CHAPTER - II

PREPARATION, PROPERTIES AND IR SPECTRA OF ORGANOTIN COMPLEXES OF 5-ARYLAZO-8-QUINOLINOLS:

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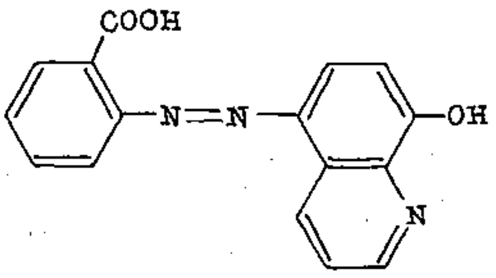
BIBLIOGRAPHY

IIA. Introduction

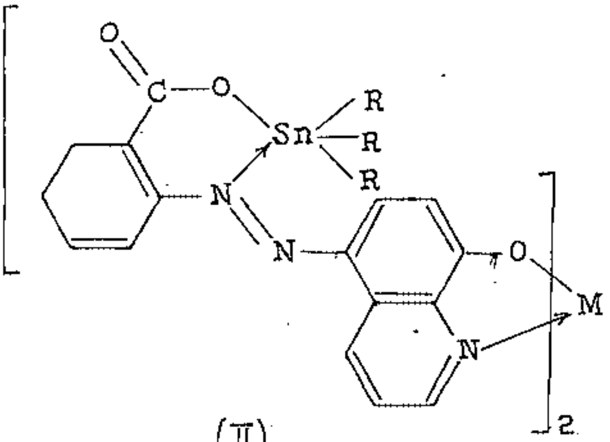
It was discussed in chapter - I that the Arylazoquinolinols are extremely efficient analytical reagents[1-5]. This class of azodyes forms complexes in solution with a wide variety of metals. However, there is no report in the extant literature of any metal complex having been isolated and characterised apart from a very recent example of organotin complexes of 5-phenyl-azo-8-quinolinol[6].

5-Arylazo-8-quinolinols, particularly the o-carboxy derivative 5-(2'-carboxyphenyl) azo-8-quinolinols (I) appears to be a very suitable ligand for preparing organotin as well as organotin-transitional metal mixed complexes. This ligand contains two functional groups capable of coordination with metal ion/organometal group and are situated at different sites within the molecule. Such a heterofunctional ligand provides a rare opportunity of synthesising not only mixed metal complexes (II) but



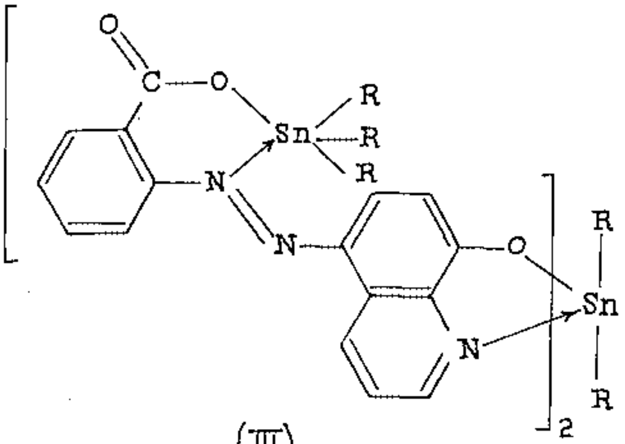
(I)

organotin complexes (III) having tin atoms of different coordination numbers in the same molecule.



(II)

(M = Cu, Ni etc. and R = alkyl or aryl groups)



(III)

(R = alkyl or aryl groups)

In addition, simple organotin complexes like the organotin carboxylates and the organotin quinolinolates can also formed. This prompted us to undertake the synthesis and spectro-chemical studies on the organotin complexes and mixed complexes of o-carbaoxine.

The reason for choosing 5-(2'-carboxy phenyl) azo-8-quinolinol or o-carbaoxine may be summarised as follows:

(i) The presence of the 8-quinolinol group is certain to impart high reactivity towards many metal ions as well as organotin group.

(ii) The compound has intense light absorption in the visible region which may be utilised in the study of the complexes.

(iii) The much higher reactivity of the metal ions, e.g., Cu(II), Ni(II) etc. towards the quinolinol part compared to the carboxylate group offers a favourable chance for synthesising the novel transition metal-organotin mixed complexes (II). In general transition metal ions reacts with organotin complexes through a facile replacement of the organotin group by the fomrer primarily due to the higher stability of the complexes due to lower effective size. Presumably, of this, no report of organotin-transition metal mixed complex is still available in the literature.

(iv) The influence of the triorganotin group in the electronic spectral characteristics can be easily ascertained by a comparative study of the complexes of 5-phenyl azo-8-quinolinols.

(v) The organotin quinolinolate type derivatives may be made water soluble by treating with aqueous sodium bicarbonate solution. Such water soluble organotin complexes are likely to find wide use because of their biocidal properties of organotin compounds.

(vi) The ligand can be easily prepared in high yield by coupling 8-hydroxy-quinoline with diazotised anthranilic acid.

In the present chapter, methods of preparation of the ligands and their organotin complexes are described.

IID. Ligands used in the present study

The ligands used in the present study are given in Table 1.

Table 1

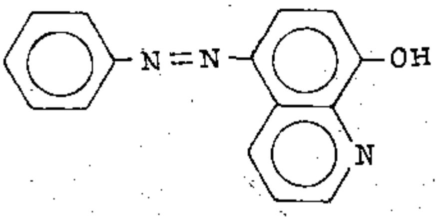
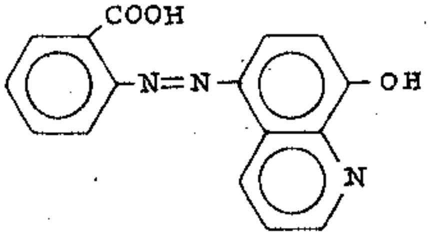
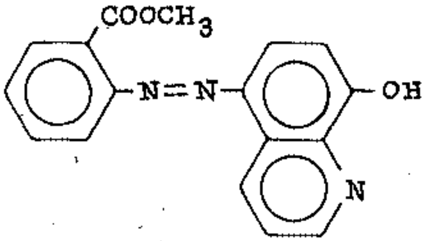
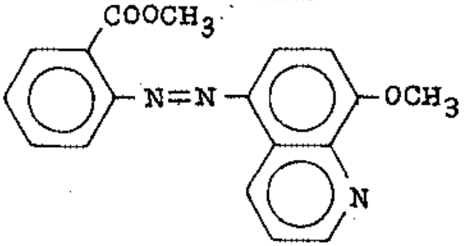
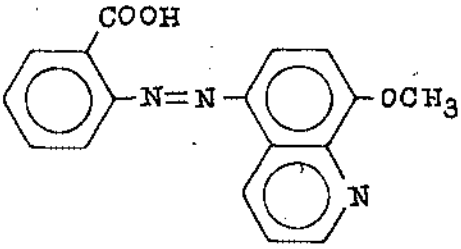
Structure	Name	Abbreviation^{a}
A.		
1. 	Phenyl-5-azo-8-quinolinol	LH^{b}

Table 1 (Contd..)

	Structure	Name	Abbreviation[a]
8.		5-(2'-carboxyphenyl) azo-8-quinolinol	L'HH'
B.			
1.		5-(2'-carbomethoxy-phenyl)azo-8-quinolinol	L'MeH
2.		5-(2'-carbomethoxy-phenyl)azo-8-methoxy quinoline	L'Me$_2$
3.		5-(2'-carboxyphenyl) azo-8-methoxy-quinoline	L'MeH'

a) H and H' denote, respectively, the phenolic (-OH) and carboxyl (-COOH) protons of the ligand to specify the site of complexation in their organotin complexes.

b) Several organotin complexes of this ligand have been recently reported (see ref. 6).

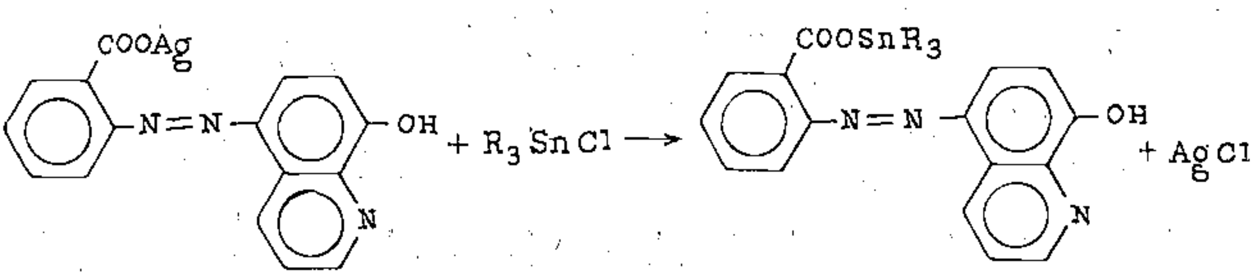
IIC. Methods of preparation of organotin complexes:

While the mono basic ligand LH, forms only one type of organotin complexes, viz., the organotin quinolinolates[6], the dibasic ligand L'HH' can form three types, viz, the organotin carboxylate, organotin quinolinolate and the binuclear di/tri-organotin (triorganotin carboxyphenyl) azo-quinolinolates.

(A) In order to prepare the triorganotin carboxylates, the following methods were employed:

(i) Reaction of the organotin halide with the silver salt of the 5-(2'-carboxyphenyl) azo-8-quinolinol.

Ag - salt of the ligand and R_3SnCl (1:1) were taken in dry benzene and the mixture was refluxed. The reaction mixture was filtered off and the benzene solution was concentrated and then pet -ether was gradually added. The crystallised compound was purified from unreacted dye by extraction with cold benzene followed by recrystallisation from benzene-petroleum ether mixture. The reaction may be represented as follows:

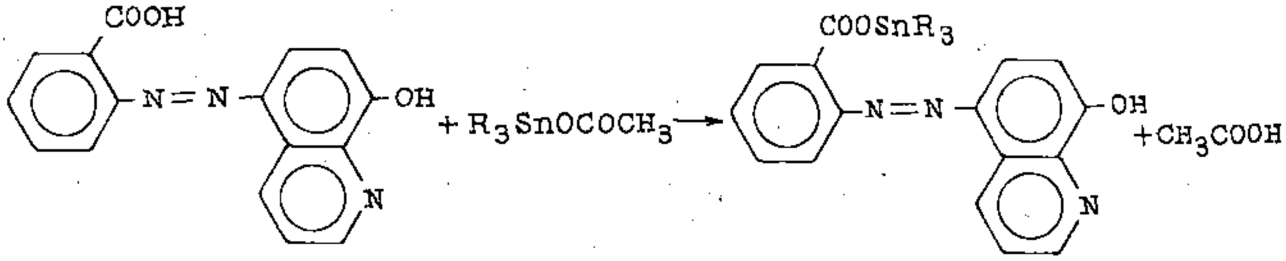


... (1)

This reaction was found particularly suitable for preparing the triphenyl tin derivative. With other triorganotin compounds, the reaction was too slow to be of any practical value.

(ii) Reaction of the organotin acetate with the 5-(2'-carboxyphenyl) azo-8-quinolinol.

The ligand and $R_3SnOCOCH_3$ (1:1) were taken in dry THF and the mixture was stirred. The reaction mixture was filtered and evaporated. Solid was extracted with cold benzene and concentrated, petroleum ether was gradually added. The crystallised compound was purified from unreacted dye by extraction with cold benzene and 2% $NaHCO_3$ solution, followed by recrystallisation from benzene-pet. ether mixture. The reaction may be represented as follows:



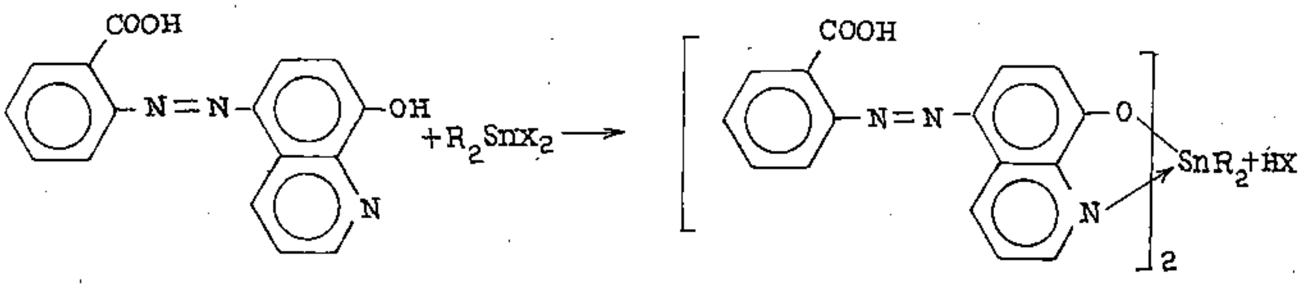
... (2)

This offers a convenient route for the preparation of the tributyl tin derivative.

(B) Preparation of the quinolinate derivatives of the type $R_2Sn(L'H')_2$ and $R_2Sn(L'Me)_2$:

(1) Reaction of diorganotin dihalide with the 5-(2'-carboxyphenyl) azo-8-quinolinol.

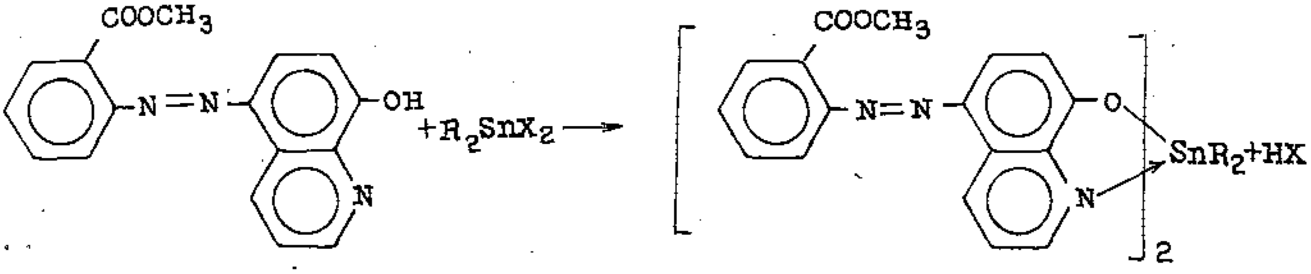
The ligand and R_2SnX_2 (2:1) were taken in dry THF and mixture was stirred. The reaction mixture was filtered and distilled off. Solid was extracted with cold benzene and concentrated, petroleum ether was gradually added. The crystallised compound was purified from unreacted dye by extraction with cold benzene and recrystallised from benzene - pet.ether mixture. The reaction may be represented as follows:



... (3)

(ii) Reaction of diorganotin dihalide with the 5-(2'-carbomethoxyphenyl) azo-8-quinolinol.

The ester (L'MeH) and R_2SnX_2 (2:1) were taken in dry benzene and refluxed. On addition of petroleum ether to the concentrated benzene solution, the diorganotin derivative could be obtained.



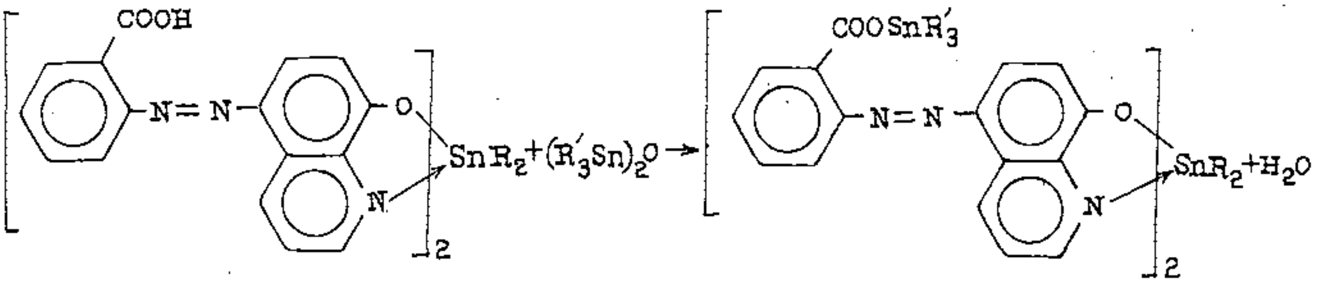
... (4)

(R = Phenyl, Octyl, Butyl and Methyl)

(C) The binuclear di/tri-organotin (triorganotin carboxyphenyl) azo-quinolinolates are conveniently prepared by the following methods:

(i) Reaction of diorganotin complexes of the ligand [$(L'H')_2SnR_2$] with the Bis-(triorganotin)oxide:

The $(L'H')_2SnR_2$ and $(R_3'Sn)_2O$ (1:1) were taken in dry benzene and refluxed. On addition of petroleum ether to the concentrated benzene solution, the binuclear di/tri-organotin (triorganotin) azo-quinolinolates could be obtained.



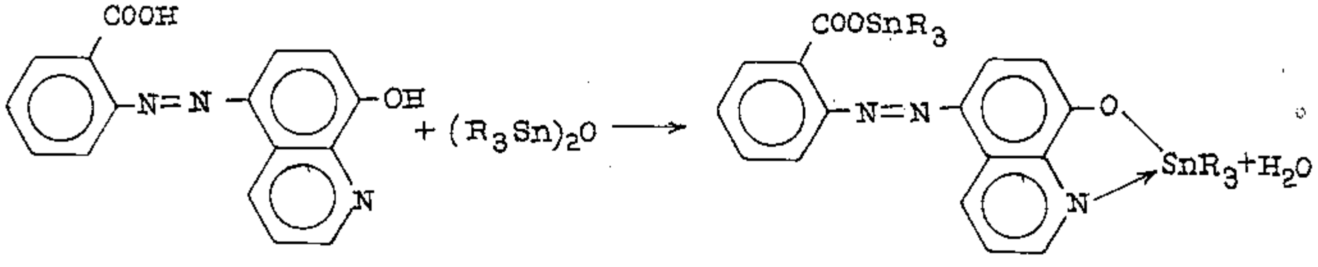
... (5)

R = Phenyl, Octyl, Butyl and methyl

R' = Phenyl and butyl

(ii) Reaction of the 5-(2'-carboxyphenyl) azo-8-quinolinols with Bis-(tri-organotin) oxide.

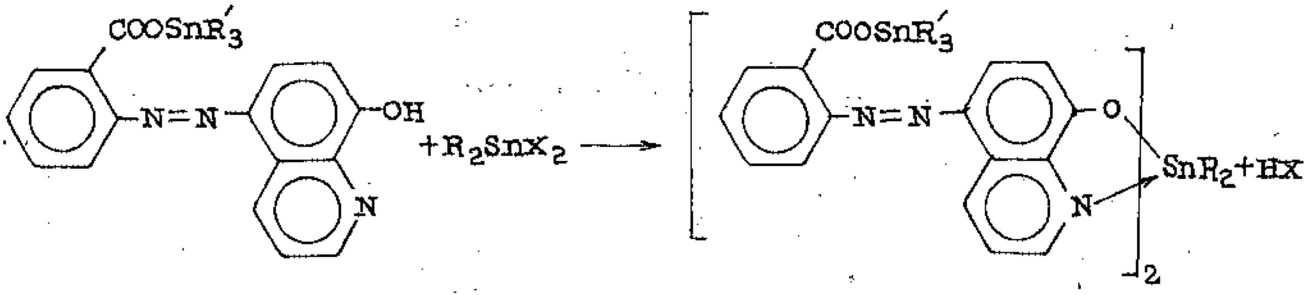
The ligand and $(R_3Sn)_2O$ (1:1) were taken in dry benzene and refluxed. On addition of pet. ether to the concentrated benzene solution, the organotin derivatives could be isolated. The reaction may be written as:



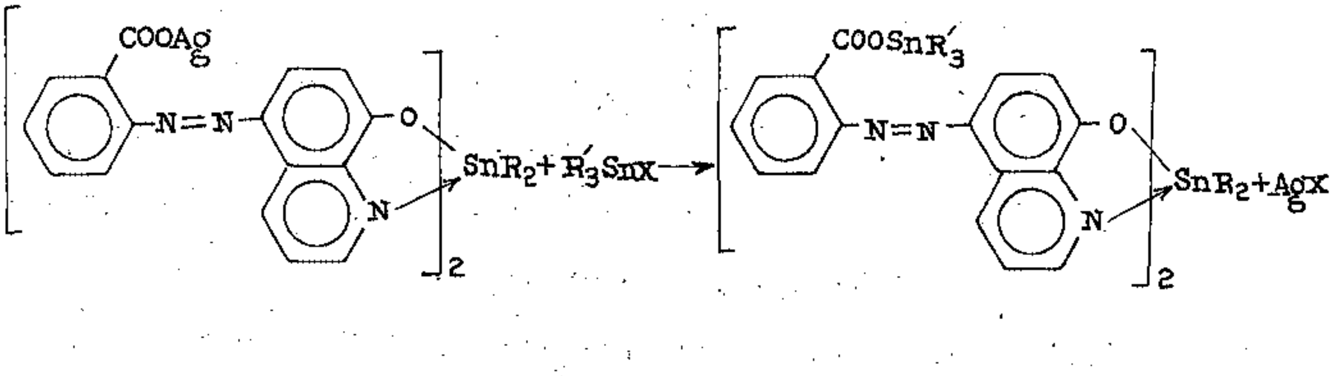
... (6)

(R = Phenyl and Butyl)

(iii) Reaction (7) and (8) were also tried for the preparation of the binuclear organotin complexes. However, reaction (5) is found to be the best one for the preparation of $R_2Sn(L'SnR'_3)_2$ type complexes.



... (7)



... (8)

[R' = Phenyl and Butyl
R = Phenyl, Butyl, Octyl and Methyl]

A reference to the methods of preparation of organotin complexes (III) would show that the yield of the desired organotin carboxylate and quinolinolate are dependent on the nature of the group R and R' and also on the method employed. The addition of a small amount of pyridine to the reaction mixture to neutralise the acid formed in reaction (2), (3), (4) and (7) improves the yield. However, in the case of stannylation of the quinolinolates this method gives considerably lower yields and increase of reaction time even with refluxing does not increase the yield significantly.

The binuclear di/tri-organotin (triorganotin carboxyphenyl) azo quinolinolates were obtained in 20-70% yield by the reaction (5) and (6). The yield in reaction (7) is not good though the reaction time is short. The reverse holds good for reaction (8).

A summary of the reaction products together with the yields and the experimental condition used in the present investigation are given in Table 2.

Table 2

Reactants^{a} (Mole ratio)	Experimental condition used	Product (m.p.°C, yield %)
1. L'H -Ag + Ph_3SnCl (1:1)	Refluxing for 25 hours in dry benzene, product crystallised from benzene-pet. ether mixture.	$Ph_3SnL'H$ (> 300°, 75)

Table 2 (Contd..)

Reactants^c (Mole ratio)	Experimental condition used	Product (m.p. °C, yield %)
2. $L'HH' + Bu_3SnOCOCH_3$ (1:1)	Stirring at RT for 8 hours in dry THF^a, product crystallised from benzene-pet. ether mixture.	$Bu_3SnL'H$ (220°, 40)
3. $L'HH' + Ph_2SnCl_2$ (2:1)	Stirring at RT for 10 hours in dry THF^a, product crystallised from benzene-pet. ether mixture.	$Ph_2Sn(L'H')_2$ (259°^{b}, 46)
4. $L'HH' + Bu_2SnBr_2$ (2:1)	Stirring at RT for 15 hours in dry THF^a, product crystallised from benzene-pet. ether mixture.	$Bu_2Sn(L'H')_2$ (163°, 25)
5. $L'HH' + Oct_2SnCl_2$ (2:1)	Stirring at RT for 10 hours in dry THF^a, product crystallised from benzene-pet. ether mixture.	$Oct_2Sn(L'H')_2$ (144°, 35)

Table 2 (Contd..)

Reactants[c] (Mole ratio)	Experimental condition used	Product (m.p. °C, yield %)
6. $L'HH' + Me_2SnCl_2$ (2:1)	Stirring at RT for 10 hours in dry THF[a], product crystallised from benzene-pet. ether mixture.	$Me_2Sn(L'H')_2$ (163°, 40)
7. $L'MeH + Ph_2SnCl_2$ (2:1)	Refluxing for 10 hours in dry benzene[a], product crystallised from benzene-pet. ether mixture.	$Ph_2Sn(L'Me)_2$ (178°, 55)
8. $L'MeH + Bu_2SnBr_2$ (2:1)	Refluxing for 10 hours in dry benzene[a], product crystallised from benzene-pet. ether mixture.	$Bu_2Sn(L'Me)_2$ (174°, 45)

Table 2 (Contd..)

Reactants (Mole ratio)	Experimental condition used	Product (m.p. °C, yield %)
9. $L'MeH + Oct_2SnCl_2$ (2:1)	Refluxing for 10 hours in dry benzene[a], product crystallised from benzene-pet. ether mixture.	$Oct_2Sn(L'Me)_2$ (175°, 80)
10. $L'MeH + Me_2SnCl_2$ (2:1)	Refluxing for 10 hours in dry benzene[a], product crystallised from benzene-pet. ether mixture.	$Me_2Sn(L'Me)_2$ (175°, 80)
11A. $Ph_2Sn(L'H')_2$ + $(Ph_3Sn)_2O$ (2:1)	Refluxing in dry benzene for 15 hours, product crystallised from benzene-pet. ether mixture.	$Ph_2Sn(L'SnPh_3)_2$ ($>300^\circ$, 65)

Table 2 (Contd..)

Reactants (Mole ratio)	Experimental condition used	Product (m.p. °C, yield %)
11B. $Ph_3SnL'H$ + Ph_2SnCl_2 (2:1)	Stirring in dry benzene[a] for 5 hours, product crystallised from benzene-pet. ether mixture	$Ph_2Sn(L'SnPh_3)_2$ ($>300^\circ$, 25)
11C. $(L'Ag)_2SnPh_2$ + Ph_3SnCl (1:2)	Refluxing in dry benzene for 15 hours, product crystallised from benzene-pet. ether mixture.	$Ph_2Sn(L'SnPh_3)_2$ ($>300^\circ$, 35)
12. $Bu_2Sn(L'H')_2$ + $(Ph_3Sn)_2O$ (1:1)	Refluxing in dry benzene for 25 hours, product crystallised from benzene-pet. ether mixture.	$Bu_2Sn(L'SnPh_3)_2$ ($211^{\circ b}$, 35)

Table 2 (Contd..)

Reactants (Mole ratio)	Experimental condition used	Product (m.p. °C, yield %)
13. $Oct_2Sn(L'H')_2$ + $(Ph_3Sn)_2O$ (1:1)	Refluxing in dry benzene for 20 hours, product crystallised from benzene-pet. ether mixture.	$Oct_2Sn(L'SnPh_3)_2$ (165^{ob}, 40)
14. $Me_2Sn(L'H')_2$ + $(Ph_3Sn)_2O$ (1:1)	Refluxing in dry benzene for 15 hours, product crystallised from benzene-pet. ether mixture.	$Me_2Sn(L'SnPh_3)_2$ (175^{o}, 50)
15. $Ph_2Sn(L'H')_2$ + $(Bu_3Sn)_2O$ (1:1)	Refluxing in dry benzene for 25 hours, product crystallised from benzene-pet. ether mixture.	$Ph_2Sn(L'SnBu_3)_2$ (242^{o}, 30)

Table 2 (Contd..)

Reactants (Mole ratio)	Experimental condition used	Product (m.p. °C, yield %)
16. $Bu_2Sn(L'H')_2$ + $(Bu_3Sn)_2O$ (1:1)	Refluxing in dry benzene for 30 hours, product crystallised from benzene-pet. ether mixture.	$Bu_2Sn(L'SnBu_3)_2$ (102°, 80)
17. $Oct_2Sn(L'H')_2$ + $(Bu_3Sn)_2O$ (1:1)	Refluxing in dry benzene for 25 hours, product crystallised from benzene-pet. ether mixture.	$Oct_2Sn(L'SnBu_3)_2$ (182°, 40)
18. $L'HH'$ + $(Ph_3Sn)_2O$ (1:1)	Refluxing in dry benzene for 25 hours, product crystallised from benzene-pet. ether mixture.	$Ph_3SnL'SnPh_3$ (180°, 70)

a) The acid formed in the reaction was neutralised with pyridine.

b) Decomposition point.

c) Ph- phenyl; Bu - n-butyl; Oct - n - Octyl; and Me- methyl.

IID. Analytical data

Analytical data on the organotin derivatives are given in Table -3. Analytical data clearly indicate the formation of well defined organotin compounds.

Table - 3

Formula*	Found (calculated) (%) C	H	N	Sn
1. $C_{34}H_{25}O_3N_3Sn$ ($Ph_3SnL'H$)	63.35 (63.58)	3.80 (3.89)	6.50 (6.54)	18.62 (18.49)
2. $C_{29}H_{37}O_3N_3Sn$ ($Bu_3SnL'H$)	57.72 (57.76)	6.30 (6.36)	7.28 (7.22)	20.12 (20.40)
3. $C_{44}H_{30}O_6N_6Sn$ [$Ph_2Sn(L'H')_2$]	60.98 (61.63)	3.52 (3.50)	9.79 (9.80)	13.90 (13.85)
4. $C_{40}H_{38}O_6N_6Sn$ [$Bu_2Sn(L'H')_2$]	58.75 (58.77)	4.60 (4.65)	10.12 (10.28)	14.70 (14.53)
5. $C_{48}H_{54}O_6N_6Sn$ [$Cot_2Sn(L'H')_2$]	61.95 (62.02)	6.02 (5.81)	9.15 (9.04)	12.50 (12.78)
6. $C_{34}H_{26}O_6N_6Sn$ [$Me_2Sn(L'H')_2$]	56.01 (55.63)	3.60 (3.54)	11.50 (11.46)	16.23 (16.20)
7. $C_{46}H_{34}O_6N_6Sn$ [$Ph_2Sn(L'Me)_2$]	62.42 (62.39)	3.90 (3.84)	9.36 (9.49)	13.39 (13.41)

Contd..

Table - 3 (Contd..)

Formula*	Found (Calculated) (%)			
	C	H	N	Sn
8. $C_{42}H_{42}O_6N_6Sn$ [$Bu_2Sn(L'Me)_2$]	59.50 (59.66)	4.08 (4.97)	10.10 (9.94)	14.12 (14.05)
9. $C_{50}H_{58}O_6N_6Sn$ [$Oct_2Sn(L'Me)_2$]	63.57 (62.71)	6.10 (6.06)	7.97 (8.78)	12.34) (12.40)
10. $C_{36}H_{30}O_6N_6Sn$ [$Me_2Sn(L'Me)_2$]	57.10 (56.78)	3.90 (3.94)	10.73 (11.04)	15.96 (15.60)
11. $C_{80}H_{58}O_6N_6Sn_3$ [$Ph_2Sn(L'SnPh_3)_2$]	61.70 (61.77)	3.70 (3.75)	5.39 (5.40)	22.50 (22.91)
12. $C_{76}H_{57}O_6N_6Sn_3$ [$Bu_2Sn(L'SnPh_3)_2$]	60.70 (60.59)	3.19 (3.78)	5.72 (5.58)	23.69 (23.65)
13. $C_{84}H_{82}O_6N_6Sn_3$ [$Oct_2Sn(L'SnPh_3)_2$]	62.50 (61.93)	5.25 (5.04)	5.30 (5.16)	21.09 (21.90)
14. $C_{70}H_{54}O_6N_6Sn_3$ [$Me_2Sn(L'SnPh_3)_2$]	57.95 (58.75)	3.60 (3.77)	5.62 (5.87)	25.10 (24.90)
15. $C_{68}H_{82}O_6N_6Sn_3$ [$Ph_2Sn(L'SnBu_3)_2$]	57.25 (56.89)	5.80 (5.71)	6.12 (5.85)	24.05 (24.83)

Contd..

Table - 3 (Contd..)

Formula*	Found (Calculated) (%)			
	C	H	N	Sn
16. $C_{64}H_{90}O_6N_6Sn_3$ [$Bu_2Sn(L'SnBu_3)_2$]	54.50 (55.03)	6.62 (6.45)	6.22 (6.02)	25.79 (25.54)
17. $C_{72}H_{106}O_6N_6Sn_3$ [$Oct_2Sn(L'SnBu_3)_2$]	56.92 (57.36)	6.96 (7.03)	5.50 (5.57)	24.10 (23.64)
18. $C_{52}H_{39}O_3N_3Sn_2$ ($Ph_3SnL'SnPh_3$)	63.50 (63.00)	3.92 (3.90)	4.10 (4.24)	24.15 (23.97)

* The abbreviated structural formulae are given in parenthesis.
Ph- phenyl; Bu - n-butyl; Me-methyl; Oct - n-octyl.

IIB. Infrared Spectra:

The IR spectra of 5-phenyl azo-8-quinolinol (LH) and 5-(2'-carboxy phenyl)-azo-8-quinolinol (L'HH') and their organotin derivatives are very complex due to the presence of a large number of vibrational modes due to ring stretch, deformation, in plane and out of plane ring and CH deformations[11,12 etc.]. However, these modes are of little value in the understanding of the structure and bonding in the complexes. Valuable information can, however, be obtained from the frequencies of carboxylate stretch, Sn-O stretch, Ar - OH (C - O vibration involving the 8-hydroxy group) and the N = N stretch. Unfortunately, even those modes can not be identified with certainity in all the cases because of the presence of strong ligand vibrations in the regions where these modes are expected. For example, the N = N stretch mode is of little use though variation of $\nu(N = N)$ in the complexes is expected to provide valuable clue to the participation or otherwise of the azo group in the organotin complexes. This is because the substitution on the azo group in dyes are fairly symmetrical (as far as the local symmetry is concerned, the grouping in azo-dyes always being $>C-N = N - C<$) and is, therefore, likely to be weak in IR spectrum. Although this vibration has been reported by some authors to occur at 1400-1450 cm^{-1} region[13], Miller[14] has emphasised that no diagnostically useful band can be found in this region in azo dyes. The later studies involving complexes of aryl azo benzoic acids[15-18] also confirm this. In view of this we shall confine our discussion primarily to ν(COO), ν(Sn-O) and ν(Ar-O) modes.

The O-H stretch in LH occurs at 3380 cm^{-1} as broad band and at 3460 cm^{-1} and ~ 3560 cm^{-1} (very broad, shoulder) in L'HH' indicating the presence of H-bonding interactions involving the -OH group. The two frequencies in the L'HH' are presumably due to the carboxylic -OH and phenolic -OH groups respectively. Since the 3480 cm^{-1} absorption disappears on methylation of the carboxyl group, this may be assigned to carboxyl O-H stretch while the very broad band at ~ 3360 cm^{-1} to the phenolic -OH group which is known to form intra molecular H- bond with the quinoline N-atom in such systems[19].

As expected, the OH stretching modes disappears in the esters or the organotin derivatives (Figs. 2,3,9-11) confirming bonding through the O-atom of the ligand.

The carboxylate stretch, ν_{as}(COO) occurs at ~ 1650 cm^{-1} in the free ligand (L'HH'). The lower value of ν_{as}(COO) is due to H-bonding involving the H-atom of the COOH group since methylation of the carboxyl group results in the shift of ν_{as}(COO) to the normal position 1700 cm^{-1} (Fig. 2, 8).

In the carboxylate derivatives of the type $R_3SnL'H$ or $(R_3SnL')_2SnR_2$, the asymmetric carboxylate stretch is lowered to 1630-35 cm^{-1} (Fig. 4,9-11) organotin carboxylates, which are not polymeric, are known to absorb in this region[20-23]. Organotin aryl azobenzoates which are closely similar to these compounds also absorb in this region. This suggests a similar 5-coordinated structure at the tin atom involving the azo-N-atom[15-18].

A strong absorption at 1235 cm^{-1} in LH which moves to ~ 1245 cm^{-1} in the organotin derivatives of the type R_2SnL_2 can be assigned to the C(aryl)-O [C_6 - O]. An upward shift of this stretching frequency is expected in the organotin compounds because the large polarity of -O-Sn$\leftarrow$ bond[24] increases the conjugative interaction of the oxygen atom with the π-ring resulting in an increase of the C-O bond order.

All organotin derivatives are characterised by a strong band at 1290 - 1310 cm^{-1}.

However, this band can not be assigned to ν_{as}(OCO) as the band is present even in the R_2SnL_2 type compounds which contain no carboxylate group.

Both ν(Sn-O) and ν(Sn-O) are expected to occur in ~ 400-600 cm^{-1} region[20-23,26]. ν(Sn-O) is probably very weak in these compounds. However, medium to strong intensity bands in 480-500 cm^{-1} are found in R_2SnL_2, $R_2Sn(L'H')_2$, $R_2Sn(LMe)_2$ and $R_2Sn(LSnR'_3)_2$ type compounds. One can, therefore, assign this band to ν(Sn-O) [oxygen of the C-OH group] with reasonable certainty. Another weaker band is also observed at ~440 cm^{-1} in the triorganotin carboxylate derivatives of the type $R_3SnL'H$ and $(R'_3SnL')_2SnR_2$ only.

Presumably, this represents take ν(Sn-OCO) stretch. The appearance of new absorptions in the organotin complexes assignable to ν(Sn-O) confirms the formation of O-Sn bonds.

As most of the spectra were run in nujol mull using KBr optics, the region below 400 cm^{-1}, where ν(N ⟶ Sn) is expected[21,26,27], could not be explored. The electronic spectra of the Organotin derivatives (Chapter - III), however, suggests the formation of complexes through N ⟶ Sn bond.

The characteristics vibrational frequencies in the organotin complexes studied in this work are given in Table - 4 and some typical spectra are shown in Figures.

The important vibrational modes that could be identified with reasonable certainty are given in Table -4.

Table - 4.

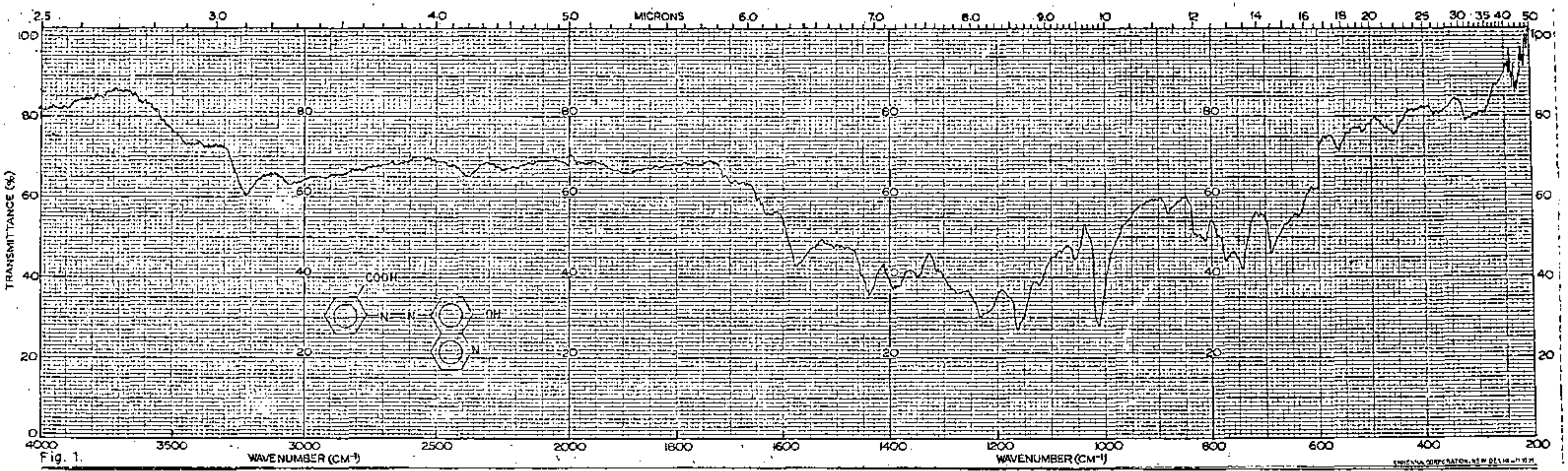
Compound	Frequencies (in cm^{-1}) of [a]			
	$\nu_{as}(OCO)$	$\nu^{b}_{Sn-O_{I}}$	$\nu^{c}_{Sn-O_{II}}$	$\nu_{C(Ar)-O}^{d}$
1. Me_2SnL_2		495		1250
2. Bu_2SnL_2		495		1250
3. Oct_2SnL_2		495		1350
4. Ph_2SnL_2		485		1250
5. Ph_3SnL		480		1250
6. $Ph_3SnL'H$	1630		440	1250

Table – 4 (Contd..)

Compound	Frequencies (in cm^{-1}) of ^{a}			
	$\nu_{as}(COO)$	$\nu^b_{Sn-O_I}$	$\nu^c_{Sn-O_{II}}$	$\nu_{C(Ar)-O}^d$
7. $Bu_3SnL'H$	1635			1245
8. $Me_2Sn(L'H')_2$	1720	495		1250
9. $Bu_2Sn(L'H')_2$	1725	495		1250
10. $Oct_2Sn(L'H')_2$	1725	495		1250
11. $Ph_2Sn(L'H')_2$	1725	495		1250
12. $Me_2Sn(L'Me)_2$	1720	495		1255
13. $Bu_2Sn(L'Me)_2$	1720	495		1255
14. $Oct_2Sn(L'Me)_2$	1720	490		1250
15. $Ph_2Sn(L'Me)_2$	1720	490		1250
16. $Ph_2Sn(L'SnPh_3)_2$	1650	490	445	1240
17. $Bu_2Sn(L'SnPh_3)_2$	1630	485	440	1240
18. $Oct_2Sn(L'SnPh_3)_2$	1630	490	445	1245
19. $Me_2Sn(L'SnPh_3)_2$	1630	500	445	1250
20. $Ph_2Sn(L'SnBu_3)_2$	1635	485	440	1245
21. $Bu_2Sn(L'SnBu_3)_2$	1630	500		1245
22. $Oct_2Sn(L'SnBu_3)_2$	1635	490		1245
23. $Ph_3SnL'SnPh_3$	1630	495	445	1245

a) Values may be in error by ± 5 cm^{-1}.
b) Refers to the oxygen atom at 8-position of the quinoline ring.
c) Refers to carboxylate O-atom.
d) Refers to C_8 – O stretch of the quinoline ring.

IR SPECTRA



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25
30
35
40
50
TRANSMITTANCE (%)
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OH
N
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800
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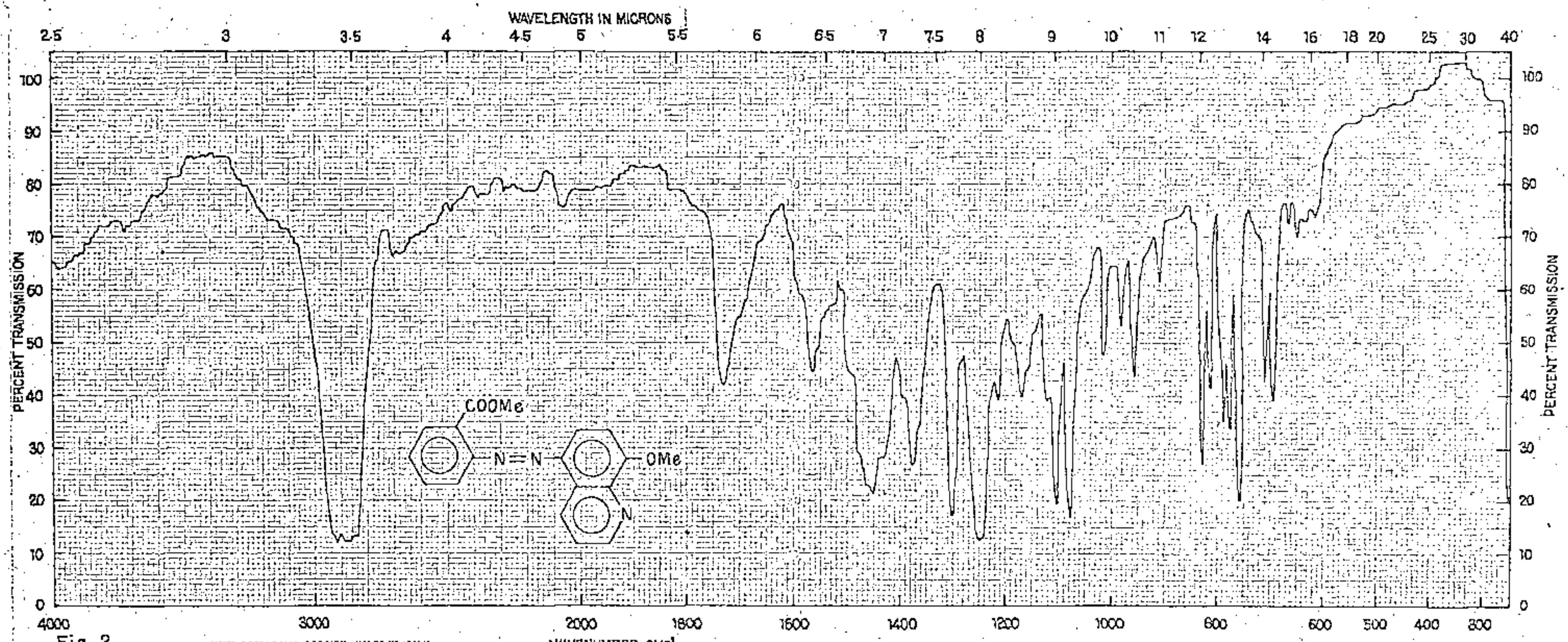
WAVENUMBER (CM⁻¹)

Fig. 1.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5.5
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10
11
12
14
16
18
20
25
30
40
PERCENT TRANSMISSION
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90
80
70
60
50
40
30
20
10
0
WAVENUMBER CM^{-1}
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400
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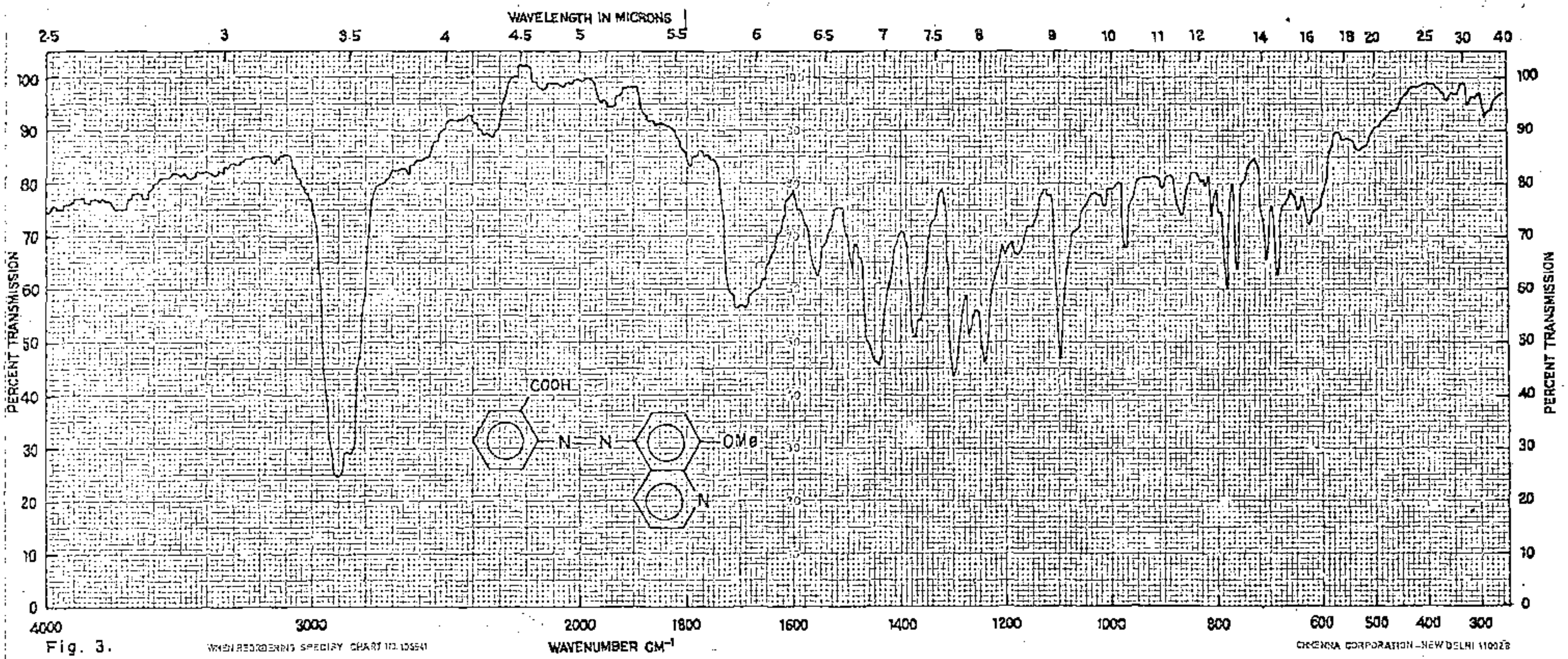
OMe
N

Fig. 2.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10
11
12
14
16
18
20
25
30
40
PERCENT TRANSMISSION
100
90
80
70
60
50
40
30
20
10
0
4000
3000
2000
1800
1600
1400
1200
1000
800
600
500
400
300
WAVENUMBER CM⁻¹
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OMe
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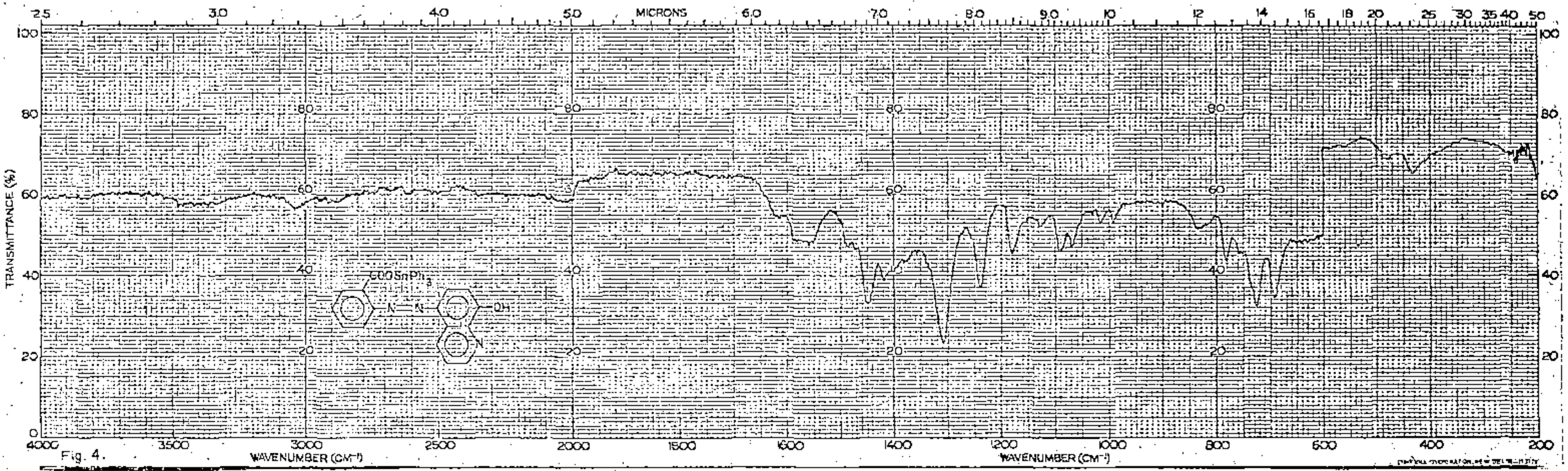
CHEMNA CORPORATION—NEW DELHI 110028

Fig. 3.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20
25
30
35
40
50
TRANSMITTANCE (%)
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80
60
40
20
0
WAVENUMBER (CM⁻¹)
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800
600
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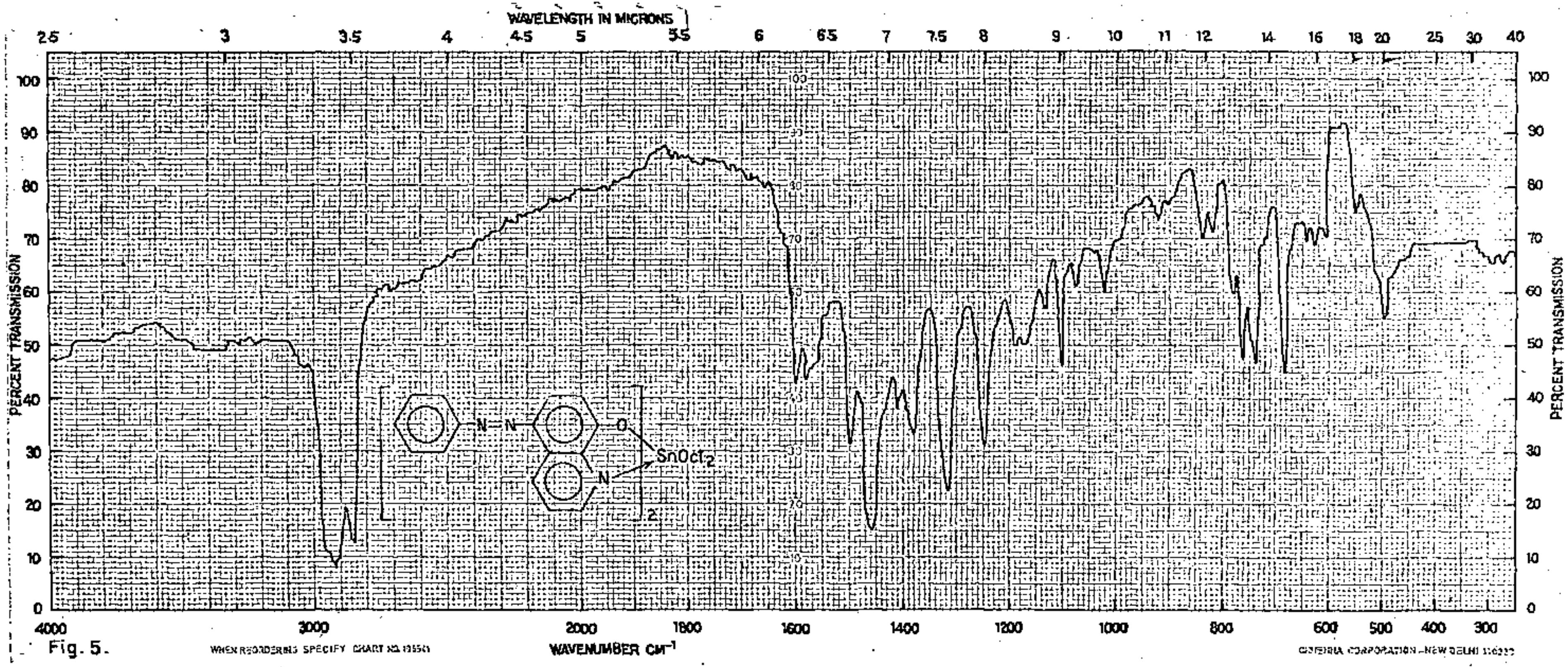
COOSnPh3
N
N
OH
N

Fig. 4.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9
10
11
12
14
16
18
20
25
30
40
PERCENT TRANSMISSION
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60
50
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30
20
10
0
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400
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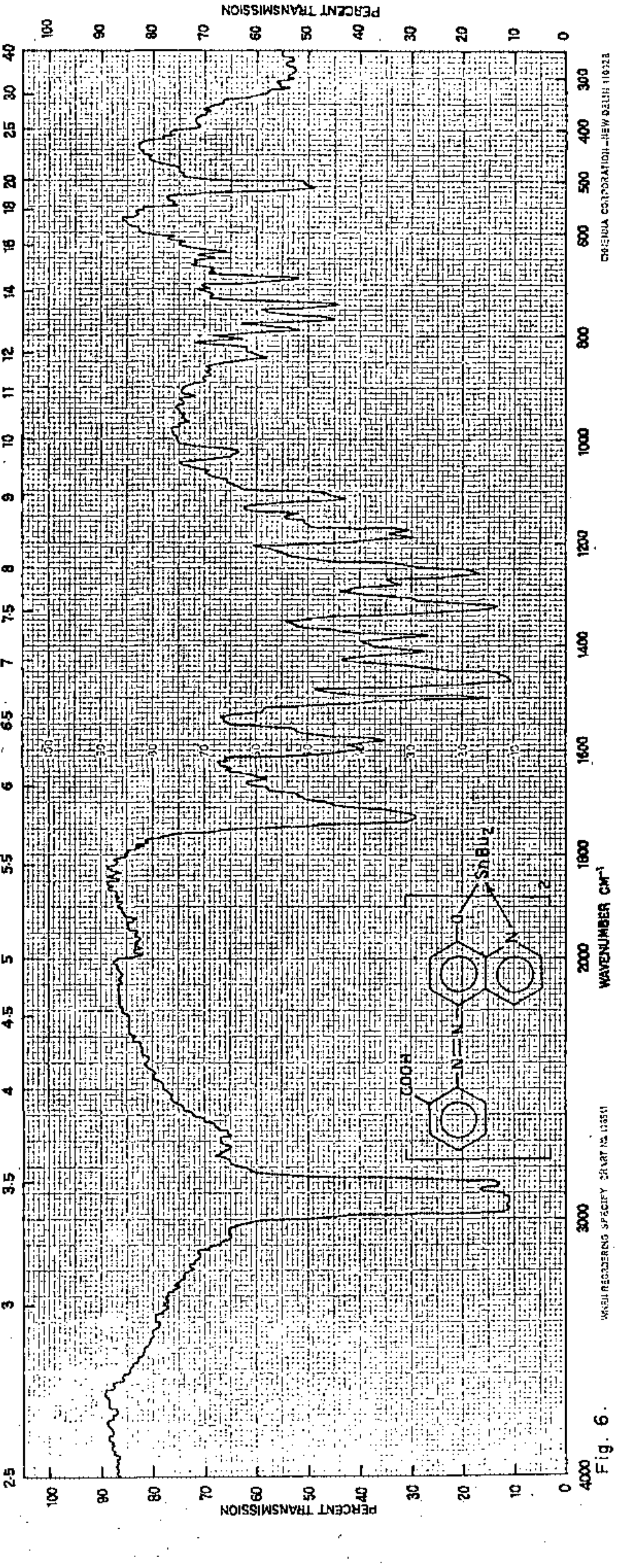
CISTERRA CORPORATION - NEW DELHI 110022

Fig. 5.



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9
10
11
12
14
16
18
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25
30
40
PERCENT TRANSMISSION
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SnBu$_2$
N
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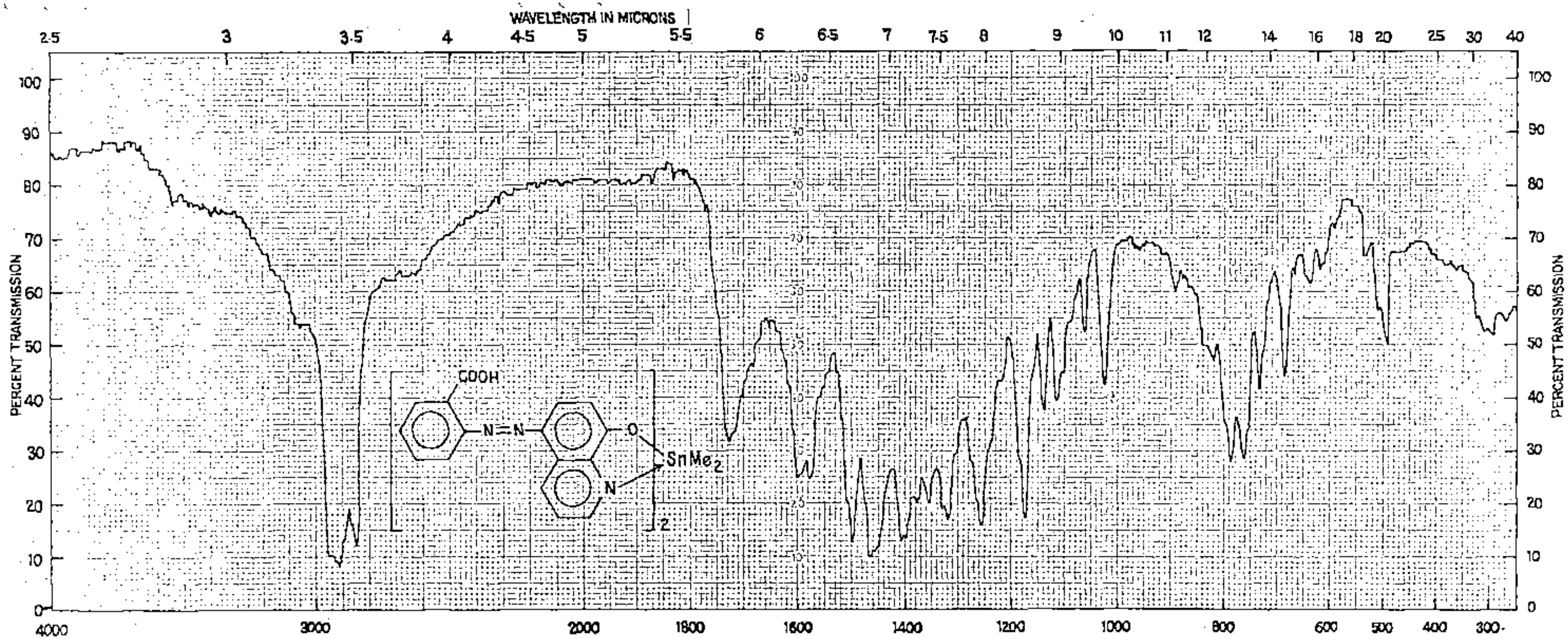
Fig. 6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18
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PERCENT TRANSMISSION
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1600
1400
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WAVENUMBER CM⁻¹
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O
SnMe₂
N
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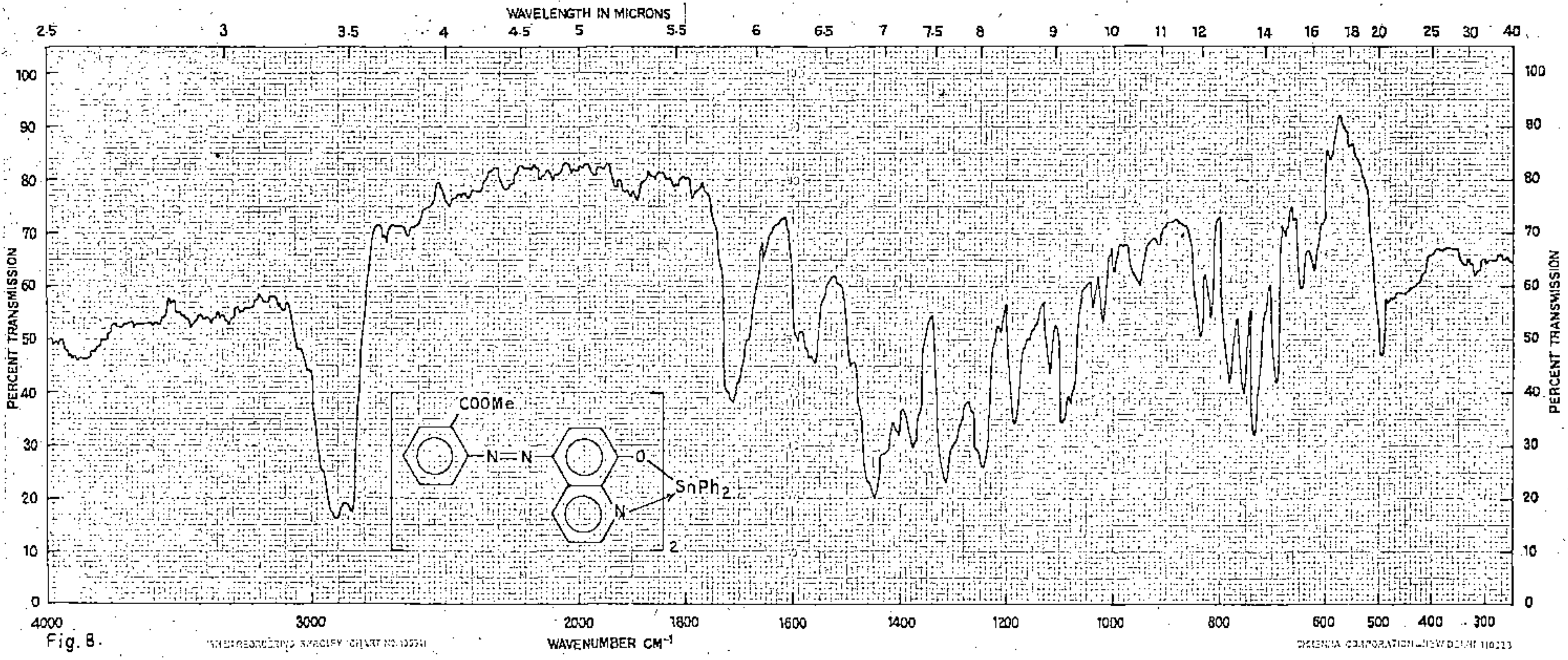
Fig. 7.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11
12
14
16
18
20
25
30
40
PERCENT TRANSMISSION
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10
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30
40
50
60
70
80
90
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WAVENUMBER CM^{-1}
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3000
2000
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1400
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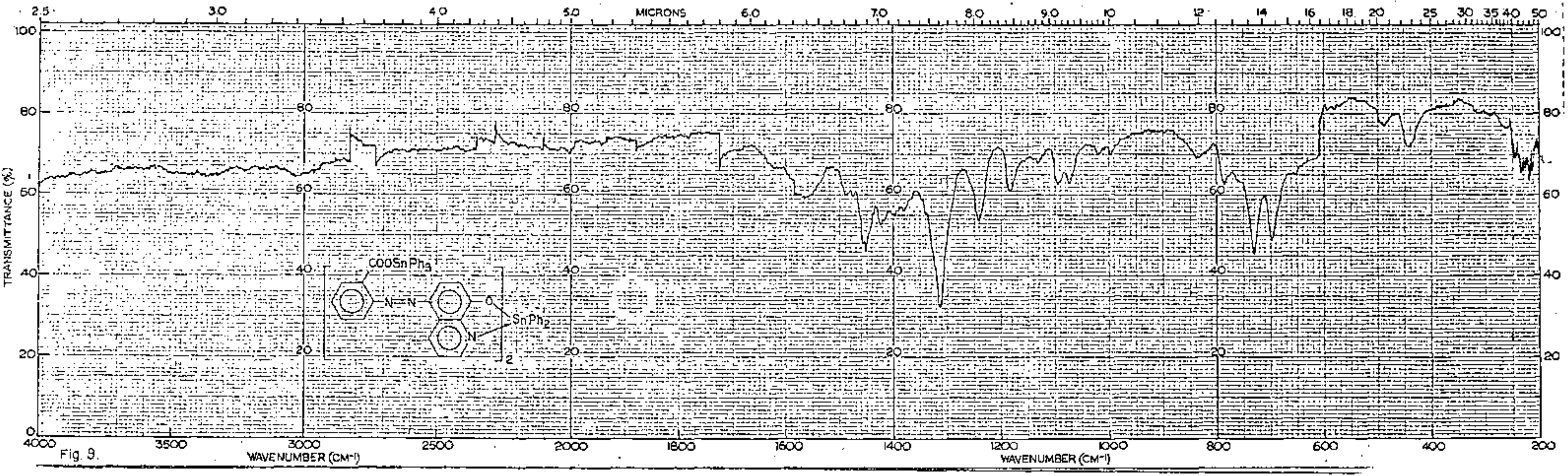
400
300
COOMe
N=N
O
SnPh$_2$
N
2

Fig. 8.



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30
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40
50
TRANSMITTANCE (%)
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60
40
20
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WAVENUMBER (CM-1)
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3500
3000
2500
2000
1800
1600
1400
1200
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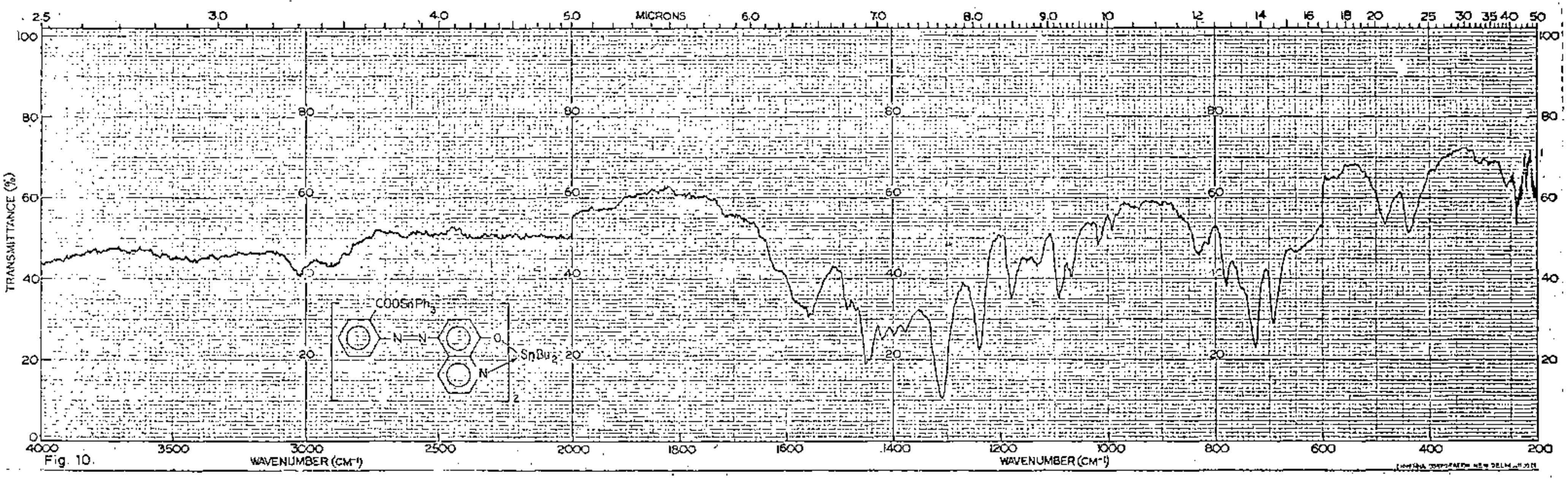
800
600
400
200
COOSnPh$_3$
N=N
O
SnPh$_2$
N
2

Fig. 9.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20
25
30
35
40
50
TRANSMITTANCE (%)
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80
60
40
20
0
COOSnPh$_3$
N
N
O
N
SnBu$_2$
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3500
3000
2500
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1000
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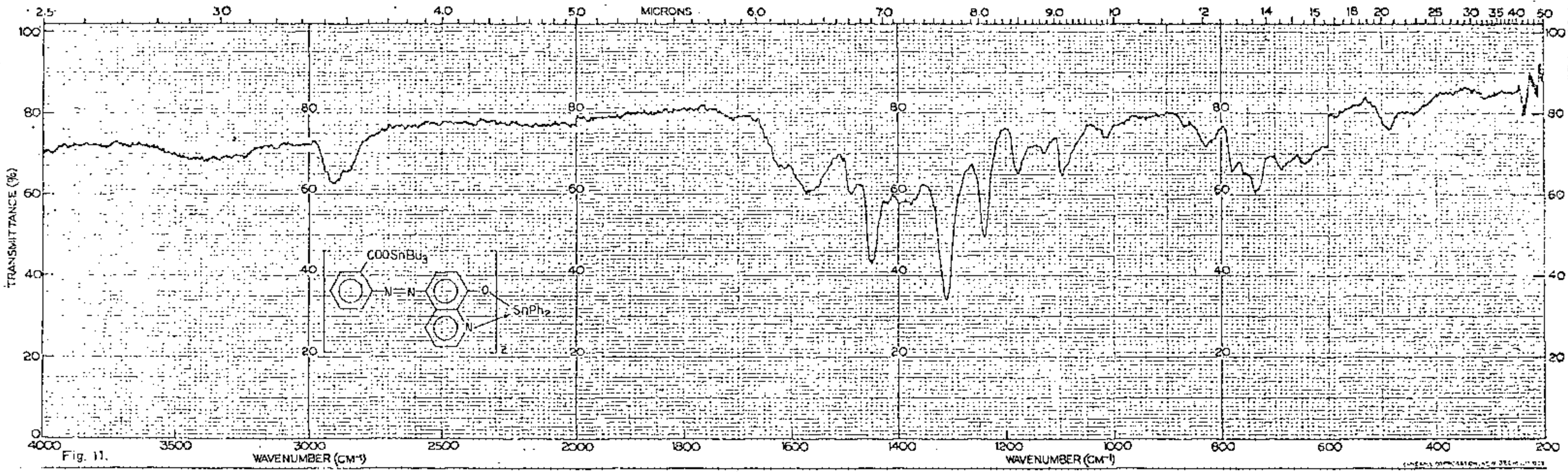
600
400
200
WAVENUMBER (CM^{-1})
WAVENUMBER (CM^{-1})

Fig. 10.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8.0
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10
12
14
15
18
20
25
30
35
40
50
TRANSMITTANCE (%)
100
80
60
40
20
0
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
WAVENUMBER (CM⁻¹)
COOSnBu3
N=N
O
SnPh2
N
2

Fig. 11.

III. Experimental

The preparation of the ligands, organotin compounds used for the synthesis of the organotin complexes, are described in this section.

All solvents were purified and dried as described in Vogel[7] unless otherwise stated. Petroleum ether used in the present investigation refers to the fraction with the boiling range 60-80°C. All melting points are uncorrected.

All IR spectra were recorded in Nujol mull/CsI using Beckman IR-20/Perkin Elmer Spectrophotometer.

(i) Preparation of the ligand:

1. Preparation of [L'HH'][2-5]

5 gm of anthranilic acid was dissolved in a little water with 6-8 ml of concentrated hydrochloric acid, was diazotised with 12 ml of cold 20% sodium nitrite. 5 gm of 8-hydroxy quinoline was dissolved in aqueous 2N sodium hydroxide solution and was cooled to 5°C in an ice bath which was then added to the cold diazonium salt solution with vigorous stirring when a red colour developed. It was kept overnight in a refrigerator followed by 2 hrs. at R.T. and then acidified with conc. hydrochloric acid when a deep red precipitate separated out. It was filtered, washed several times with water, dried in air. Crystallisation from methanol yielded L'HH'.

m.p.	: $235^{0}C$			
Yield	: 80%			
IR	: $\nu_{as}(COO)$	1645 cm^{-1} (broad)		
$\frac{m}{e}$ (M^{+})	: 293			
Analytical data Found:		C 65.27	H 3.70	N (%) 14.32
Calculated for				
$C_{16}H_{11}O_{3}N_{3}$:		65.30	3.74	14.28

2. Preparation of $[LH]^{2-3}$:

5 ml. of concentrated hydrochloric acid was mixed with 3.2 gm of aniline and was dissolved with the addition of 50 gm of ice. Then it was cooled and added 25 ml. of a 20% solution of sodium nitrite. 5 gm of 8-hydroxy quinoline was dissolved in 2N sodium hydroxide and cooled to $5^{0}C$ in an ice bath which was then added to the cold diazonium salt solution with vigorous stirring. It was kept over night in a refrigerator followed by 2 hrs. at R.T. It was filtered, washed several times with water, dried in air. Crystallisation from methanol yields the desired product.

m.p. : $170^{0}C$

Yield : 80%

3. Preparation of [L'MeH][8]:

A diazotised solution of methyl anthranilate in aqueous hydrochloric acid was added to a stirred cold solution of 8-hydroxyquinoline in methanol. Enough potassium acetate was added to neutralise the hydrochloric acid. The mixture was kept below 5°C for 12 hours after which the mixture was filtered and washed thoroughly with water. Several crystallisations from methanol gave an orange coloured product of the dye.

m.p	: 164°C			
Yield	: 80%			
IR	ν_{as}(COO) 1720 cm^{-1}			
$\frac{m}{e}$ (M)	: 307			
		C	H	N (%)
Analytical data				
Found	:	66.45	4.31	13.50
Calculated for				
$C_{17}H_{13}O_3N_3$	:	66.44	4.23	13.68

4. Preparation of [$L'Me_2$]:

Methylation of L'HH' was done using standard procedure[7].

2 gms of L'HH' was dissolved in 5 ml. of methanol and little amount of concentrated sulphuric acid was added. Then the mixture was refluxed for 5 hours. Enough sodium bicarbonate was added to

neutralise the acid. The mixture was extracted with cold benzene, washed several times with water and benzene layer was separated. On evaporation on water bath, a gummy paste was obtained which was extracted with solvent ether. Repeated crystallisations gave the desired orange coloured product.

m.p. : 112^{0}C
Yield : 85%
PMR (δ) : 3.78 ($COOCH_3$), 4.03 (aryl - OCH_3)
IR : ν_{as}(COO) : 1730 cm^{-1}
$\frac{m}{e}$ (M^+) : 321

6. Preparation of [L'MeH']

L'MeH' was prepared by saponification of $L'Me_2$ using standard procedure[7].

1 gm of $L'Me_2$ was dissolved in 30 ml. 10% sodium hydroxide. Then the mixture was refluxed for 1 hour. Acetic acid was added to neutralise the alkali. The mixture was extracted with cold benzene, washed successively with 5% sodium hydroxide and finally with water. To the concentrated benzene solution was added petroleum ether, an orange coloured product separated as a crystal. Product was further purified by repeated crystallisation.

m.p. : 205^{0}C

Yield : 73%

$\frac{m}{e}$ (M^+) : 307

(ii) Source of organotin compounds used for synthesising the organotin complexes:

Triphenyl tin chloride (MERCK - Schuchardt) was used after recrystallisation from petroleum ether, m.p. 105° - 106°C (Lit. m.p. 106°C) and when necessary, triphenyl tin chloride was also prepared from tetraphenyl tin by the reaction of stannic chloride[9].

Bis-(triphenyl tin) oxide (m.p. 122° - 124°C) was prepared by the reaction of triphenyl tin chloride and sodium hydroxide[10]. The product was purified by crystallisation.

Tributyl tin chloride, b.p. 152°C/10 mm (Fluka A.G.) was used without further purification.

Bis-(tributyl tin) oxide, b.p. 210-4°C/10 mm (RIEDEL - DE HAEN AG SEELZE - HANNOVER), Tributyl tin acetate (Fluka A.G.), Dibutyl tin dibromide (Alfa - Division, Ventron Corporation), and Dimethyl tin dichloride (Fluka A.G.) were used without further purification. Diphenyl tin dichloride was prepared by the method of Gilman et al[11] from tetraphenyl tin.

Dioctyl tin dichloride was obtained as a gift from Dr. S. Banerjee of ALA Industry, Bombay, was used without further purification.

(iii) Synthesis of organotin derivatives:

(1) Preparation of $Ph_3SnL'H$:

A mixture of triphenyl tin chloride (2.03 g, 5.2 m. mole) and silver salt of L'HH' (2.1 g, 5.2 m. mole) in 250 ml dry benzene was refluxed for about 25 hours. The reaction mixture was cooled and filtered. To the concentrated filtrate was added petroleum ether when an orange coloured solid separated out which was filtered off and washed with hot petroleum ether. The solid was then washed with 2% sodium bicarbonate solution followed by water to remove any unreacted ligand. The solid was extracted with cold benzene and concentrated by evaporation. On addition of petroleum ether to concentrated solution, orange coloured solid separated. The product was purified by several recrystallisation from benzene-petroleum ether mixture. $Ph_3SnL'H$ was obtained as a bright orange solid. The purified solid was dried in vacuum over calcium chloride.

m.p. : > 300 °C

Yield : 70%

Analytical data		C	H	N	Sn (%)
Found	:	63.85	3.80	6.50	18.62
Calculated for					
$C_{34}H_{25}N_3O_3Sn$	:	63.58	3.89	6.54	18.49

I.R. : ν_{as}(COO) 1630 cm^{-1}

2. Preparation of $Bu_3SnL'H$:

A mixture of tributyl tin acetate (1.18g, 3.4 m.mole) and L'HH' (1.0g, 3.4 m.mole) were taken in 150 ml dry THF and a few drops of pyridine were added for the neutralisation of acid formed in the reaction. The reaction mixture was stirred for 8 hours at room temperature. The volume was reduced to about 70 ml by distillation, cooled and filtered. On addition of petroleum ether to the concentrated filtrate, a brown coloured product separated which was filtered. The solid was washed with hot petroleum ether, followed by 2% sodium bicarbonate solution to remove unreacted ligand and finally with water. The solid was extracted with cold benzene and concentrated. To the concentrated solution was added petroleum ether, cooled and filtered. The brown coloured product was further purified by recrystallisation from benzene-petroleum ether mixture.

m.p. : 220°C

Yield : 55%

Analytical data	C	H	N	Sn (%)
Found :	57.73	6.30	7.28	30.12
Calculated for $C_{28}H_{37}N_3O_3Sn$:	57.76	6.36	7.22	20.40

I.R. : $\nu_{as}(OCO)$ 1635 cm^{-1}

3. Preparation of Ph_3SnL :

A mixture of bis-(triphenyl tin) oxide (0.71g, 1.0 m.mole) and LH (0.5g, 2.0 m. mole) in 75 ml dry benzene was refluxed for 20 hours. The solution on hot filtration gave a residue of unreacted ligand. The filtrate was concentrated by evaporation on water bath followed by addition of hot petroleum ether. On cooling, an orange coloured solid was obtained which was extracted with 25 ml of cold and dry benzene. The extract was concentrated, hot petroleum ether was added to reprecipitate the product which was separated and dried in vacuum. The product was purified by recrystallisation from benzene-petroleum ether mixture.

m.p. : 166°C

Yield : 80%

Analytical data:	C	H	N	Sn (%)
Found :	66.20	4.10	7.0	19.80
Calculated for				
$C_{33}H_{25}N_3OSn$	65.95	4.20	7.1	19.62

4. Preparation of Ph_2SnL_2 :

A mixture of bis-(diphenyl tin) oxide (0.35g, 1.5 m.mole) and LH (0.75g, 3.0 m.mole) in 100 ml dry benzene was refluxed for 20 hours. The reaction mixture was cooled and filtered. The filtrate was concentrated by evaporation and hot petroleum ether was added when a precipitate appeared. On cooling, the orange coloured product was separated by decantation and dried in a vacuum desiccator. This was treated with a little cold and dry benzene and filtered. The filtrate was treated as before when an orange coloured solid was obtained.

m.p. : 143°C (d)

Yield : 80%

Analytical data :	<u>C</u>	<u>H</u>	<u>N</u>	<u>Sn</u> (%)
Found :	65.50	3.90	10.90	15.40
Calculated for				
$C_{42}H_{30}N_6O_2Sn$:	65.25	3.50	10.95	15.36

5. <u>Preparation of Bu_2SnL_2</u> :

A mixture of dibutyl tin dibromide (1.03g, 2.6 m.mole) and LH (1.3g, 5.2 m.mole) were taken in 200 ml of dry benzene. To this reaction mixture was added few drops of pyridine for the neutralisation of acid formed in the reaction. This reaction mixture was then refluxed for 25 hours. The volume of the solution was reduced to about 90 ml by evaporation on water bath and filtered. The filtrate was concentrated to about 50 ml followed by addition of hot petroleum ether. On cooling a gummy material was obtained which was separated by decantation. The gummy material was treated with about 25 ml of cold and dry benzene and filtered. The filtrate was concentrated, hot petroleum ether added. The precipitate was separated and dried in vacuum. The brown coloured product was further purified by recrystallisation from benzene-petroleum ether mixture.

Decomposition point: 70°C

Yield : 60%

Analytical data:	C	H	N	Sn (%)
Found :	62.70	4.90	11.50	16.30
Calculated for $C_{38}H_{36}N_6O_2Sn$:	62.69	4.79	12.60	16.22

6. Preparation of Oct_2SnL_2 :

A mixture of dioctyl tin dichloride (1.24g, 3.0 m. mole) and LH (1.6g, 6.0 m. mole) were taken in 250 ml of dry benzene containing a few drops of pyridine and refluxed for 23 hours. The solution was then evaporated almost to dryness. The solid was extracted with cold, dry benzene, boiled for 15 minutes and then allowed to cool and filtered. The filtrate was concentrated, added a little hot petroleum ether, cooled and filtered. The concentrated filtrate afforded a brown coloured solid. The solid product was treated with a little volume of cold and dry benzene and filtered. The product was reprecipitated by adding hot petroleum ether to the cold concentrated solution. The brown coloured product was dried in vacuum. Oct_2SnL_2 was further purified by recrystallisation from benzene-pet ether mixture.

m.p. : 93°C

Yield : 65%

Analytical data :	<u>C</u>	<u>H</u>	<u>N</u>	<u>Sn</u> (%)
Found :	66.60	6.20	9.70	13.70
Calculated for $C_{48}H_{54}N_6O_2Sn$:	66.25	6.35	9.72	13.50

7. Preparation of Me_2SnL_2 :

A mixture of dimethyl tin dichloride (0.36g, 1.6 m.mole) and LH (0.8g, 3.2 m.mole) were taken in 150 ml of dry benzene containing a few drops of pyridine and the mixture was then refluxed for 25 hours. The volume of the solution was reduced to 50 ml by distillation, cooled and filtered. On addition of petroleum ether to the concentrated filtrate, a reddish brown product separated which was filtered off and the filtrate was concentrated. To the hot filtrate was added hot petroleum ether, cooled and filtered. The product was dried, washed several times with hot petroleum ether. It was then boiled with 60 ml of benzene-petroleum ether mixture (20:80) and filtered. The reddish brown coloured product was further purified by repeated crystallisation from benzene-petroleum ether mixture.

M.p. : 187°C

Yield : 65%

Analytical data :	C	H	N	Sn (%)
Found :	59.50	4.0	13.0	18.40
Calculated for $C_{32}H_{26}N_6O_2Sn$:	60.20	3.95	13.20	18.35

8. *Preparation of $Ph_2Sn(L'H')_2$* :

L'HH' (2.8g, 8.5 m. mole) was extracted by soxhlet in 300 ml Tetrahydrofuran. To the solution of L'HH' was added diphenyl tin dichloride (1.46g, 4.2 m. mole) containing a few drops of pyridine and the mixture was stirred at room temperature for 10 hours. The solvent was distilled off and the residue dried in vacuum, boiled with dry benzene for about 15 minutes and extracted. The benzene extract was concentrated, added petroleum ether, cooled and filtered. The orange coloured solid was boiled with petroleum ether for 10 minutes and filtered. The solid was extracted with cold benzene and concentrated by evaporation. Upon addition of petroleum ether a bright orange coloured solid separated which was purified by recrystallisation from benzene-petroleum ether. The solid was dried in vacuum over calcium chloride.

Decomposition point : 259°C

Yield : 46%

Analytical data:	C	H	N	Sn (%)
Found :	60.92	3.52	9.72	13.90
Calculated for $C_{44}H_{30}N_6O_6Sn$:	61.63	3.50	9.80	13.85

I.R. : $\nu_{as}(COO)$ 1725 cm^{-1}

9. Preparation of $Bu_2Sn(L'H')_2$:

L'HH' (2.5g, 8.5 m. mole) was extracted by soxhlet in 300 ml tetrahydrofuran. To the solution of L'HH' was added dibutyl tin dibromide (1.67g, 4.3 m. mole) and a few drops of pyridine. The mixture was stirred at room temperature for 15 hours, tetrahydrofuran was distilled off and the residue was dried in vacuum. The solid obtained was dissolved in dry benzene and filtered. The filtrate was concentrated, hot petroleum ether added, allowed to cool and the precipitate A, reddish brown powder (m.p. 159-160°C) was separated by filtration. The filtrate was concentrated, hot petroleum ether was added and cooled when a gummy material was obtained. This, on trituration with petroleum ether, gave a product B; (m.p. 157-158°C). Both the product (A and B) were dissolved in boiling benzene, concentrated, hot petroleum ether added, cooled and filtered. The solid obtained was washed with hot petroleum ether by boiling. The solid was then extracted with cold benzene and concentrated and petroleum ether was added when a reddish brown product separated. The product was purified by recrystallisation from benzene-pet. ether mixture and dried in vacuum.

m.p. : 163°C

Yield : 25%

Analytical data :	C	H	N	Sn (%)
Found :	58.75	4.60	10.18	14.70
Calculated for $C_{40}H_{36}N_6O_6Sn$:	58.77	4.65	10.28	14.53

IR : $\nu_{as}(COO)$ 1725 cm^{-1}

10. Preparation of $Oct_2Sn(L'H')_2$:

L'HH' (2.5 g, 8.5 m. mole) was extracted by soxhlet in 300 ml THF. To this solution was added (1.75g, 4.3 m. mole) dioctyl tin dichloride and few drops of pyridine. The reaction mixture was stirred at room temperature for about 10 hours. THF was then distilled off. The residue was washed with hot petroleum ether and extracted with cold benzene. Addition of petroleum ether to the concentrated solution furnished a brick red coloured solid which was recrystallised several times from benzene-petroleum ether mixture and dried in vacuum.

m.p. : 144°C

Yield : 35%

Analytical data:	<u>C</u>	<u>H</u>	<u>N</u>	<u>Sn</u> (%)
Found :	61.95	6.02	9.15	12.50
Calculated for				
$C_{48}H_{54}N_6O_6Sn$:	62.02	5.81	9.04	12.78

IR : ν_{as}(COO) 1725 cm^{-1}

11. <u>Preparation of $Me_2Sn(L'H')_2$:</u>

L'HH' (2.5g, 8.8 m. mole) was extracted by soxhlet in about 350 ml THF. To the solution was added dimethyl tin dichloride (0.94g, 4.2 m. mole) and few drops of pyridine. The reaction mixture was stirred at room temperature for 10 hours. THF was then distilled off, the solid washed with hot petroleum ether and extracted with cold benzene. On addition of petroleum ether to the concentrated solution a red coloured solid, m.p. 166°C separated which after several recrystallization from benzene-petroleum ether mixture afforded the desired product.

m.p. : 169°C

Yield : 40%

Analytical data:	<u>C</u>	<u>H</u>	<u>N</u>	<u>Sn</u> (%)
Found :	56.01	3.50	11.50	16.25
Calculated for				
$C_{34}H_{26}N_6O_6Sn$:	55.68	3.54	11.46	16.20

IR : ν_{as}(COO) 1730 cm^{-1}

12. Preparation of $Ph_2Sn(L'Me)_2$:

A mixture of L'MeH (1.3g, 4.2 m. mole), diphenyl tin dichloride (0.73g, 2.1 m. mole) and few drops of pyridine in 150 ml dry-benzene was refluxed for 10 hours, cooled and filtered off. To the concentrated filtrate was added petroleum ether, when a solid separated out. The solid was filtered, washed successively with hot petroleum ether, 2% sodium bicarbonate solution and finally with water. The residue was extracted with cold benzene and concentrated. On addition of petroleum ether, an orange product separated. The product was purified by recrystallisation from benzene-petroleum ether mixture and dried in vacuum.

m.p. : 178°C

Yield : 55%

Analytical data:	C	H	N	Sn (%)
Found :	62.42	3.90	9.36	13.89
Calculated for $C_{46}H_{34}N_6O_6Sn$:	62.39	3.84	9.49	13.41

IR : $\nu_{as}(COO)$ 1720 cm^{-1}

13. Preparation of $Bu_2Sn(L'Me)_2$:

A mixture of L'MeH (1.3g, 4.2 m. mole), dibutyl tin dibromide (0.83g, 2.1 m. mole) were taken in 150 ml dry benzene containing a few drops of pyridine. The reaction mixture was refluxed for 10 hours, cooled and filtered. Addition of petroleum ether to the concentrated filtrate yielded the crude product which was filtered, washed with hot petroleum ether, 2% sodium-bicarbonate solution and finally with water. The product was extracted with cold benzene and concentrated. To this solution was added petroleum ether, the brown coloured product was separated and crystallised from benzene and petroleum-ether.

m.p. : 174°C

Yield : 45%

Analytical data :	C	H	N	Sn (%)
Found :	59.50	4.52	10.1	14.12
Calculated for :				
$C_{42}H_{42}N_6O_6Sn$:	59.66	4.97	9.94	14.05

IR : ν_{as}(COO) : 1720 cm^{-1}

14. Preparation of $Oct_2Sn(L'Me)_2$:

A mixture of L'MeH (1.3g, 4.2 m. mole) and dioctyl tin dichloride (0.87g, 2.1 m. mole) were taken in 200 ml dry benzene containing a few drops of pyridine. The mixture was refluxed for 10 hours, cooled and filtered. Addition of petroleum ether to the concentrated filtrate yielded the crude product which was filtered, washed with hot petroleum ether. The product was then washed with aqueous 2% sodium bicarbonate and finally with water to remove unreacted ligand. The brown coloured compound was then extracted with cold benzene, concentrated and reprecipitate by adding petroleum-ether. The process was repeated several times.

m.p. : 178°C

Yield : 50%

Analytical data:	C	H	N	Sn (%)
Found :	63.57	6.10	7.97	12.34
Calculated for $C_{50}H_{58}N_6O_6Sn$:	62.71	6.06	8.78	12.40

IR : $\nu_{as}(C=O)$: 1720 cm^{-1}

15. Preparation of $Me_2Sn(L'Me)_2$:

A mixture of L'MeH (1.3g, 4.2 m. mole), dimethyl tin dichloride (0.47g, 2.1 m. mole) and few drops of pyridine in 175 ml dry benzene was refluxed for 10 hours and the residue was filtered off. To the concentrated filtrate was added petroleum ether when a solid separated which was filtered, washed successively with hot petroleum ether, 2% sodium bicarbonate solution and finally with water. The solid was extracted with cold benzene and concentrated. On addition of petroleum ether a brown coloured product separated. The product was purified by repeated crystallisation from benzene-petroleum ether mixture.

m.p. : 175°C

Yield : 60%

Analytical data:	C	H	N	Sn (%)
Found :	57.10	3.80	10.73	15.96
Calculated for				
$C_{36}H_{30}N_6O_6Sn$:	56.73	3.94	11.04	15.60

IR : ν_{as} (OCO) : 1720 cm^{-1}

18. Preparation of $Ph_2Sn(L'SnPh_3)_2$:

A. To a suspension of the silver salt of $R_2Sn(L'H')_2$ (0.5g, 0.47 m. mole) in 100 ml of dry benzene was added (0.350g, 0.91 m. mole) of triphenyl tin chloride and the mixture was refluxed for 20 hours. Benzene was distilled off to about 50 ml and filtered. To the concentrated solution was added petroleum ether, cooled and filtered. The solid was extracted with cold and dry benzene and filtered. The filtrate was further concentrated, added a little petroleum ether, cooled and filtered. The product was purified by recrystallisation from benzene-petroleum ether mixture. The orange product was dried in vacuum.

m.p. : > 300°C

Yield : 30%

B. To a solution of (0.3g, 0.78 m. mole) of $Ph_3SnL'H$ in 100 ml of dry benzene was added (0.134g, 0.39 m. mole) of diphenyl tin dichloride and a few drops of pyridine for the neutralisation of acid formed in the reaction. The reaction mixture was then stirred for about 10 hours at room temperature. Benzene was distilled off to about 50 ml, cooled and filtered. To the concentrated filtrate was added hot petroleum ether, cooled and filtered. The product was separated by filtration and washed with hot petroleum ether, 2% aq. solution of sodium bicarbonate and finally with water to remove unreacted $Ph_2Sn(L'H')_2$. Then the solid was extracted with cold dry benzene and filtered. The filtrate was concentrated, added petroleum ether when an orange coloured solid separated. The orange product was purified by repeated crystallisation from benzene-petroleum ether mixture and dried in vacuum.

m.p.	: > 300°C
Yield	: 32%

C. A mixture of $Ph_2Sn(L'H')_2$ (1.0g, 1.1 m. mole) and bis-(triphenyl tin) oxide (0.83g, 1.1 m. mole) in 200 ml of dry benzene was refluxed for 15 hours. Then the reaction mixture was concentrated on water bath and filtered. To the concentrated filtrate was added petroleum ether. The orange coloured precipitate was filtered, washed successively with hot petroleum ether, 2% aq. solution of sodium bicarbonate and finally with water to remove unreacted $Ph_2Sn(L'H')_2$. The residue was extracted with cold, dry benzene and concentrated. The concentrated filtrate was treated as before. The orange solid was further purified by recrystallisation from benzene-petroleum ether mixture and dried.

M.p. : >300°C

Yield : 65%

Analytical data :	C	H	N	Sn (%)
Found :	61.70	3.70	5.39	22.30
Calculated for $C_{80}H_{58}N_6O_6Sn_3$:	61.77	3.73	5.40	22.91

IR : $\nu_{as}(OCO)$: 1630 cm^{-1}.

17. Preparation of $Bu_2Sn(L'SnPh_3)_2$:

A mixture of $Bu_2Sn(L'H')_2$ (1.0g, 1.2 m.mole) and bis-(triphenyl tin) oxide (0.83g, 1.2 m. mole) in about 250 ml dry benzene was refluxed for 26 hours, cooled and filtered. Addition of petroleum ether to the concentrated filtrate yielded the crude product which was filtered, washed with hot petroleum ether. The product was further purified by washing with 2% sodium-bicarbonate solution and finally with water. The product was purified by repeated crystallisation from benzene-petroleum ether mixture.

Decomposition point : 211°C

Yield : 40%

Analytical data:	<u>C</u>	<u>H</u>	<u>N</u>	<u>Sn</u> (%)
Found :	60.70	3.19	5.78	23.63
Calculated for				
$C_{76}H_{57}N_6O_6Sn_3$:	60.59	3.78	5.58	23.65

IR : ν_{as} (COO) : 1630 cm^{-1}

18. <u>Preparation of $Cot_2Sn(L'SnPh_3)_2$:</u>

A mixture of $Cot_2Sn(L'H')_2$ (1.0g, 1.0 m. mole) and bis-(triphenyl tin) oxide (0.77g, 1.0 m. mole) in 200 ml dry benzene was refluxed for 20 hours, cooled and filtered. Addition of petroleum ether to the concentrated filtrate yielded the crude product which was filtered and washed successively with hot petroleum ether, 2% sodium bicarbonate solution and water. The solid was extracted with cold benzene and the solution was concentrated. On addition of petroleum ether to the concentrated benzene solution, an orange coloured solid separated which after several recrystallisation from benzene-petroleum ether mixture afforded the pure product. The solid was dried in vacuum.

Decomposition point : 165°C

Yield : 40%

Analytical data:	<u>C</u>	<u>H</u>	<u>N</u>	<u>Sn</u> (%)
Found :	62.50	5.25	6.30	21.89
Calculated for				
$C_{84}H_{82}N_6O_6Sn_3$:	61.98	5.04	5.16	21.90

IR : ν_{as}(COO) : 1630 cm^{-1}

19. Preparation of $Me_2Sn(L'SnPh_3)_2$:

A mixture of $Me_2Sn(L'H')_2$ (1.0g, 1.4 m. mole) and bis-(triphenyl tin) oxide (0.98g, 1.4 m. mole) in 300 ml dry benzene was refluxed for 15 hours, cooled and filtered. The filtrate was concentrated to about 75 ml, and pet. ether was added when the crude product m.p. 173°C separated. The product was filtered and washed successively with 2% sodium bicarbonate solution, and water. The reddish orange solid was purified by repeated crystallisation from benzene-petroleum ether mixture.

m.p. : 175°C

Yield : 50%

Analytical data:	<u>C</u>	<u>H</u>	<u>N</u>	<u>Sn</u> (%)
Found :	57.95	3.50	5.62	25.10
Calculated for $C_{70}H_{54}N_6O_6Sn_3$:	58.73	3.77	5.87	24.9

IR : $\nu_{as}(COO)$ 1630 cm^{-1}

20. Preparation of $Ph_2Sn(L'SnBu_3)_2$:

A mixture of $Ph_2Sn(L'H')_2$ (1.0g, 1.1 m. mole) and bis-(tributyl tin) oxide (0.7g, 1.2 m. mole) in 300 ml dry benzene was refluxed for 25 hours, cooled and filtered and concentrated. Addition of petroleum ether to the concentrated filtrate yielded the crude product, which was filtered, washed successively with hot petroleum ether, 2% sodium bicarbonate solution and water. The orange solid was extracted with cold benzene and the filtrate was treated as before. The product was further purified by crystallisation from benzene-petroleum ether mixture.

m.p. : 242°C

Yield : 30%

Analytical data:	C	H	N	Sn (%)
Found :	57.25	5.60	6.12	24.92
Calculated for $C_{63}H_{82}N_6O_6Sn_3$:	56.89	5.71	5.95	24.83

IR : $\nu_{as}(COO)$ 1635 cm^{-1}

21. Preparation of $Bu_2Sn(L'SnBu_3)_2$:

A mixture of $Bu_2Sn(L'H')_2$ (1.0g, 1.2 m. mole) and bis-(tributyl tin) oxide (0.73g, 1.2 m. mole) in 300 ml dry benzene was refluxed for 30 hours, cooled and filtered. Addition of petroleum ether to the concentrated filtrate yielded a product m.p. ~160°C, which was filtered and washed successively with hot petroleum ether, 2% sodium bicarbonate solution and water. The product was then purified by recrystallisation from benzene-petroleum ether mixture. The product was obtained as orange coloured crystals.

m.p. : 162°C

Yield : 30%

Analytical data:	C	H	N	Sn (%)
Found :	54.50	6.62	6.22	25.79
Calculated for				
$C_{64}H_{90}N_6O_6Sn_3$:	55.08	6.45	6.02	25.54

IR : ν_{as}(COO) 1630 cm^{-1}

22. Preparation of $Oct_2Sn(L'SnBu_3)_2$:

A mixture of $Oct_2Sn(L'H')_2$ (1.0g, 1.0 m. mole) and bis-(tributyl tin) oxide (0.64g, 1.0 m. mole) in 250 ml dry benzene was refluxed for 25 hours, cooled and filtered. Addition of petroleum ether to the concentrated filtrate yielded the crude product which was filtered and washed with hot petroleum ether, 2% sodium bicarbonate solution and finally with water. The orange coloured product was then purified by repeated crystallisation from benzene-petroleum ether mixture.

m.p. : 182°C

Yield : 40%

Analytical data:	C	H	N	Sn (%)
Found :	56.92	6.96	5.50	24.10
Calculated for				
$C_{72}H_{106}N_6O_6Sn_3$:	57.36	7.03	5.57	23.64

IR : ν_{as}(COO) 1635 cm^{-1}

23. Preparation of $Ph_3SnL'SnPh_3$:

A mixture of L'HH' (1.5g, 5.1 m. mole) and bis-(triphenyl tin) oxide (3.7g, 5.2 m. mole) in 500 ml dry benzene was refluxed for 25 hours. The reaction mixture was cooled and filtered. The filtrate was concentrated, petroleum ether added when the crude product, m.p. 178°C separated. This was filtered, washed with hot petroleum ether, 2% sodium bicarbonate solution, and finally with water to remove unreacted L'HH'. The orange product was extracted with cold dry benzene and concentrated. Filtrate was treated as before. The product was purified by crystallisation from benzene-petroleum ether mixture. The orange crystals of triphenyl tin derivatives was dried in vacuum.

m.p. : 180°C

Yield : 70%

Analytical data:	C	H	N	Sn (%)
Found :	62.50	3.92	4.10	24.15
Calculated for				
$C_{52}H_{39}N_3O_3Sn_2$:	63.0	3.90	4.24	23.97

IR : ν_{as} (COO) 1630 cm^{-1}.

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