DISCUSSION:

Triphenyltin N-substituted benzohydroxamates and diorganotin bis-N-substituted benzohydroxamates have been prepared by the two methods:

Azeotropic distillation of water from a mixture of organotin oxide and N-substituted benzohydroxamic acid in 1:2 mole ratio in benzene:

$$(Ph_3Sn)_2O + 2R'CO.NOHR'' \longrightarrow H_2O + 2Ph_3Sn(R'CO.NOR'')$$

$$R_2SnO + 2R'CO.NOHR'' \longrightarrow H_2O + R_2Sn(R'CO.NOR'')_2$$

And reaction of one mole of organotin chloride with one or two moles of N-substituted benzohydroxamic acid:

$$Ph_3SnCl + R'CO.NOHR'' \longrightarrow HCl + Ph_3Sn(R'CO.NOR'')$$

$$R_2SnCl_2 + 2R'CO.NOHR'' \longrightarrow 2HCl + R_2Sn(R'CO.NOR'')_2$$

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

The N-substituted benzohydroxamic acids all contain one labile hydrogen per molecule, which attack the oxygen or chlorine of the organotin oxides or chlorides in equilibrium reaction to give water or hydrochloric acid respectively along with the formation of

the organotin derivatives of N-substituted benzohydroxamic acids.

It has been reported (117) that the triphenyltin N-phenylbenzohydroxamate is moisture-stable, crystalline solid which is monomeric in benzene (cryoscopy). The crystal structure of this compound has been determined (166). The $Ph_3SnONPhCOPh$ possesses a trigonal bipyramidal arrangement of groups about Sn, with two equatorial and one axial phenyl groups:

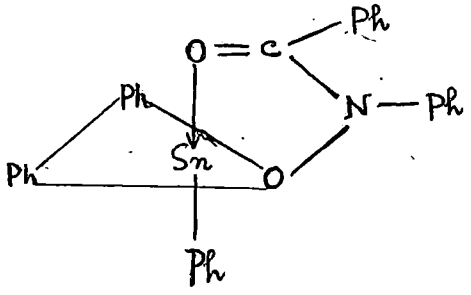


Fig. 12

The hydroxylamine residue is covalently bound at an equatorial site, and the carbonyl group coordinates intramolecularly to the tin atom via the remaining axial site. This is consistent with the lowering of the IR carbonyl stretching frequency from 1630 cm^{-1} in parent hydroxamic acid to 1540 cm^{-1} in the triphenyltin derivative. It seems (117) likely that whereas $Ph_3SnONPhCOPh$ is monomeric in both the crystal and solution phases, the trimethyltin derivatives are associated in the solid. The intramolecular forces must however be fairly weak since monomeric species, which presumably also have the trigonal bipyramidal structure, are present in solution. Mass

spectral data suggested dimerisation via the formation of distannoxane rings.

All the five triphenyltin N-substituted benzohydroxamates prepared here show a shift of the ν(C = O) band of 60-90 cm^{-1} to lower frequencies with a concomitant increase of 10-30 cm^{-1} in the N-O frequencies. Also, the ν(O-H) frequency due to intramolecular hydrogen bonding in the ligand at ~3150 cm^{-1} is absent in the triphenyltin derivatives. All these compounds can then be suggested to have an analogous penta-coordinated tin atom, the arrangement of the groups around tin atom being in trigonal bipyramidal one.

Harrison (117) has reported a m.p. of 115.5 - 116.5° for triphenyltin N-phenylbenzohydroxamate which has been prepared by the azeotropic distillation of water from a mixture of the ligand and the triphenyltin hydroxide and crystallised from benzene. The same compound was prepared here by two procedures mentioned previously and crystallisation of the product from either benzene or methanol, shows a m.p. of 133°. The analysis of this compound corresponds to that prepared by Harrison. This discrepancy in m.p. of this compound is not clear at present.

Harrison et al (166) have determined the crystal structure of $Me_2Sn(MeCO.NOMe)_2$ by X-ray method. The compound has been shown to be a distorted octahedral, the overall symmetry approximating to C_{2v}. The two N-acylhydroxylamine residues functions as bidentate ligands forming one short covalent and one long coordinate bond to

Sn whilst the Me-Sn-Me group is not linear, the C-Sn-C bond angle being 145.6°. Bond distances within the two ligand residues indicate significant multiple-bond character for the C-N bonds and single bond zwitterionic character for the C = O bond:

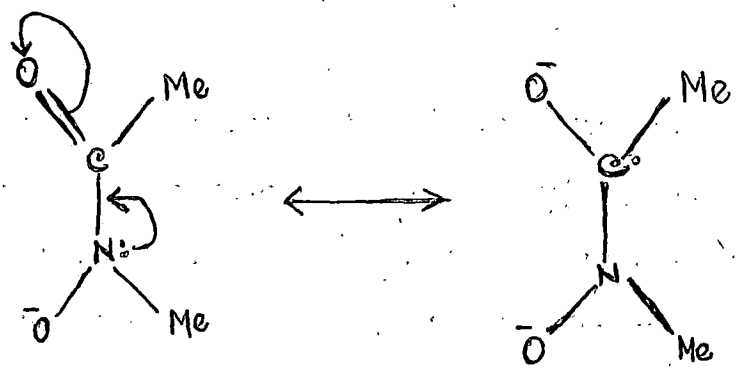


Fig. 13

For diorganotin bis-N-substituted benzohydroxamtes the strong absorptions in the IR spectra at 1550 cm^{-1} have been assigned to ν(C = O) frequency except for the compounds derived from the ligand, N-ethylparachlorobenzohydroxamic acid in which case the corresponding ν (C = O) band appears at 1565±5cm^{-1}. A strong band around 930 cm^{-1} in the IR spectra of all these complexes has been assigned as due to the ν(N-O) mode.

The ligands studied in the present investigation have a large number of absorption bands particularly in the region of 900-400 cm^{-1}. The presence of so many bands in this region has made the assignments for Sn-O, Sn-C, etc. rather difficult in the organotin compounds derived from these ligands.

Poller and Ruddick (163) have suggested tentative assignments for $R_2Sn(Ox)_2$ compounds the band at 640-651 cm^{-1} as $\nu_{as}(OSnO)$ and band at 443-446 cm^{-1} as $\nu_{s}(OSnO)$. For acetylacetonato compounds of the type $RR'Sn(acac)_2$, Kawasaki and his co-workers (239) have assigned the band at 404-401 cm^{-1} as due to $\nu(Sn-O)$ mode. The assignment of tin-phenyl stretching frequencies $\nu_{as}(Sn-Ph)$ in Ph_3Sn compounds at ~450 cm^{-1} (240) has been accepted by some workers (241-242). But Poller has suggested (243) that this band at ~ 450 cm^{-1} is, in fact, a benzene ring vibration, the tin-phenyl stretching frequencies should occur at below 300 cm^{-1} (243-245). In a letter publication Poller and Ruddick (163) have readily assigned the 16b phenyl ring mode for the oximates as follows:

$Ph_2Sn(Ox)_2$	442-450 cm^{-1}	} all are intense absorptions
$Ph_2SnCl(Ox)$	450 cm^{-1}	
$PhSnCl(Ox)_2$	444 cm^{-1}	

All the hydroxamic acid ligands studied here show absorptions at 450 ±25 cm^{-1} . But the corresponding triphenyl and diphenyltin derivatives show a medium to strong intensity absorption band at 440 ±10 cm^{-1}, which is absent in the dibutyltin derivatives. Thus this band in these compounds can be assigned as due to the phenyl ring vibration characteristic of the phenyltin compounds. In almost all of these compounds a new band appeared at 300 ± 5 cm^{-1} which is absent in the ligands. This band can be assigned as due to $\nu_{s}(OSnO)$ mode in these compounds. In the case of dibutyltin N-ethylparachloro-

benzohydroxamate this mode of vibration appeared at 580 cm^{-1}. The corresponding asymmetric stretching vibration $\nu_{as}(O_2Sn)$ can be assigned to the band at ~ 600 cm^{-1} since no other band between 000-600 cm^{-1} region is found more suitable for this mode in these compounds.

The intense broad band at 490 cm^{-1} in $Bu_2Sn(PhCO.NOPh)_2$ compound which is absent in the ligand, can be assigned as due to $\nu_s(Sn-O)$ mode, since no such band is present in the corresponding phenyltin compound and the corresponding asymmetric stretching vibration $\nu_{as}(Sn-O)$ can be assigned to the weak absorption at 565 cm^{-1}. The IR spectrum of $(CH_3)_2Sn(acac)_2$ shows only the antisymmetric stretching vibration of the SnO_2 moiety near 560 cm^{-1}. The symmetric vibration is observed near 510 cm^{-1} in the Raman spectrum and hence the CH_3 groups in this compound have been suggested to occupy trans positions with respect to the central tin atom (63, 73, 104, 247). McGrady and Tobias studied the proton NMR spectra of $Me_2Sn(Ch)_2$ compounds (247) which strongly support the trans methyl structure. The absence of a symmetric Sn-O stretching vibration in the IR spectrum of solid $(CH_3)_2SnCl_2$. Spy and $(CH_3)_2SnCl_2$.bipy in the 580-500 cm^{-1} region has been suggested to have trans alignment of the CH_3 groups for the hexa-coordinated tin atom (248-249).

Hence on the basis of the above results, the $Bu_2Sn(PhCO.NOPh)_2$ can be suggested to have a configuration in which the two butyl groups are probably cis though the analogous $Me_2Sn(MeCO.NOMe)_2$ has been shown to have trans methyl groups (166). On the other hand, the related dimethyltin bis(oximate), $(CH_3)_2Sn(Ox)_2$, has been shown

to have a structure with a cis-dimethyl-tin group (110.7°) (163). The Sn-C stretching frequencies for other dibutyltin bis(N-substituted benzohydroxamates) could not be assigned due to the presence of similar bands in the corresponding ligands.

For the N-phenylparanitrobenzohydroxamic acid the strong absorption bands at 1512 cm^{-1} and 1342 cm^{-1}, which are absent in the N-phenylbenzohydroxamic acid, have been assigned as due to $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ modes since a range of 1525-1490 cm^{-1} and 1350-1340 cm^{-1} has been suggested for corresponding frequencies for aromatic nitro compounds which have para-substituted donor groups (350). In the triphenyl-and diphenyltin derivatives of this ligand, these bands remain practically intact indicating that the NO_2 group does not involve in anyway in the coordination with tin.

Yamasaki and his collaborators (251-255) have studied UV spectra of the metallic complex salts of 2,2'-dipyridyl and 1,10-phenanthroline and reported that very strong absorption bands (logϵ 4-5) in the UV region were due to the organic ligand molecules and these bands were shifted towards longer wavelengths in the complex compared to the free ligand molecules. Similar ligand absorption band shift to longer wavelengths due to chelation have been studied for metal chelate compounds of 8-hydroxyquinoline, salicylaldehyde, salicylaldoxime, salicylaldimine, dimethyl- and diphenylglyoxime (256-257). As is shownin table I and II, the tri- and di-organotin compounds of N-substituted benzohydroxamic acids (except the N-phenylparanitrobenzohydroxamic acid) all show strong absorptions (broad

band) and the longest wavelength absorption maxima of the free ligand have been shifted to the longer wavelength region (bathochromic shift). Hence these di-and tri-organotin compounds are chelated in solution. In polar solvent e.g. in methanol, the triphenyltin N-phenylbenzohydroxamate shows no shift; this may be due to possible solvolysis of the compound in polar solvent resulting in the liberation of the ligand. There is evidence for solvolysis of triphenyltin oxinate in methanol, which has been studied by Datta, Majee and Ghosh (253). In the case of N-phenylparanitrobenzohydroxamic acid practically no shift of the ligand absorption band was observed either in non-polar or in polar solvents. Interestingly, for this ligand a new absorption peak at 339 mm is found in the di- and triphenyltin compounds in cyclohexane is absent in methanol. No interpretation is made possible for these observations at present.

Hence, the triphenyltin and di-organotin derivatives of N-substituted benzohydroxamic acids are all chelated compounds with penta- and hexa-coordinated tin like their oxinate and acetylacetonate analogues.

It has been shown by Datta, Majee and Ghosh (31) that the penta-coordinated compound triphenyltin oxinate, $Ph_3Sn(Ox)$ reacts readily with mercuric halides at room temperature to produce phenyltin halide dioxinates, $PhSnX(Ox)_2$, phenylmercuric halides, $PhHgX$ and triphenyltin halides, Ph_3SnX. Triphenyltin carboxylates which are also penta-coordinated with Sn-O linkage like their oxinato counterpart react with mercuric halides to produce phenyltin halide dicarboxylates, phenylmercuric halides and triphenyltin halides. However,

no phenyltin halide dicarboxylates have been isolated though PhHgX and Ph_3SnX were isolated (63). And it has been suggested that dicarboxylates were formed which, unlike their oximate analogous, were unstable and were easily hydrolysed to polymeric compounds of the type $[RSn(OH)_2OCOR']_n$.

Triphenyltin N-substituted benzohydroxamates are all pentacoordinated compounds with Sn-O moiety. So, it is expected that these compounds should also react with mercuric halides to produce, like oximates, the compounds of the type, e.g. for PBHA, $PhSnX(PBHA)_2$ along with the phenylmercuric halides and triphenyltin halides. Thus, this method would be a convenient way of preparing phenyltin halide bis-N-substituted benzohydroxamates. Reactions of triphenyltin N-phenylbenzohydroxamate with mercuric chloride, mercuric bromide and mercuric iodide gave quantitative yield of the respective phenyltin halide bis-N-phenylbenzohydroxamates together with phenylmercuric halides and triphenyltin halides.

Thus the mechanism of this conversion would be like that as proposed for oximates (61),

$$Ph_3Sn(PBHA) + HgX_2 \longrightarrow Ph_3Sn(PBHA)X + PhHgX$$

$$Ph_3Sn(PBHA)X + HgX_2 \longrightarrow PhSn(PBHA)X_2 + PhHgX$$

$$PhSn(PBHA)X_2 + Ph_3Sn(PBHA) \longrightarrow PhSn(PBHA)_2X + Ph_3SnX$$

The overall reaction is therefore,

$$2Ph_3Sn(PBHA) + 2HgX_2 \longrightarrow 2PhHgX + Ph_3SnX + PhSnX(PBHA)_2$$

(where X = Cl, Br, I).

Phenyltin thiocyanate bis (N-phenylbenzohydroxamato) has been prepared from the corresponding chloride by the displacement of chloride by thiocyanate:

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

All the other compounds of this series reported here have been prepared by the above method by reacting the triphenyltin derivative with mercuric halides.

Since the Sn-X (X = Cl, Br, I) modes are known to appear at lower frequency (below 320 cm^{-1}) in most cases) the spectra of $PhSnL_2$ (L = N-substituted benzohydroxamic acid) are very similar for a particular ligand. For all compounds of this series the very strong and broad band at ~ 1530 cm^{-1} has been assigned due to ν (C = O) mode and another strong band at ~ 930 cm^{-1} is assigned due to the ν (N-O) mode. As indicated previously for the triphenyl and diphenyltin derivatives the band at ~ 435 cm^{-1} in the IR spectra of these compounds can be assigned as due to phenyl ring mode. That each of these compounds contains at least one phenyl group is further supported by the fact that all show moderately intense absorption band at 1065 - 1070 cm^{-1}. This band at ~ 1065 cm^{-1} has been assigned

by Henry and Holtes (246) to be perturbed phenyl vibrational absorption; probably a C-H in plane deformation and is believed to be characteristic of phenyl group bonded to tin atom. The intense ~~of~~ bands at ~ 560 cm^{-1} and ~ 620 cm^{-1} have been assigned as ν_s(OSnO) and ν_{as}(OSnO) respectively for these complexes.

The IR spectrum of the thiocyanate complex, $Ph_2Sn(SCN)(PBHA)_2$, is exactly identical with those of the corresponding halide complexes except that a very intense absorption band appeared at 2035 cm^{-1}. The ambident ligand -SCN- can coordinate to metal either through S or through N or it can act as a bridge. Sabatini and Bertini (263) have suggested the following criteria to distinguish between these two types of co-ordinations:

ν(C≡N)	M-N≡C-S below 2100 cm^{-1} (broad)	M-S-C≡N 2100 cm^{-1} (sharp)
ν(C-S)	860 - 780 cm^{-1}	690-720 cm^{-1}
δ (NCS)	490 - 450 cm^{-1}	440-400 cm^{-1}

Though the C-S stretching frequency is more useful in distinguishing these two isomers (263-265), the N-phenylbenzohydroxamic acid has so many absorptions in this region that they may obscure the C-S stretching band. Hence on the basis of the C≡N stretching frequency the thiocyanate group may be thought to be linked to tin atom through the nitrogen atom of the group. This is further supported by the fact that ν(C≡N) frequency is at 2035 cm^{-1} in KBr compared to

that at 2045 cm^{-1} in chloroform solution(Fig. 8e).

$Ph_2SnX(Ox)_2$ (X = Cl, Br, I) like $R_2Sn(Ox)_2$ have been shown to possess an octahedral arrangement of groups around tin. Similar complexes of other bidentate chelating agents have the similar octahedral arrangement around tin. On the basis of all these data the present phenyltin halide bis-N-substituted benzohydroxamates can have the following structure, e.g. for PBHA :

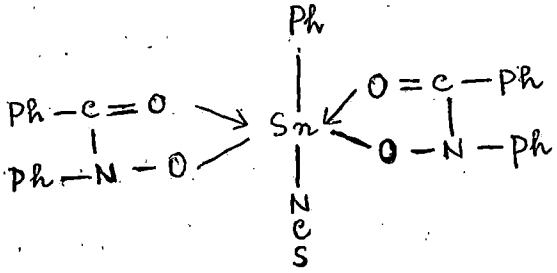


Fig. 14a

and

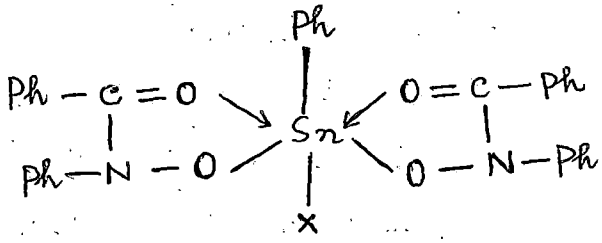


Fig. 14b

Diorganotin halide N-phenylbenzohydroxamates, $R_2SnX(PBHA)$ (R = Ph, X = Cl, I, SCN, and R = Bu, X = SCN) have been prepared. While $Ph_2SnX(PBHA)$ (X = Cl,I) and $Bu_2Sn(SCN)(PBHA)$ have been prepared by the reaction:

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

$Ph_2Sn(SCN)(PBHA)$ has been prepared by replacement of the chloride from the corresponding complex:

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

Analytical data of these N-phenylbenzohydroxamate complexes suggest the composition to be $R_2SnX(PBHA)$. But when similar reactions were done with the ligand, N-phenylparanitrobenzohydroxamic acid and the compounds were crystallized from benzene the analytical data correspond to $Ph_2SnX(p\text{-}NO_2BPHA).C_6H_6$ (X = Cl, I).

In the IR spectra of $Ph_2SnX(PBHA)$ (X = Cl, I, SCN) the band at 1525 ± 10 cm^{-1} has been assigned due to ν (C = O) and the band at ~ 925 cm^{-1} has been assigned to the ν (N-O) mode. For the $Ph_2SnX(p\text{-}NO_2BPHA)$ (X = Cl, I), the ν(C = O) band is at ~ 1550 cm^{-1}. And as for the other N-substituted benzohydroxamates discussed previously the bands at 600 cm^{-1} and 560 cm^{-1} have been assigned due to ν_{as}(OSnO) and ν_s(OSnO) modes respectively for all these complexes of this category.

Mullins and Curran (71) have shown that $Ph_2Sn(SCN)(Ox)$ does not contain any -NCS-bridging in the solid since absorption by this compound is at 2025 cm^{-1} in KBr compared to 2035 cm^{-1} in benzene solution and they have suggested a penta-coordinated tin in $Ph_2Sn(SCN)(Ox)$. They have also suggested from dipolemoment measurement a cis arrangement of hydrocarbon groups for this compound. From Mossbauer spectra $Ph_2SnX(Ox)$(X = SCN, Cl) have been shown (163) to have a preferable penta-coordinated structure. In view of these data $Ph_2SnX(PBHA)$ (X = Cl, I) can have the following penta-coordinated structure:

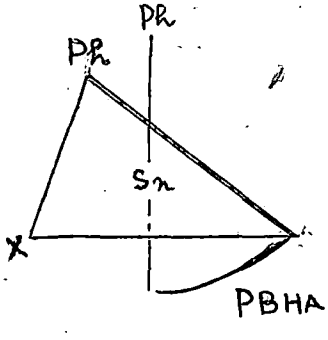


Fig. 15a

But in the case of $Ph_2Sn(SCN)(PBHA)$ the IR spectrum indicates very strong (C≡N) absorption at 2080 cm^{-1} with a medium intensity band at 1982 cm^{-1}. These data indicates, as stated previously, that the coordination of SCN group to tin is through the N atom. And in view of the second absorption band for C≡N mode which is absent in other thiocyanate complexes where SCN does not involve in bridging, a dimeric hexa-coordinated structure can be proposed for this compound:

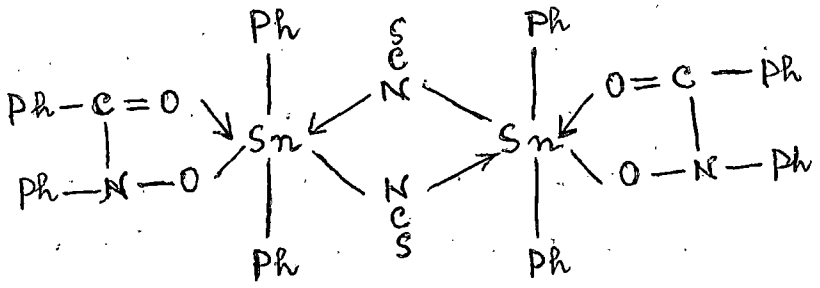


Fig. 15b

in the solid in which nitrogen bridges between the two tin atoms. This is supported by the similar assignment of N≡C stretching vibrations near 2040 cm^{-1} and 1960 cm^{-1} for $(SCN)R_2SnOSnR_2(NCS)$ (239), which has been interpreted as due to an increased contribution of form (b) (the resonance hybrid form):

$$Sn - \bar{N} = C = S \qquad\qquad Sn - \bar{N} - C \equiv \overset{+}{S}:$$

(a) (b)

which indicates the occurance of nitrogen bridging between the two tin atoms. But in solution of $Ph_2Sn(NCS)(PBHA)$ in chloroform, the lower frequency band (1932 cm^{-1} band) has been found to be completely absent and only one strong absorption band due to $\nu(C\equiv N)$ has been observed at 2040 cm^{-1} (Fig. 9e). Thus no -NCS- bridging occure in solution, which suggests a penta-coordinated trigonal bipyramidal structure for this compound in solution.

Dibutyltin thiocyanate N-phenylbenzohydroxamate has similar IR spectrum as that of the corresponding phenyl compound. A very strong band at 2060 cm^{-1} is found to be associated with a weak band at 1990 cm^{-1} in nujol mull. But the weak band disappeared when the spectrum was taken in solution in chloroform and the strong band shifted to 2040 cm^{-1} (Fig. 9e). These data suggest for this compound an analogous structure as proposed for the corresponding phenyl compound. Similar dimeric structure involving -NCS- bridging with hexa-coordinated tin has been suggested for $Bu_2Sn(NCS)(Ox)$ in the solid by Mullins and Curran (71) and this structure is supported by Mossbauer spectra (168).

Kawakami and Okawara (70) have shown that penta-coordinated diorganotin chloride oximates disproportionate to the more stable hexa-coordinated tin compounds. Thus, in polar solvents e.g. in pyridine they suggested the disproportionation:

$$2(CH_3)_2SnCl(Ox) \xrightarrow{\text{Pyridine}} (CH_3)_2Sn(Ox)_2 + (CH_3)_2SnCl_2.2py.$$

When the same reaction was carried out by heating at 160° for one hour in a sealed tube they identified the product $CH_3Sn(Ox)_2$ and suggested the presence of $(CH_3)_3SnCl$ from its characteristic odour in pet-ether washings i.e. the above reaction proceeds further as

$$(CH_3)_2Sn(Ox)_2 + (CH_3)_2SnCl_2 \cdot 2py \longrightarrow (CH_3)_3SnCl + CH_3Sn(Ox)_2 + 2py.$$

When diphenyltin chloride N-phenylbenzohydroxamate was refluxed in a nonpolar solvent (benzene) for a long time (11 hrs.) only two products had been identified; one was phenyltin chloride bis(N-phenylbenzohydroxamate) and the other was triphenyltin chloride. The products were obtained in almost quantitative yield. These products were identified by mixed melting point determinations with authentic analysed samples. In the case of diphenyltin thiocyanate N-phenylbenzohydroxamate one of the products, the phenyltin thiocyanate bis (N-phenylbenzohydroxamate) has been isolated and characterised by mixed melting point determination with authentic analysed sample and the other product, $Ph_3Sn(SCN)$ could not be isolated. However, as has been stated previously, $Ph_3Sn(SCN)$ was formed in the reaction and the complete separation of it from the starting material, diphenyltin thiocyanate N-phenylbenzohydroxamate, was not possible.

It can then be suggested that like the analogous pentacoordinated oxinates, the $Ph_2SnX(PBHA)$ (X = SCN, Cl) disproportionate to the more stable hexa-coordinated tin complexes; but in this case

the change is effected by heating only since the non-polar solvent has probably nothing to do with the reaction. In other words, it can be said that the diphenyltin halide N-phenylbenzohydroxamates are thermally unstable and disproportionate as

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

$$(X = Cl,\ SCN)$$

In polar solvents like methanol, $Ph_2SnX(PBHA)$ was found not to give any triphenyltin halide and $PhSnX(PBHA)_2$ instead another hexa-coordinated compound phenyltin halide methoxy N-phenylbenzohydroxamate was formed along with the liberation of one equivalent of benzene. If solvents have had no effect on the above disproportionation reaction then it is expected that this reaction could lead to the products $Ph_2Sn(PBHA)_2$ and Ph_2SnX_2 or $PhSnX(PBHA)_2$ and Ph_3SnX, none of which can liberate benzene when refluxed in methanol. Here probably the thermally unstable $Ph_2SnX(PBHA)$ is susceptible to nucleophilic attack in polar solvents and before having any chance of disproportionation the compound is attacked by nucleophile methanol itself giving the easily formed another hexa-coordinated stable dimeric methoxy compound with the liberation of benzene resulting from one tin-phenyl bond cleavage.

Tin-carbon bond may be cleaved by a number of reagents e.g. acids, bases, halides, halogens, acidic chelating agents like oxine etc. and in the case of phenyltin or substituted phenyltin cleavage always benzene or substituted benzene respectively are among the products. These have been discussed earlier. There it has been said

that in polar solvents like methanol, the most nucleophilic species available in solution is the solvent itself, which can react with the organotin molecule forming a "Collision Complex":

$$C\text{-}Sn + MeOH \rightleftharpoons C - \overset{(-)}{Sn} - \overset{(+)}{O}Me \quad (H)$$

which can lead to the products resulting in tin-carbon bond cleavage:

$$C - \overset{(-)}{Sn} - \overset{(+)}{O}Me \quad (H) \longrightarrow C\text{-}H + Sn - OMe$$

Thus, the reaction of Ph_2SnX_2(DBEA) with methanol may be represented as:

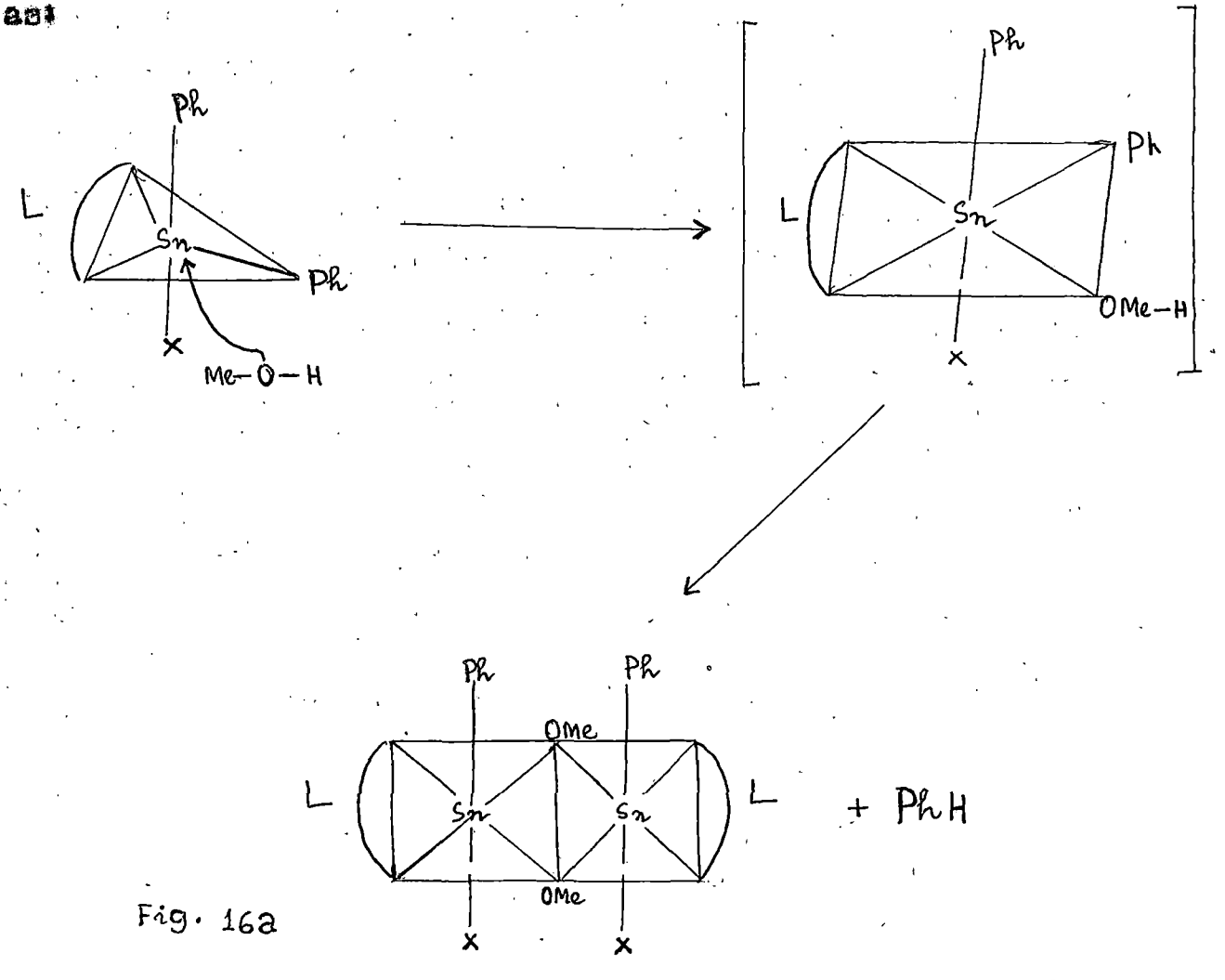


Fig. 16a

The same phenyltin halide methoxy N-substituted benzohydroxamate was obtained with simultaneous liberation of ligand when phenyltin halide bis(N-substituted benzohydroxamate) was refluxed in methanol for a long time. Here the conversion was not complete possibly due to the higher stability of the parent compound and involvement of the same coordination number of tin for both the compounds.

All the phenyltin halide methoxy N-substituted benzohydroxamates were easily obtained by refluxing either the diphenyltin halide N-substituted benzohydroxamates or the phenyltin halide bis(N-substituted benzohydroxamates) with methanol:

$$Ph_2SnXL + MeOH \longrightarrow PhSnX(OMe)L + C_6H_6$$

$$PhSnXL_2 + MeOH \longrightarrow PhSnX(OMe)L + HL$$

These reactions are very simple and the methoxy compounds were easily separated out since either benzene or ligands were the other products which were easily removed by washings with hot methanol which also removes unconverted, if any, reactants which are soluble in methanol. These methoxy compounds have insufficient solubility in benzene and chloroform and hence the molecular weight could not be determined. Analytical data of phenyltin chloride methoxy N-phenylbenzohydroxamate suggest that one phenyl, one methoxy, one chloride and one ligand must be attached to each tin atom. These methoxy compounds, unlike many monomeric alkoxy compounds, are moisture-stable. They have high melting points (above 210°) and all decompose at their

melting points. These data indicate that these methoxy compounds are not monomeric.

Kawasaki and Okawra (173) have prepared dimeric methoxy (acetylacetonato) tin dihalides by the reaction:

$$(Acac)_2SnX_2 + MeOH \text{ (large excess)} \longrightarrow AcacH + (acac)(OMe)SnX_2$$

(X = Cl, Br, I)

in which one ligand has been replaced by a methoxy group. They have determined the molecular weight of these compounds by ebullioscopic method and have shown that these are dimeric. All alkoxides absorb strongly near 1000 cm^{-1} due to modes variously described as ν(C-O) or ν(M - C - O) (266-270). For this frequency there must be considerable "mixing" of ν(C-O) and ν(M-O) although the ν(C-O) contribution will undoubtedly dominate in the 1000 cm^{-1} band. Butcher and his co-workers (271) and Lorberth and Kula (130) independently assigned bands near 1035 cm^{-1} and 1060 cm^{-1} to the symmetric and asymmetric modes, respectively in dialkoxides. In the IR spectra of methoxy(acetylacetonate) tin dihalides Kawasaki and Okawara have assigned the new band at 970 - 1000 cm^{-1} to the ν(H_3C-O) mode. Another lower frequency band which appeared at 520-530 cm^{-1} in these complexes have been assigned as due to the ν(Sn-OCH_3) mode, which is intermediate between the two extreme cases of dimethyltin dimethoxide [ν_{as}(Sn-OCH_3) 644 cm^{-1} and ν_s(Sn-OCH_3) 609 cm^{-1}] and bis-acetylacetonato dihalides [ν(Sn-O) 460-440 cm^{-1}]. They suggested a dimeric structure in which each tin atom is hexa-coordinated in

conformity with the fact that these compounds are not easily hydrolysed in moist air. In a latter publication they (102) have assigned the characteristic 531-491 band in the methoxylbridged acetylacetonates to the 4-membered $\overline{OSnOSn}$ ring system which frequently occur in dimeric tin compounds.

The IR spectra of the phenyltin halide methoxy N-substituted benzohydroxamates all show an intense broad absorption band at 490 ± 10 cm^{-1}, which is not present or present as a very small absorption in either of the parent compounds. This suggests the presence of $\overline{OSnOSn}$ ring systems in these methoxy compounds. The assignment of the higher frequency band at ~1000 cm^{-1} due to stretching vibrations of the O-CH_3 group is not possible here because of the presence of similar bands in this region in the parent compounds. However, the bands at ~1010 cm^{-1} in the parent compounds have been intensified in all the methoxy compounds derived from them. Hence, consistent with these facts the structures of these novel type of methoxy compounds can be written (e.g. for PMHA) similar to that of the methoxyl-bridged acetylacetonates:

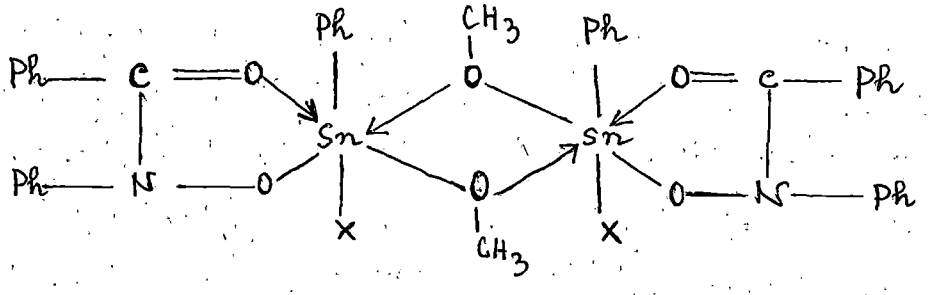


Fig. 16b

The presence of the same intense band at 400 cm^{-1} indicative of the OSnOSn ring is also present in the phenyltin chloride complex when the ligand was N-phenylparanitrobenzohydroxamic acid. But a broad weak band at≈3400 cm^{-1} which indicates the presence of an OH group in this compound is also present. Thus this compound is probably a hydroxyl bridged compound resulting from the hydrolysis of the methoxy compound.

The structure (Fig.16b ; X = Cl) assigned for phenyltin chloride methoxy N-phenylbenzohydroxamate is also supported by its NMR spectrum. (Fig. 16c) The proton NMR spectrum (60 MHz) of the compound taken in $CDCl_3$ showed peaks at δ 7.37, 7.30 and 7.25 for the phenyl protons and a signal (singlet) at δ 3.43 due to the $-OCH_3$ protons. From the integration of the curve the ratio of the phenyl protons and methoxy protons is approximately 5:1, which is consistent with the structure assigned.

The stability of all these five types of compounds taking the case of phenyltin derivatives of N-phenylbenzohydroxamic acid $Ph_3Sn(PBHA)$, $Ph_2Sn(PBHA)_2$, $Ph_2SnCl(PBHA)$, $PhSnCl(PBHA)_2$ and $PhSnCl(OMe)(PBHA)$, can roughly be compared following the shifting of the longest wavelength absorption maxima in the ultraviolet region of the spectra.

Sone and his co-workers (256-257) have studied a number of metal chelates compounds and have shown that the ligand absorption band is shifted to longer wave length due to chelate formation and the extent of this shift parallels the stability of the chelate complex. Kawakami and Okawara (70) have shown that the organotin oximates

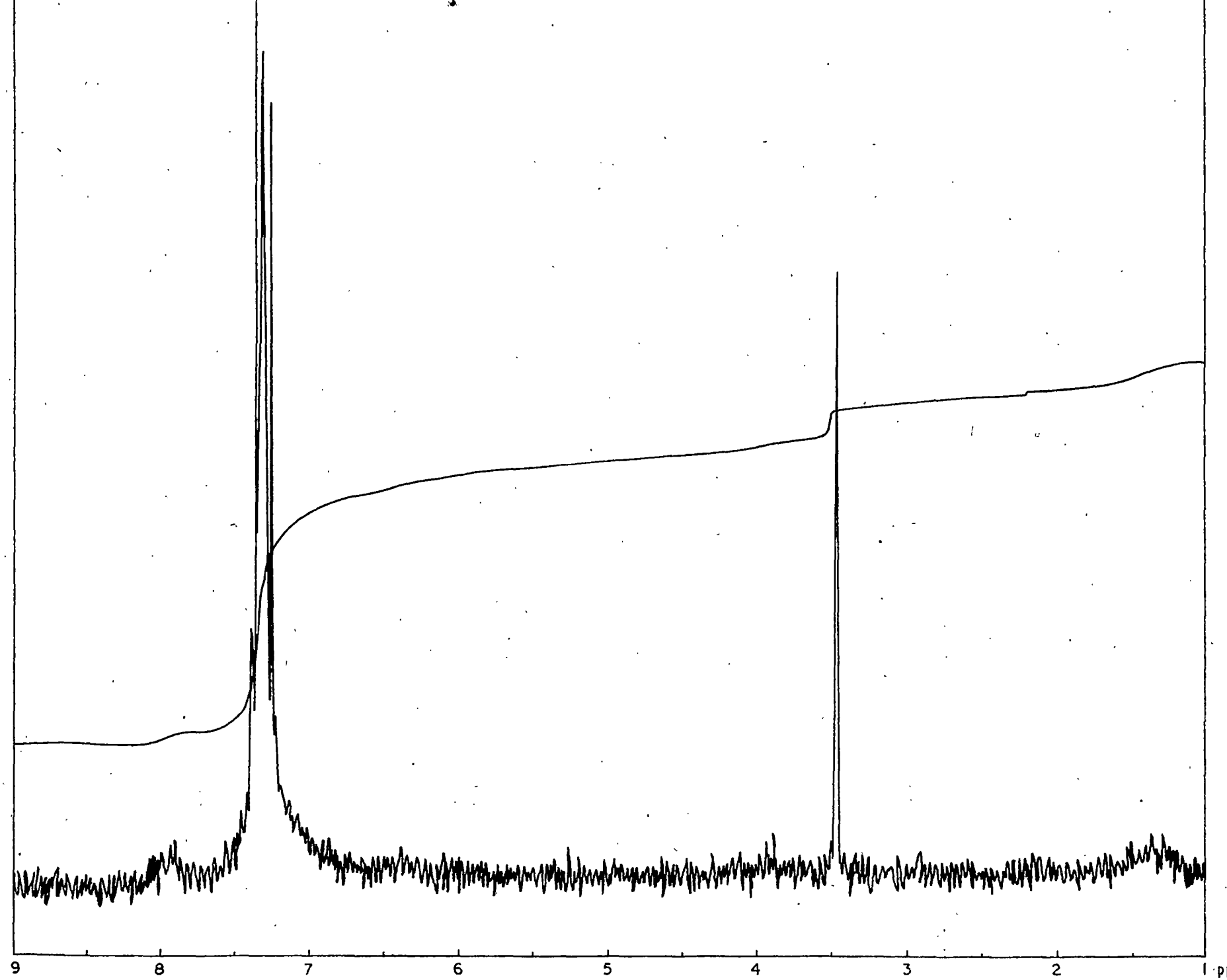


FIG. 16e: PMR SPECTRUM OF PHENYLTIN CHLORIDE METHOXY N – PHENYLBENZOHYDROXAMATE IN $CDCl_3$ (60 MHz)

are chelated compounds in solution since the peak of oxine in the UV region shifts to longer wavelengths in the complexes. And the sequence of the stability constants of these oxinates have been drawn from the band shifts in non polar solvents.

As shown (Table -III), all the five N-substituted benzohydroxamates mentioned above show strong absorptions in the UV region and the longest wavelength absorption maxima of the free ligand show bathochromic shift in non polar solvent, cyclohexane. Thus, all these phenyltin N-substituted benzohydroxamates are chelated compounds in solution. And, if the relationships between the band shift and the stability of the chelates are applicable here, then the sequence of the stability of these complexes would be $Ph_2Sn(PBHA)_2 > Ph_3Sn(PBHA) > Ph_2SnCl(PBHA) \simeq PhSnCl(PBHA)_2 \simeq PhSnCl(Oxe)(PBHA)$.

During the investigation of the reaction of tetraphenyldiltin 1,2-diacetate with N-substituted benzohydroxamic acids and 8-hydroxyquinoline it was observed that reaction of tetraphenyldiltin 1,2-diacetate with N-phenylbenzohydroxamic acid yielded a compound of m.p. 160°, which was found to be identical with that of the diphenyltin bis(N-phenylbenzohydroxamate) (identified by mixed m.p. determination). Whatever be the ratio of the reactants (1:2, 1:3, 1:4) one of the products was diphenyltin bis(N-phenylbenzohydroxamate) in each case. Thus 1.33 gm (0.002 mole) of tetraphenyldiltin 1,2-diacetate was taken in benzene and to it was added 0.85 gm (0.004 mole) of N-phenylbenzohydroxamic acid and the mixture was heated on a water bath for ten minutes. This was then concentrated to a pasty mass,

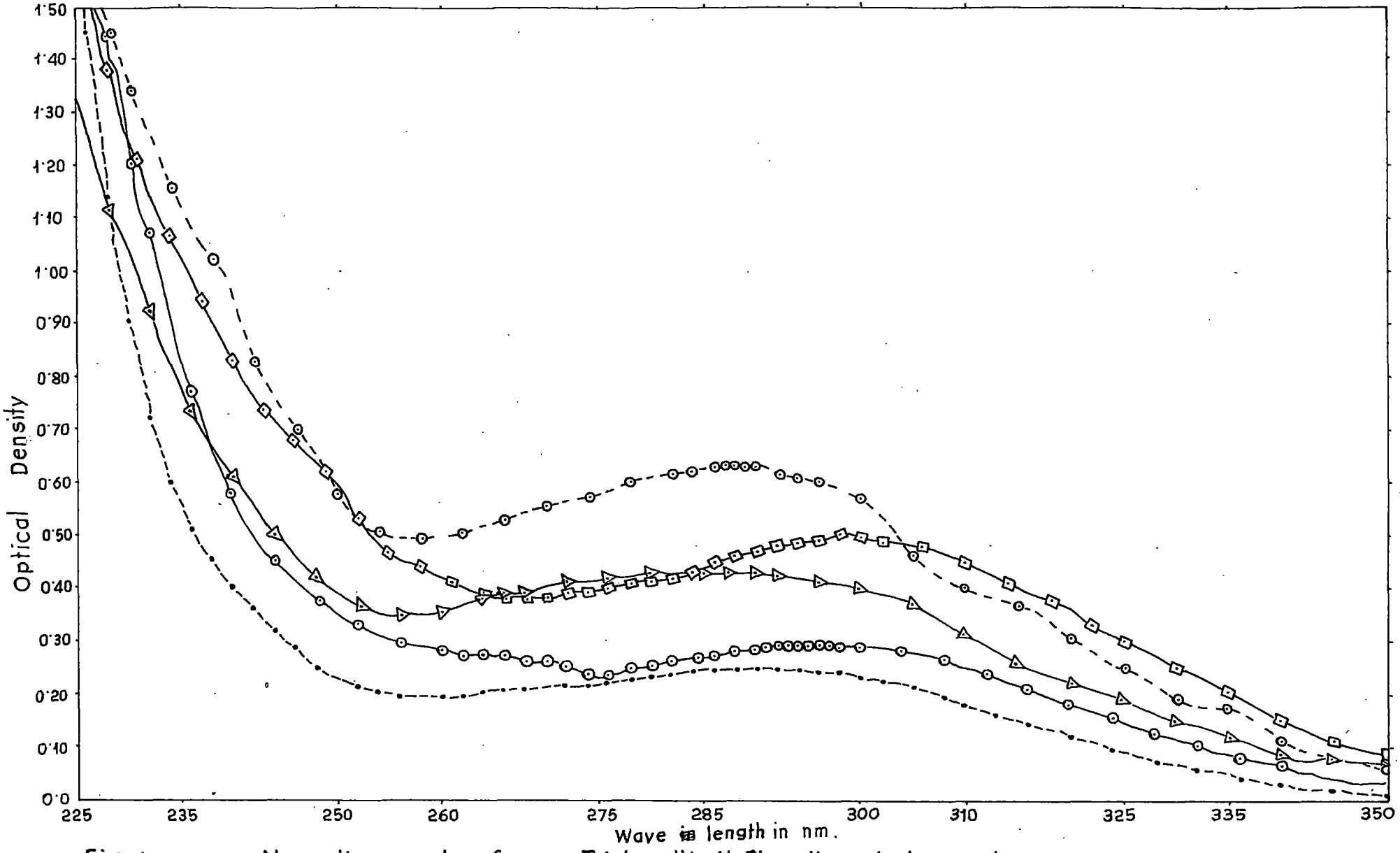


Fig-17 Absorption spectra of —o-o— Triphenyltin N-Phenylbenzohydroxamate, —□-□— Diphenyltin bis-N-Phenylbenzohydroxamate, —·—·— Diphenyltin chloride N-Phenylbenzohydroxamate, (IV) --o--o-- Phenyltin chloride bis-N-Phenylbenzohydroxamate, —▷-▷— Phenyltin Chloride methoxy N-Phenylbenzohydroxamate in the UV region in Cyclohexane.

which on crystallisation from methanol gave fine white crystals (0.51 gm) of m.p. 160°. Similarly, when 1.33 gm (0.002 mole) of tetraphenyldiitin 1,2-diacetate and 0.91 gm (0.004 mole) of N-para-tolylbenzohydroxamic acid taken in 40 ml of benzene were heated on a water bath for twenty minutes and then concentrated to a pasty mass gave a white compound (0.86 gm) of m.p. 166-67° after repeated precipition from methanol. This compound was found to be diphenyltin bis-N-paratolylbenzohydroxamate (identified by mixed melting point determination). Thus, diphenyltin bis-N-phenylbenzohydroxamate and diphenyltin bis-N-paratolylbenzohydroxamate have been obtained when tetraphenyldiitin 1,2-diacetate was reacted with any equivalent of the corresponding N-substituted benzohydroxamic acid ligands. This reaction can be taken as the cleavage of the tin-tin bond by the hydroxamic acid ligands which can act as oxidising agents. Since, Sn-Sn bond in organopolytin compounds can be cleaved readily by many common reagents e.g. halogens (1,234-236):

$$R - \underset{\underset{R}{|}}{\overset{R}{|}}{Sn} - \underset{\underset{R}{|}}{\overset{R}{|}}{Sn} - R + X_2 \longrightarrow 2R_3SnX$$

$$\underset{\underset{OAc}{|}}{\overset{R_2Sn}{|}} - \underset{\underset{OAc}{|}}{\overset{SnR_2}{|}} \xrightarrow{Br_2} 2R_2Sn\begin{matrix}Br\\OAc\end{matrix}$$

(R = Bu, Ph)

by oxidising agents e.g. with benzoyl peroxide (237):

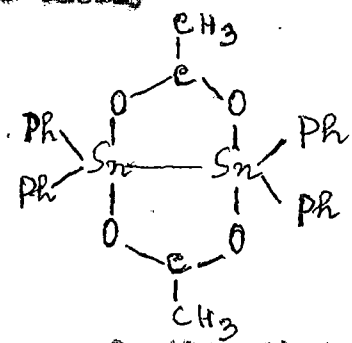
$$(Bu_2Sn)_n \xrightarrow[\text{(in benzene at room temp.)}]{\text{benzoyl peroxide}} Bu_2Sn(OOCPh)_2$$

by acids (233) e.g. :

$$(Bu_2Sn)_n \xrightarrow[(X = Br, I)]{HX} Bu_2SnX_2 + H_2$$

etc.

And Blakeley et al (219) have shown that N-substituted benzohydroxamic acids act as an oxidising agent. Hence both the acidic and oxidising properties of these N-substituted benzohydroxamic acids can be thought to be responsible for the cleavage of the Sn-Sn bond so easily

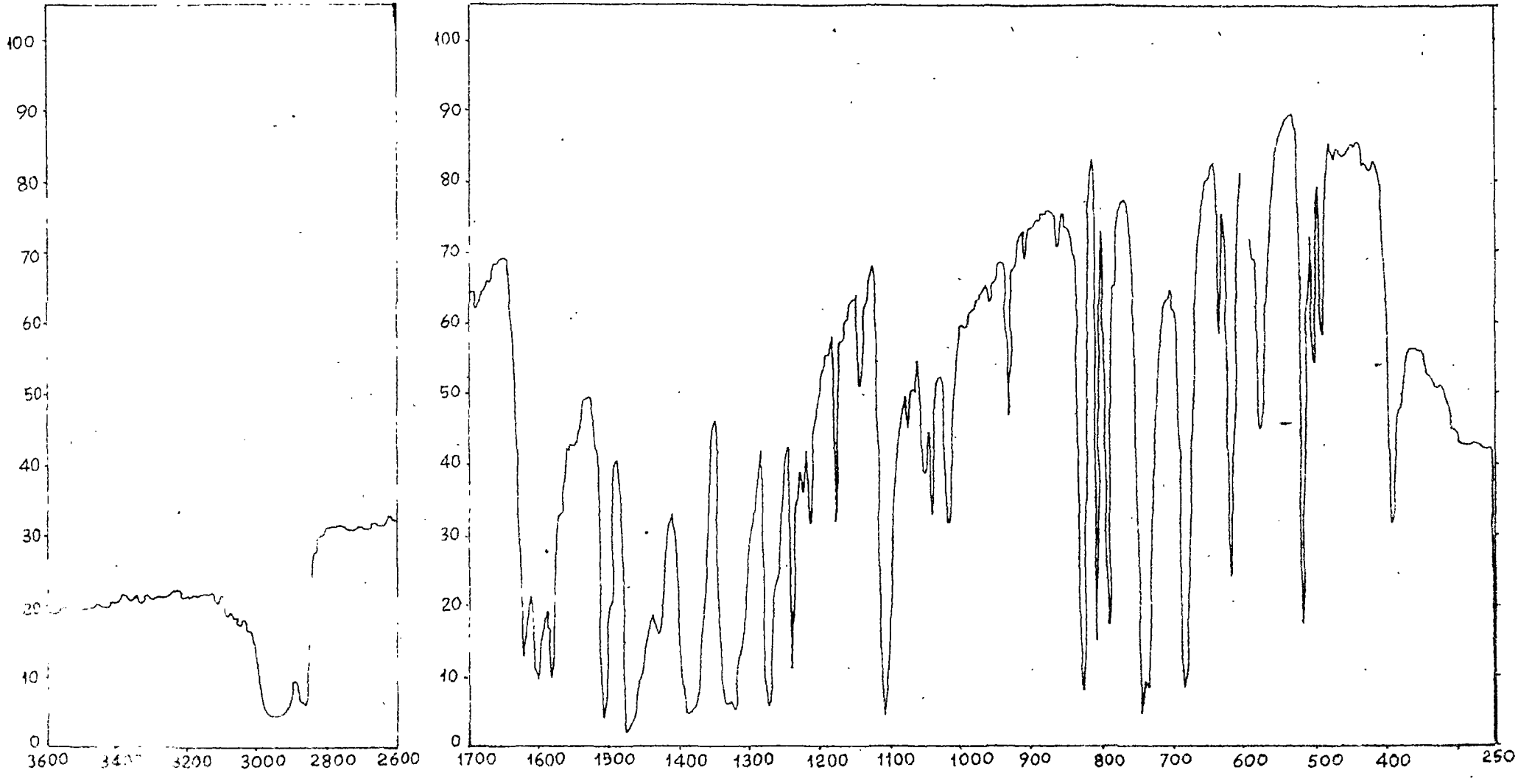


$$+ \quad 2LH \longrightarrow Ph_2SnL_2 + Ph_2Sn(OAc)_2 + H_2 .$$

On the other hand, when tetraphenylditin diacetate and oxine (1:2 mole ratio) taken in benzene were heated just to boiling and shaken fine yellow crystals started to come having a m.p. of 224-30°. This on crystallisation twice from benzene showed a m.p. 235° and mixed with diphenyltin bis(oxinate) (m.p. 252°) had m.p. of 210-15°. Analysis of this compound gave : C = 40.97, H = 2.06, N = 5.07, Sn = 36.53% and calculated for $C_{22}H_{18}N_2O_6Sn_2$: C = 41.02, H = 2.82, N = 4.35, Sn = 36.89%. The analytical data of this compound conform with a formula of $(OAc)_2Sn_2(Ox)_2$, diacetate ditin bisoxinate, which can be supported by the IR and UV spectral data.

The IR spectra of 1,1,2,2-tetraphenyl-1, 2-diacyloxyditin compounds have been studied by Teglavini et al (260). For the acetate compound the band at 1530 cm^{-1} has been assigned due to $\nu_{as}(COO)$ vibration , the symmetric stretching vibration of which, $\nu_{s}(COO)$ has been assigned at 1405 cm^{-1}. These frequencies have been shown to be unchanged in nujol mulls, in solid and in solution in chloroform and carbon tetrachloride. A five-coordinated trigonal bipyramidal structure with the two acetate ligands bridging the two tin atoms have been proposed. In the spectrum of the present compound these two bands have been missing and a new intense band at 1630 cm^{-1} has been appeared. Monomeric diorganotin bis(acetate) $R_2Sn(OAc)_2$ (R = CH_3, C_3H_7, C_4H_9) have been shown to give $\nu_{as}(COO)$ at 1607 cm^{-1} which was attributed to a chelating acetate group. For $Sn(OAc)_4$ the bands at 1628 cm^{-1} and 1725 cm^{-1} have been interpreted as (COO) vibrations involving a chelating and an ester-like acetate configuration respectively. Also, the ν_{as} (C = O) stretching band of CH_3COOEt at 1741 cm^{-1} is shifted to 1613 cm^{-1} upon coordination of the C = O group through the oxygen to the tin atom (262). Hence in the present compound the acetate group is not a bridging one as in the parent ditin compound but a chelating one.

Tin-nitrogen stretching vibration in $(CH_3)_2Sn(Ox)_2$ has been shown to occur at 395 cm^{-1} and the band at 617 has been assigned to ν(Sn-O) mode (70). Similar band assignments have been made for $R_2SnX(Ox)$ compounds (168). The present compound contains two strong bands at 390 cm^{-1} and 515 cm^{-1} which were absent in the tetraphenyl-ditin diacetate and hence these bands can be assigned as ν (N→Sn)



I.R Spectrum of Diacetate ditin dioxinate.

Fig---18a

and ν(Sn-O) modes respectively arising from the coordination of the oxine group to the tin atom. The band at 575 cm^{-1} which is present in both the $Ph_2Sn(Ox)_2$ and $Ph_4Sn_2(OAc)_2$ compounds appeared as intense absorption and can be assigned as due to ν_s(OCnO) mode. All the phenyltin compounds have been found to have a medium to intense absorption band at ~450 cm^{-1} which has been assigned to phenyl ring mode (100). Since the present compound has no absorption band between 390 cm^{-1} to 490 cm^{-1} corresponding to the intense band at ~450 cm^{-1} in the $Ph_2Sn(Ox)_2$ and $Ph_4Sn_2(OAc)_2$ compounds it can be suggested that the compound lacks the phenyl group. This is supported by the fact that dicarboxylatotin bis(oxinates) which contain no phenyl ring did not show any band at ~450 cm^{-1}. It has also been generally found that medium to strong intensity absorption bands appear at ~3060 cm^{-1} for compounds which contain phenyl group. But such band is absent in the present compound.

It is now well known, due largely to the research of Gilman, Kumada and their co-workers, that catenated metal-metal bonds of Group IV metals absorb as chromophores in the near ultraviolet. And, in organoditetannanes, there is intense absorption around 245 nm in cyclohexane, which is associated with the Sn-Sn bond and is independent of the presence of aromatic groups (112, 272-273). The UV spectra of tetraphenylditindiacetate and the present compound in cyclohexane were taken (Fig.18b). Both the compounds show absorption maxima at 242-243 nm suggesting that the present compound contains a tin-tin bond as that of tetraphenylditindiacetate. The extinction could not be determined due to insufficient solubility of the compound in cyclohexane. But in chloroform solution this compound shows

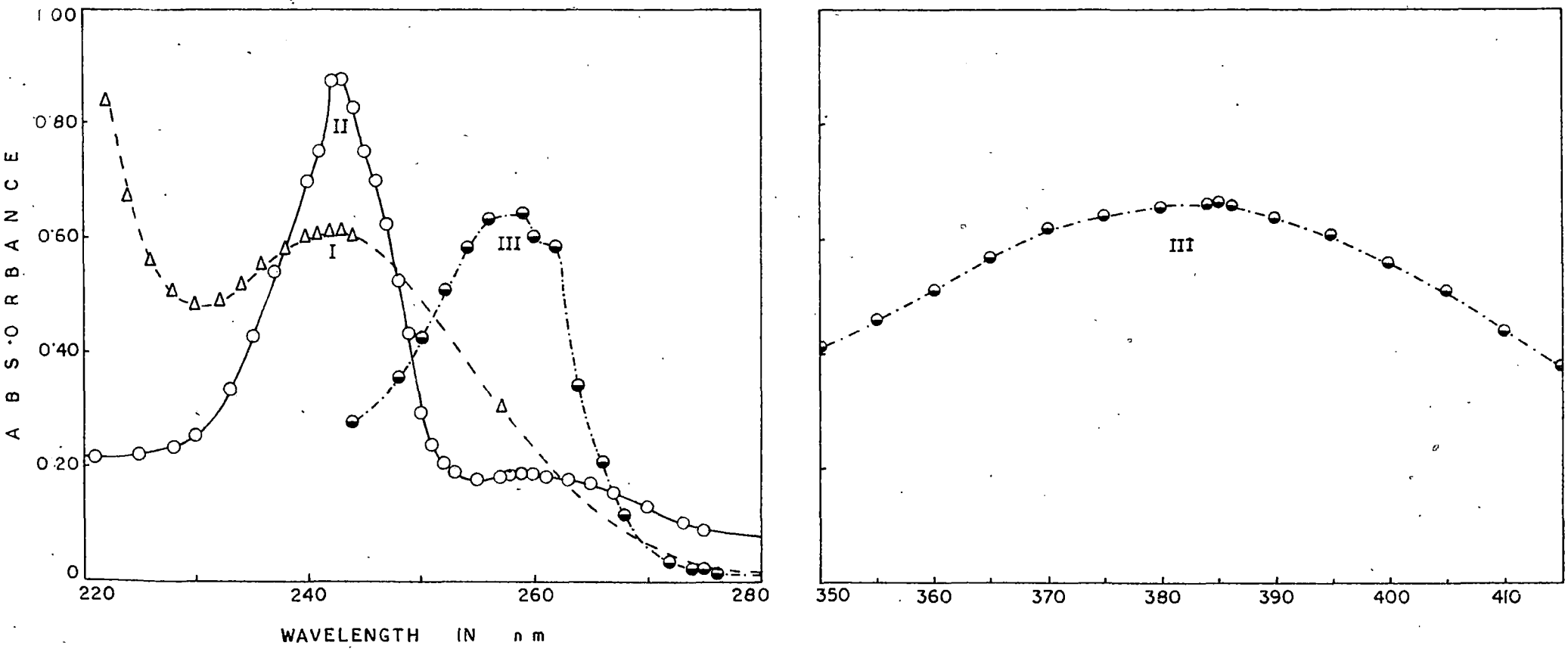


FIG. 18b TETRAPHENYLDITIN DIACETATE IN CYCLOHEXANE (I)
DIOXINATE DITIN DIACETATE IN CYCLOHEXANE (II) AND IN CHLOROFORM (III).

absorption maxima at 259 nm (log ϵ_{max} = 4.79) and a broad band at 335 nm (log ϵ_{max} = 3.50). The nature of the compound in the ultraviolet and visible region of the spectra in chloroform solution (Fig. 18b) clearly demonstrates the presence of the chelating oxinate groups in the compound (261).

Hence on the basis of the above discussion the present compound may be suggested to have a penta-coordinated trigonal bipyramidal structure with chelating acetate and oxinate groups in conformity with the analytical data:

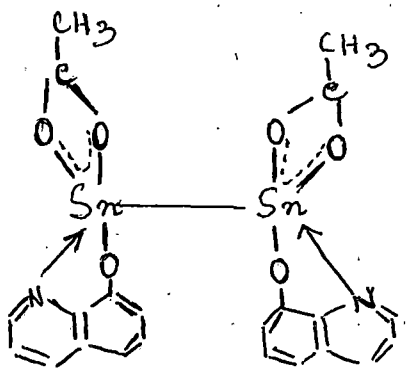


Fig. 18c