, 550m, 510m, 490s, 435m, 410vw.

Diphenyltin bis(N-phenylparachlorobenzohydroxamate): 3060m, 1590m, 1575m, 1525s,b, 1490w, 1475w, 1435m, 1423m, 1300w, 1280w, 1260vw, 1190vw, 1150m, 1090m, 1070w, 1040m, 1012m, 1000w, 932s, 910w, 832m, 770m, 760w, 720s, 695s,sh, 625vw, 595w, 560m, 555m, 520w, 490m, 470w, 440m.

Diphenyltin bis(N-phenylparanitrobenzohydroxamate): 3055m, 1590w, 1540s,b, 1530s,sh, 1485w, 1450m, 1420m, 1392w, 1340s, 1308w, 1290m, 1180vw, 1150m, 1100w, 1068m, 1038s, 1015m, 990w, 918w, 930s, 910w, 850m, 842s, 770m, 752m, 710m,sh, 693s, 690s, 680m, 565m,b, 550w, 520w, 492vw, 475w, 445w, 420w.

Diphenyltin bis(N-ethylparachlorobenzohydroxamate): 3060m, 1590m, 1570s,b, 1558m,sh, 1490m, 1444s, 1430m, 1420m, 1390w, 1342m, 1290vw, 1280m, 1210w, 1170m, 1090m, 1080s, 1070m, 1008w, 990vw, 970m, 960m, 930s, 850w, 840m, 830m, 825m, 815m, 740w, 718s, 690s, 660s, 600w, 580m, 570m, 543m, 504s, 440m.

Dibutyltin bis(N-phenylbenzohydroxamate): 3060m, 1590s, 1550s,b, 1490m, 1440m, 1420m, 1300w, 1290w, 1275w, 1249vw, 1160m,sh, 1070m, 1030m, 1010s, 995m, 960vw, 920s,sh, 900m, 872w, 860vw, 842vw 825w, 775s, 760s, 715m, 700s, 690s, 660s, 600m, 570w, 540m, 490s,b, 430s.

Dibutyltin bis(N-phenylparachlorobenzohydroxamate): 1600m, 1580s, 1540s,b, 1490m, 1430m, 1300vw, 1270vw, 1240vw, 1160w, 1150w, 1080m, 1030m, 1010s, 960vw, 920s, 902m, 870w, 838s, 770s, 725s, 703w, 684m,sh, 670m, 660vw, 600m, 575w, 550s, 523w, 495s, 435w,vb.

Dibutyltin bis(N-parachlorophenylbenzohydroxamate): 3060w, 1580m, 1540s,b, 1480m, 1440m, 1423m, 1390w, 1235w, 1205vw, 1148m, 1090w, 1080m, 1070w, 1030w, 1015m, 1002m, 960vw, 922m,sh, 910m, 870w, 828s, 775m, 772m, 760m, 720w, 710m, 702m, 603m, 632s, 625m, 670m, 600m, 560m, 495m,sh, 435w,vb.

Dibutyltin bis(N-ethylparachlorobenzohydroxamate): 3040w, 1582s,b, 1560s,b, 1500vw, 1450s,sh, 1355m, 1336m, 1220w, 1170m,sh, 1000w, 1033s, 1012m, 970m, 932s,sh, 830m, 832m, 818m, 790vw, 760vw, 742vw, 730w, 700vw, 670m, 650vw, 620vw, 580m, 520m, 500s, 460m,b.

Phenyltin chloride bis(N-phenylbenzohydroxamate): 3060m, 1582m, 1530s,b, 1490m, 1450s, 1424s,sh, 1306vw, 1290w,sh, 1180m, 1068m, 1038m, 1014m, 996w,sh, 963vw, 935s, 912m, 844w, 770s,sh, 735s, 712m, 688s, 660m, 560s,sh, 510m, 472vw, 440s.

Phenyltin bromide bis(N-phenylbenzohydroxamate): 3060m, 1578m, 1525s,b, 1490m, 1450m, 1422s,sh, 1300vw, 1286w,sh, 1144m, 1064m, 1030m, 1010m, 990w, 930s, 910m, 830w, 765s, 722s, 710m, 680s, 660m, 560s,sh, 500w, 434m,b.

Phenyltin iodide bis(N-phenylbenzohydroxamate) : 3060m,

1580m, 1515s,b, 1492m, 1482w, 1440w, 1423s, 1328vw, 1312w, 1290w,sh, 1145m, 1068m, 1038m, 1010m,sh, 993w, 970w, 935s, 922m, 910m,sh, 845w, 775s, 763s, 730s, 722s, 715m, 694s,sh, 662m, 610w, 599m, 570m, 560m, 493vw, 465vw, 435s,b, 370w.

Phenyltin thiocyanate bis(N-phenylbenzohydroxamate): 3060vw, 2040s,sh, 1582m, 1528s,b, 1492m, 1480w, 1442w, 1430m,sh, 1315vw, 1290w, 1280vw, 1150m, 1070m, 1040m, 1015m, 1000w, 940s, 918m, 772m, 730m, 720m, 690s, 668m, 615w, 600m, 565m,b, 500vw, 465vw, 432m.

Phenyltin bromide b is(N-phenylparanitrobenzohydroxamate): 1600m, 1585w, 1535s,b, 1520s, 1490w, 1450s,b, 1430m, 1392w, 1340s, 1310vw, 1290m, 1150m,sh, 1100w, 1003w, 1034m, 1010m, 990w, 920s, 915m, 850m, 840s, 770m, 760m, 730m, 700m, 690m, 678s, 600m, 565m,b, 520w, 475m,b.

Phenyltin chloride bis(N-phenylparanitrobenzohydroxamate): 1600m, 1583m, 1540s,b, 1512s, 1490w, 1450s,b, 1395w, 1340s, 1310vw, 1290m, 1150m, 1100w, 1070w, 1035m, 1012m, 990w, 965vw, 932s, 915m, 845s,sh, 765m,sh, 750m, 730m, 700m, 690s, 680s, 660vw, 650vw, 610vw, 600m, 564m,b, 522w, 474m,b, 432w,b, 390vw.

Phenyltin iodide bis(N-phenylparanitrobenzohydroxamate): 3400w,vb, 3060w, 1600w, 1542s,b, 1520s, 1470w, 1440m, 1425m, 1335vw, 1342s, 1310w, 1290m, 1150m, 1100w, 1068w,sh, 1040m,sh, 1010m, 993w, 935s, 915w, 860m, 845s, 763m, 730m, 710m, 690s, 660vw, 650vw, 600m, 570m,sh, 520w,b, 435w,b, 425w,b, 400vw.

Phenyltin bromide bis(N-phenylparachlorobenzohydroxamate): 3060m, 1584m, 1570s, 1518s,b, 1490m, 1450s, 1423s,sh, 1380w, 1302w, 1274w, 1170vw, 1160vw, 1144m, 1100w, 1060m, 1062w, 1030m, 1004s, 990w, 950w, 926s, 904m, 836m, 822m, 760m, 730m, 680s,sh, 660vw, 650vw, 615w, 595m, 590w, 575m, 560m, 525m, 490m, 470w,b, 430w,b.

Phenyltin iodide bis(N-phenylparachlorobenzohydroxmate): 3050m, 1590m, 1572m, 1520s,b, 1495m, 1472m, 1455s,sh, 1392w, 1300w, 1280w, 1190w, 1165w, 1150m, 1110w, 1038m, 1065w, 1034m, 1010s, 996w, 960w, 930s, 910m, 840m, 833s, 770s, 730m, 720m, 694s,sh, 660vw, 650vw, 620w, 585m, 562m,sh, 524m, 490s, 470w,b, 433w,b.

Diphenyltin chloride N-phenylbenzohydroxamate: 3050m,sh, 1582s,sh, 1535s,b, 1490m, 1474m, 1440m, 1424s, 1330vw, 1295w, 1270vw, 1190w, 1152vw, 1140m, 1100vw, 1065m, 1030m, 1010s,sh, 990w, 930s, 920w, 910m, 850vw, 830vw, 770s, 730s, 720s, 713w, 688s,sh, 662m, 665s, 445m,b.

Diphenyltin iodide N-phenylbenzohydroxamate: 3060m, 1590m, 1580s,b, 1480vw, 1450m, 1430m, 1420s, 1320vw, 1290vw, 1290w, 1180w, 1135m, 1060m, 1030w, 1000m,sh, 985w,sh, 990vw, 960vw, 922m, 910m, 909m, 840vw, 820vw, 770s, 760s, 720s, 710m, 692s, 635m, 600m, 555m, 510vw, 490vw, 435m,b, 390m,vw.

Diphenyltin thiocyanate N-phenylbenzohydroxamate: 3060m, 3020w, 2030s,b, 1982m, 1560s,sh, 1515s,b, 1490m, 1473m, 1425s,b,

1330w, 1305w, 1290m, 1275w, 1260w, 1190s,sh, 1165m, 1144s, 1090vw, 1068s, 1030m, 1010s, 990m,sh, 965vw, 930s, 922s, 910m, 880w, 838w, 824w-770s, 760s, 725s, 710s, 685s,b, 660m, 615m, 610m, 580s, 500vw, 436w, 470vw, 430s,b.

Dibutyltin thiocyanate N-phenylbenzohydroxamate: 3030w, 2060s,b, 1990w, 1880m, 1335s,b, 1485w, 1450s,b, 1455s, 1405w, 1330w, 1285w, 1145m,sh, 1068m, 1030m, 1003m, 980w, 930s, 910m, 855w, 760s, 712m, 680s, 650m, 605m, 590vw, 560m, 500m, 430m.

Diphenyltin chloride N-phenylparanitrobenzohydroxamate: 3400w,vb, 3050w, 1595m, 1565s, 1555s,sh, 1503s,sh, 1433vw, 1450s,sh, 1422s, 1358s, 1300w, 1286m, 1270w, 1190w, 1150m, 1090vw, 1060m, 1030m, 1005m, 990m, 930s, 910m, 852m, 840m, 825vw, 760m, 750m, 720s, 710m, 680s, 600s, 600m, 562m, 520w,b, 475m,b, 440w,b.

Diphenyltin iodide N-phenylparanitrobenzohydroxamate: 3060m, 3020w, 1593m, 1580w, 1562s, 1550s,b, 1508s, 1490w, 1470vw, 1450m, 1433w, 1420s, 1390w, 1338s, 1305s,w, 1285w, 1180w, 1142m, 1100w, 1060m, 1025m, 1002m, 990m, 924s, 910m, 845s, 838s, 823w, 760m, 750m, 720s, 700m, 680s, 650s, 598m, 560m,b, 515w,b, 470m,b, 440m,sh.

Phenyltin chloride methoxy N-phenylbenzohydroxamate: 3040w, 1590m, 1530s,b, 1500m, 1430m, 1440w, 1430s, 1380w,b, 1132vw, 1155m,sh, 1070w, 1042m, 1010m,sh, 940s, 932m, 925m, 840vw, 776s, 763w, 743s, 724m, 697s, 670m, 620w, 580m,b, 490s,b, 435m,b, 393vw.

Phenyltin thiocyanate methoxy N-phenylbenzohydroxamate: 3060m, 2020s,b, 1600m, 1590m, 1540s,b, 1500m, 1493m, 1450m, 1435s, 1390m, 1355vw, 1320vw, 1300w, 1280w, 1160s,sh, 1095w, 1078m, 1044s, 1030s, 1020m, 1000m, 970vw, 940s, 920m, 890s, 780s, 770s, 730s, 720m, 692s,b, 670s, 600m, 575m,b, 530w, 500m,b, 470w,b, 435s,b.

Phenyltin bromide methoxy N-phenylbenzohydroxamate: 3050w, 1578m, 1520s,b, 1490m, 1470m, 1450s,sh, 1435w, 1420s, 1305vw, 1285vw, 1270vw, 1170vw, 1140m, 1068w, 1052w, 1030m, 1002s, 988m, 930s, 920w, 910w, 780s, 750m, 710w, 680s, 659m, 600m, 570m,b, 492s,b, 438m, 392vw.

Phenyltin chloride hydroxy N-phenylparanitrobenzohydroxamate: 3400w,vb, 3060w,b, 1600m, 1580vw, 1540s,b, 1512s, 1490vw, 1450s,b, 1430w, 1420w, 1340s, 1300w, 1284m, 1150m, 1148m, 1100w, 1068m, 1030m, 1008s, 985m, 930s, 910m, 880m, 840s, 768s, 750w, 720m, 700m, 684s,sh, 645vw, 600m, 565m, 490s,b, 440vw, 405vw.

Tetraphenyldiitin 1,2-diacetate: 3080m, 3060w, 3040w, 1590w, 1530s,b, 1490s, 1480m,b, 1440s, 1415s, 1390m, 1310s, 1300w, 1190ww 1085s, 1072w, 1030m, 1010m, 750s, 740s,sh, 700s,sh, 666s, 620m, 580w,b, 525vw,b, 450s.

Diphenyltin bis (oxinate): 3070m, 3050w, 3030w, 1605m, 1580s, 1502s, 1485w, 1470s,b, 1442m, 1393s, 1330s, 1285s, 1240m, 1230m, 1195vw, 1120s, 1080m, 1040w, 1060vw,sh, 1040w, 1030w, 1000w, 980vw, 930s, 810m, 700s, 770s, 735m, 708m, 680m, 660w, 640w,

625m, 575w,b, 523s, 500w, 450m,b, 380m.

Diacetate ditin bis(oximate): 1620s, 1600s, 1580s, 1510s, 1475s,b, 1430m, 1390s,b, 1325s,b, 1272s, 1240m, 1210m, 1180m, 1145m, 1110s, 1090ws, 1060m, 1045m, 1020m, 938m, 830s, 810s, 795s, 750s,sh, 685s, 640m, 620s, 580m, 560s, 505m, 495m, 308s.

The UV spectral data for some representative organotin benzohydroxamates along with the benzohydroxamic acids are presented in the tabular form. The spectra were taken in Beckman DU-2 spectrophotometer, using 1 cm. cells. The solvents used were all of spectral grade (Uvasol). The absorption bands are broad and in some cases extinction coefficients could not be calculated due to insufficient solubility in the solvents concerned.

TABLE-I

UV spectral data of some N-substituted benzohydroxamic acids in different solvents.

Compounds	Solvents used	λ_{max}(nm)	log ϵ_{max}
PhCO.NOHPh	cyclohexane	276	3.81
	dichloromethane	271	3.87
	methanol	265	3.95
p-ClC_6H_4CO.NOHPh	cyclohexane	227,281	—
	methanol	227	4.03
		267	3.98

Contd...