CHAPTER-III

ORGANOTIN DERIVATIVES OF α-KETO CARBOXYLIC ACIDS.

ORGANOTIN DERIVATIVES OF α-KETO CARBOXYLIC ACIDS :

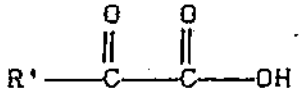
(Preparation, Properties and Spectroscopic Studies).

III.1. *Introduction :*

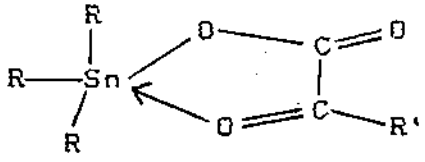
A survey of literature shows that although tremendous amount of work has already been done on the synthesis and structure of organotin carboxylates with almost all conceivable type of substituents on both the tin atom and the carboxyl moiety, the organotin esters of α-keto acids [I] are yet to be adequately investigated. Only a few reports on the preparation[1] and spectral studies[2] on the triphenyl and tributyltin esters of pyruvic acid have appeared so far. Organotin derivatives of α-keto carboxylic acids would be of interest in two respects :

(i) Organotin carboxylates, unlike organotin halides, are somewhat reluctant to form addition complexes with Lewis bases, although a number of their adducts with N, O and S containing ligands have, recently, been reported[3-10]. Apart from the hydrate adducts of di and tri organotin carboxylates[16-18] and the anionic acetate adduct of $Me_2Sn(OAc)_2$[19], the organotin carboxylate moiety, in majority of these complexes reported so far, is a derivative of a trihalocarboxylic acid such as CF_3COOH or CCl_3COOH[6,7,10,12-15]. Most obviously, the electronegativity of the $RCOO^-$ moiety in these carboxylates profoundly influences the Lewis acidity of the tin atom[15], thereby making it susceptible to nucleophilic attack. The

α-keto acids, possessing a suitably placed keto group and high acid strength (electronegativity) appear to be suitable for the realisation of organotin carboxylates of the type II, in which the carboxylato group is part of a chelated ring structure, formed as a result of intra molecular nucleophilic attack. It is therefore, of great interest to know whether, such coordination would occur in organotin derivatives of α-keto carboxylic acids, or not.



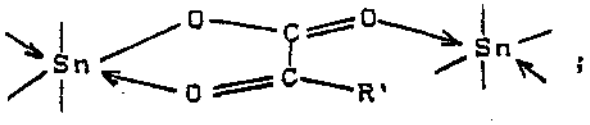
I



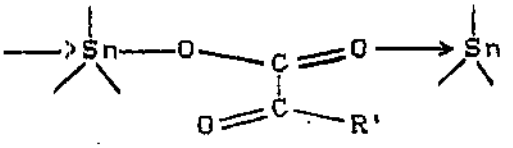
II

It should be pointed out here, that the formation of such a chelate ring does not necessarily exclude the possibility of intermolecular coordination in these organotin derivatives of the α-keto acids. The enhanced Lewis acidity of the tin atom due to high electronegativity of the $R'COCOO^-$ moiety makes it equally susceptible to intra molecular as well as intermolecular nucleophilic attack. Thus, favourable electronic and steric factors are likely to introduce intermolecular coordination leading to either of the following structures III or IV, without regard to the role of the keto group in the complex.

(ii) Pyruvic acid, the first member of the α-keto acid series, is very important biologically since it is an intermediate product



III



IV

in the metabolism of carbohydrates and proteins. Recently, Pt-complexes of pyruvic acid have been found to possess remarkable anti-tumour activity[21-24]. Therefore, synthesis and study of the tin complexes of pyruvic acid and its homologues are important from the biological point of view as well.

Moreover, it is also interesting to know the various factors which influence the course of the reaction between the keto acids and organostannoxanes.

These considerations led us to investigate the organotin derivatives of α-keto carboxylic acids. The keto acids used in the present investigation have been named and abbreviated as shown below.

Sl.no.	Structure	Name	Abbreviation
1.	$CH_3-C(=O)-C(=O)-OH$	Pyruvic acid (2-Oxo-Propanoic acid)	PvH
2.	$PhCH_2-C(=O)-C(=O)-OH$	Phenyl Pyruvic acid (2-Oxo-3-Phenyl Propanoic acid)	PPvH
3.	$Ph-C(=O)-C(=O)-OH$	Benzoyl Formic acid (2-Oxo-2-Phenyl Acetic acid)	BFH

III.2. *Experimental :*

The organotin compounds used were purchased from Fluka (Switzerland) and Aldrich (USA) and were used without further purification except Ph_3SnCl, which was purified by repeated recrystallisation from petroleum ether (Bp. 60-80°c) until the product attained the mp. 106°c. Ph_3SnCl was also prepared from Ph_4Sn by standard method[25] and purified in the same manner. $(PhCH_2)_3SnCl$ was prepared by the method described by Sisido et.al.[26] and recrystallised from ethyl acetate.

All solvents were purified by standard methods[27] as and when necessary. Unless otherwise stated, petroleum ether used refers to the fraction boiling at 60-80°c. All melting points were observed by open capillary method and are uncorrected.

III.2A. Preparation Of The Ligands :

(i) Pyruvic acid (PvH) :

Pyruvic acid was prepared according to the method described by Gilman and Blatt[28a], and purified by fractional distillation. The fraction boiling at 75-80°C/25 mm was collected.

(ii) Phenyl Pyruvic acid (PPvH) :

Phenyl pyruvic acid was prepared according to the method described by Gilman and Blatt[28b], and dried in a vacuum desiccator over $CaCl_2$ and KOH. Mp. 156-158°C.

(iii) Benzoyl Formic acid (BFH) :

Benzoyl formic acid was purchased from Fluka (Switzerland) and used without further purification. Mp. 62-64°C.

III.2B. Preparation of the Organotin Derivatives :

1. Reaction of NaPv with Ph_3SnCl :

0.77 g (0.002 mole) of Ph_3SnCl was stirred with large excess of NaPv (0.5 g,0.005 mole) in dry ether containing some methanol at room temperature for 8 hours. The solvent was completely removed at room temperature under vacuum and the resultant mass extracted with hot pet.ether. The pet.ether extract was allowed to stand and the first fraction of product was repeatedly recrystallised from pet.ether.

Yield :0.085 g (ca.10%). Mp. 114-6°C.

Analysis :	%Sn	%C	%H
Found :	26.1	58.8	4.6
Calculated for Ph_3SnPv :	27.06	57.7	4.13

2. Reaction of PvH with $(Ph_3Sn)_2O$:

(i) 1.79 g (0.0025 mole) of $(Ph_3Sn)_2O$ was dissolved in 40 ml dry dry ether, 0.44 g (0.005 mole) of PvH was added and refluxed using Dean and Stark water separator for about 1 hour and filtered. The filtrate was evaporated to dryness at room temperature and the

resulting mass extracted with pet.ether. The pet.ether extract on evaporation and recrystallisation from the same solvent gave 0.065 g (3%) white solid melting at 114-6°C.

Analysis :	%Sn	%C	%H
Found :	25.8	59.1	4.8
Calculated for Ph_3SnPv :	27.06	57.7	4.13

The residue obtained after reflux and after extraction with pet.ether were repeatedly washed with benzene and ether and dried. Both were found to be identical on the basis of IR and analytical data. The combined mass of the residue was 1.75 g (80%) and it did not melt.

Analysis :	% Sn	% C	% H
Found :	30.1	48.1	3.8
Calculated for $Ph_2Sn(Pv)OH$:	31.38	47.87	3.72

(ii) The same amount of $(Ph_3Sn)_2O$ and PvH as above were taken in benzene-free solvent ether and refluxed under the same condition and the solvent ether was carefully distilled out completely. The UV spectrum of the distillate was recorded in the 280-230 nm region using a Shimadzu UV240 spectrophotometre. The UV spectrum showed the presence of benzene in the distillate indicating that one of the reaction products is benzene.

(iii) The same amount of $(Ph_3Sn)_2O$ and PvH as above were taken in 40 ml dry benzene and refluxed using water separator for 12 hours. Filtered and the residue washed with ether. On

recrystallisation from methanol 0.8 g of yellow solid, which decomposed above 280°C without melting, was obtained.

Analysis :	% Sn	% C	% H
Found :	38.5	34.8	2.8
Calculated for $[PhSn(Pv)O]_n$:	39.6	36.2	2.7

The filtrate was evaporated to dryness and extracted with hot benzene-pet.ether mixture (80:20). The solution was concentrated and allowed to crystallise. On repeated recrystallisation from the same solvent 0.19 g of crystalline solid, melting at 227-8°c, were obtained. This was found to be Ph_4Sn from analytical data and mixed melting point determination with an authentic sample of Ph_4Sn.

The residue after extraction with benzene-pet.ether mixture was washed with ether and dried. The yellow solid weighed 0.5 g and did not melt.

Analysis :	% Sn	% C	% H
Found :	30.9	49.3	3.4
Calculated for $Ph_2Sn(Pv)OH$:	31.38	47.87	3.72

3. Reaction of NaPv with Bu_3SnCl :

0.32 g (0.001 mole) of Bu_3SnCl was added to a suspension of excess NaPv (0.2 g, ~ 0.002 mole) in 20 ml ether and stirred for 8 hours using magnetic stirrer. The solvent was then removed at room temperature and the residue was extracted with pet.ether.

The pet.ether solution was evaporated and the resulting mass recrystallised from the same solvent.

Yield : 0.04 g (ca. 11%). Mp. 80-82°C.

Analysis :	% Sn	% C	% H
Found :	31.02	49.0	8.5
Calculated for Bu_3SnPv :	31.38	47.9	7.98

4. Reaction of PvH with $(Bu_3Sn)_2O$:

1.49 g of $(Bu_3Sn)_2O$ (0.0025 mole) was dissolved in 40 ml dry benzene and refluxed with 0.46 g (>0.005 mole) of PvH for 16 hours using water separator. The yellow solution was filtered and shaken vigorously with $NaHCO_3$. Filtered and the filtrate was evaporated to very small volume (3-4 ml), diluted with 5 ml pet.ether and stored at 5°C. A viscous dark yellow liquid settled at the bottom. The clear supernatant liquid was decanted and further diluted with little pet.ether and kept at 5°C. The same process was repeated till no more viscous liquid separated. The supernatant liquid on evaporation at room temperature gave yellowish crystals which were recrystallised from pet.ether and dried under vacuum over $CaCl_2$.

Yield : 0.36 g (ca. 20%). Mp. 80-82°C.

Analysis :	% Sn	% C	% H
Found :	31.1	48.8	8.4
Calculated for Bu_3SnPv :	31.38	47.9	7.98

5.(i) Reaction of NaPv with $(PhCH_2)_3SnCl$:

0.426 g (0.001 mole) of $(PhCH_2)_3SnCl$ was stirred with excess NaPv (0.27 g, ~ 0.003 mole) in dry ether containing some methanol at room temperature for 6 hours. The solvent was completely removed at room temperature and the residue extracted with cold ether and allowed to stand. The first crop of product was rejected and the second crop recrystallised from ether.

Yield :0.04 g (ca. 8%). Mp. 104-108^{o}C.

Analysis :	% Sn	% C	% H
Found :	-	61.3	4.8
Calculated for $(PhCH_2)_3SnPv$:	24.69	60.25	5.02

(ii) Reaction of PvH with $[(PhCH_2)_3Sn]_2O$:

1.0 g (0.00125 mole) oxide was dissolved in 40 ml dry benzene and refluxed with 0.22 g (<0.0025 mole) PvH for 10 hours. The light yellow solid deposited was filtered out, washed with ether and recrystallised from methanol. The product weighed 0.55 g and did not melt.

Analysis :	% Sn	% C	% H
Found :	36.26	39.2	3.5
Calculated for $[BzSn(Pv)O]_n$:	37.82	38.46	3.2

6. Reaction of PvH with Oct_2SnO :

(i) 0.45 g (0.00125 mole) of Oct_2SnO was suspended in about 15 ml dry benzene, warmed and 0.22 g (0.0025 mole) of PvH added

drop wise with shaking. The oxide went into solution. Allowed to stand for 1-2 minutes and the solution was carefully decanted leaving behind unreacted substances. Precipitation was completed by addition of pet.ether and allowed to settle. The supernatant liquid decanted off and the residue washed with benzene. It was then dissolved in ether and reprecipitated with pet.ether. The light yellow precipitate was filtered and washed with ether-pet.ether mixture. It was dried first in air and then in vacuum over $CaCl_2$.

Yield : 0.47 g (ca. 80%). Did not melt (decomposed above 150°C).

Analysis :	% Sn	% C	% H
Found :	25.2	51.6	7.5
Calculated for $Oct_2Sn(Pv)OH$:	26.34	50.89	8.48

(ii) 0.45 g of Oct_2SnO and 0.22 g of PvH were taken in 40 ml dry benzene and refluxed for 10 hours using water separator. The yellow solution was filtered and the filtrate shaken vigourously with $NaHCO_3$. Filtered and the filtrate evaporated to a small volume, diluted with equal volume of pet.ether and stored at 5°C. The first fraction of precipitate (a small amount of yellow solid) was discarded and the clear solution on cooling for several days gave a white product. It was recrystallised from benzene-pet.ether mixture.

Yield : 0.25 g (ca. 40%). Mp. 112-114°C.

Analysis :	% Sn	% C	% H
Found :	23.72	51.7	8.02
Calculated for $Oct_2Sn(Pv)_2$:	22.78	50.96	7.72

7. Reaction of PvH with Bu_2SnO :

(i) 0.62 g (0.0025 mole) of Bu_2SnO was suspended in 15 ml benzene-ether mixture (80:20), warmed and shaken with 0.44 g (0.005 mole) of PvH added drop wise. Shaking continued for 2-3 minutes, when the oxide went into solution. Allowed to stand for 1-2 minutes and the solution carefully decanted leaving behind traces of unreacted substances. Pet.ether was then added to the solution and the precipitate formed allowed to settle. The supernatant liquid was decanted off and the residue washed repeatedly with ether. The yellowish white residue was dried first in air and then under vacuum over $CaCl_2$.

Yield : 0.82 g (ca. 84%). Decomposed above 234°C.

Analysis :	% Sn	% C	% H
Found :	34.64	40.45	6.1
Calculated for $Bu_2Sn(Pv)OH$:	35.1	39.3	6.54

(ii) 0.62 g of Bu_2SnO and 0.44 g of PvH were taken in 40 ml dry benzene and refluxed for 20 hours using water separator. The yellow solution was filtered and shaken vigourously with $NaHCO_3$. Filtered and the filtrate evaporated to a small volume and diluted with equal volume of pet.ether and stored at 5°C, when a viscous dark yellow liquid settled at the bottom. The clear upper layer

was decanted and again kept at 5°C. The same process was repeated till no more viscous liquid separated. The supernatant liquid on dilution with more pet.ether and cooling gave a white product. This was recrystallised from benzene-pet.ether mixture.

Yield : 0.22 g (ca. 23%). Mp. 157°C

Analysis :	% Sn	% C	% H
Found :	30.82	42.1	6.5
Calculated for $Bu_2Sn(Pv)_2$:	29.06	41.4	5.9

8. Reaction of PvH with Me_2SnO :

(i) 0.41 g (0.0025 mole) of Me_2SnO was suspended in 15 ml hot benzene-ether mixture (80:20) and reacted with 0.44 g (0.005 mole) of PvH, following the same procedure used for the reaction 7(i) above. The product was collected and dried in the same manner.

Yield : 0.63 g (ca. 80%). Did not melt.

Analysis :	% Sn	% C	% H
Found :	46.16	23.3	4.4
Calculated for $Me_2Sn(Pv)OH$:	46.82	23.81	3.97

(ii) 0.41 g of Me_2SnO and 0.44 g of PvH were refluxed in 40 ml dry benzene for 16 hours using water separator. The benzene solution was filtered and shaken vigourously with $NaHCO_3$. Filtered, the filtrate concentrated and allowed to stand overnight. The yellowish white solid deposited was filtered and washed with benzene and ether, then dried.

Yield : 0.15 g (ca. 18%). Did not melt.

Analysis :	% Sn	% C	% H
Found :	34.9	29.28	3.8
Calculated for $Me_2Sn(Pv)_2$:	36.64	29.8	3.7

9. Reaction of PvH with Ph_2SnO :

(i) 0.72 g (0.0025 mole) of Ph_2SnO was reacted with 0.44 g of PvH following the same procedure as for the reaction 7(i) above and 0.8 g (ca. 78%) of a yellowish white product, which did not melt, was obtained.

Analysis :	% Sn	% C	% H
Found :	30.47	49.85	3.9
Calculated for $Ph_2Sn(Pv)OH$:	31.38	47.87	3.72

(ii) 0.72 g Ph_2SnO and 0.44 g PvH were refluxed in 40 ml dry benzene for 8 hours using water separator. The yellow solid deposited was filtered, washed with ether and recrystallised from methanol and dried. 0.62 g of yellow solid which decomposed above 280^{o}C were obtained.

Analysis :	% Sn	% C	% H
Found :	38.1	35.7	2.9
Calculated for $[PhSn(Pv)O]_n$:	39.6	36.2	2.7

10. Reaction of NaPPv with Ph_3SnCl :

0.38 g (~ 0.001 mole) of Ph_3SnCl and 0.28 g (> 0.001 mole) of NaPPv were taken in dry ether containing small amount of

methanol and stirred at room temperature for 6 hours. Evaporated to dryness at r.t. and extracted with cold ether and allowed to stand overnight at 5°C. First crop of products rejected and the second crop was recrystallised from ether.

Yield : 0.35 g (68%). Mp. 139-140°C.

Analysis :	% Sn	% C	% H
Found :	22.9	63.8	3.7
Calculated for Ph_3SnPPv :	23.0	63.15	4.28

11. Reaction of PPvH with $(Ph_3Sn)_2O$:

(i) 0.35 g (~ 0.0005 mole) of $(Ph_3Sn)_2O$ was dissolved in 5 ml dry benzene(or ether) and shaken with 0.16 g (0.001 mole) of PPvH for 2-3 minutes. The faint yellow solution obtained was diluted with 2-3 ml pet.ether and allowed to stand at 5°C. The first crop of product was rejected and the second crop washed with cold ether and dried, first in air and then under vacuum over $CaCl_2$.

Yield :0.375 g (70%). Mp. 139-140°C.

Analysis :	% Sn	% C	% H
Found :	22.9	63.79	3.65
Calculated for Ph_3SnPPv :	23.0	63.15	4.28

(ii) 1.4 g (~ 0.002 mole) of $(Ph_3Sn)_2O$ was dissolved in 20 ml dry benzene and 0.65 g (~ 0.004 mole) PPvH added. the light yellow solution was then refluxed using water separator for 12 hours. The yellow solid separated was filtered and washed with

ether. The solid weighed 0.98 g on drying and did not melt.

Analysis :	% Sn	% C	% H
Found :	32.6	47.3	3.7
Calculated for $[PhSn(PPv)O]_n$:	31.55	48.12	3.2

The filtrate was evaporated at room temperature, washed with cold ether and extracted with hot benzene-pet.ether mixture (80:20). The solution was concentrated and allowed to crystallise. On repeated recrystallisation from benzene-pet.ether mixture 0.17 g of crystalline solid melting at 227-8^{o}C were obtained. This was found to be Ph_4Sn from analytical data and mixed melting point determination.

The residue after extraction with benzene-pet.ether mixture weighed 0.43 g on drying and did not melt.

Analysis :	% Sn	% C	% H
Found :	27.56	57.4	3.7
Calculated for $Ph_2Sn(PPv)OH$:	26.1	55.75	3.98

When the reaction 11.(ii) was carried out in solvent ether and the solvent was carefully distilled out, benzene could be spectroscopically detected in the distillate, indicating that benzene was one of the products of the reaction.

12. Reaction of NaPPv with Bu_3SnCl :

0.32 g (0.001 mole) of Bu_3SnCl and 0.27 g (>0.001 Mole) of NaPPv were taken in dry ether containing little methanol and stirred at room temperature for 8 hours.Filtered, evaporated at

r.t. and extracted with cold pet.ether. The pet.ether extract on evaporation gave a colorless liquid product weighing 0.44 g (98%) containing no halogen.

Analysis :	% Sn	% C	% H
Found :	26.84	56.65	5.8
Calculated for Bu_3SnPPv :	26.1	55.75	7.52

13. Reaction of PPvH with $(Bu_3Sn)_2O$:

0.6 g (~ 0.001 mole) of $(Bu_3Sn)_2O$ and 0.4 g (>0.002 mole) of PPvH were taken in 20 ml dry benzene and refluxed for 10 hours using Dean and Stark water separator. The yellow solution obtained was shaken with $NaHCO_3$ and filtered. The filtrate was concentrated, diluted with pet.ether and kept at 5^oC overnight. Pasty yellow mass settled down and the clear upper layer decanted. The decant was allowed to evaporate at room temperature to a semisolid mass and then extracted with cold pet.ether. The pet.ether extract on evaporation gave a colorless viscous liquid weighing 0.49 g (55%).

Analysis :	% Sn	% C	% H
Found :	26.65	56.6	5.7
Calculated for Bu_3SnPPv :	26.1	55.75	7.52

14. Reaction of NaPPv with $(PhCH_2)_3SnCl$:

0.42 g (~ 0.001 mole) of $(PhCH_2)_3SnCl$ and 0.27 g (>0.001

mole) of NaPPv were taken in dry ether containing little methanol and stirred at room temperature for 7 hours and filtered. The filtrate was evaporated to dryness at r.t. and extracted with cold ether. The ether solution was stored at 5°C. The first crop of products was rejected and the second crop, recrystallised from ether, weighed 0.24 g (44%) on drying and melts at 134°C.

Analysis :	% Sn	% C	% H
Found :	21.86	64.25	5.6
Calculated for Bz_3SnPPv :	21.3	64.98	5.05

15. Reaction of PPvH with $[(PhCH_2)_3Sn]_2O$:

0.4 g (0.0005 mole) of the oxide was dissolved in 10 ml benzene-ether mixture (50:50) and 0.17 g (~ 0.001 mole) acid added. Warmed and shaken for 2-3 minutes. The clear solution obtained was diluted with pet.ether and kept overnight at 5°C. The solid deposited was recrystallised from cold ether and dried.

Yield : 0.42 g (78%). Mp. 134°C.

Analysis :	% Sn	% C	% H
Found :	22.1	64.56	5.4
Calculated for Bz_3SnPPv :	21.3	64.98	5.05

16. Reaction of PPvH with Bu_2SnO :

(i) 0.25 g (0.001 mole) of Bu_2SnO and 0.33 g (0.002 mole) of PPvH were shaken in 10 ml warm benzene-ether mixture (50:50) for 10 minutes and filtered. The filtrate was diluted with pet.ether

and allowed to stand at 5°C. The solid deposited was recrystallised from benzene-pet.ether mixture and the product obtained was washed with cold ether and dried.

Yield : 0.4 g (ca. 72%). Decomposed above 170°C.

Analysis :	% Sn	% C	% H
Found :	22.49	54.8	5.6
Calculated for $Bu_2Sn(PPv)_2$:	21.15	55.91	5.73

(ii) 0.25 g Bu_2SnO and 0.33 g PPvH were refluxed in 20 ml benzene-ether mixture (50:50) for 8 hours. The residue was filtered and recrystallised from acetone and dried under vacuum.

Yield : 0.14 g (ca. 25%). Mp. 191°C.

Analysis :	% Sn	% C	% H
Found :	30.15	48.8	5.4
Calculated for $Bu_2Sn(PPv)OH$:	28.64	49.51	6.3

The filtrate was shaken with $NaHCO_3$, filtered, concentrated and diluted with pet.ether and allowed to stand at 5°C. The first crop of products was rejected and the second crop recrystallised from benzene-pet.ether mixture.

Yield : 0.38 g (ca. 68%). Decomposed above 170°C.

Analytical data identical with that of $Bu_2Sn(PPv)_2$.

17. Reaction of PPvH with Oct_2SnO :

(i) 0.18 g (0.0005 mole) of Oct_2SnO was suspended in 10 ml hot ether and shaken with 0.16 g (0.001 mole) of PPvH for 5 minutes. The solution was filtered, diluted with 5 ml pet.ether and stored

at 5°C. The white product obtained was recrystallised from ether-pet.ether mixture and dried under vacuum over $CaCl_2$.

Yield : 0.2 g (ca. 60%). Mp. 74-6°C.

Analysis :	% Sn	% C	% H
Found :	18.65	59.02	6.85
Calculated for $Oct_2Sn(PPv)_2$:	17.61	60.89	7.13

(ii) 0.36 g (0.001 mole) of Oct_2SnO and 0.35 g (>0.002 mole) of PPvH were taken in 20 ml benzene-ether mixture (50:50) and refluxed for 9 hours. Filtered and the residue recrystallised from acetone. The solid on drying weighed 0.37 g (ca. 55%). Mp. 124°C.

Analysis :	% Sn	% C	% H
Found :	23.76	58.74	7.5
Calculated for $Oct_2Sn(PPv)OH$:	22.52	57.25	8.01

The filtrate was shaken with $NaHCO_3$, concentrated, diluted with pet.ether and kept at 5°C. The first crop was discarded and the second crop was recrystallised from ether-pet.ether mixture. The product was found to be identical with $Oct_2Sn(PPv)_2$ on the basis of melting point, analytical data and IR spectra.

Yield : 0.1 g (ca. 15 %).

18. Reaction of PPvH with Me_2SnO :

(i) 0.16 g (~ 0.001 mole) of Me_2SnO was suspended in hot benzene-ether mixture (50:50) and shaken with 0.32 g (0.002 mole) of PPvH for 2-3 minutes. The clear supernatant solution was

decanted and allowed to stand. The solid precipitated from the solution was washed with ether and dried.

Yield : 0.225 g (ca. 46 %). Decomposes above 200°C.

Analysis :	% Sn	% C	% H
Found :	26.2	49.85	4.1
Calculated for $Me_2Sn(PPv)_2$:	24.89	50.63	4.22

(ii) 0.16 g of Me_2SnO and 0.32 g PPvH were refluxed in bez-ether mixture for 8 hours and filtered. The filtrate was shaken with $NaHCO_3$, filtered, concentrated, diluted with pet.ether and stored at 5°C. The yellowish white precipitate obtained was washed with ether and dried. Yield : 0.05 g (ca. 16%). Mp. 172°C.

Analysis :	% Sn	% C	% H
Found :	-	41.07	3.8
Calculated for $Me_2Sn(PPv)OH$:	35.97	40.24	4.26

19. Reaction of PPvH with Ph_2SnO :

0.28 g (~ 0.001 mole) of Ph_2SnO and 0.32 g (~ 0.002 mole) of PPvH were refluxed in benzene-ether mixture (50:50) for 1 hour and filtered. The filtrate was shaken with $NaHCO_3$, concentrated and allowed to stand. The precipitate obtained was washed with ether and dried.

Yield : 0.055 g (ca. 12%). Does not melt.

Analysis :	% Sn	% C	% H
Found :	-	57.16	4.3
Calculated for $Ph_2Sn(PPv)OH$:	26.1	55.75	3.98

20. Reaction of NaBF with Ph_3SnCl :

0.19 g (~ 0.0005 mole) of Ph_3SnCl and 0.095 g (>0.0005 mole) of NaBF were stirred at room temperature for 6 hours in dry ether containing little methanol. The resultant suspension was evaporated at room temperature, extracted with cold bez-pet.ether mixture (50:50) and stored at 5^oC. The first crop of products was rejected and the second crop was recrystallised from benzene-pet.ether.

Yield : 0.1 g (ca. 42 %). Mp. 149-50^oC.

Analysis :	% Sn	% C	% H
Found :	23.1	61.8	4.5
Calculated for Ph_3SnBF :	23.69	62.65	4.02

21. Reaction of BFH with $(Ph_3Sn)_2O$:

0.35 g (~ 0.0005 mole) $(Ph_3Sn)_2O$ was dissolved in 10 ml benzene-ether mixture (50:50) by warming and the solution shaken with 0.15 g (~ 0.001 mole) BFH for 5 minutes.The clear solution was diluted with pet.ether and stored at 5^oC. The white product obtained was recrystallised from cold benzene-pet.ether mixture and dried under vacuum over $CaCl_2$. The product was identified with Ph_3SnBF on the basis of melting point, analytical data and IR spectra.

Yield : 0.45 g (ca. 90%).

22. Reaction of NaBF with Bu_3SnCl :

0.32 g (~ 0.001 mole) of Bu_3SnCl was added to a suspension of excess NaBF (0.3 g, ~ 0.002 mole) in 20 ml ether and stirred for 10 hours using a magnetic stirrer and filtered. The solvent was evaporated to a small volume (~ 5 ml), diluted with equal volume of pet.ether and stored at $5^{o}C$ for several days. No precipitation occurred and the solvent was removed at room temperature. The colorless viscous liquid obtained, after drying under vacuum, weighed 0.43 g (ca. 100 %).

Analysis :	% Sn	% C	% H
Found :	26.5	55.3	7.6
Calculated for Bu_3SnBF :	26.94	54.79	7.3

23. Reaction of BFH with $(Bu_3Sn)_2O$:

0.3 g (~ 0.0005 mole) of $(Bu_3Sn)_2O$ and 0.2 g (>0.001 mole) of BFH were refluxed in 20 ml dry benzene for 4 hours using water separator. The solution was shaken vigourously with $NaHCO_3$, filtered, concentrated to about 5 ml, diluted with pet.ether and stored at $5^{o}C$ for a week. The slight turbidity formed was removed by filtration and evaporated at room temperature. The colorless viscous liquid was dried under vacuum. Yield : 0.38 g (ca. 96 %).

Analysis :	% Sn	% C	% H
Found :	26.6	55.1	7.7
Calculated for Bu_3SnBF :	26.94	54.79	7.3

24. Reaction of NaBF with Bz_3SnCl :

0.42 g (~ 0.001 mole) of Bz_3SnCl was added to a suspension of excess NaBF (0.3 g ~ 0.002 mole) in 20 ml ether and stirred magnetically for 6 hours. The solvent was removed at room temperature and the residue extracted with bez-pet.ether mixture. The extract was concentrated and stored at 5^oC. The first crop of solids on recrystallisation from benzene-pet.ether mixture and drying gave 0.24 g (ca. 45%) of product melting at 152-4^oC.

Analysis :	% Sn	% C	% H
Found :	20.96	64.68	5.0
Calculated for Bz_3SnBF :	21.85	64.4	4.8

25. Reaction of BFH with $(Bz_3Sn)_2O$:

0.4 g (~ 0.0005 mole) of $(Bz_3Sn)_2O$ and 0.15 g (~ 0.001 mole)of BFH were refluxed in benzene for 15-20 minutes. The faint yellow solution was shaken with $NaHCO_3$, filtered and allowed to stand when slight turbidity appeared.Turbidity was removed by filtration, diluted with pet.ether and stored at 5^oC overnight. The first crop of product was recrystallised from bez-pet.ether mixture and was identified as Bz_3SnBF on the basis of mixed melting point, IR and analytical data. Yield : 0.3 g (ca. 55 %).

26. Reaction of BFH with Bu_2SnO :

0.26 g (>0.001 mole) of Bu_2SnO and 0.3 g (0.002 mole) of BFH

were shaken for 5 minutes in 10 ml warm benzene-ether mixture (50:50) and filtered. The filtrate was diluted with pet.ether and allowed to stand at 5°C. The white precipitate obtained was recrystallised from benzene-pet.ether mixture and dried.

Yield : 0.44 g (ca. 82 %). Mp. 65-68°C.

Analysis :	% Sn	% C	% H
Found :	20.86	54.9	5.4
Calculated for $Bu_2Sn(BF)_2$:	22.26	54.34	5.28

27. Reaction of BFH with Oct_2SnO :

0.18 g (0.0005 mole) of Oct_2SnO and 0.15 g (0.001 mole) of BFH were shaken for 5 minutes in 10 ml warm benzene-ether mixture (50:50). The clear solution was diluted with pet.ether and stored at 5°C. The white solid obtained was recrystallised from benzene-pet.ether mixture and dried.

Yield : 0.25 g (ca. 80 %). Mp. 73-49°C.

Analysis :	% Sn	% C	% H
Found :	18.72	59.2	5.9
Calculated for $Oct_2Sn(BF)_2$:	18.38	59.81	6.85

28. Reaction of BFH with Me_2SnO :

0.08 g (~ 0.0005 mole) of Me_2SnO and 0.15 g (~ 0.001 mole) of BFH were taken in 5ml benzene-ether mixture (50:50) and shaken for 5 minutes. Filtered and the filtrate allowed to stand at 5°C.

The white solid separated was recrystallised from ether and dried.

Yield : 0.155 g (ca. 70 %). Mp. 182^{o}C.

Analysis :	% Sn	% C	% H
Found :	-	48.75	3.5
Calculated for $Me_2Sn(BF)_2$:	26.46	48.43	3.59

29. Reaction of BFH with Ph_2SnO :

0.15 g (~ 0.0005 mole) of Ph_2SnO and 0.15 g (0.001 mole) of BFH were reacted following the same method as for reaction 28 above and the product collected in the same way.

Yield : 0.18 g (ca. 64%). Mp. 117^{o}C.

Analysis :	% Sn	% C	% H
Found :	-	59.4	4.15
Calculated for $Ph_2Sn(BF)_2$:	20.7	58.95	3.5

III.2.C. Physical measurements :

All analytical work were carried out at C.D.R.I.,Lucknow, India. The IR spectra were recorded in KBr discs using PERKIN ELMER 983 and 783 spectrophotometers at R.S.I.C., NEHU and I.A.C.S. Jadavpur, India, respectively. IR spectra in Nujol mull were recorded using a PYE UNICAM SP3-300S spectrophotometer at North Bengal University, Dist. Darjeeling ,India.

All UV spectra were recorded with a SHIMADZU UV240 spectrophotometer using 1 cm quartz cells at North Bengal University.

^{1}H NMR spectra were recorded with VARIAN XL-200 and EM-390 spectrometers at I.A.C.S., Jadavpur and R.S.I.C., NEHU and JEOL GSX 400 NB at I.I.T., Madras, India.

III.3. *Results and discussion :*

In order to prepare the organotin α-keto carboxylates the following two methods were used :

(i) Reaction of the Na -salt of the α-keto acid with the triorganotin halides in ether or methanol,

$$R'\text{-}\overset{O}{\overset{\|}{C}}\text{-}COONa + R_3SnCl \longrightarrow 2\ R_3SnOCO\overset{O}{\overset{\|}{C}}\text{-}R' + H_2O \quad \text{------[1]}$$

and (ii) reaction of the α-keto acid (HL) with the appropriate organostannoxane in dry benzene/solvent ether,

$$2\ R'\text{-}\overset{O}{\overset{\|}{C}}\text{-}COOH + (R_3Sn)_2O \longrightarrow 2\ R_3SnOCO\overset{O}{\overset{\|}{C}}\text{-}R' + H_2O \quad \text{-----[2]}$$

$$2\ R'\text{-}\overset{O}{\overset{\|}{C}}\text{-}COOH + R_2SnO \longrightarrow R_2Sn(OCO\overset{O}{\overset{\|}{C}}\text{-}R')_2 + H_2O \quad \text{-----[3]}$$

While the reaction between triorganotin halides and the Na-salts of the acids proceeded as expected giving triorganotin carboxylates, the reaction between the acids and organotin oxides yielded a variety of apparently unexpected products in addition to the carboxylates, depending on the reactants and reaction conditions used. In fact, the yield of the triorganotin

carboxylates were almost negligible (<10 %) in some of the latter case indicating a profound influence of the α-keto group on the reaction. In order to understand the rather surprising results of these reactions, it is necessary to first discuss the different products obtained.

The most interesting feature of these reactions is the formation of addition complexes of the type $R_3SnOH.HL$. The reactions of $CH_3COCOOH$ (PvH) and $PhCH_2COCOOH$ (PPvH) with some hexaorgano distannoxanes under very mild conditions, leading to the addition products, deserve special attention. For example, when a solution of $(Ph_3Sn)_2O$ in benzene/ether is stirred with PvH in 1:2 proportion for 2-3 minutes a white solid is precipitated immediately. This product has an empirical formula of $Ph_3SnOH.PvH$ on the basis of elemental analysis and possesses very interesting

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chemical and spectroscopic properties. Because of the uniqueness of these compounds their preparation and characterisation will be discussed separately.

These acids also produce other interesting compounds of the type $R_2Sn(L)OH$, which are hydrolysates of the diorganotin dicarboxylates. Incidentally, $Ph_2Sn(L)OH$ type of compounds have also been formed during the reaction of $(Ph_3Sn)_2O$ with the acids, presumably, through the cleavage of Ph—Sn bonds.

Interestingly, the reaction of PhCOCOOH (BFH) with the stannoxanes has produced only the carboxylate derivatives of the type $R_nSn(OCOCOR')_{4-n}$ (n = 2,3).

In the present chapter, characterisation of the tri- and diorganotin keto carboxylates and the hydrolysates of the diorganotin derivatives are being presented. A summary of the reaction conditions used for the preparation of the keto carboxylates, their yields and melting points are given in table-III.1. Analytical data and the solubilities of the compounds are recorded in table-III.2.

III.3.1. Characterisation Of The Products :

A reference to the table-III.3. would reveal that the reaction of triorganotin halides with the Na-salts of benzoyl formic acid (BFH) and phenyl pyruvic acid (PPvH) gives moderately

Table:-III.1.

Summary of reaction conditions and products.

Sl. no.	Reactants and mole ratio	Reaction conditons	Time	Product	% yield, Mp.
1.	Ph_3SnCl + NaPv (1:1)	Stirred in ether containing little methanol and excess NaPv. Evaporated to dryness and extracted with pet.ether. Solid obtained from the extract recrystallised from same solvent.	8 hrs.	Ph_3SnPv	10, 114-6°C
2. (i)	$(Ph_3Sn)_2O$ + PvH (1:2)	Refluxed in ether. Filtered, and filtrate evaporated at r.t. The resultant mass extracted with pet.ether. Pet. ether extract on evaporation and recrystallisation from the same solvent gave (a)	1 hr.	(a) Ph_3SnPv	3, 114-6°C
		The residue after reflux and that from the pet.ether extract on washing with bez. and ether gave identical products (b)		(b) $Ph_2Sn(Pv)OH$	-
		When the ether was distilled out completely after the reaction, the distillate was found to contain benzene in ether (c).		(c) C_6H_6	

Table-III.1(contd.).

2. (ii)	$(Ph_3Sn)_2O$ + PvH (1:2)	Refluxed in bez. Filtered, residue washed with bez. and ether gave (a) Filtrate evaporated at r.t. and washed with cold ether. The remaining solid was extracted with hot bez., concentrated and allowed to crystallise. Product recrystallised with bez-pet.ether (b). The residue from the bez.-extract on washing with ether and recrystallisation from methanol gave (c).	12 hrs.	(a) $[PhSn(Pv)O]_n$	-
				(b) Ph_4Sn	227°C
				(c) $Ph_2Sn(Pv)OH$	-
3.	Bu_3SnCl + NaPv (1:1)	Stirred in ether with excess NaPv. Evaporated to dryness at r.t. and extracted with pet.ether. Solid separated from the extract was recrystallised.	8 hrs.	Bu_3SnPv	11, 80-2°C
4.	$(Bu_3Sn)_2O$ + PvH (1:2)	Refluxed in dry bez. Solution shaken with $NaHCO_3$ and filtered. Filtrate concentrated to a small volume, diluted with pet.ether and stored at 5°C. Thick yellow liquid separated. Upper pet.ether-bez layer crystallised.	16 hrs.	Bu_3SnPv	20, 80-2°C

Table-III.1(contd.).

5. (i)	Bz_3SnCl + NaPv (1:1)	Stirred in ether containing little methanol with excess NaPv. Evaporated to dryness at r.t. and extracted with cold ether and allowed to crystallise. The second crop recrystallised from cold ether.	6 hrs.	Bz_3SnPv	8, 104-8°C
5. (ii)	$(Bz_3Sn)_2O$ + PvH (1:2)	Refluxed in bez. and filtered. Residue washed with ether and recrystallised from methanol.	10 hrs.	$[BzSn(Pv)O]_n$	-
6. (i)	Oct_2SnO + PvH (1:2)	Oxide and acid shaken in bez. Decanted and precipitated with pet.ether. Solid dissolved in ether and reprecipitated with pet.ether.	5 min.	$Oct_2Sn(Pv)OH$	80, Decomp. >150°C
6. (ii)	,,	Refluxed in bez. Solution shaken with $NaHCO_3$, concentrated, diluted with pet.ether. Product recrystallised from bez.-pet.ether.	10 hrs.	$Oct_2Sn(Pv)_2$	32, 112-4°C
7. (i)	Bu_2SnO + PvH (1:2)	Organotin and acid shaken in warm bez-ether (1:1) mixture. Solution decanted and precipitated with pet.ether. Solid washed with ether.	2-3 min.	$Bu_2Sn(Pv)OH$	84, Decomp. >234°C

Table-III.1(contd.).

7. (ii)	,,	Refluxed in dry bez. Solution shaken with $NaHCO_3$, concentrated, diluted with pet.ether and stored at 5°C. Thick yellow liquid separated. Upper pet.-bez layer crystallised.	14 hrs.	$Bu_2Sn(Pv)_2$	23, 157°C
8. (i)	Me_2SnO + PvH (1:2)	Organotin and acid shaken in warm bez-ether mixture. Solution decanted and precipitated with pet.ether. Solid washed with ether	2-3 min.	$Me_2Sn(Pv)OH$	80, -
8. (ii)	,,	Refluxed in bez. Solution shaken with $NaHCO_3$, and concentrated.	8 hrs.	$Me_2Sn(Pv)_2$	18, -
9. (i)	Ph_2SnO + PvH (1:2)	Organotin and acid shaken in warm bez-ether (1:1) mixture. Solution decanted, precipitated with pet.ether. Solid washed with ether.	2-3 min.	$Ph_2Sn(Pv)OH$	78, -
9. (ii)	,,	Refluxed in bez. Residue washed with ether and recrystallised from methanol.	8 hrs.	$[PhSn(Pv)O]_n$	-
10.	Ph_3SnCl + NaPPv (1:1)	Stirred in ether containing little methanol. Evaporated and extracted with cold ether. Recrystallised from bez-pet.ether.	6 hrs.	Ph_3SnPPv	68, 139-40°C

Table-III.1(contd.).

11. (i)	$(Ph_3Sn)_2O$ + PPvH (1:2)	Solution of stannoxane in bez/ ether shaken with acid, diluted with pet.ether, allowed to stand at 5°C for several hrs. Product washed with cold ether.	5 min.	Ph_3SnPPv	70, 139-40°C
11. (ii)	$(Ph_3Sn)_2O$ + PPvH (1:2)	Refluxed in bez. Filtered, residue washed with ether, gave (a). Filtrate evaporated at r.t. and washed with cold ether and residue extracted with hot bez. Bez. extract gave (b) on recrystallisation from bez. -pet.ether. Remaining residue (c) was recrystallised from methanol. When refluxed in ether, the above reaction [11.(ii)] gave C_6H_6 as one of the products, along with (a) and (c).	12 hrs.	(a) $[PhSn(PPv)O]_n$	-
				(b) Ph_4Sn	227°C
				(c) $Ph_2Sn(PPv)OH$	-
12.	Bu_3SnCl + NaPPv (1:1)	Stirred in ether containing little methanol with excess of NaPPv. Filtered, evaporated at r.t. and extracted with pet.ether and evaporated.	8 hrs.	Bu_3SnPPv	98, Liq.
13.	$(Bu_3Sn)_2O$ + PPvH (1:2)	Refluxed in bez. with excess acid. Solution shaken with $NaHCO_3$ and filtered. Evaporated at r.t. and extracted with cold pet.ether and the solvent allowed to evaporate.	10 hrs.	Bu_3SnPPv	55, Liq.

Table-III.1(contd.).

14.	Bz_3SnCl + NaPPv (1:1)	Stirred in ether containing MeOH. Filtered, Evaporated at r.t. and extracted with ether. The extract stored at 5^oC.	7 hrs.	Bz_3SnPPv	45, 134^oC
15.	$(Bz_3Sn)_2O$ + PPvH (1:2)	Shaken in Bez.-ether mixture. Solution kept at 5^oC. The solid product obtained was washed with cold ether.	5 min.	Bz_3SnPPv	78, 134^oC
16. (i)	Bu_2SnO + PPvH (1:2)	Shaken in warm bez.-ether mix. Filtered, diluted with ether and allowed to stand at 5^oC.	10 min.	$Bu_2Sn(PPv)_2$	72, Decomp $>170^oC$
16. (ii)	,,	Refluxed in bez.-ether mixture and filtered. Residue recrystallised from acetone, gave (a). Filtrate shaken with $NaHCO_3$, filtered, concentrated, diluted with pet.ether and stored at 5^oC. First crop of products rejected and the second crop recrystallised from bez.-pet.-ether (b).	8 hrs.	(a) $Bu_2Sn(PPv)OH$	25, 191^oC
				(b) $Bu_2Sn(PPv)_2$	68, Decomp $>170^oC$
17. (i)	Oct_2SnO + PPvH (1:2)	Shaken in hot ether, filtered, concentrated, diluted with pet -ether and kept in freeze. Product recrystallised from ether-pet.ether mix.	5 min.	$Oct_2Sn(PPv)_2$	60, $74-6^oC$
17. (ii)	,,	Refluxed in bez.-ether mixture and filtered. Residue rec-	9 hrs.	(a) $Oct_2Sn(PPv)OH$	55, 124^oC

Table-III.1(contd.).

		rystallised from acetone (a). Filtrate shaken with $NaHCO_3$, concentrated, diluted with pet. -ether and stored at 5°C. First crop recrystallised from acetone (a) and the second crop (b) recrystallised from ether-pet.ether mix.		(b) $Oct_2Sn(PPv)_2$	15, 74-6°C
18. (i)	Me_2SnO + PPvH (1:2)	Stannoxane and acid shaken in bez.-ether mix. Solution decanted and allowed to stand. Ppt. washed with ether.	2-3 min.	$Me_2Sn(PPv)_2$	46, Decomp >200°C
18. (ii)	,,	Refluxed in bez.-ether mix. filtered, shaken with $NaHCO_3$, concentrated, diluted with pet.ether and stored at 5°C.	8 hrs.	$Me_2Sn(PPv)OH$	16, 172°C
19.	Ph_2SnO + PPvH (1:2)	Refluxed in bez.-ether mix. Solution shaken with $NaHCO_3$, and allowed to stand. Ppt. washed with ether.	1 hr.	$Ph_2Sn(PPv)OH$	12, -
20.	Ph_3SnCl + NaBF (1:1)	Stirred in ether containing little MeOH, with excess Na-salt. Evaporated at r.t. and extracted with bez.-pet.ether mix., concentrated and allowed to crystallise. 2nd crop of products recrystallised from bez.-pet.ether.	6 hrs.	Ph_3SnBF	42, 149°C

Table-III.1(contd.).

21.	$(Ph_3Sn)_2O$ + BFH (1:2)	Solution of stannoxane in bez.-ether mix. shaken with acid. Diluted with pet.ether and kept at 5°C. product recrystallised from cold bez.-pet.ether.	5 min.	Ph_3SnBF	90, 149-50°C
22.	Bu_3SnCl + NaBF (1:1)	Stirred in ether with excess NaBF and filtered. Solvent evaporated at r.t. Redissolved in pet.ether, filtered and again evaporated at r.t.	10 hrs.	Bu_3SnBF	100, Liq.
23.	$(Bu_3Sn)_2O$ + BFH (1:2)	Refluxed in bez. with excess acid. Shaken with $NaHCO_3$, concentrated, diluted with pet. ether and stored at 5°C. Slight turbidity formed was removed by filtration. Solvent removed from the filtrate at r.t.	4 hrs.	Bu_3SnBF	96, Liq.
24.	Bz_3SnCl + NaBF (1:1)	Stirred in ether with excess NaBF and solvent removed at r.t. Extracted with bez.-pet. ether mixture, concentrated and allowed to crystallise. First crop recrystallised from bez.-pet.ether.	6 hrs.	Bz_3SnBF	45, 152-4°C
25.	$(Bz_3Sn)_2O$ + BFH (1:2)	Refluxed in bez.-ether mixture. Shaken with $NaHCO_3$, concentrated and allowed to stand. Sli-	20 min.	Bz_3SnBF	55, 152-4°C

Table-III.1(contd.).

		ght turbidity appeared, removed by filtration. Diluted with pet.ether and stored at 5°C. First crop of products recrysllised from bez.-pet.ether mix.			
26.	Bu_2SnO + BFH (1:2)	Shaken in hot bez.-ether mix., with small excess of oxide, filtered, diluted with pet.-ether and stored at 5°C. Product recrystallised from bez.-pet.ether mixture.	5 min.	$Bu_2Sn(BF)_2$	82, 65-8°C
27.	Oct_2SnO + BFH (1:2)	,,	5 min.	$Oct_2Sn(BF)_2$	80, 73-4°C
28.	Me_2SnO + BFH (1:2)	Shaken in hot bez.-ether mix., with small excess of oxide. Filtered and allowed to stand at 5°C. Product recrystallised from ether.	5 min.	$Me_2Sn(BF)_2$	70, 182°C
29.	Ph_2SnO + BFH (1:2)	,,	5 min.	$Ph_2Sn(BF)_2$	64, 117°C

Table:-III.2.

Analytical data and Solubilities of the Products.

Sl. No.	Compound	% Found / (Calculated) Sn	C	H	Solubilities
1.	Ph_3SnPv	26.1	58.8	4.6	Bez., P.eth., $CHCl_3$
		(27.06)	(57,8)	(4,13)	Et_2O, Ace.,Alc.
2.	Bu_3SnPv	31.02	49.0	8.5	,,
		(31.38)	(47.9)	(7.98)	
3.	Bz_3SnPv	-	61.3	4.8	,,
		(24.69)	(60.25)	(5.02)	
4.	$Bu_2Sn(Pv)_2$	30.82	42.1	6.5	,,
		(29.06)	(41.4)	(5.9)	
5.	$Me_2Sn(Pv)_2$	34.9	29.28	3.8	Alc.; slightly soluble
		(36.64)	(29.8)	(3.7)	in Et_2O, Bez., Ace.
6.	$Oct_2Sn(Pv)_2$	23.72	51.7	8.02	Bez., P.eth., $CHCl_3$,
		(22.78)	(50.96)	(7.72)	Et_2O, Ace., Alc.
7.	$Bu_2Sn(Pv)OH$	34.64	40.45	6.1	Alc.
		(35.1)	(39.3)	(6.54)	
8.	$Me_2Sn(Pv)OH$	46.16	23.3	4.4	,,
		(46.82)	(23.81)	(3.97)	
9.	$Oct_2Sn(Pv)OH$	25.2	51.6	7.5	Alc., Et_2O., Ace.
		(26.34)	(50.89)	(8.48)	
10.	$Ph_2Sn(Pv)OH$	30.1	48.1	3.8	Alc.
		(31.38)	(47.87)	(3.72)	
11.	$[PhSn(Pv)O]_n$	38.5	34.8	2.8	,,
		(39.6)	(36.2)	(2.7)	
12.	$[BzSn(Pv)O]_n$	36.26	39.2	3.48	,,
		(37.82)	(38.46)	(3.2)	
13.	Ph_3SnPPv	22.9	63.8	3.7	Alc., Ace., Et_2O, Bez.,
		(23.0)	(63.15)	(4.28)	Sl.sol.in $CHCl_3$(h).
14.	Bu_3SnPPv	26.84	56.65	5.8	Bez., P.eth, $CHCl_3$,
		(26.1)	(55.75)	(7.52)	Et_2O, Ace.,Alc.

Table-III.2(contd.).

15. Bz_3SnPPv	22.1 (21.3)	64.56 (64.98)	5.4 (5.05)	Alc., Ace., Et_2O. Bez., Sl.sol.in $CHCl_3$(h).
16. $Bu_2Sn(PPv)_2$	22.49 (21.15)	54.8 (55.91)	5.6 (5.73)	Alc., Ace., Et_2O, Bez., Sl.sol.in $CHCl_3$(h).
17. $Oct_2Sn(PPv)_2$	18.65 (17.61)	59.02 (60.89)	6.85 (7.13)	,,
18. $Me_2Sn(PPv)_2$	26.2 (24.89)	49.85 (50.63)	4.1 (4.22)	Alc., Sl.sol. in Ace., Et_2O, Bez.
19. $Bu_2Sn(PPv)OH$	30.15 (28.64)	48.8 (49.51)	5.4 (6.3)	Alc., Ace., Et_2O.
20. $Oct_2Sn(PPv)OH$	23.76 (22.52)	58.74 (57.25)	7.5 (8.01)	,,
21. $Me_2Sn(PPv)OH$	- (35.97)	41.07 (40.24)	3.8 (4.26)	Alc.
22. $Ph_2Sn(PPv)OH$	27.56 (26.1)	57.4 (55.75)	3.7 (3.98)	,,
23. $[PhSn(PPv)O]_n$	32.6 (31.55)	47.3 (48.12)	3.7 (3.2)	,,
24. Ph_3SnBF	23.1 (23.69)	61.8 (62.65)	4.5 (4.02)	Bez., $CHCl_3$, CCl_4(h), Et_2O, Ace., Alc.
25. Bu_3SnBF	26.6 (26.94)	55.1 (54.79)	7.7 (7.3)	,,
26. Bz_3SnBF	20.96 (21.85)	64.68 (64.4)	5.0 (4.8)	,,
27. $Bu_2Sn(BF)_2$	20.86 (22.26)	54.9 (54.34)	5.4 (5.28)	,,
28. $Me_2Sn(BF)_2$	- (26.46)	48.75 (48.43)	3.5 (3.59)	Bez.(h), $CHCl_3$, Et_2O,
29. $Oct_2Sn(BF)_2$	18.72 (18.38)	59.2 (59.81)	5.9 (6.85)	Bez., P.eth., CCl_4, $CHCl_3$, Et_2O, Ace., Alc.
30. $Ph_2Sn(BF)_2$	- (20.7)	59.4 (58.95)	4.15 (3.5)	Bez., $CHCl_3$, Et_2O, Ace., Alc.

good yields of the triorganotin keto carboxylates, but with the Na-salt of pyruvic acid (PvH) the yields are very poor. Although no explanation for this observation is readily forthcoming , one of the probable reasons may be the fact that the pyruvate ion is susceptible to extensive polymerisation, catalysed by base[29], traces of which are produced due to absorption of moisture, by the extremely hygroscopic Na-pyruvate, during handling.

This method of reacting organotin halides with the Na-salts, has however, not been found to be suitable for the preparation of

Table-III.3.

Reaction of R_3SnCl with R'COCOONa producing $R_3SnOCOCOR'$:

	% yield of products.		
R_3SnCl / R'COCOONa	R = n-Bu	R = Ph	R = $PhCH_2$
R' = CH_3	11	10	8
R' = $PhCH_2$	98	68	44
R' = Ph	100	42	45

diorganotin derivatives of the keto acids, due to the formation of highly polymeric insoluble products, which are difficult to characterise.

The reaction between appropriate organostannoxanes and the keto acids, carried out by heating them in dry benzene/solvent ether in 1:2 mole ratio, on the other hand, have produced both tri- and diorganotin ketocarboxylates. While the carboxylate derivatives of benzoyl formic acid (BFH) and phenyl pyruvic acid (PPvH) were obtained in good yields under mild conditions, those of pyruvic (PvH) were obtained under comparatively drastic conditions and the yields were also very poor (table-III.1.). The percentage yields of the triorganotin ketocarboxylates obtained from the reaction of triorgano stannoxanes with the keto acids are shown in table-III.4.

Table:-III.4.

Reaction of $(R_3Sn)_2O$ with R'COCOOH producing $R_3SnOCOCOR'$.

	% yield of products.		
R R' (Taft's constant)	n-Bu	Ph	$PhCH_2$
CH_3 (-0.05)	20	3	-
$PhCH_2$ (0.04)	55	70	78
Ph (0.1)	90	90	55

From the data in tables III.3 and III.4 it is seen that both the methods give very high yields of the triorganotin derivatives of PhCOCOOH (BFH) and very low yields for the derivatives of $CH_3COCOOH$ (PvH) . This clearly displays a distinct pattern and if we look at the values of the Taft's constant of the R' groups (table-III.4.), we find that the yield of the carboxylates increases with increasing Taft's constant. This would suggest that electronic and other factors are responsible for the exceptionally poor yields of the triorganotin pyruvates.

These observations coupled with the fact, that pyruvic acid reacts with some bis(triorganotin) oxides giving very high yield of the addition product, whereas, benzoyl formic acid forms no such compound, shows that these acids differ remarkably in their reactions with organostannoxanes. This difference in the role of the ligand in relation to the formation of the ketocarboxylates or the addition products will be discussed latter.

The characteristics of the tri- and diorganotin ketocarboxylates and the carboxylato diorganotin hydroxides are now discussed separately.

III.3.1A. Triorganotin Keto Carboxylates ($R_3SnOCOCOR'$) :

Reference to tables-III.1 and III.2 reveals that the triorganotin ketocarboxylates have low melting points and are

fairly soluble in nonpolar organic solvents like typical organotin carboxylates. Analytical and spectroscopic data (tables III.2 and III.6, III.8, III.9) have provided valuable information regarding their composition and structure.

Before undertaking to discuss the spectroscopic properties of the triorganotin ketocarboxylates, it will be relevant as well as instructive to have a close look at the IR spectra and the molecular geometry of the free acids.

(i) IR spectra of the free acids :

The IR spectra of the α-keto acids used in the present investigation are shown in figures III.1-III.3 and the spectral data given in table-III.6A.

In free pyruvic acid (PvH) and benzoyl formic acid (BFH) there are very broad bands in the region 3600-2900 cm^{-1} indicating the presence of hydrogen bonded dimers. In CCl_4 solution of PvH this band, however, becomes sharp and absorbs moderately at 3420 cm^{-1} like monomers. The ν_{asOCO} and $\nu_{C=O}$ frequencies, which overlap into a strong broad band in the region 1750-1720 cm^{-1} in neat PvH also get split into two strong sharp bands at 1790 and 1725 cm^{-1} in CCl_4 solution. The 1790 cm^{-1} band in CCl_4 solution may reasonably be attributed to the carboxyl C=O stretch of the monomeric form of the acid[90]. Therefore, it is apparent that PvH is monomeric in CCl_4 solution and occurs as a dimeric species in

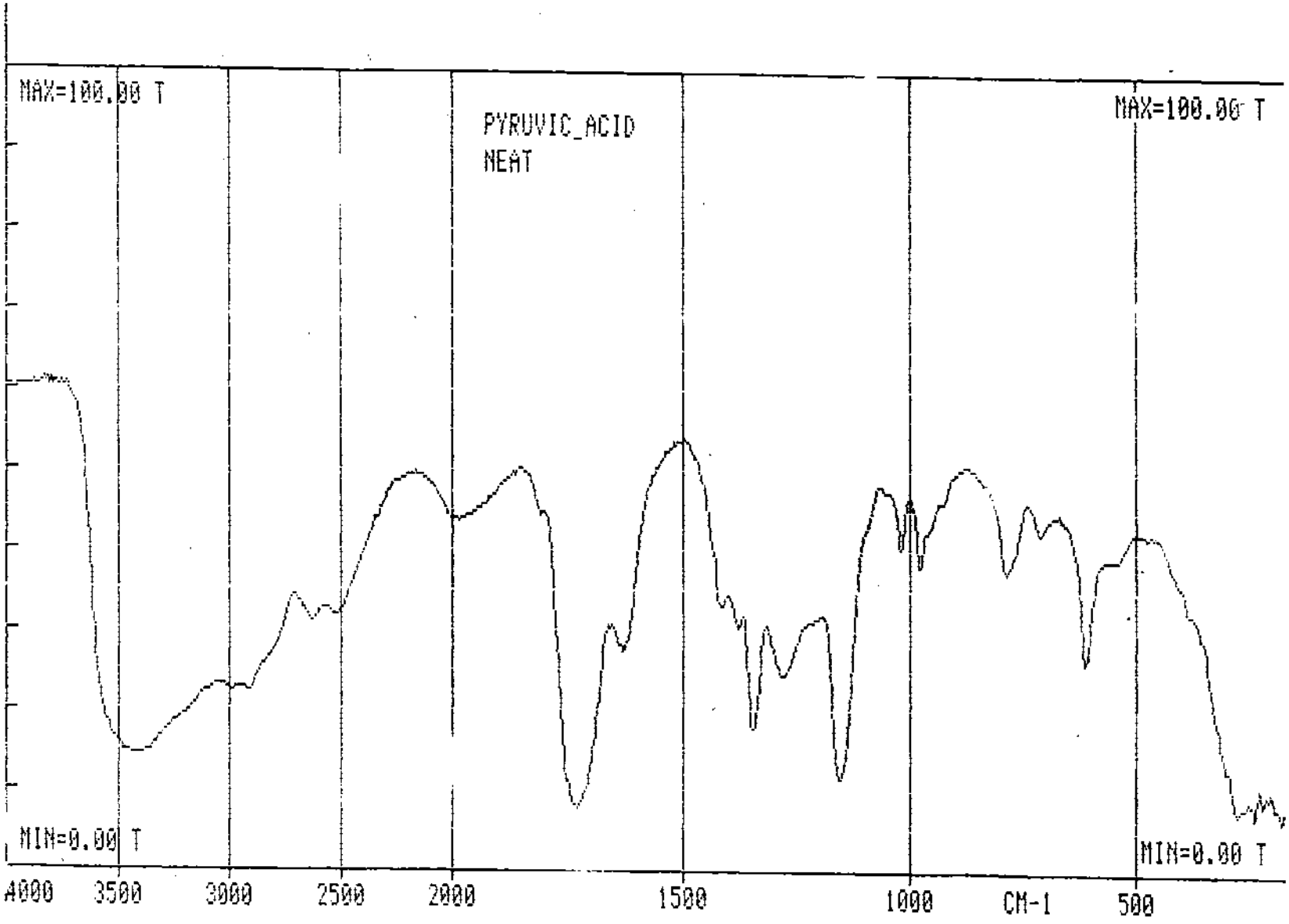


Fig.III.1. IR Spectrum of PvH (neat).

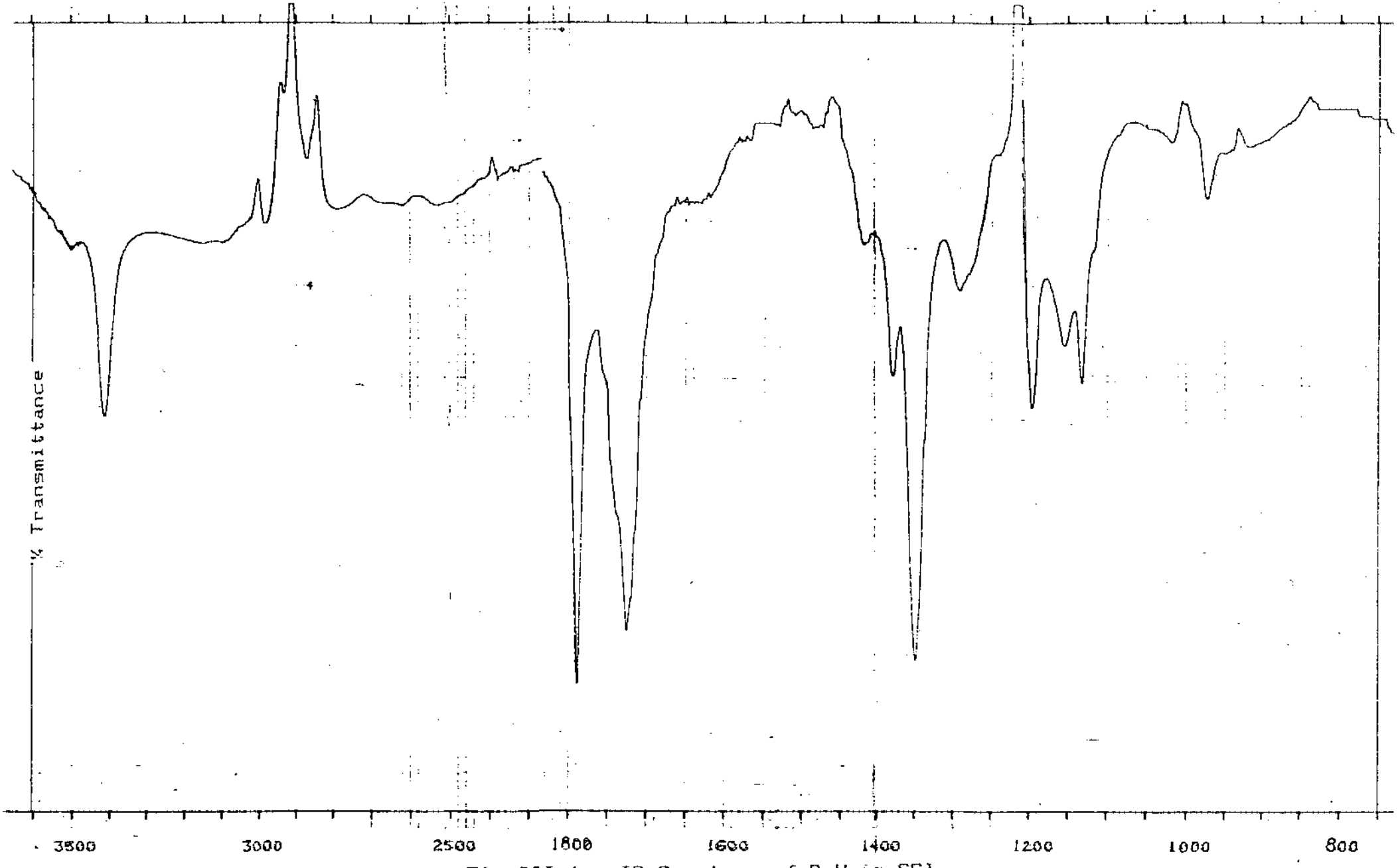


Fig.III.1a. IR Spectrum of PvH in CCl_4.

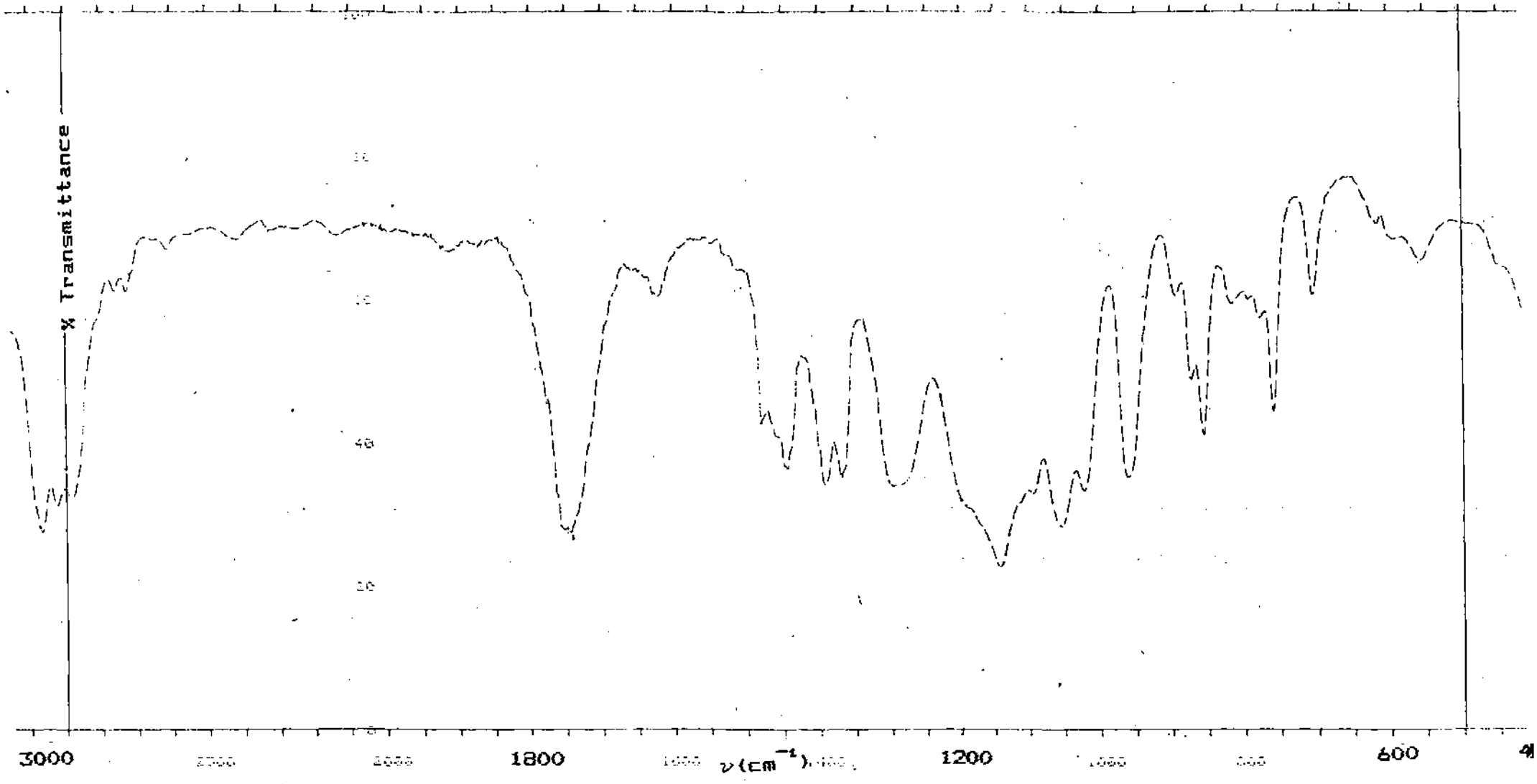


Fig.III.1b. IR Spectrum of PvEt (neat).

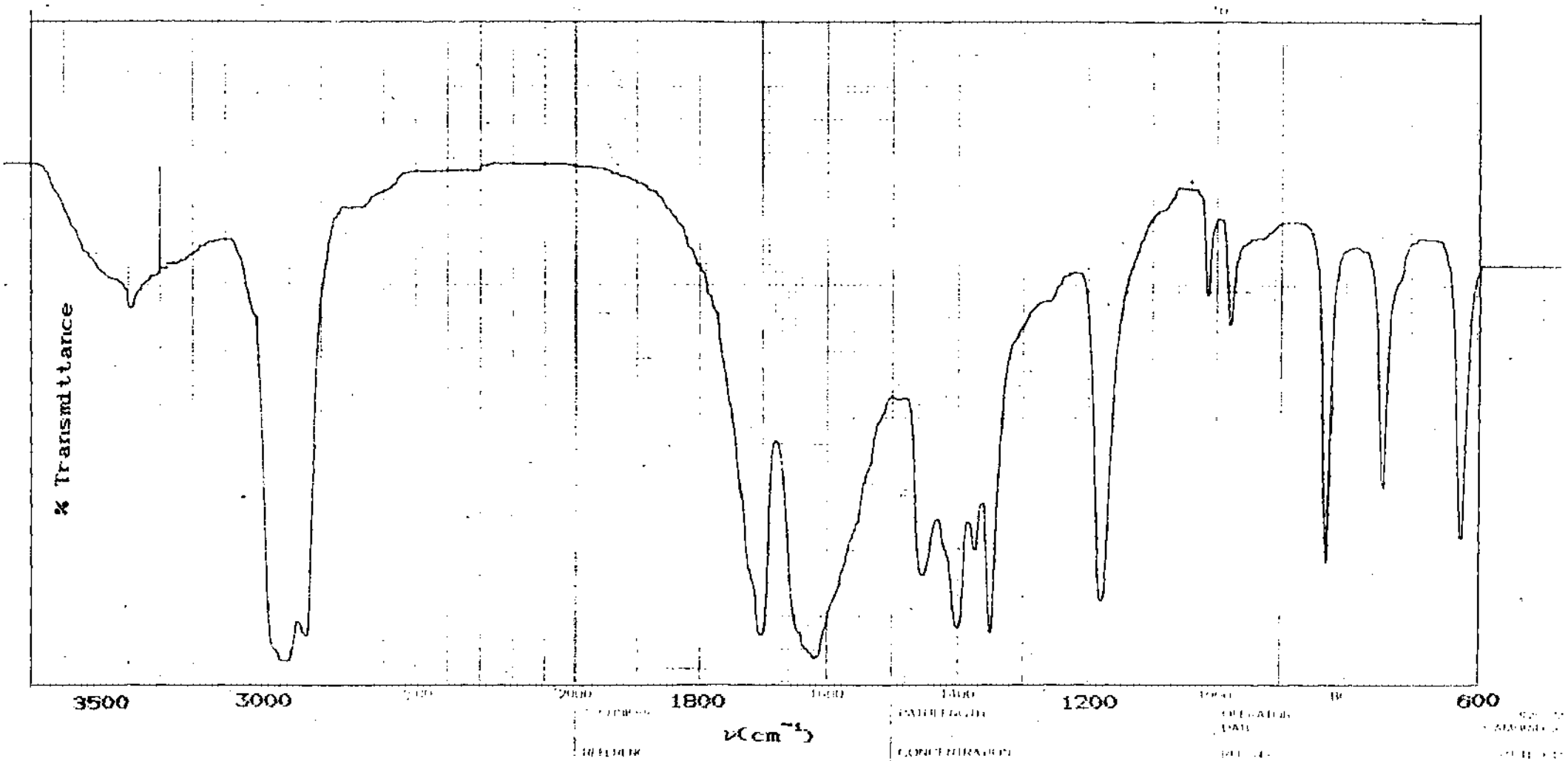


Fig.III.1c. IR Spectrum of NaPv in Nujol.

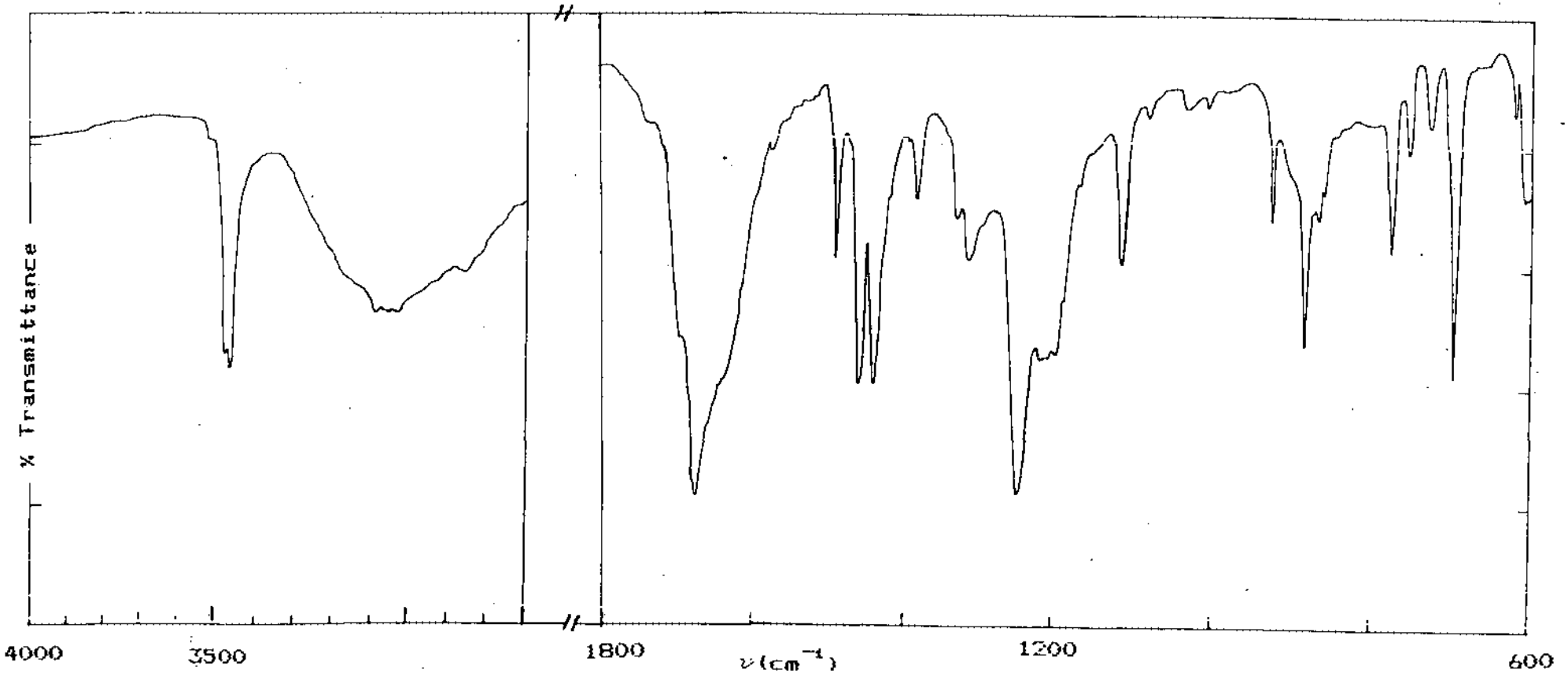


Fig.III.2. IR Spectrum of PPvH in KBr.

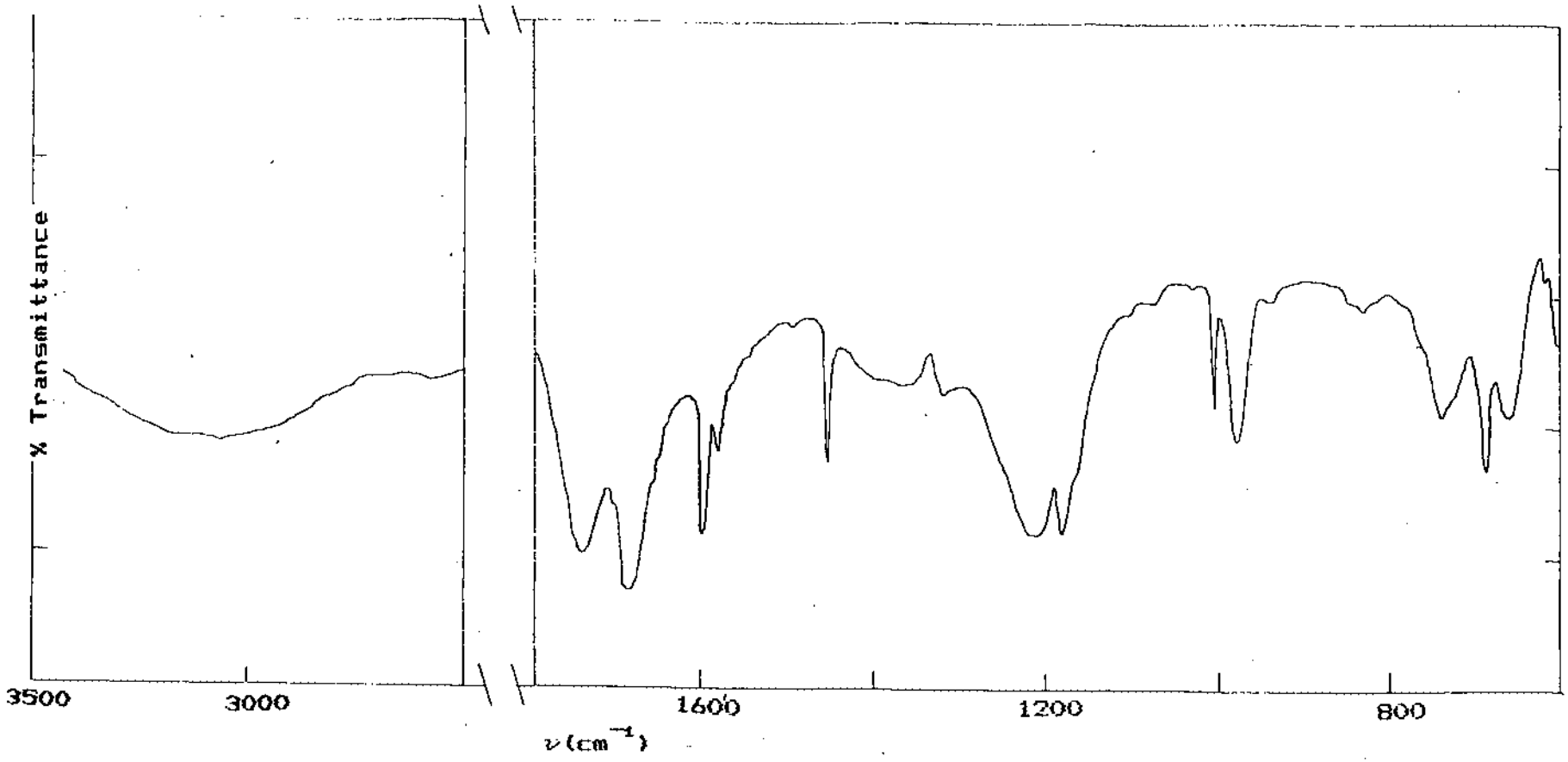


Fig.III.3. IR Spectrum of BFH in KBr.

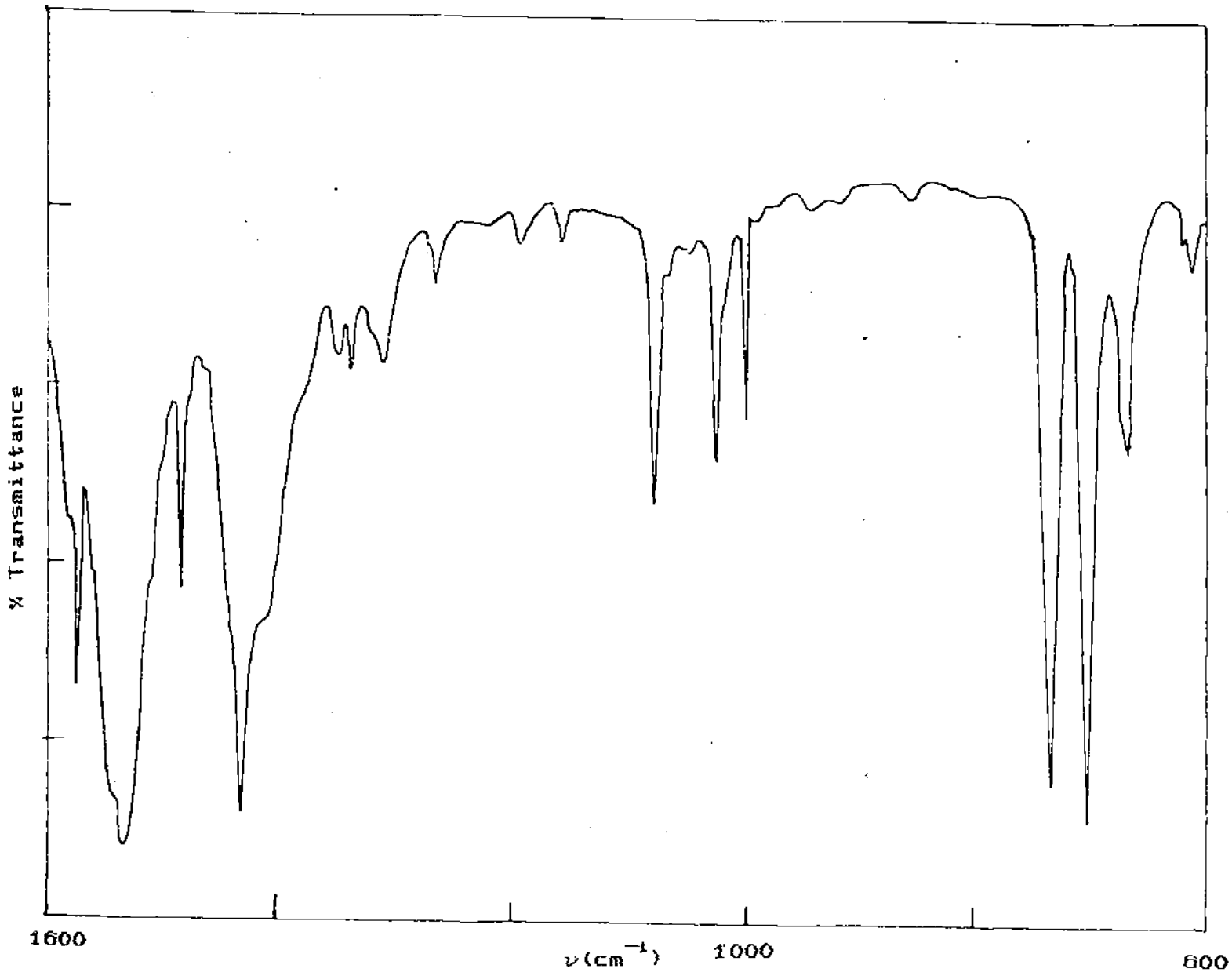


Fig.III.4. IR Spectrum of Ph_3SnPy in KBr.

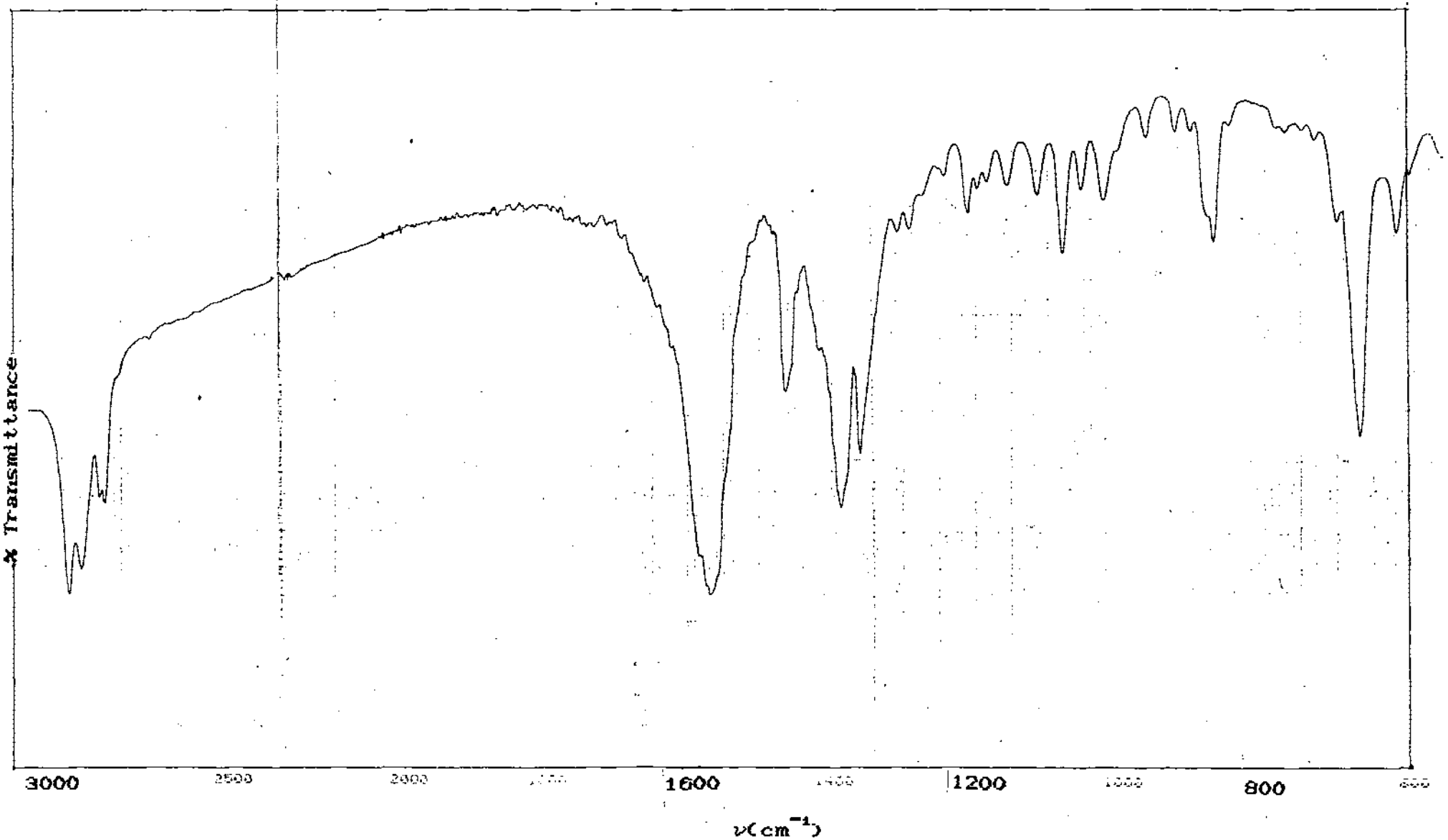


Fig.III.5. IR Spectrum of Bu_3SnPv in KBr.

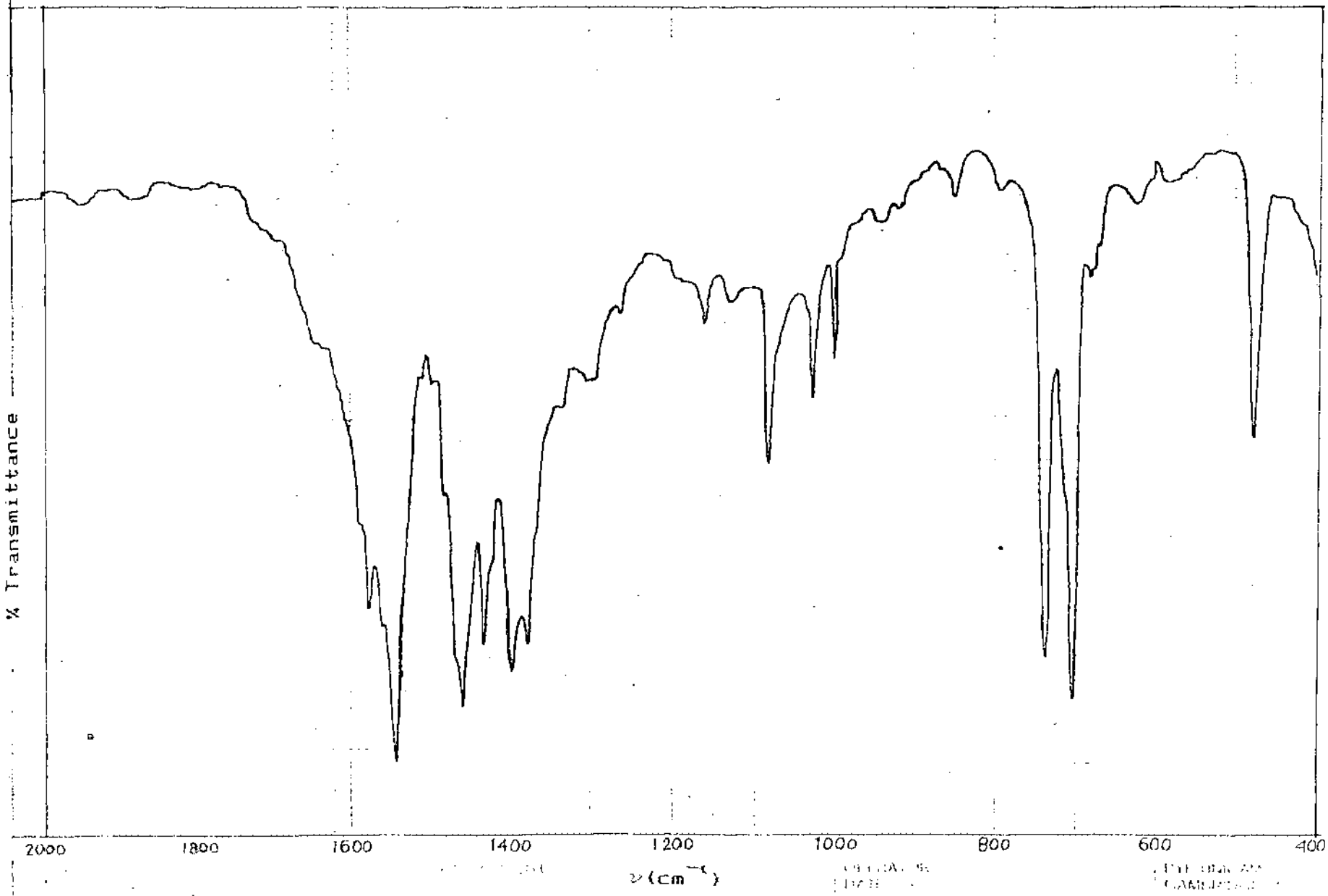


Fig.III.6. IR Spectrum of Ph_3SnPPv in Nujol.

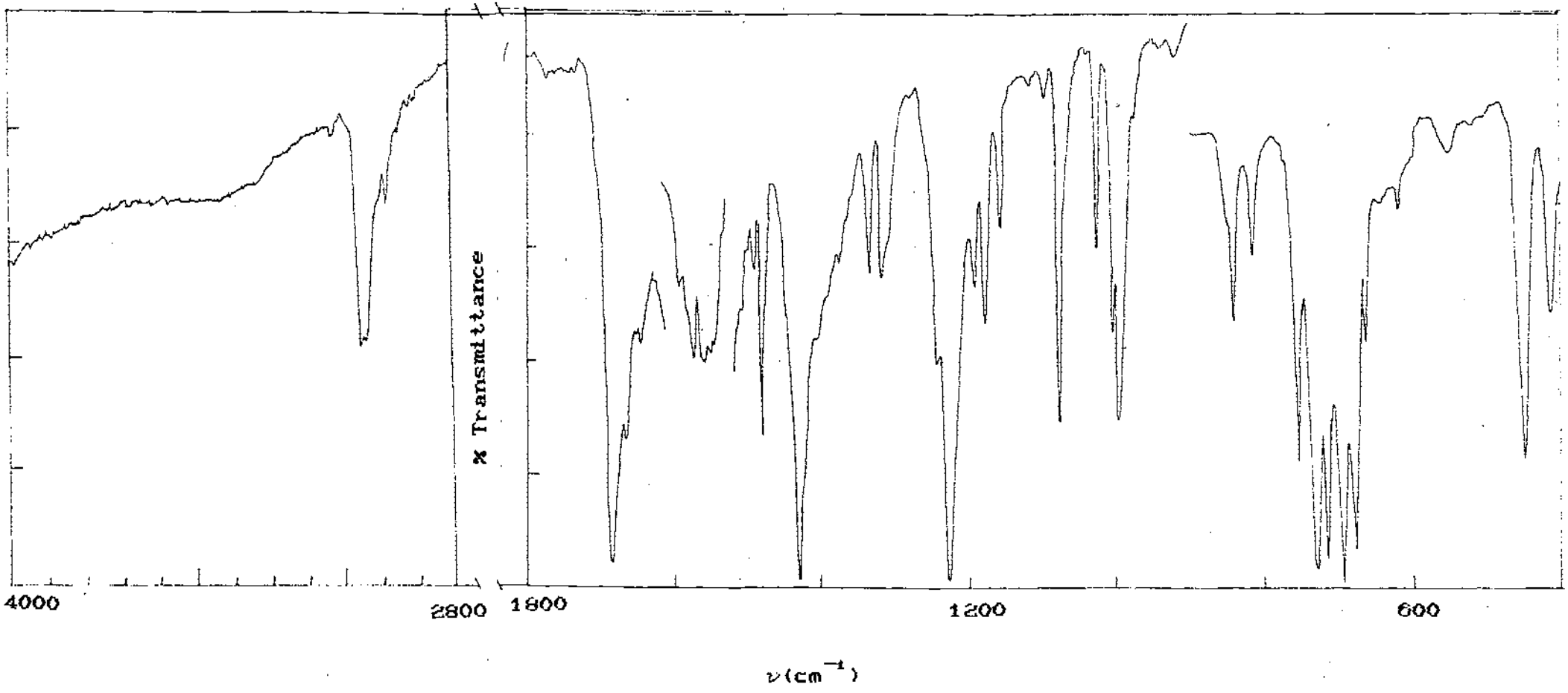


Fig.III.7. IR Spectrum of Ph_3SnBF in KBr.

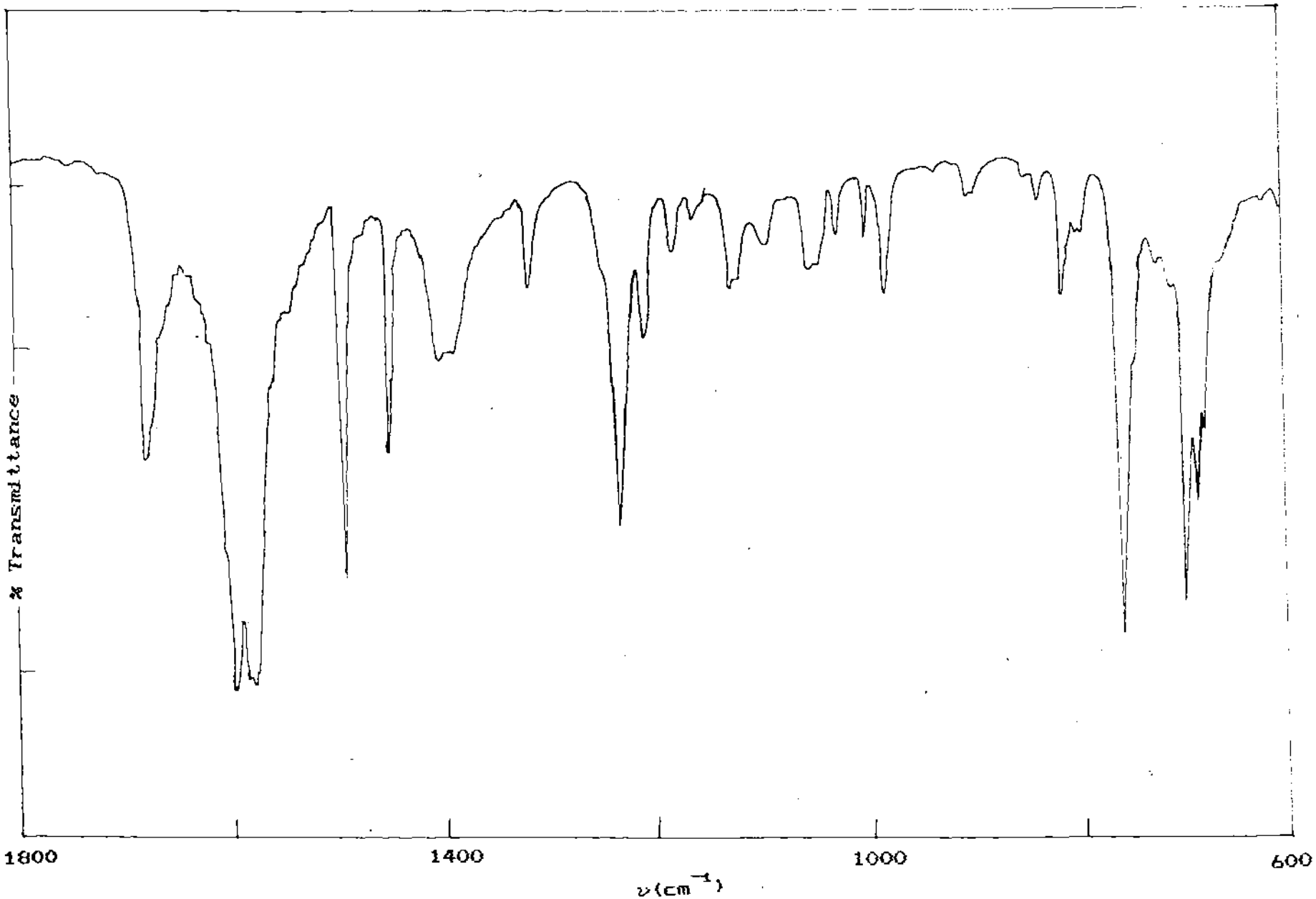


Fig.III.8. IR Spectrum of Bz_3SnBF in KBr.

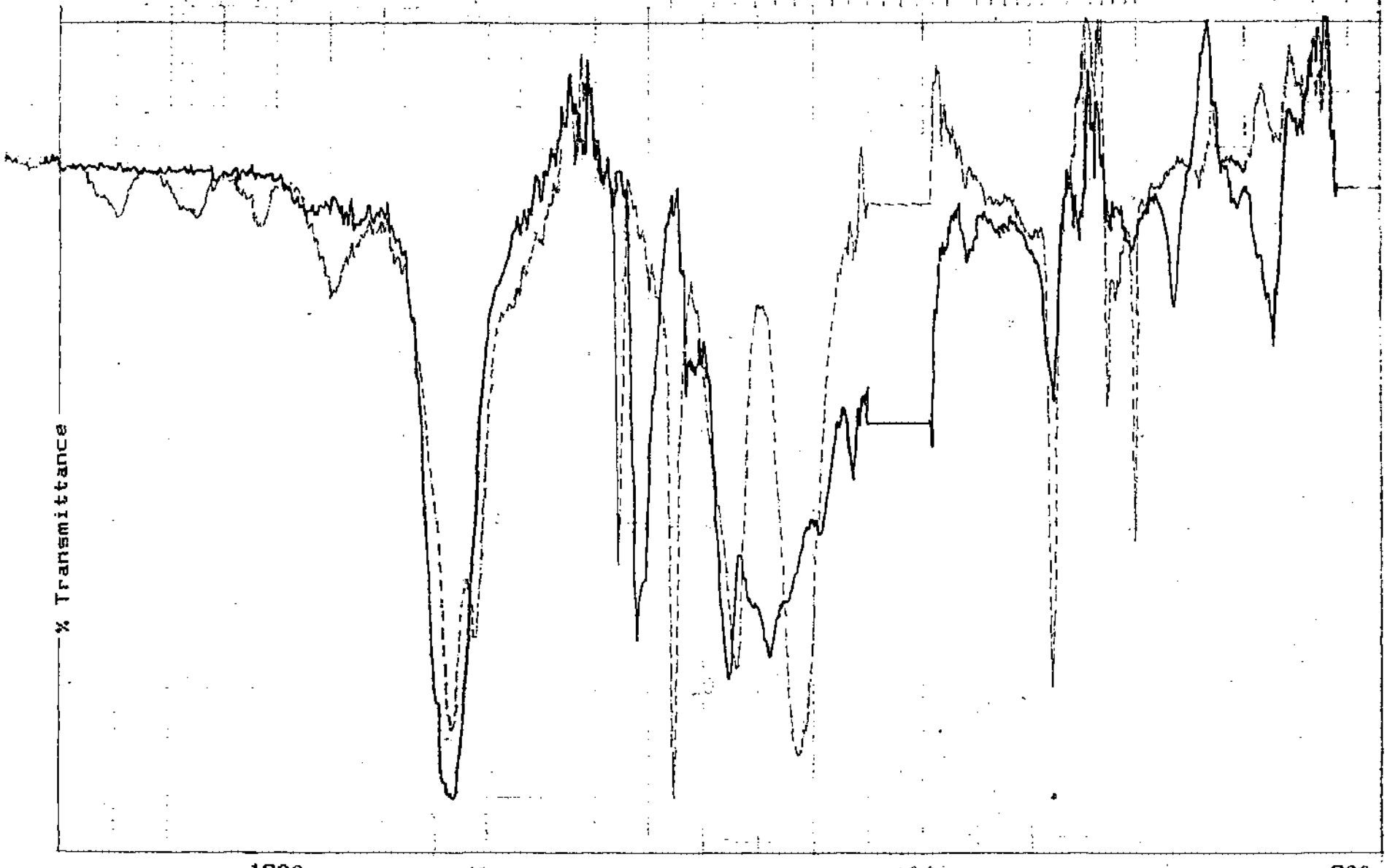


Fig.III.9. IR Spectra of Ph_3SnPv (------) and Bu_3SnPv (———) in $CHCl_3$.

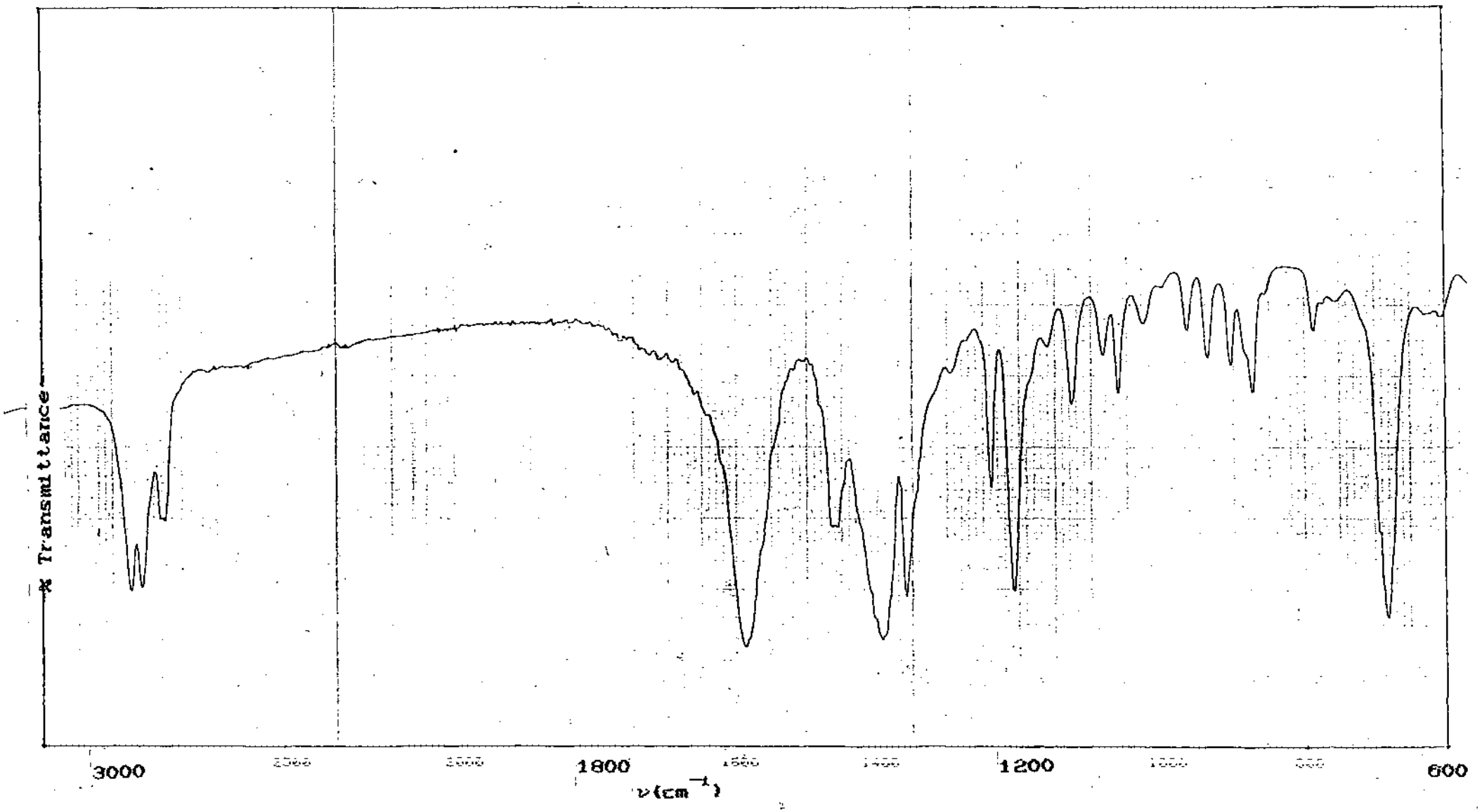


Fig.III.10. IR Spectrum of $Bu_2Sn(Pv)_2$ in KBr.

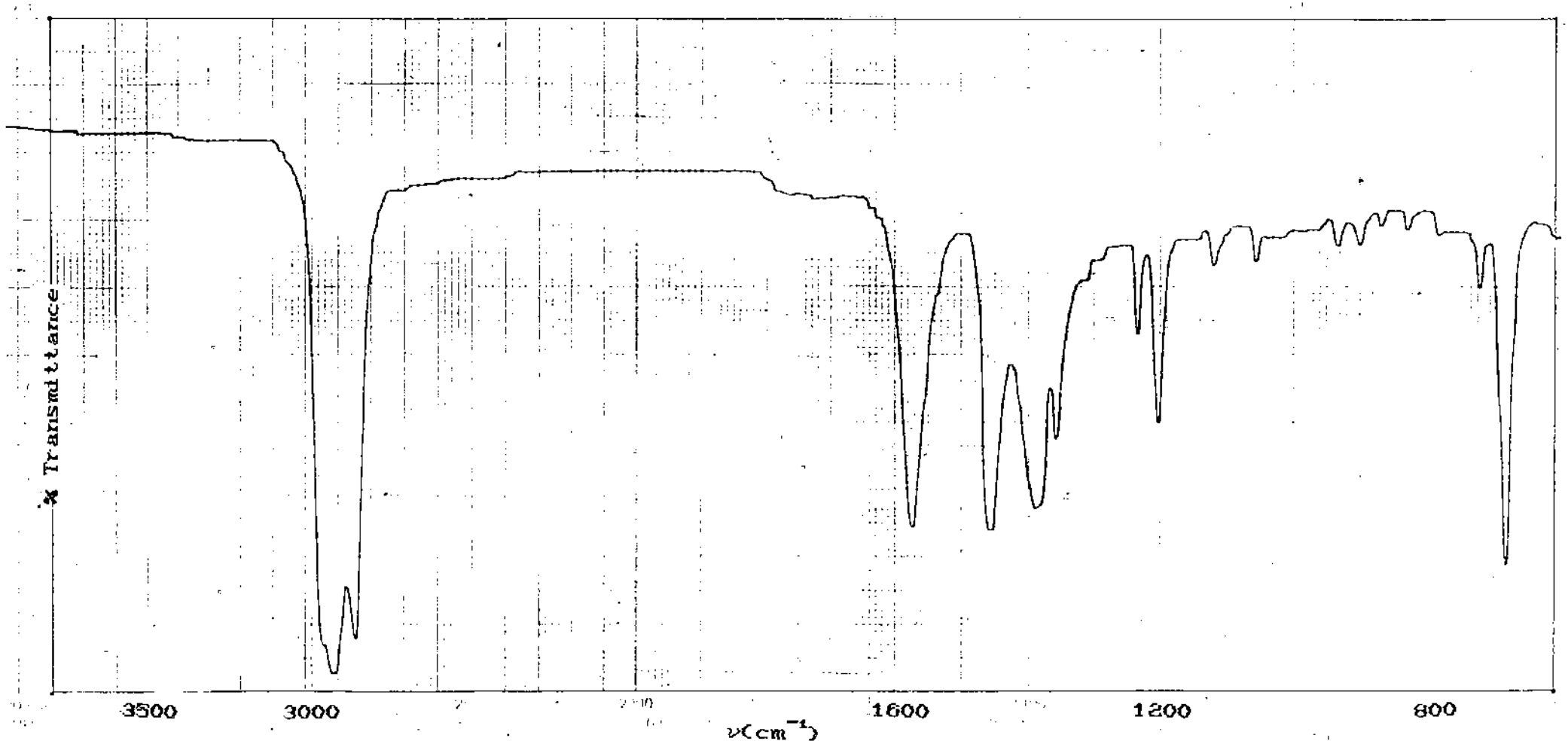


Fig.III.11. IR Spectrum of $Oct_2Sn(Pv)_2$ in Nujol.

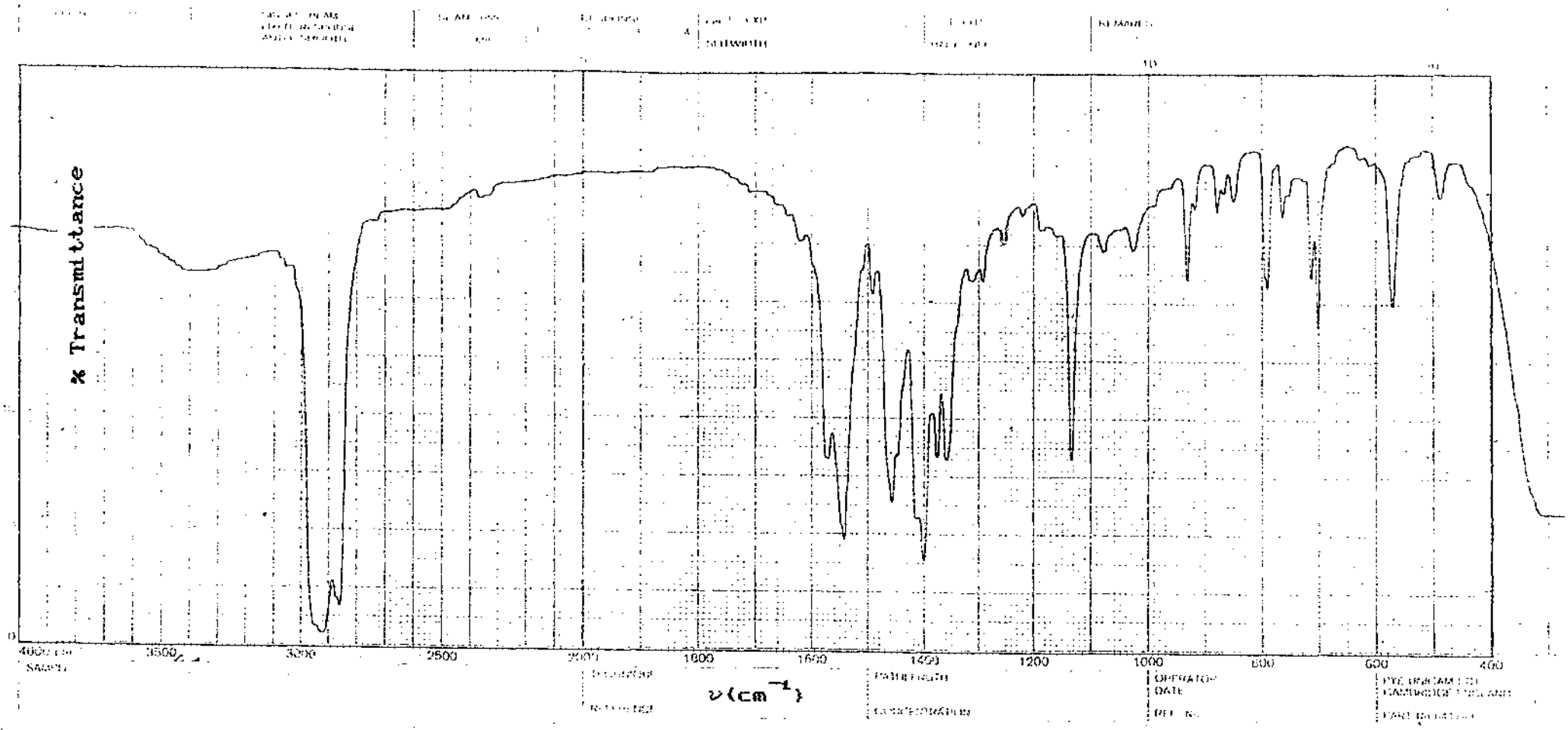


Fig.III.12. IR Spectrum of $Bu_2Sn(PPv)_2$ in Nujol.

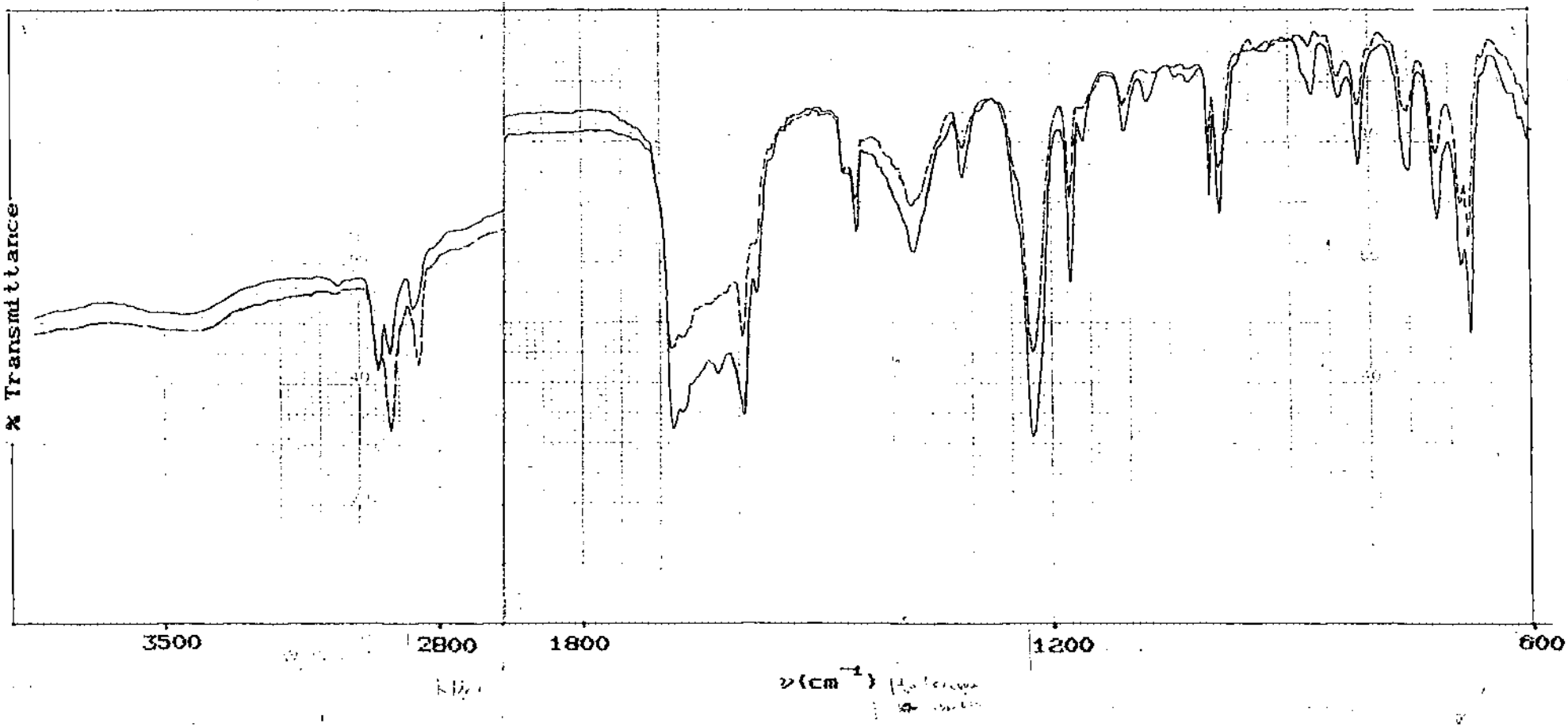


Fig.III.13. IR Spectra of $Oct_2Sn(BF)_2$ (------) and $Bu_2Sn(BF)_2$ (———) in KBr.

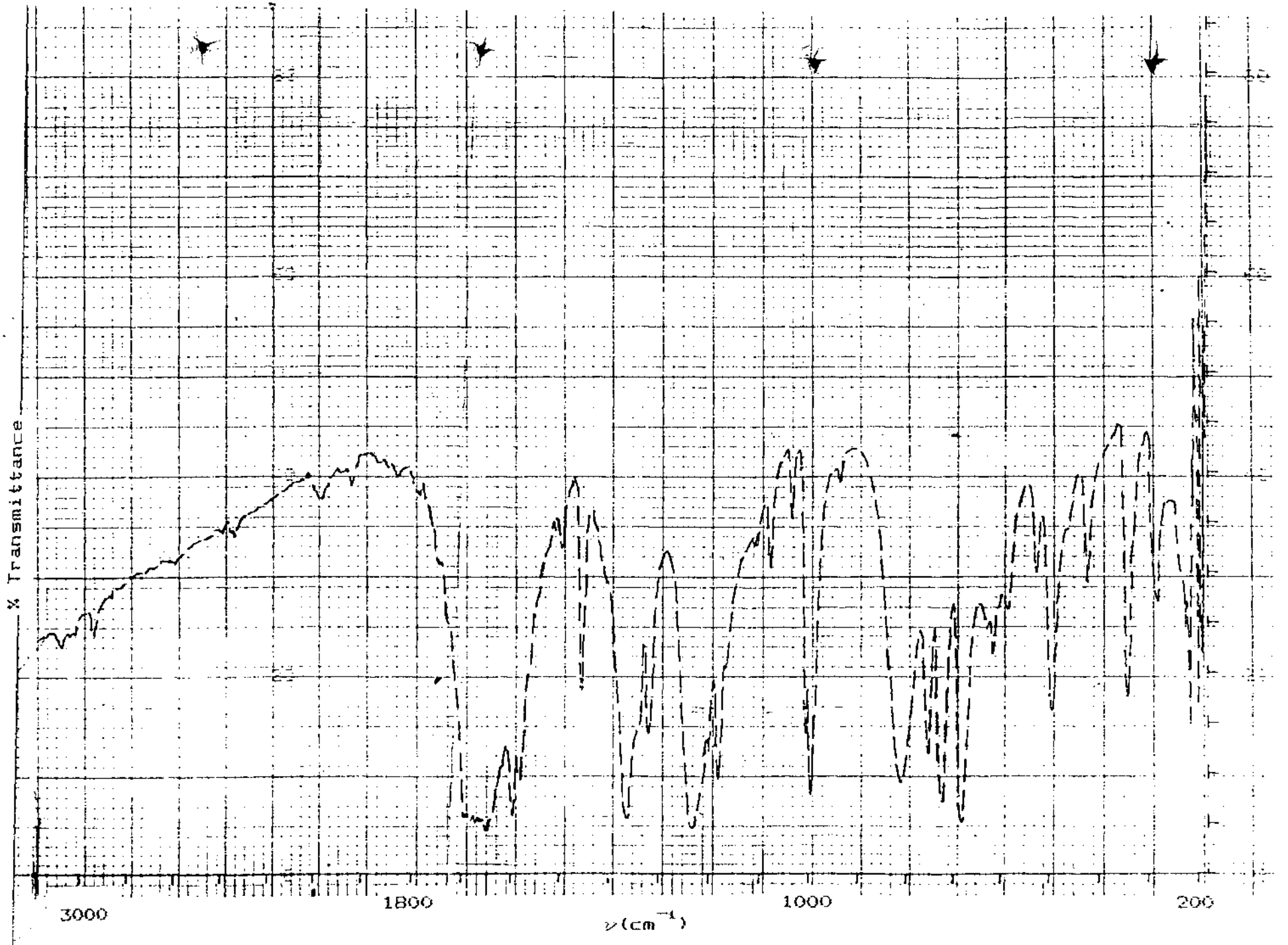


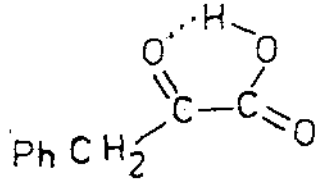
Fig.III.14. IR Spectrum of $Me_2Sn(BF)_2$ in KBr.

the neat liquid. The band occurring at 1725 cm^{-1} in CCl_4 solution may be assigned to ketonic C=O, from the comparison of the IR spectra of the acid and its ethyl ester.

In BFH the ν_{asOCO} and $\nu_{C=O}$ frequencies appear as broad bands at 1740 and 1685 cm^{-1} respectively, in the solid phase. The $\nu_{C=O}$ band occurs at a lower frequency compared to PvH due to conjugation with the phenyl ring. Because of the presence of a very broad OH stretching band centering near 3000 cm^{-1} and a medium intensity, slightly broad, out of plane OH deformation band at 975 cm^{-1}, it may be inferred that this acid exists primarily as carboxyl dimer in the solid state.

On the other hand, the presence of a medium intensity sharp band at 3460 cm^{-1}, in the case of phenyl pyruvic acid (PPvH), indicates the absence of dimeric form even in the solid state. However, the carboxyl stretch occurs as a broad band in the region 1690-1680 cm^{-1} showing a lowering of ν_{asOCO} This is, presumably, due to intramolecular hydrogen bonding as shown in structure-V. This is supported by the spectrum of the sodium salt where the $\nu_{C=O}$ (keto) is found at 1700 cm^{-1} and the ν_{asOCO} and ν_{sOCO} are found in the normal region for salts.

There are medium intensity bands in the 700-600 cm^{-1} which may be assigned to C=O wag in all these acids. In PvH and BFH this band occurs at 615 and 660 cm^{-1} respectively, whereas, in PPvH the



V

same band occurs at still higher frequency at 695 cm^{-1}. This also suggest the involvement of the ketonic C=O group in intramolecular H-bonding in PPvH.

The existence of the intramolecularly H-bonded monomeric structure [V] for PPvH requires the trans form of the acid to be more stable. Although, for PvH and BFH also, the more symmetrical trans form may be assumed to be more stable, no such inference can be drawn on the basis of IR spectra. A study of the computer generated molecular models of these acids and calculation of their energies, using Desk Top Molecular Modeller: Version 1.2[94], have shown that for all the free acids the trans-geometry offers the energetically more stable form (table-III.5). Thus, it is evident

Table-III.5.

Calculated molar energy content of the ligands.

Molecule	E in KJ/Mole. Cis-form	Trans-form
$CH_3COCOOH$	1.432	1.244
$PhCH_2COCOOH$	-4.511	-4.741
PhCOCOOH	10.769	7.784

that in these acids the potential donor O-atom of the keto group is suitably oriented for intramolecular coordination in their organotin derivatives.

(ii) IR spectra of triorganotin ketocarboxylates :

The IR spectral data of the organotin keto carboxylates are presented in table- III.6A, and some typical spectra are shown in figures III.4-III.9.

Although complete assignment of the absorption bands in the IR spectra of the triorganotin compounds is not possible due to the presence of strong ligand vibrations in all the relevant regions, important structural information may be obtained from a qualitative assignment of bands to ν_{OH}, ν_{asOCO}, $\nu_{C=O}$, ν_{sOCO} and ν_{Sn-O} vibrations. The main features of the IR spectra are noted below.

All the triorganotin derivatives are characterised by the presence of a number of strong intensity bands in the 1700-1500 cm^{-1} region, where the $\nu_{C=O}$ and ν_{asOCO} frequencies occur. These frequencies in these compounds have been identified by comparing their spectra with those of the free acids, their esters and Na-salts. However, in some cases these two frequencies overlap resulting into a broad band similar to that of the free acids, but at a lower frequency. In such cases the assignments are not precise.

Table:-III.6.A.

Characteristic IR freguencies(in Cm^{-1}) of α-keto acids & their organotin derivatives.

SL. no.	Compound.	Solid Phase(in Nujol/KBr)					Soln.Phase(in CCl_4/$CHCl_3$)			
		ν_{OH}	$\nu_{C=O}$	ν_{asOCO}	ν_{sOCO}	$\nu_{C=O}$ (wag)	ν_{OH}	$\nu_{C=O}$	ν_{asOCO}	ν_{sOCO}
1.	PvH	3600-2900[b]	1728	1740	1285 1160	615	4320	1725	1790	1280 1200
2.	PvEt	-	1745	1755	1370 1300	618		-		
3.	PvNa	-	1710	1625	1405	625		-		
4.	Ph_3SnPv	-	1572	1542 1535	1410	665		1612	1635	1370
5.	Bu_3SnPv	-	1584	1567[b]	1384	665		1635[a]	1635	1340
6.	Bz_3SnPv	-	1580	1567[b]	1403	665		-		
7.	$Bu_2Sn(Pv)_2$	-	1585[a]	1585[a]	1392	680		1608	1680	1370
8.	$Oct_2Sn(Pv)_2$	-	1580[a]	1580[a]	1395	680		1610	1678	1370
9.	$Me_2Sn(Pv)_2$	-	1628[sh] 1595	1560	1356	670		-		
10.	PPvH	3460	1686[a]	1686[a]	1248 1195	695		-		
11.	PPvNa	-	1702	1620	1395			-		
12.	Ph_3SnPPv	-	1583	1565 1547	1400			1610	1650	1370
13.	Bu_3SnPPv	-	1592[a]	1592[a]	1394			-		
14.	Bz_3SnPPv	-	1614[a]	1614[a] 1562	1386			1610	1650	1345
15.	$Bu_2Sn(PPv)_2$	-	1620[sh] 1580	1550	1406			-		

---

a - very broad band, probably due to overlap of ν_{asOCO} and $\nu_{sC=O}$.

b - broad ; sh - shoulder.

Table:-III.6.A(contd.).

SL. no.	Compound.	Solid Phase(in Nujol/KBr)					Soln.Phase(in CCl_4/$CHCl_3$)			
		ν_{OH}	$\nu_{C=O}$	ν_{asOCO}	ν_{sOCO}	$\nu_{C=O}$ (wag)	ν_{OH}	$\nu_{C=O}$	ν_{asOCO}	ν_{sOCO}
16.	$Oct_2Sn(PPv)_2$	-	1627[ah]					-		
			1577[a]	1577[a]	1394					
17.	$Me_2Sn(PPv)_2$	-	1628[ah]					-		
			1575[a]	1575[a]	1410					
18.	BFH	3400-2800[b]	1686	1742	1215[b] 1180	660		-		
19.	BFNa	-	1670	1570	1412			-		
20.	Ph_3SnBF	-	1686	1575 1550	1405	680		1690	1655	1360
21.	Bu_3SnBF	-	1648	1582 1550	1405	670		-		
22.	Bz_3SnBF	-	1678	1583	1405	680		1670	1610	1360
23.	$Bu_2Sn(BF)_2$	-	1686	1625[b]	1375[b]	680		1688	1645	1365
24.	$Oct_2Sn(BF)_2$	-	1686	1620[b]	1375[b]	675		1680	1640	1370
25.	$Me_2Sn(BF)_2$	-	1686	1647	1363	680		-		
26.	$Ph_2Sn(BF)_2$	-	1686	1635	1375[b]	678		-		

a - very broad band, probably due to overlap of ν_{asOCO} and $\nu_{sC=O}$.

b - broad ; sh - shoulder.

In most of the derivatives of PvH and PPvH both the $\nu_{C=O}$ and ν_{asOCO} frequencies appear below 1600 cm^{-1}, the lowest being for the triphenyltin derivatives, as expected. In the derivatives of BFH, however, the ketonic stretching frequency is either unchanged or shows only marginal -ve shift relative to the free acid and occurs as an unambiguously identifiable sharp band around 1680 cm^{-1}.

The symmetric carboxyl stretching vibrations in these compounds appear in the region 1410-1380 cm^{-1}, which are well above the corresponding frequencies in the free acids or their esters, but close to their Na-salts. However, identification of the ν_{sOCO} is not always unambiguous due to the presence of various other strong absorptions.

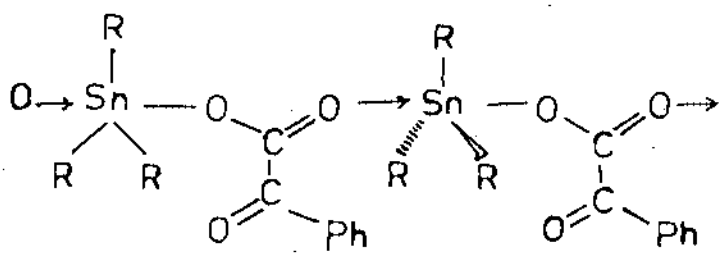
Thus, data from table-III.6A shows that both the asymmetric and symmetric carboxyl stretching vibrational bands of the parent acids, appearing in the region 1740-1688 cm^{-1} and 1280-1215 cm^{-1} respectively, get considerably shifted in the triorganotin ketocarboxylates, indicating organostannylation[32]. Like triorganotin acetates, formates etc.[33], the ν_{asOCO} and ν_{sOCO} bands of all the triorganotin ketocarboxylates appear in the 1590-1535 cm^{-1} and 1410-1380 cm^{-1} regions respectively, in the solid state. In $CHCl_3$ solution, the former band is raised to 1655-1610 cm^{-1} region and the latter is lowered to around 1370-1340 cm^{-1}. It can

also be seen from table-III.6A that the difference between ν_{asOCO} and ν_{sOCO} is always less than 200 cm^{-1} in the solid state and more than 250 cm^{-1} in solution.

These observations may be interpreted in terms of bidentate and almost symmetrical carboxyl group forming intermolecular bridges in the solid state giving rise to polymeric keto carboxylates[34], while in solution depolymerisation occurs resulting into ester like monomeric species.

All the triorganotin derivatives show weak to medium intensity bands in 600-400 cm^{-1} region. These bands may be assigned to ν_{Sn-O}, since comparison with ligand spectra showed no band attributable to ν_{Sn-C}, which is expected to occur further down the scale.

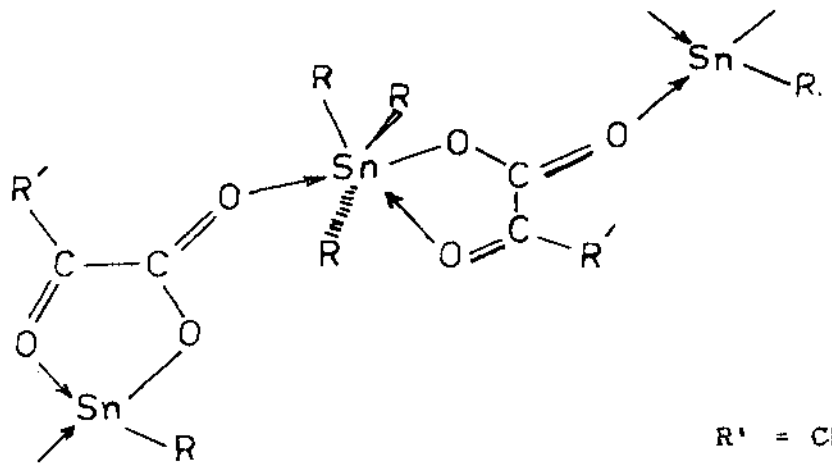
In the light of the above observations it is apparent that, the derivatives of BFH differ from the derivatives of the other acids in having the $\nu_{C=O}$ frequencies almost unaltered (at 1680 cm^{-1}), both in the solid and solution phase relative to the free acid, but having the carboxylic stretching frequencies in the same regions. Thus it may be inferred that, in the triorganotin benzoylformates, while the carboxyl group acts as intermolecular bridge giving rise to polymeric structure with trigonal bipyramidal geometry around tin in the solid state, the keto group remains free as shown in structure VI below :



VI

In the derivatives of PvH and PPvH, however, the ketonic stretching bands appear below 1600 cm^{-1} in the solid state, although the same bands in the free acids appear at 1728 cm^{-1} and 1688 cm^{-1} respectively. Such a large negative shift can only be explained by assuming the involvement of the keto group in intramolecular coordination, as the carboxyl group is less likely to act intramolecularly because of its small bite angle[35]. Thus, in the solid state the triorganotin esters of PvH and PPvH have polymeric structure, involving chelating C=O group and bridging carboxylic group, the tin atom geometry, presumably, being octahedral as shown in structure VII below.

This conclusion is supported by the fact that in $CHCl_3$ solution of these compounds, while the ν_{asOCO} frequency undergoes very large +ve shift due to depolymerisation, the $\nu_{C=O}$ is raised only slightly. In spite of the fact that in solution the ketonic C=O group remains intramolecularly coordinated, the small rise in $\nu_{C=O}$



VII

R' = CH_3, $PhCH_2$

R = n-Bu, Ph, $PhCH_2$

frequency may not be quite unlikely because of the change in the environment of the tin atom and its geometry from octahedral to trigonal bipyramidal.

Although in the +IV state tin is known to utilise its 5d orbital, hybridised with 5s and 5p orbitals, frequently in increasing its coordination number above four, the energy difference between the s or p orbital and the d orbital is such that the hybrid orbitals have relatively low d-character. In the trigonal bipyramidal geometry involving sp^3d hybrid orbitals, in complexes of the type $R_3SnX.L$ (L = ligand), the three orbitals in the equatorial plane around tin can be regarded as primarily sp^2 in character and are expected to form three strong covalent bonds with the R groups. The two apical orbitals may be regarded as

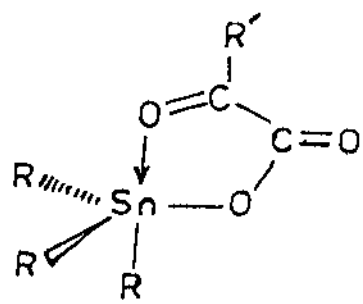
consisting of the p_z and the d orbitals, having predominant p-character and are most likely to overlap with the more electronegative X group[41,42] and the donor atom of the complexing agent. The bonds between tin and the axially placed electronegative atoms are, therefore, expected to be relatively weak. X-ray crystallographic studies by several authors on a number of $R_3SnX.L$ compounds[96-98], having trigonal bipyramidal geometry with cis-disposition of the R groups, support this contention. Tin-oxygen bond data for a few such complexes tabulated below [table-III.7] shows the weakness of the tin-axial oxygen bond.

Table:-III.7.

Tin-Oxygen bond data (A^o) in R_3Sn-Carboxylates.

Sl. no.	Compound.	Equatorial. Sn——O	Axial. Sn----O	Ref.
1.	$Ph_3Sn[O_2CC_6H_4(N_2R)-o]$ (R = 2-hdroxy 5-methyl phenyl)	2.070	2.463	36
2.	Ph_3Sn(ONPhCOPh)	2.091	2.308	,,
3.	Me_3Sn(ONPhCOPh) (mol-1)	2.064	2.392	,,
	(mol-2)	2.152	2.263	
4.	Ph_3Sn(OCPhCHPhO)	2.094	2.276	,,
5.	$Ph_3Sn[O_2CC_6H_4(XR)/(NR_2)]$			
	XR = OMe(-o)	2.054	2.781	37
	NR_2 = NH_2(-o)	2.043	2.823	38

On the basis of analogous line of reasoning, it may be inferred that in the monomeric forms of the triorganotin esters of PvH and PPvH in solution phase, the change in hybridisation from sp^3d^2 (octahedral) to sp^3d (trigonal bipyramidal) brings in a reorientation of the groups in such a way that the intramolecularly donating ketonic oxygen atom and a R group occupy axial positions. The resulting structure, with cis-disposition of R groups, in the solution phase, is shown below.



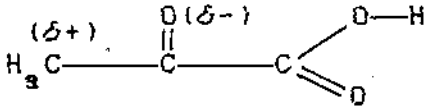
VIII

This change is expected to lower the strength of the Sn <—O (keto) bond, which is reflected in the rise of the $\nu_{C=O}$ frequency in going from solid phase (octahedral geometry) to solution (trigonal bipyramidal geometry).

From the foregoing discussion it is clear that the keto group in BFH is not involved in intramolecular coordination and thus behave differently from that of the other acids. This may,

probably, be due to steric as well as electronic reasons arising out of the presence, on the ketonic carbon atom in BFH, of a phenyl group. The delocalisation of the π electrons of C=O with the phenyl group is certain to diminish the electron density at the oxygen atom compared to that in the other cases, thereby, making intramolecular coordination unfavouable.

The values of the field effect (Taft's) constants for the three R' groups, [CH_3 (-0.05), $PhCH_2$ (0.04), and Ph (0.1)] of the carboxylic acids R'COCOOH used, clearly indicates that the basicity of the keto group is highest in $CH_3COCOOH$ (PvH) and lowest in PhCOCOOH (BFH). While the Ph group acts as an electron withdrawing group in PhCOCOOH, the electron releasing CH_3 group sufficiently enhances electron density at the ketonic oxygen atom in $CH_3COCOOH$ making it capable of coordinating to suitable electrophiles.



IX

This is in agreement with the observation that PvH can form not only intramolecularly coordinated carboxylates, but also, addition complexes. For PPvH the situation is expected to be intermediate between that of PvH and BFH. This is reflected in the fact that PPvH, in addition to forming intramolecularly coordinated

carboxylates, forms an addition complex with $(Bu_3Sn)_2O$, whose donor strength is the highest among the oxo-organotin compounds used.

(iii) Electronic Absorption Spectra :

The α-keto acids, being dicarbonyl systems, are expected to show $n-\pi^*$ transition at wavelengths well above 300 nm, in addition to the $\pi-\pi^*$ band which is expected to occur at much lower wavelength. As discussed earlier, the CO group in these acids plays an extremely important role in the formation of their organotin derivatives. Any involvement of the CO group must result in appreciable changes in either the position or intensity or both, of the $n-\pi^*$ band in these compounds. While in the simple carboxylate compounds like organotin formate or acetate etc., the $n-\pi^*$ transition occurs at a much lower wavelength, approximately at around 200 nm, and is, therefore, of little help in the elucidation of the structure of the organotin carboxylate, the present group of ligands offer a scope for studying the $n-\pi^*$ spectra of the free acids and their organotin derivatives vis-a-vis the role of the CO group in determining the structure of the carboxylates.

The electronic spectra of the keto acids in CCl_4 shows a weak band (ε ~ 10-90) at around 350-390 nm in addition to strong absorptions below 260 nm. The large hypsochromic shift of this

band in polar solvent, e.g., methanol, its low molar absorbance and the presence of vibrational structures in the spectra in non-polar solvents help to identify this band as due to $n-\pi^*$ transition. The position of the $n-\pi^*$ band in the different acids are shown in table-III.8. and some of the spectra are presented in figures III.15-III.26.

In the organotin esters of pyruvic acid (PvH) and phenyl pyruvic acid (PPvH) the $n-\pi^*$ transition bands suffer very large hypsochromic shift, indicating the stabilisation of the n-orbital on stannylation (cf. hypsochromic shift in MeOH). This, clearly indicates the participation of the carbonyl group in intramolecular coordination, which stabilises the lone pair thereby increasing the $n-\pi^*$ transition energy. The magnitude of the blue shift could be used as a measure of the strength of binding by the carbonyl group. Unfortunately, the $n-\pi^*$ bands in the organotin esters often get superimposed with the $\pi-\pi^*$ transition bands making it difficult to determine the position of the $n-\pi^*$ transition precisely in the organotin derivatives.

In the triorganotin esters of benzoyl formic acid (BFH), however, there is practically no change in the position, as well as, molar extinction of the $n-\pi^*$ transition band in comparison to the free acid. This shows the presence of non-interacting keto group in these compounds, corroborating the inference already

Table:-III.8.

Electronic spectral data of Triorganotin Keto Carboxylates:

Compounds.	$n-\pi^*$ peaks (nm) in CCl_4 Sol.	ϵ_{max}	$n-\pi^*$ peaks (nm) in MeOH Sol.	Remarks
$CH_3COCOOH$	370, 350, 335(sh)	9, 13	330	
$Ph_3SnOCOCOCH_3$	No peak above 300 nm. Inflection at 290nm.		290(sh), 275	Carbonyl gr. interacts.
$Bu_3SnOCOCOCH_3$	No peak above 300 nm.		<280	,,
$Bz_3SnOCOCOCH_3$	Inflection at 326 nm.		280	,,
$PhCH_2COCOOH$	385, 368 306	16.5, 23	345, 330, 300	
$Ph_3SnOCOCOCH_2Ph$	310, 296		320(sh), 304	,,
$Bu_3SnOCOCOCH_2Ph$	320(sh), 306, 294		320(sh), 302 288	,,
$Bz_3SnOCOCOCH_2Ph$	330, 310		280	,,
$PhCOCOOH$	393, 375	86, 93	346, 336, 292(sh)	
$Ph_3SnOCOCOPh$	395, 375, 360	58, 71 75	345, 335 ? 280	No CO interaction
$Bu_3SnOCOCOPh$	395, 375		345, 335? 280, 270	,,
$Bz_3SnOCOCOPh$	395, 375		345, 335	,,

sh-shoulder.

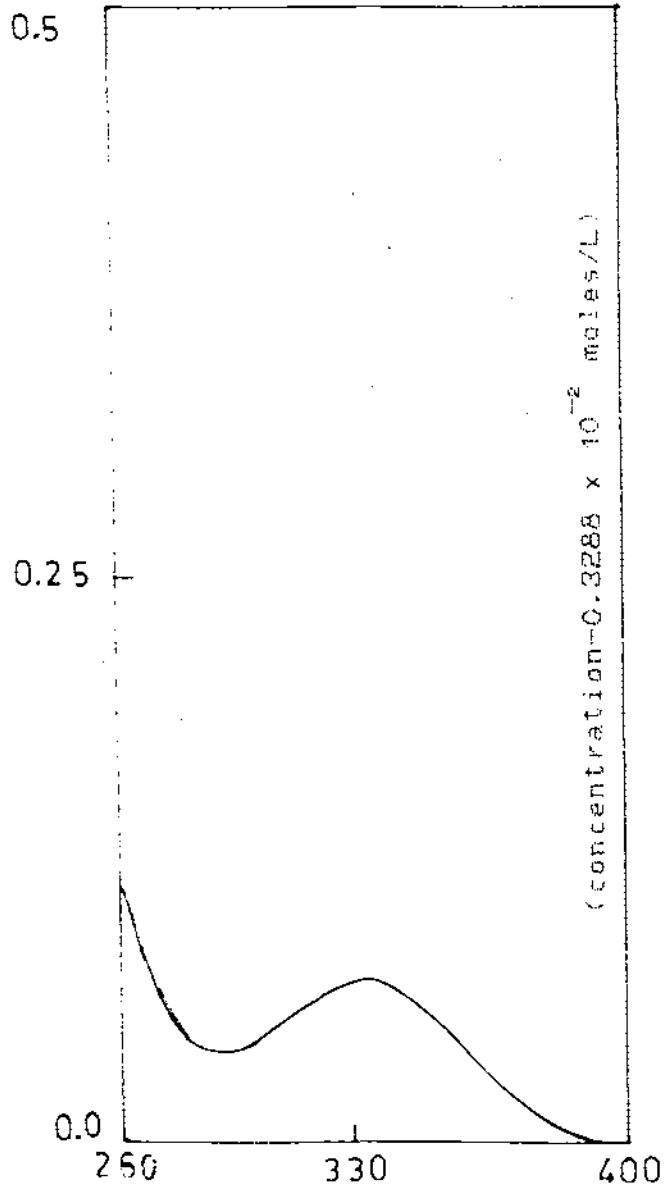


Fig.III.16. Electronic spectrum of PVH in MeOH.

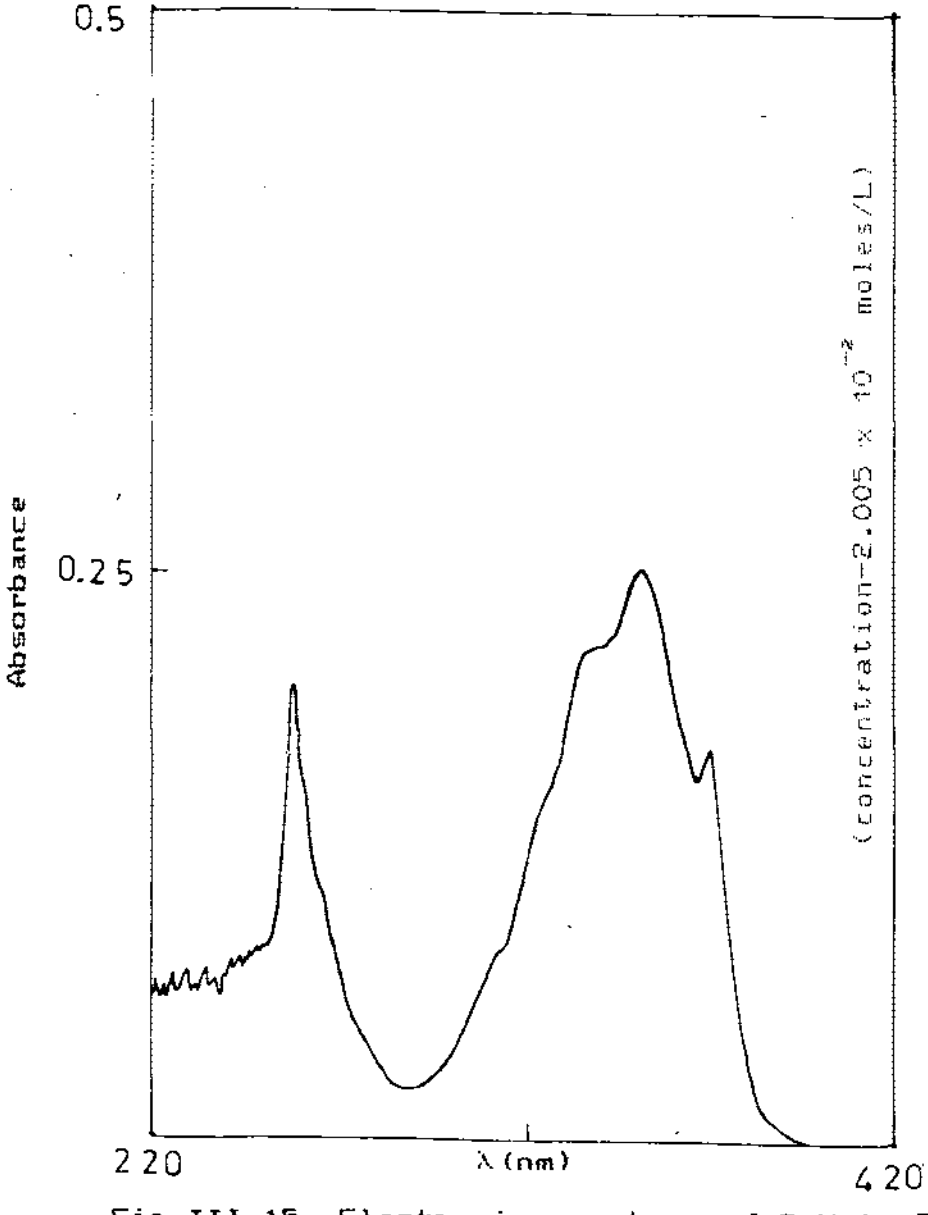


Fig.III.15. Electronic spectrum of PVH in CCl_4.

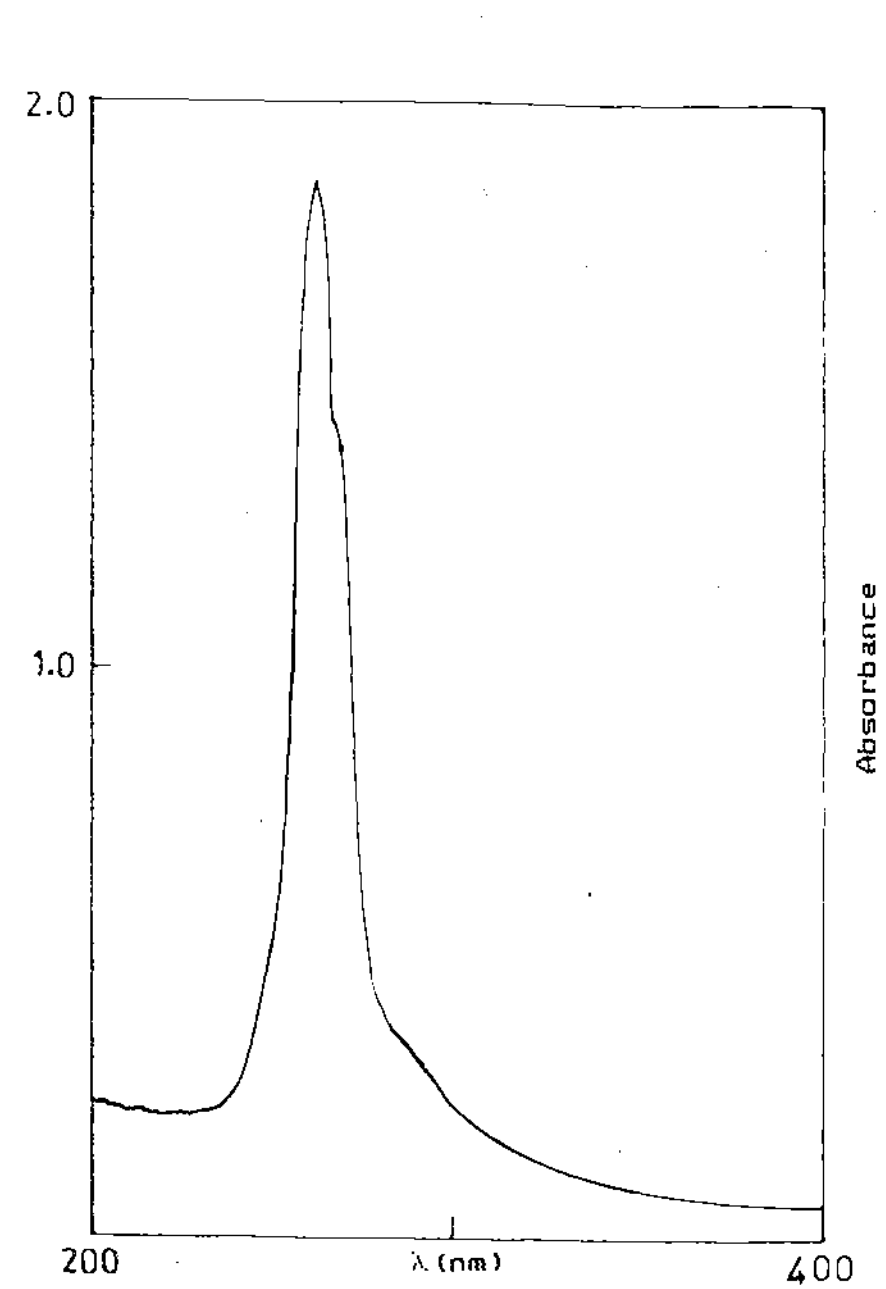


Fig.III.17. Electronic spectrum of Ph_3SnPv in CCl_4.

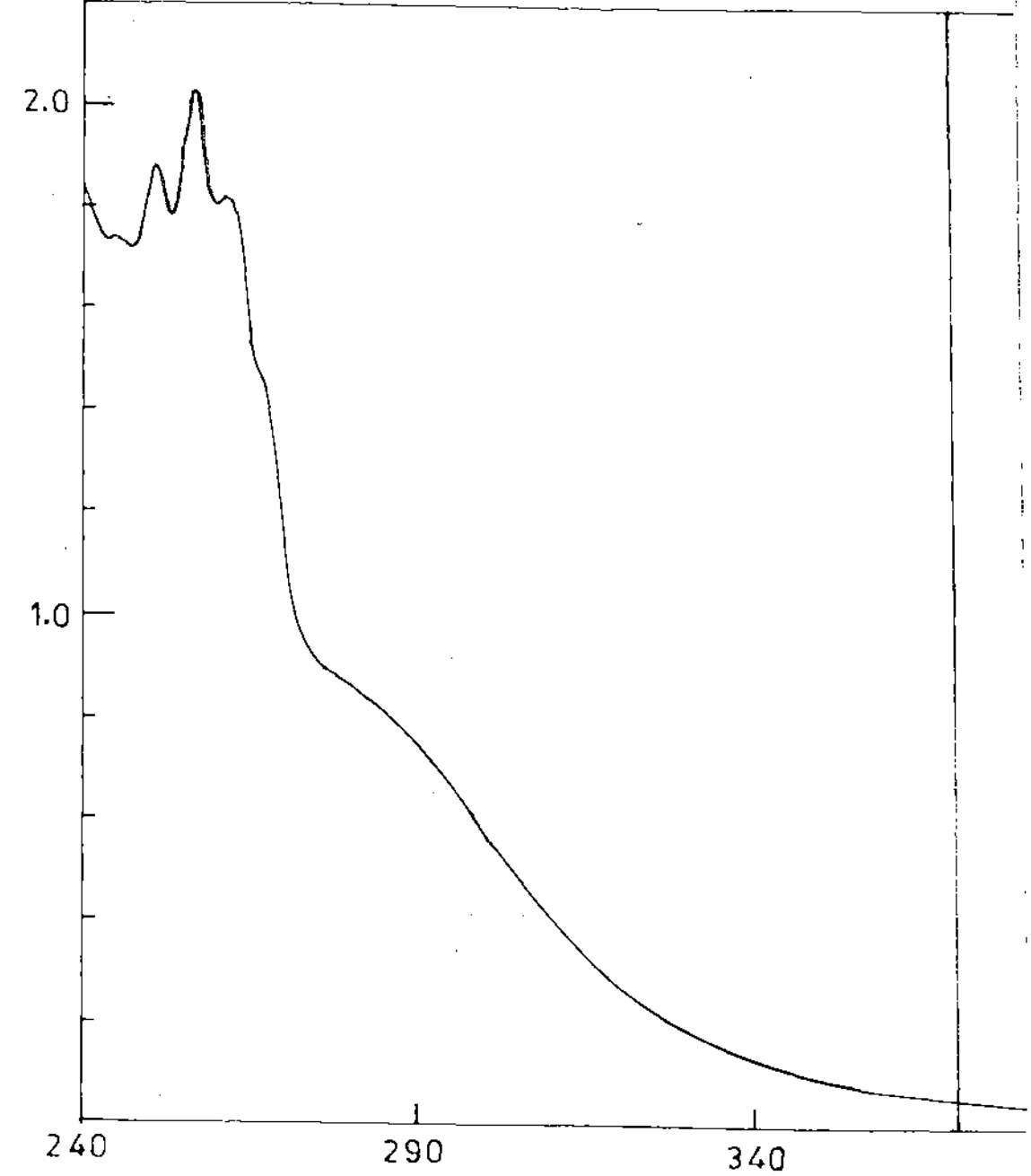
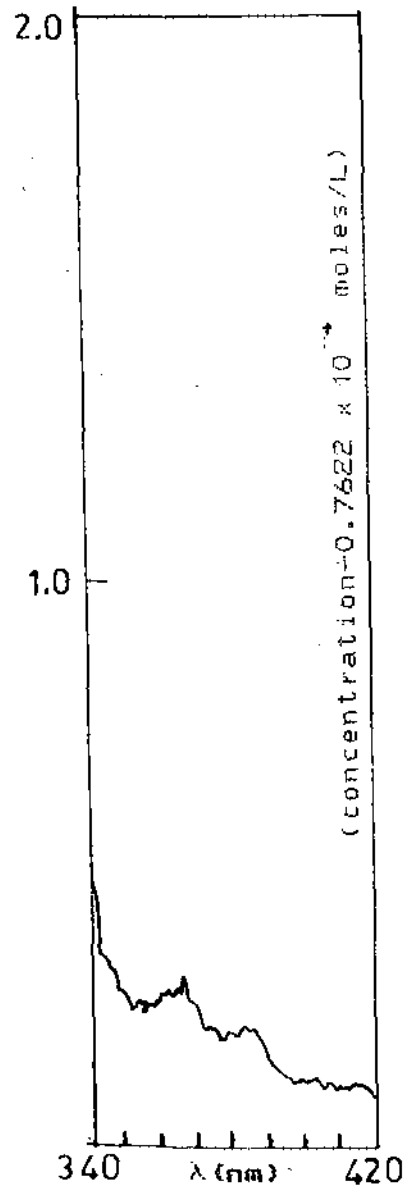


Fig.III.18. Electronic spectrum of Ph_3SnPv in MeOH.



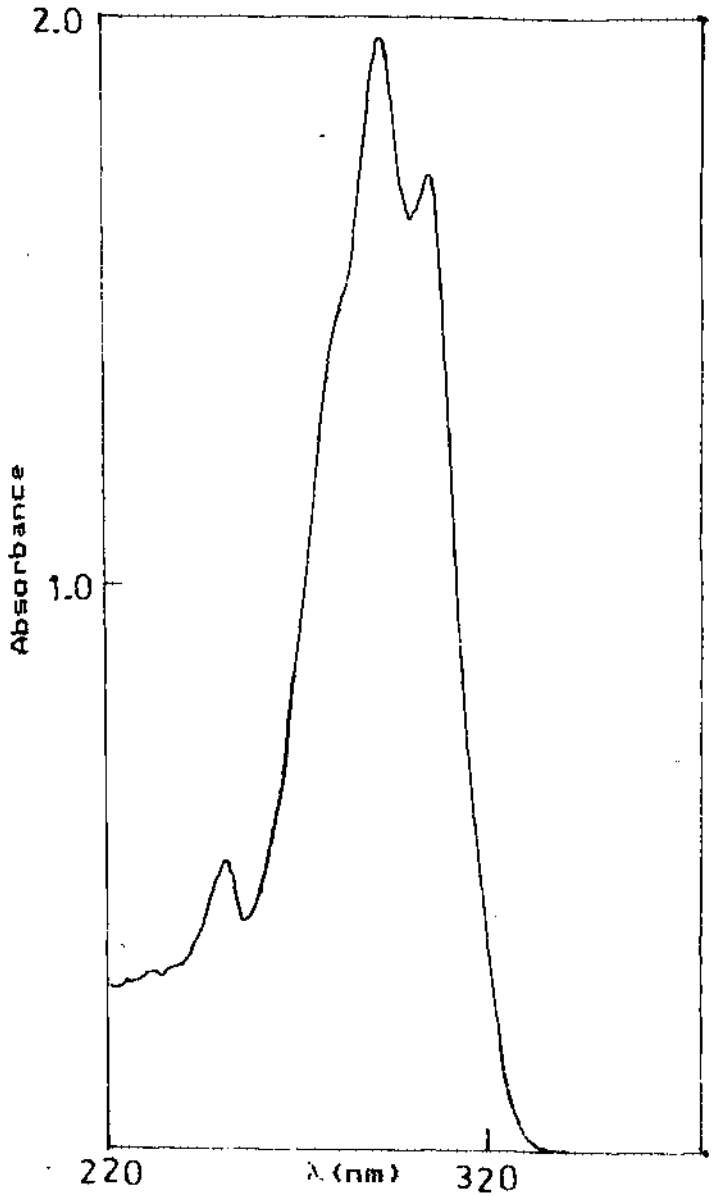


Fig.III.19. Electronic spectrum of PPvH in CCl_4.

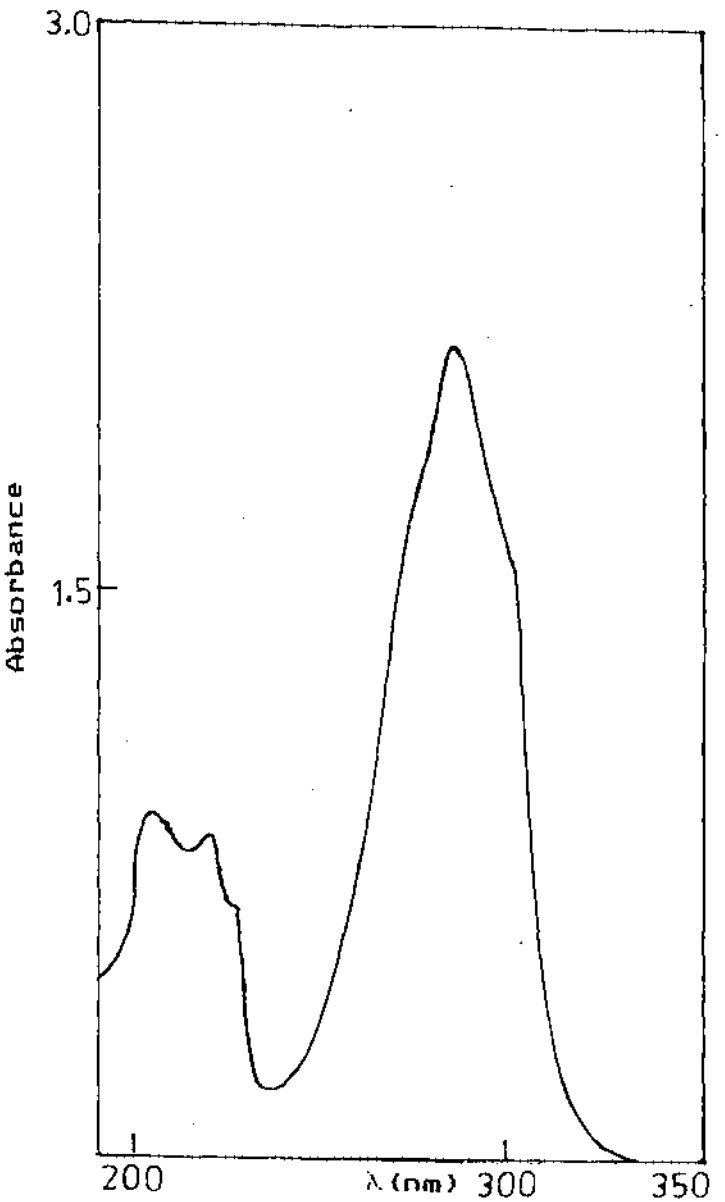


Fig.III.20. Electronic spectrum of PPvH in MeOH.

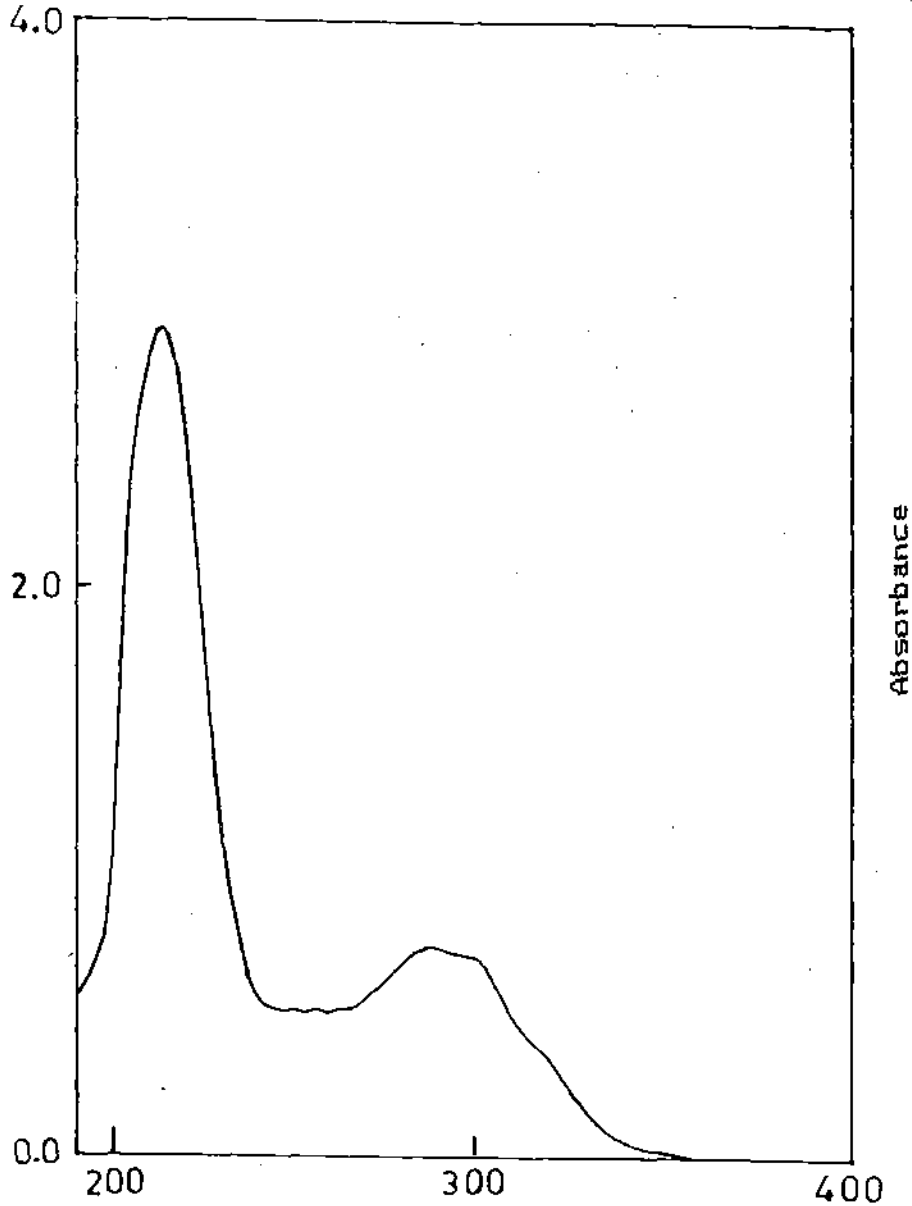


Fig.III.22. Electronic spectrum of Bu_3SnPPv in MeOH.

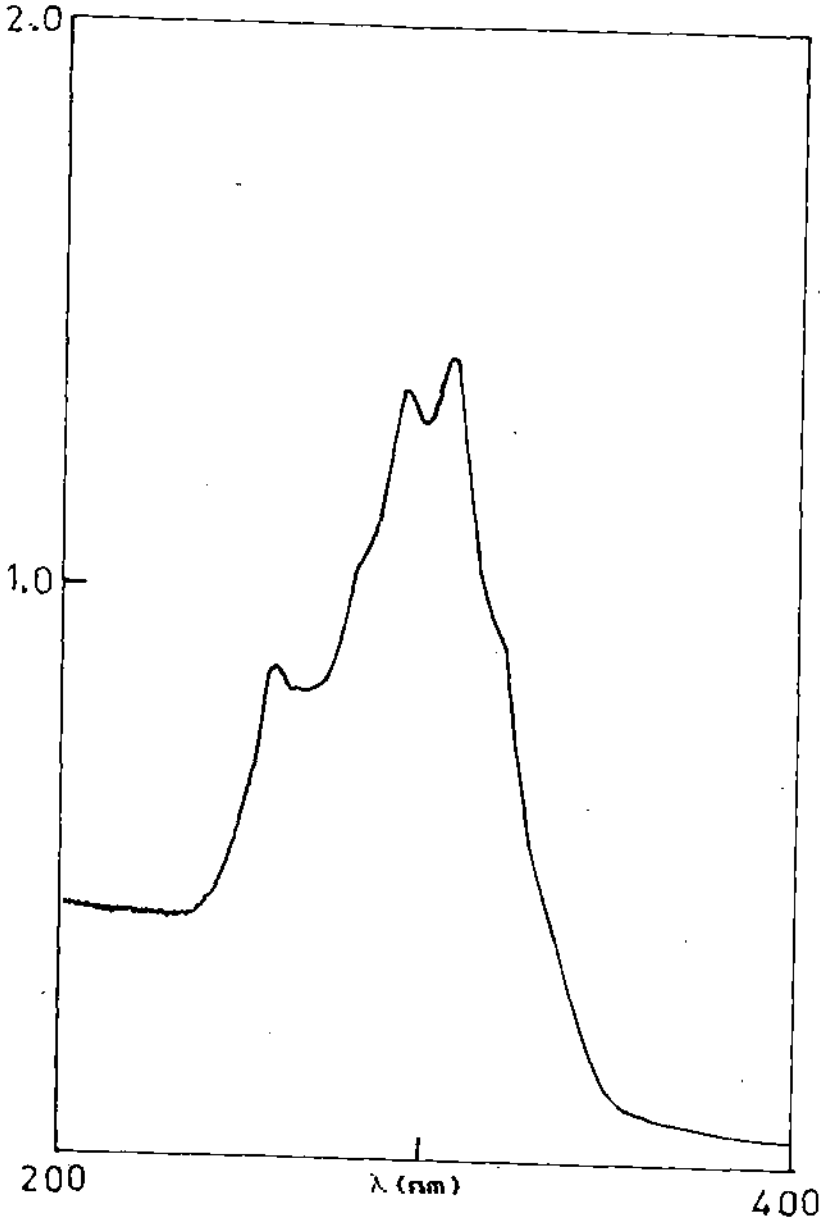


Fig.III.21. Electronic spectrum of Bu_3SnPPv in CCl_4.

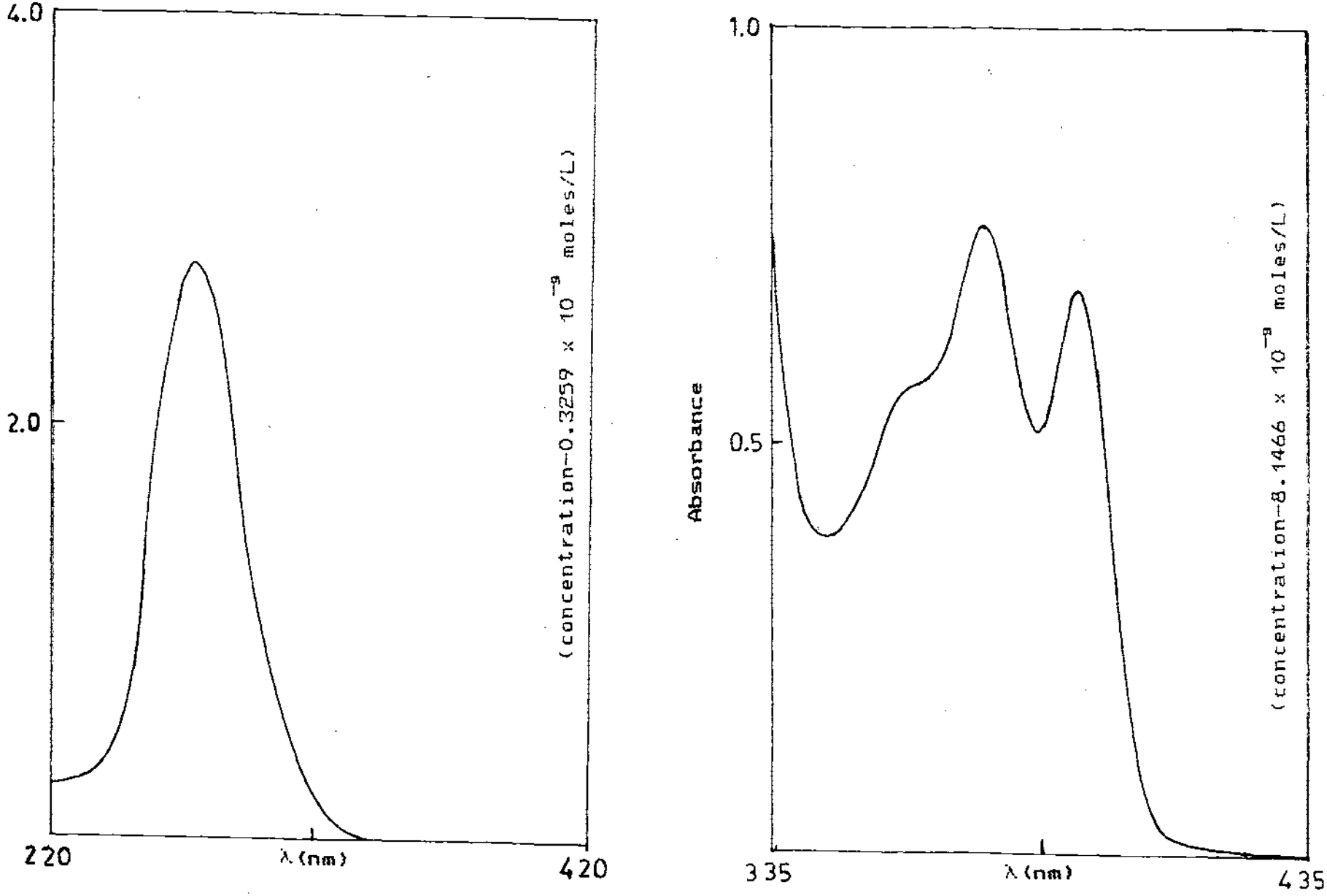


Fig.III.23. Electronic spectrum of BFH in CCl_4.

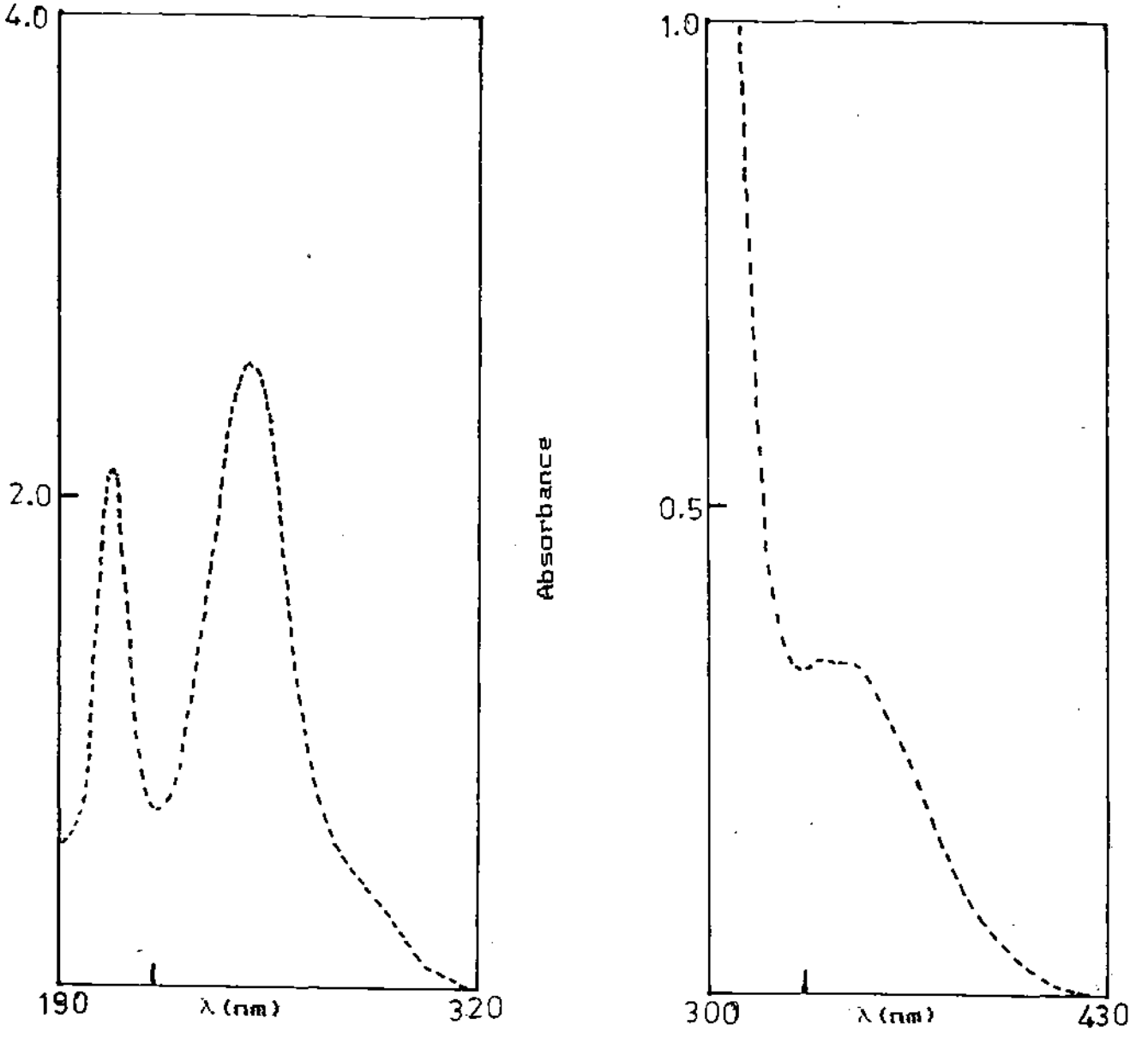


Fig.III.24. Electronic spectrum of BFH in MeOH.

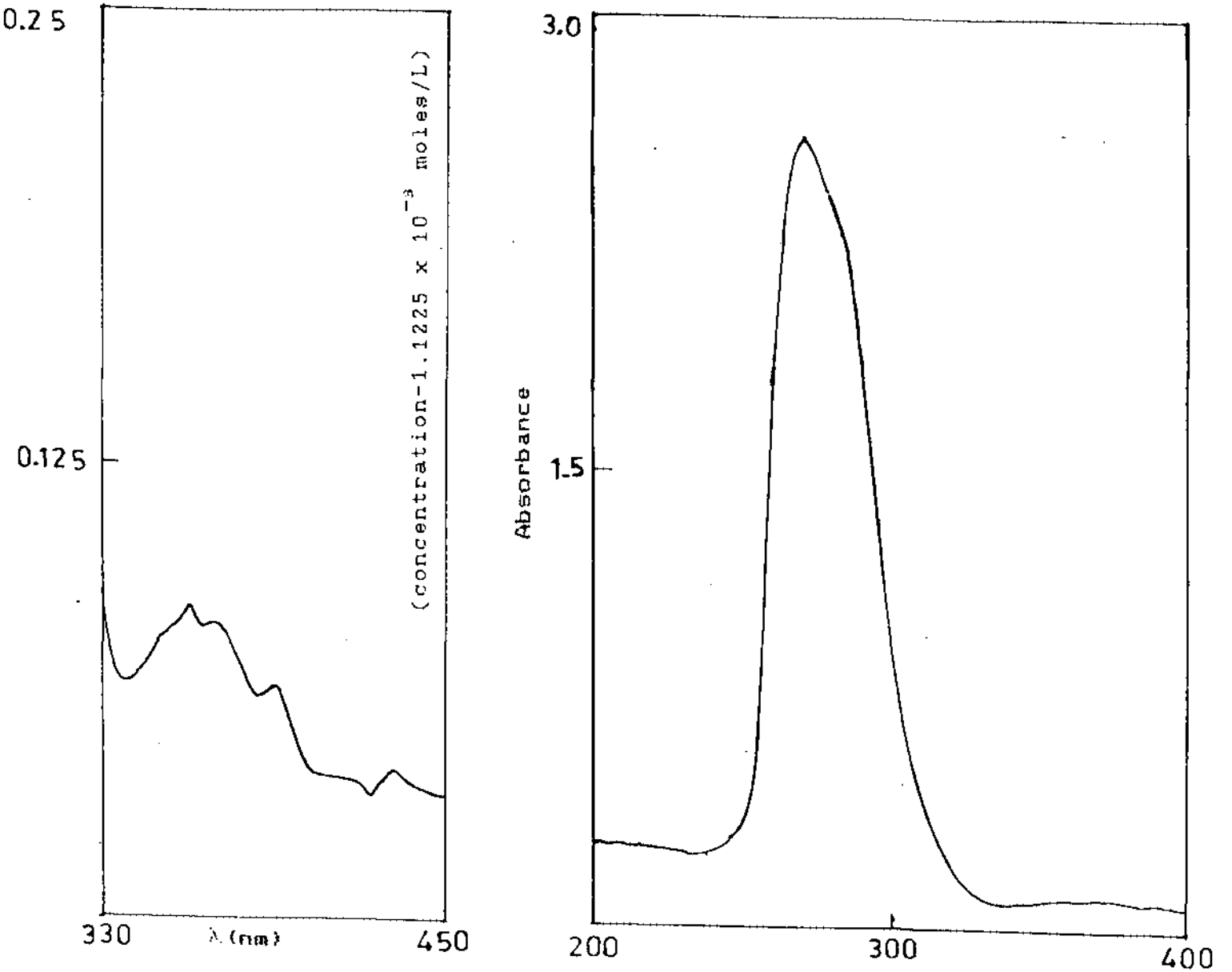


Fig.III.25. Electronic spectrum of Ph_3SnBF in CCl_4.

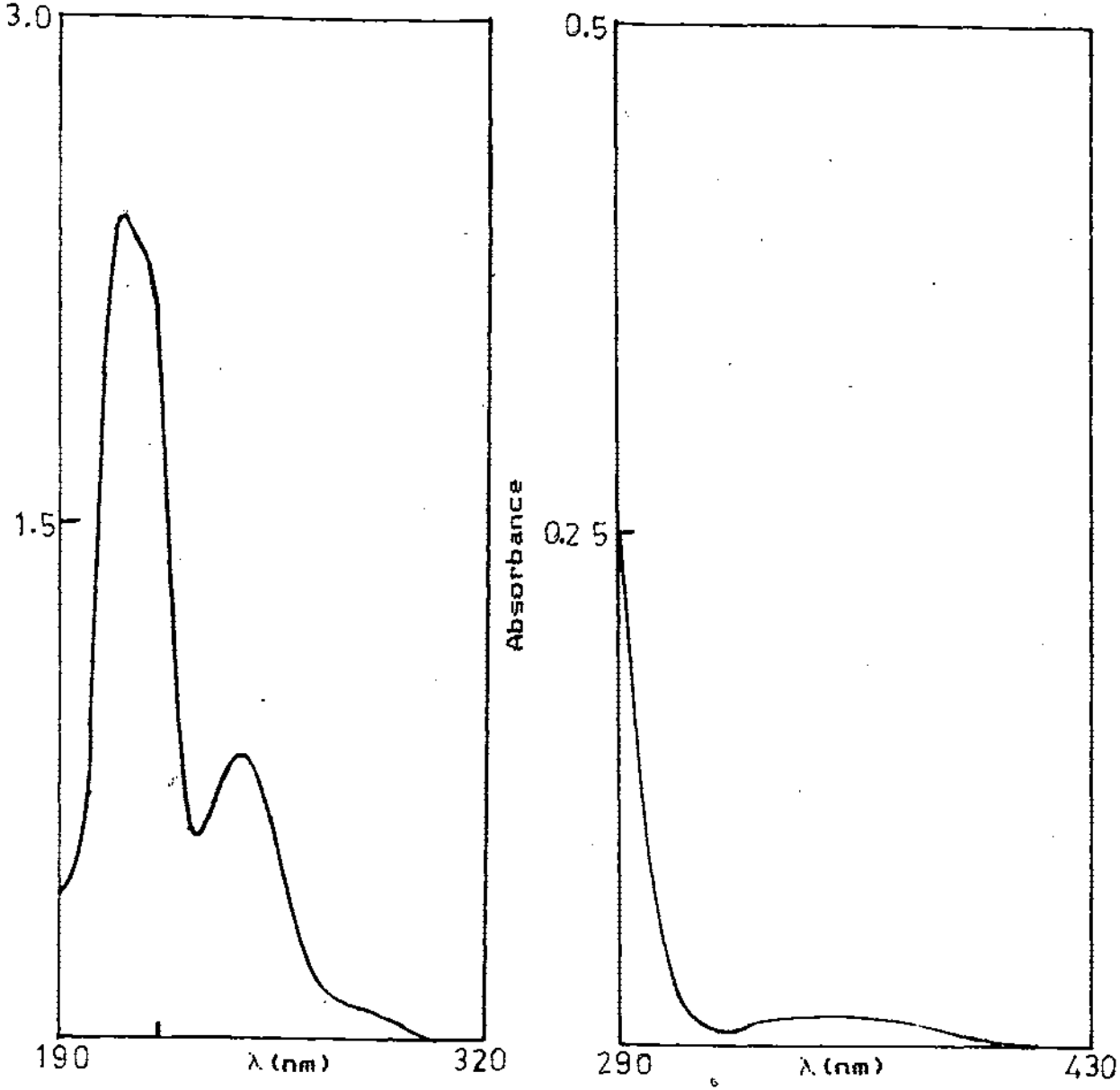


Fig.III.26. Electronic spectrum of Ph_3SnDF in MeOH.

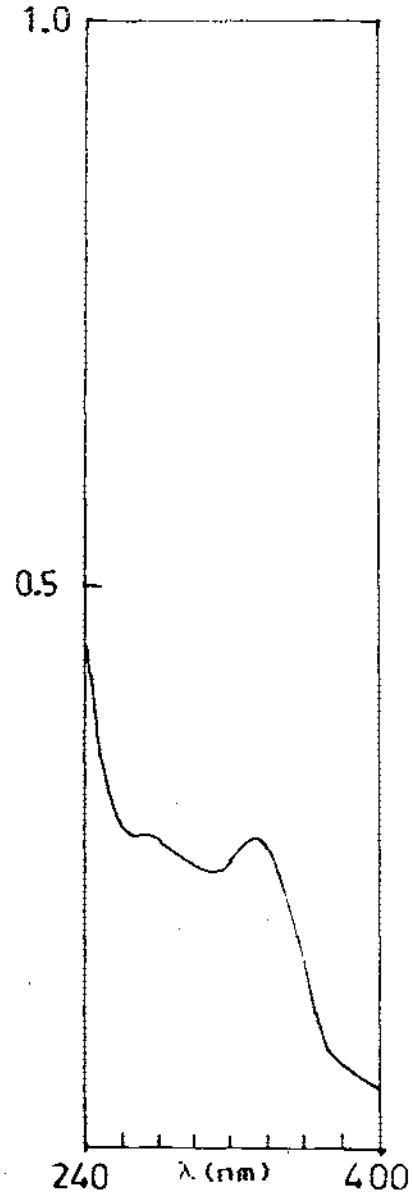


Fig.III.28. Electronic spectrum of $Bu_2Sn(Pv)_2$ in MeOH.

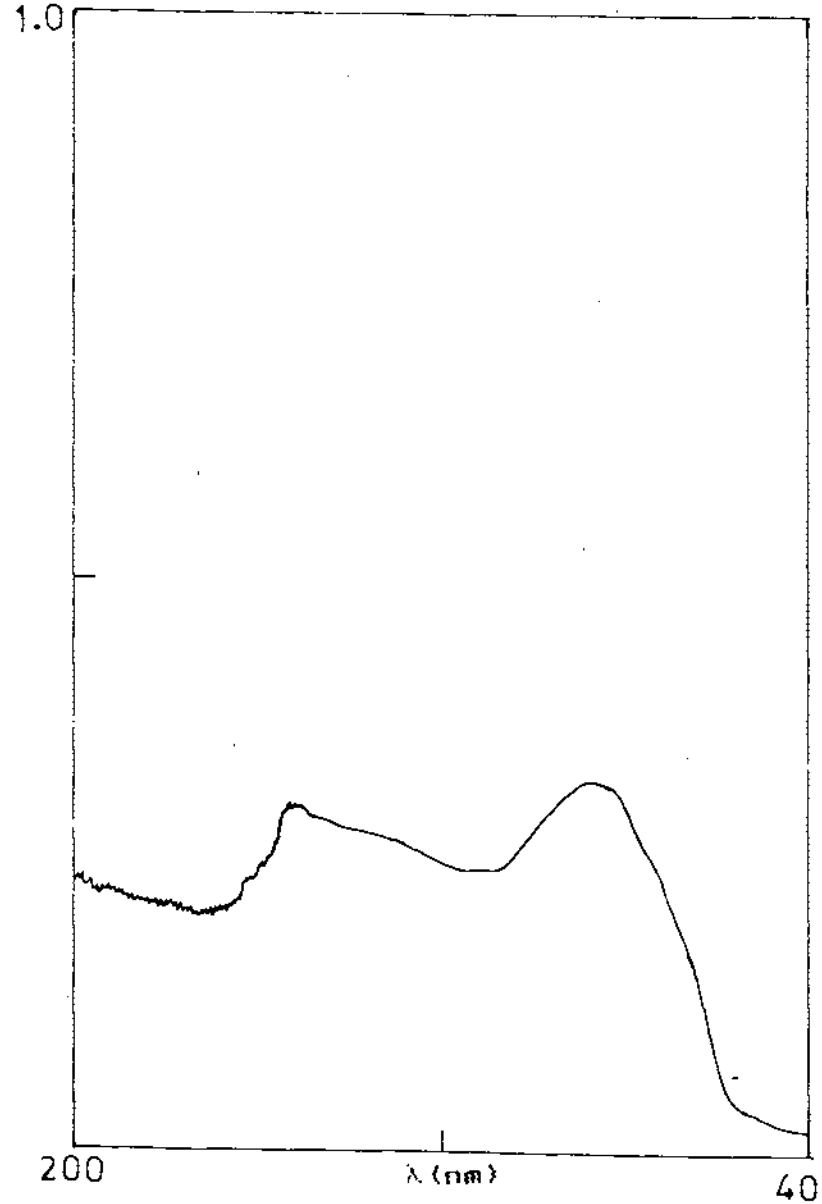


Fig.III.27. Electronic spectrum of $Bu_2Sn(Pv)_2$ in CCl_4.

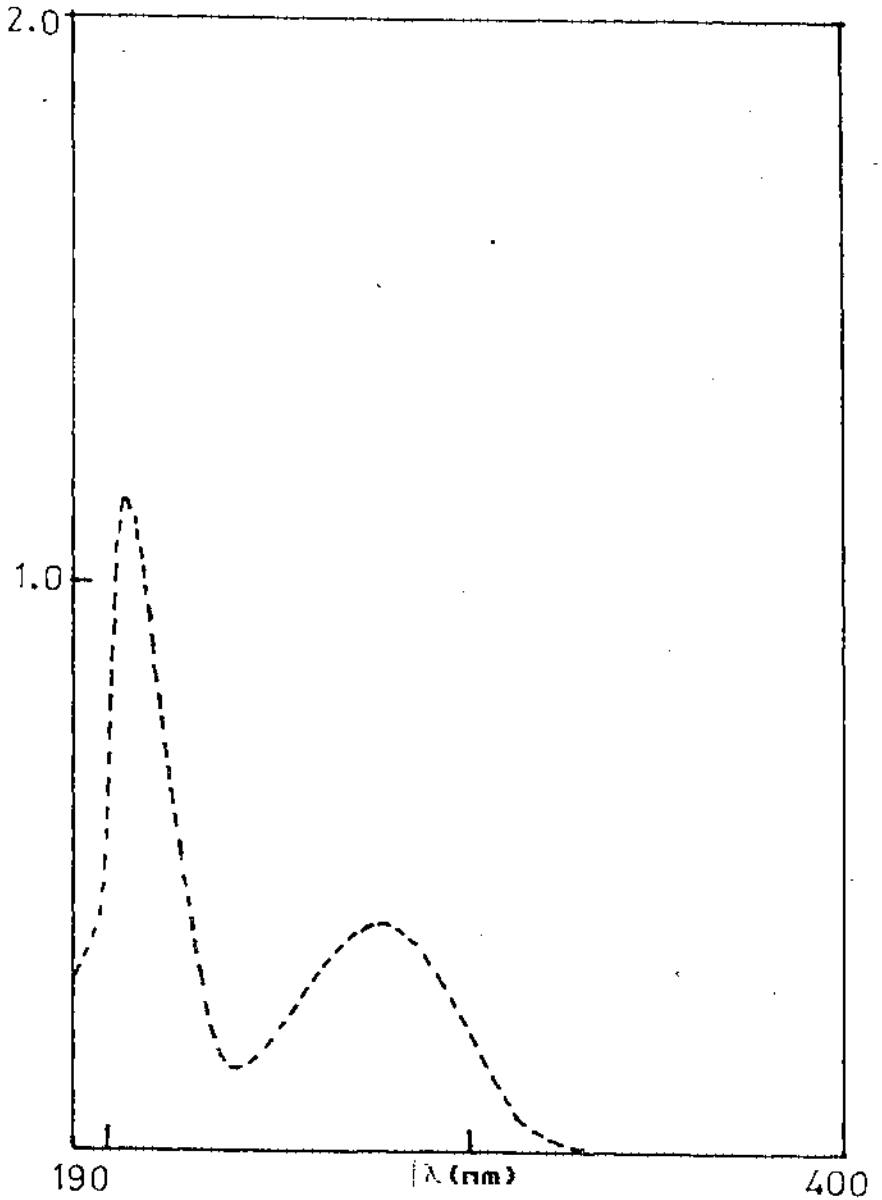


Fig.III.30. Electronic spectrum of $Oct_2Sn(PPv)_2$ in MeOH.

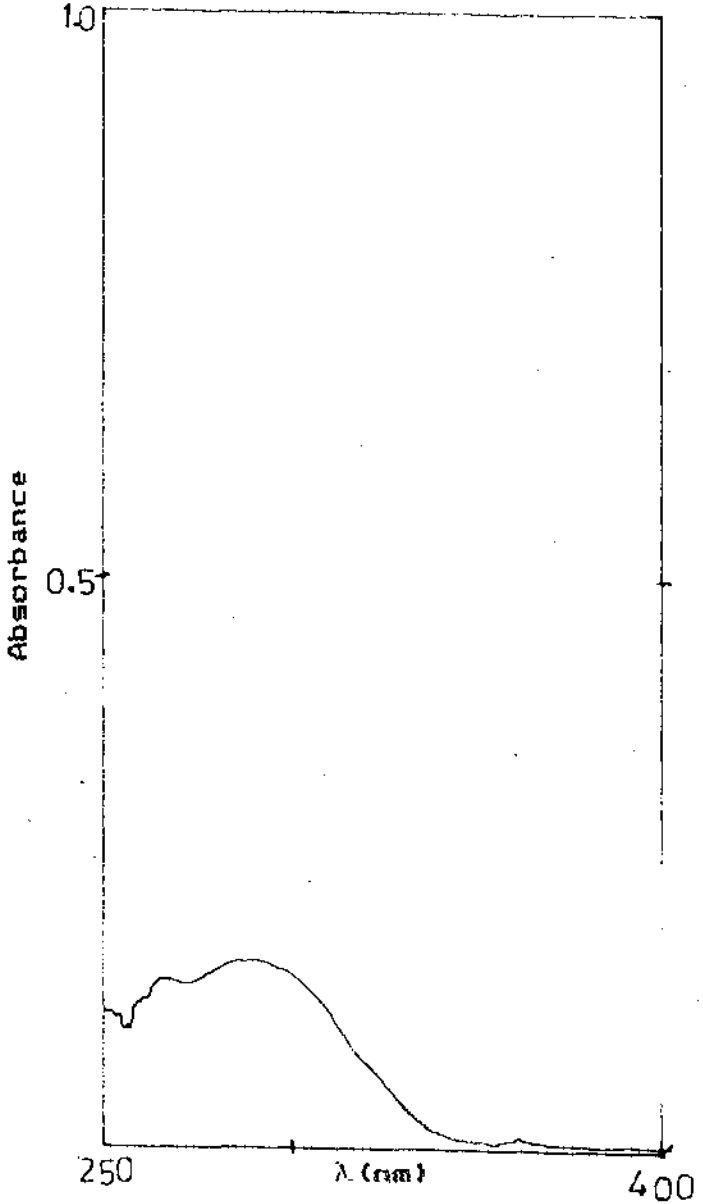


Fig.III.29. Electronic spectrum of $Oct_2Sn(PPv)_2$ in CCl_4.

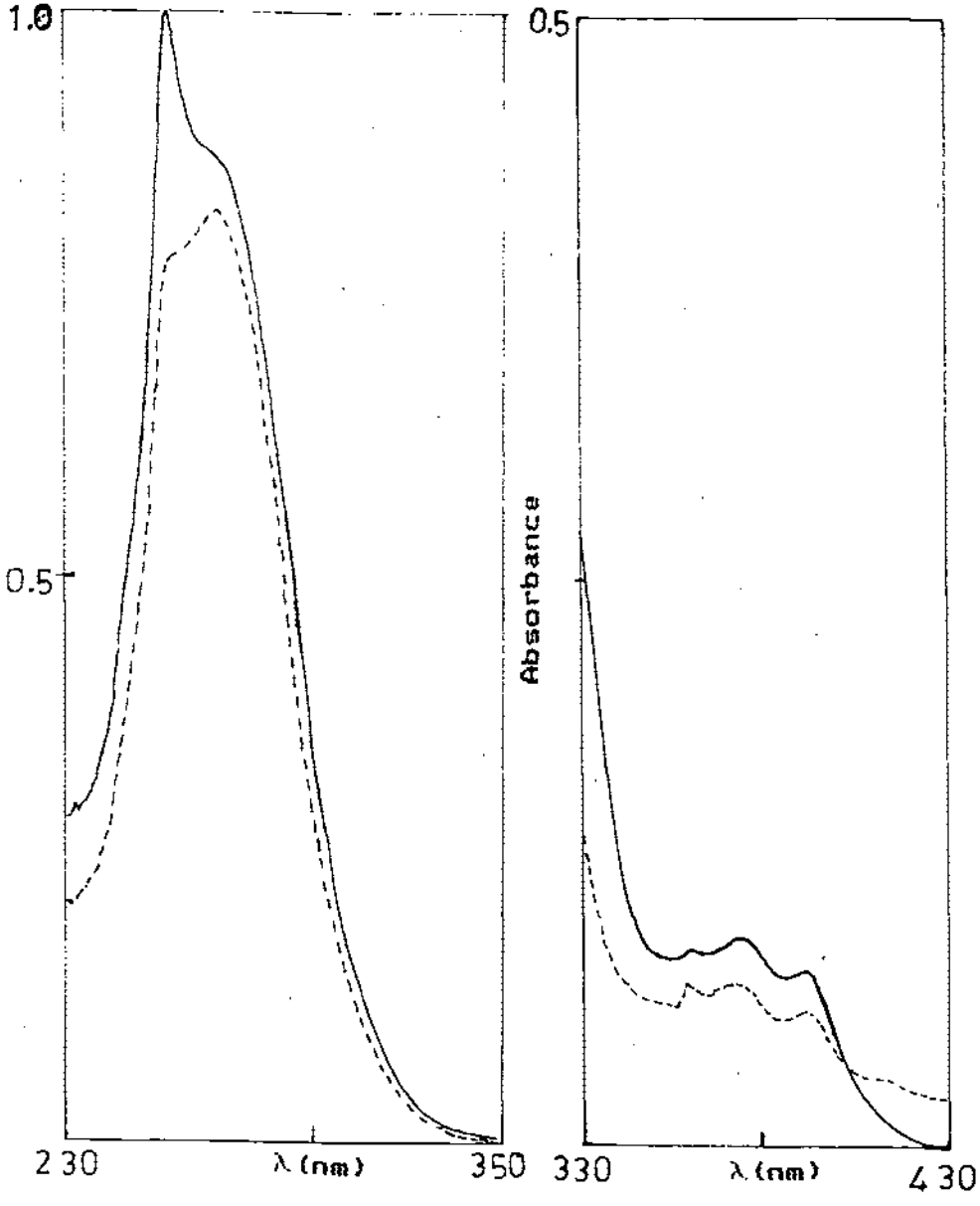


Fig.III.31. Electronic spectrum of $Bu_2Sn(BF)_2$ (———) and $Me_2Sn(BF)_2$ (- - - - -) in CCl_4.

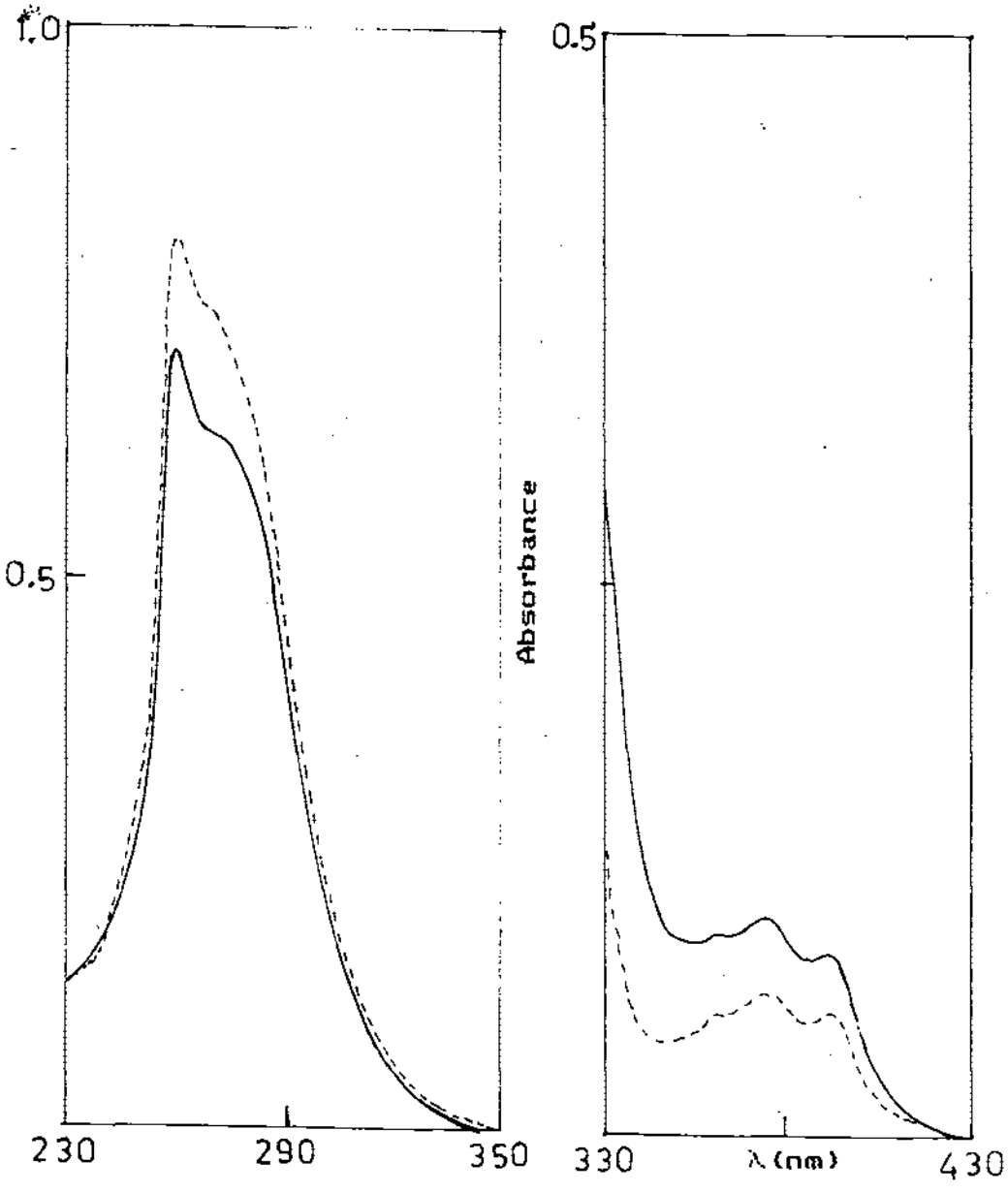


Fig.III.33. Electronic spectrum of $Oct_2Sn(BF)_2$ (———) and $Ph_2Sn(BF)_2$ (- - - - -) in CCl_4.

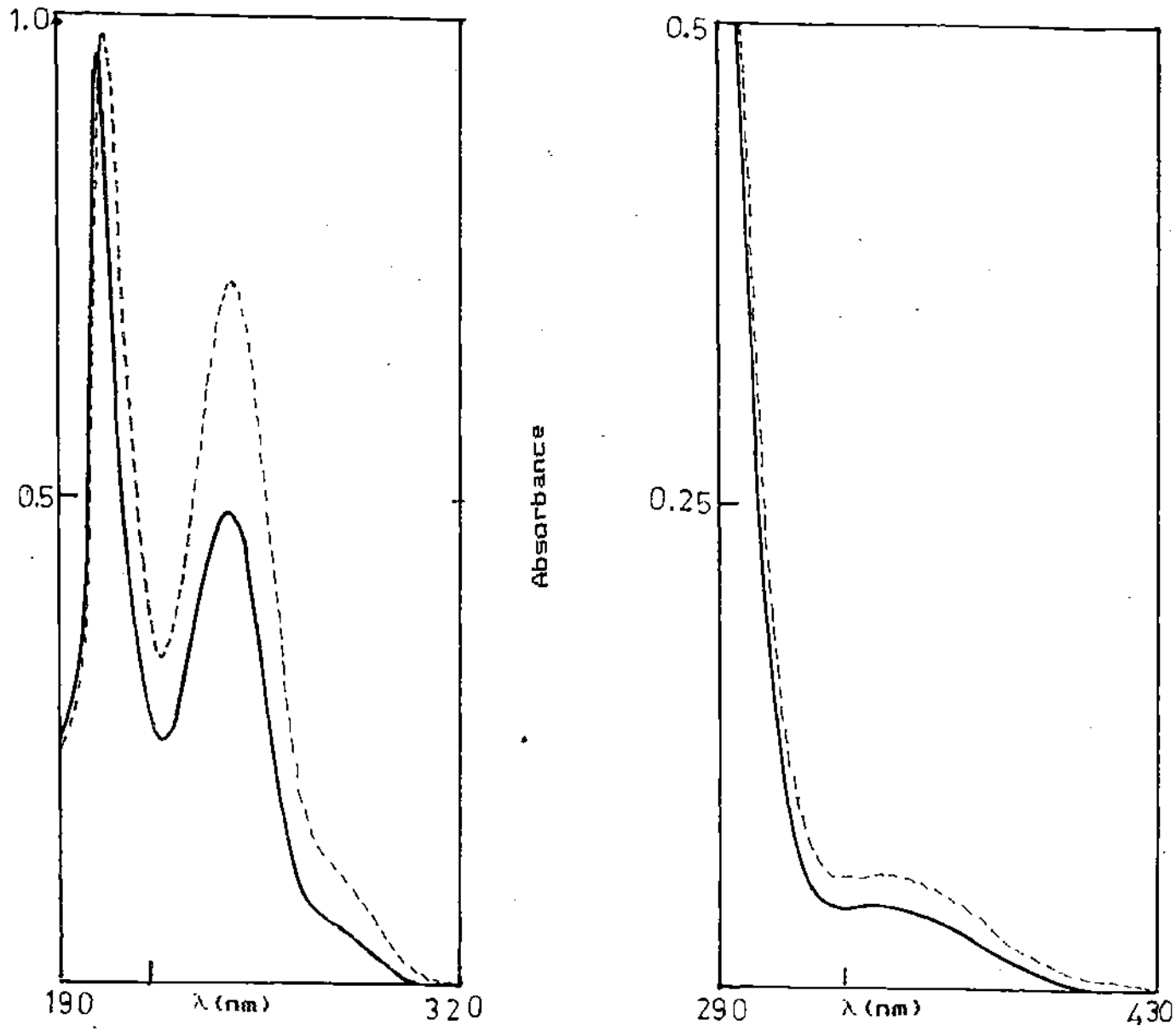


Fig.III.32. Electronic spectrum of $Bu_2Sn(BF)_2$ (——) and $Me_2Sn(BF)_2$ (------) in MeOH.

drawn from their IR spectra.

The π-π^* transitions of the carbonyl group in these organotin esters, occurring below 280 nm, are masked by the absorption bands of the Ph-ring , and therefore, provides little structural information.

(iv) ^{1}H NMR spectra :

The ^{1}H NMR spectra of the organotin keto carboxylates in $CDCl_3$ against the internal standard TMS (table-III.9.) are consistent with the structures assigned to them on the basis of IR and electronic spectral data. All the keto carboxylates exhibited expected peak multiplicities and intensities. Some of the spectra are shown in figures III.34-III.39.

Data from table-III.9. shows that the CH_3 protons in free pyruvic acid ($CH_3COCOOH$) appearing at δ 2.56ppm is only slightly shielded in ethyl pyruvate. But in the organotin pyruvates the CH_3 protons are considerably shielded due to the essentially polar nature of the Sn—O bond. The deshielding of the CH_3 protons by the adjacent C=O group is lowered due to the participation of the C=O group in intramolecular coordination. Hence, in all these compounds the CH_3 protons appear at sufficiently high field.

The signals for the resonances of the methyl and the methylene protons of the alkyl groups attached to tin appear in the same regions as reported for similar organotin

Table:-III.9

PMR data for the Organotin Keto Carboxylates:

Compounds.	Peak position (δ ppm) and assignments
$CH_3COCOOH$ (PvH)	2.56, (s), CH_3; 8.64, (s), COOH.
PvEt	1.22-1.49, (t), CH_3(Et); 2.5, (s), CH_3, (Pv); 4.13-4.5, (q), CH_2(Et).
Ph_3SnPv	2.13, (s), 3H, CH_3(Pv); 7.42-7.5, (m) and 7.68, (m), 15H, aromatic.
Bu_3SnPv	0.843-0.916, (t), (J 7.2Hz), 9H, CH_3(Bu); 1.142-1.355, (m), 15H, CH_2(Bu) and CH_3(Pv); 1.526-1.619, (m), 6H, Sn-CH_2.
$Bu_2Sn(Pv)_2$	0.834-0.906, (t), (J 7.2Hz), 6H, CH_3(Bu); 1.203-1.382, (m), (J 7 Hz), 8H, CH_2(Bu); 1.61, (s), 6H, CH_3(Pv); 2.415-2.917, (m), 4H, Sn-CH_2.
PhCOCOOH (BFH)	7.34-7.64, (m) and 8.04-8.12, (m), 5H, aromatic; 10.98, (s), COOH.
Ph_3SnBF	7.35-7.41, (m), 7.5-7.58, (m) and 7.79-7.86, (m) aromatic.
$Bu_2Sn(BF)_2$	0.89-0.96, (t), (J 7 Hz), 6H, CH_3(Bu); 1.38-1.5, (m), (J 8 Hz), 4H, Sn-CH_2; 1.68-1.92, (m), 8H, CH_2(Bu); 7.52-7.62, (m), 7.7-7.78, (m) and 8.28-8.4, (d), 10H, aromatic.
$Me_2Sn(BF)_2$	1.18, (s), 6H, CH_3(Me); 7.52-7.62, (m), 7.7-7.78, (m) and 8.28-8.4, (d), 10H, aromatic.
$Oct_2Sn(BF)_2$	0.8-0.92, (t), (J 7 Hz), 6H, CH_3(Oct); 1.1-1.48, (m), 24H, CH_2; 1.72-1.9, (m), 4H, Sn-CH_2; 7.52-7.62, (m), 7.7-7.78, (m) and 8.28-8.4, 10H, aromatic.

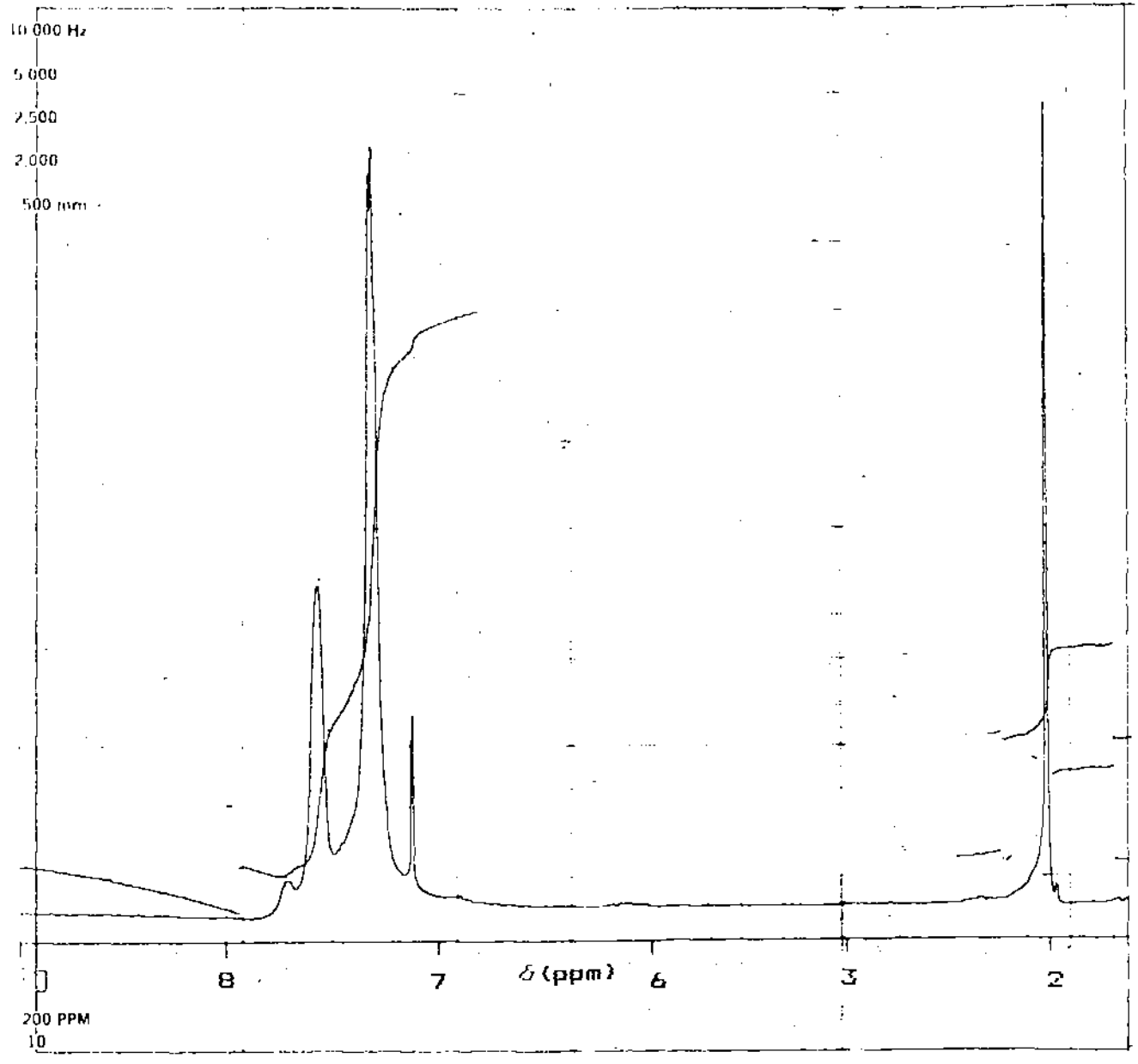


Fig.III.34. ^{1}H NMR spectrum of Ph_3SnPv in $CDCl_3$.

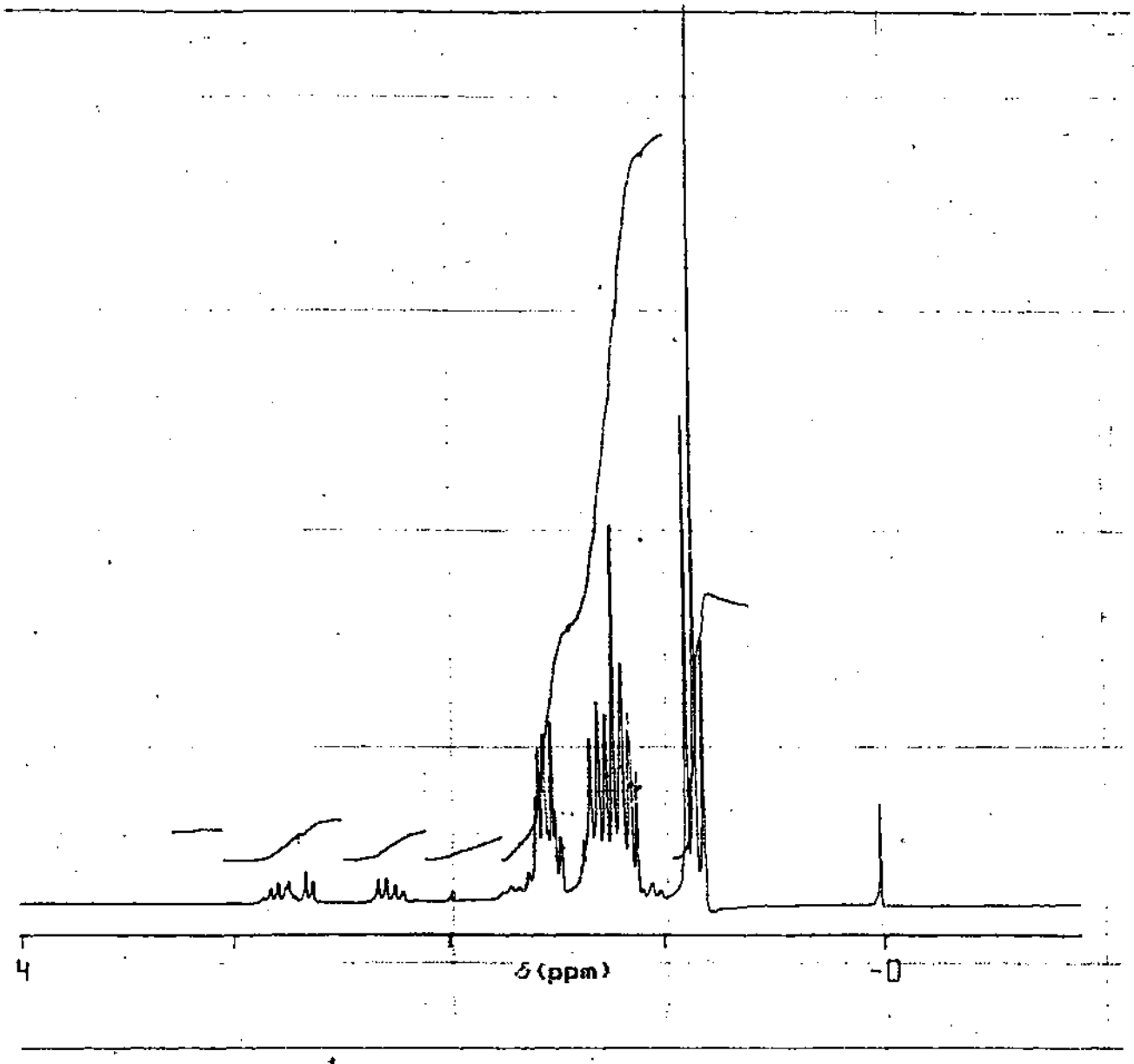


Fig.III.35. ^{1}H NMR spectrum of Bu_3SnPv in $CDCl_3$.

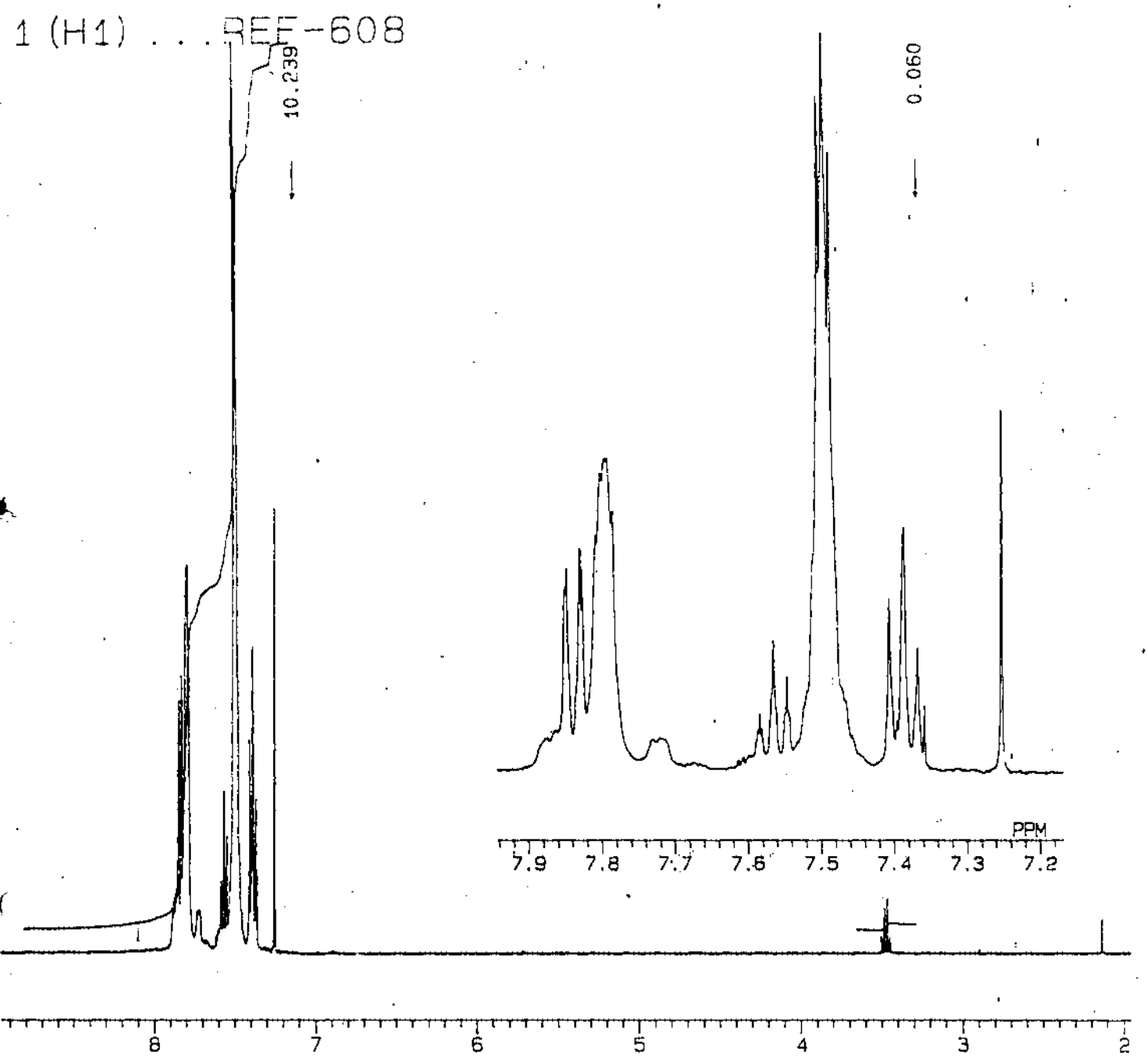


Fig.III.36. ^{1}H NMR spectrum of Ph_3SnBF in $CDCl_3$.

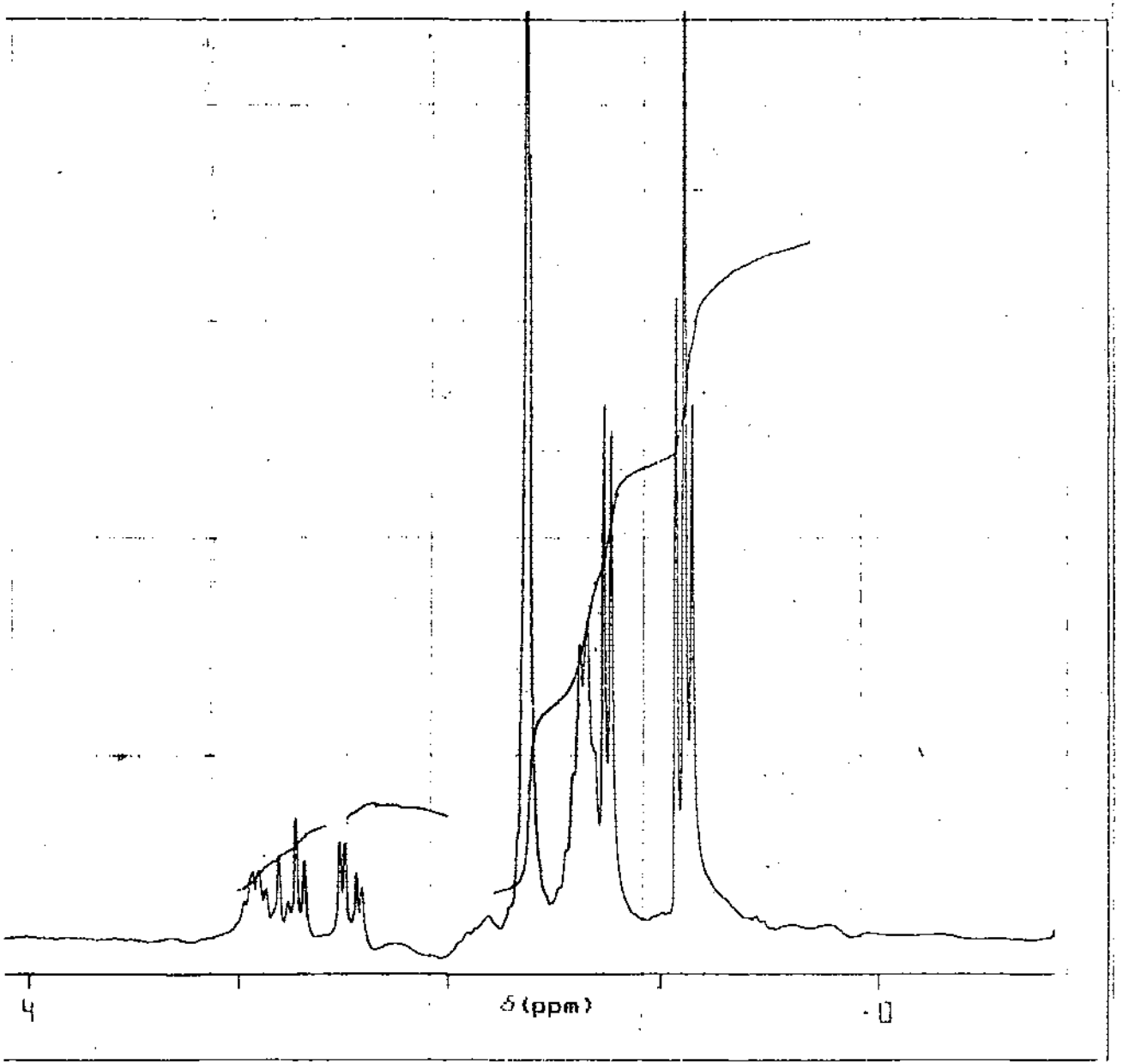


Fig.III.37. ^{1}H NMR spectrum of $Bu_2Sn(Pv)_2$ in $CDCl_3$.

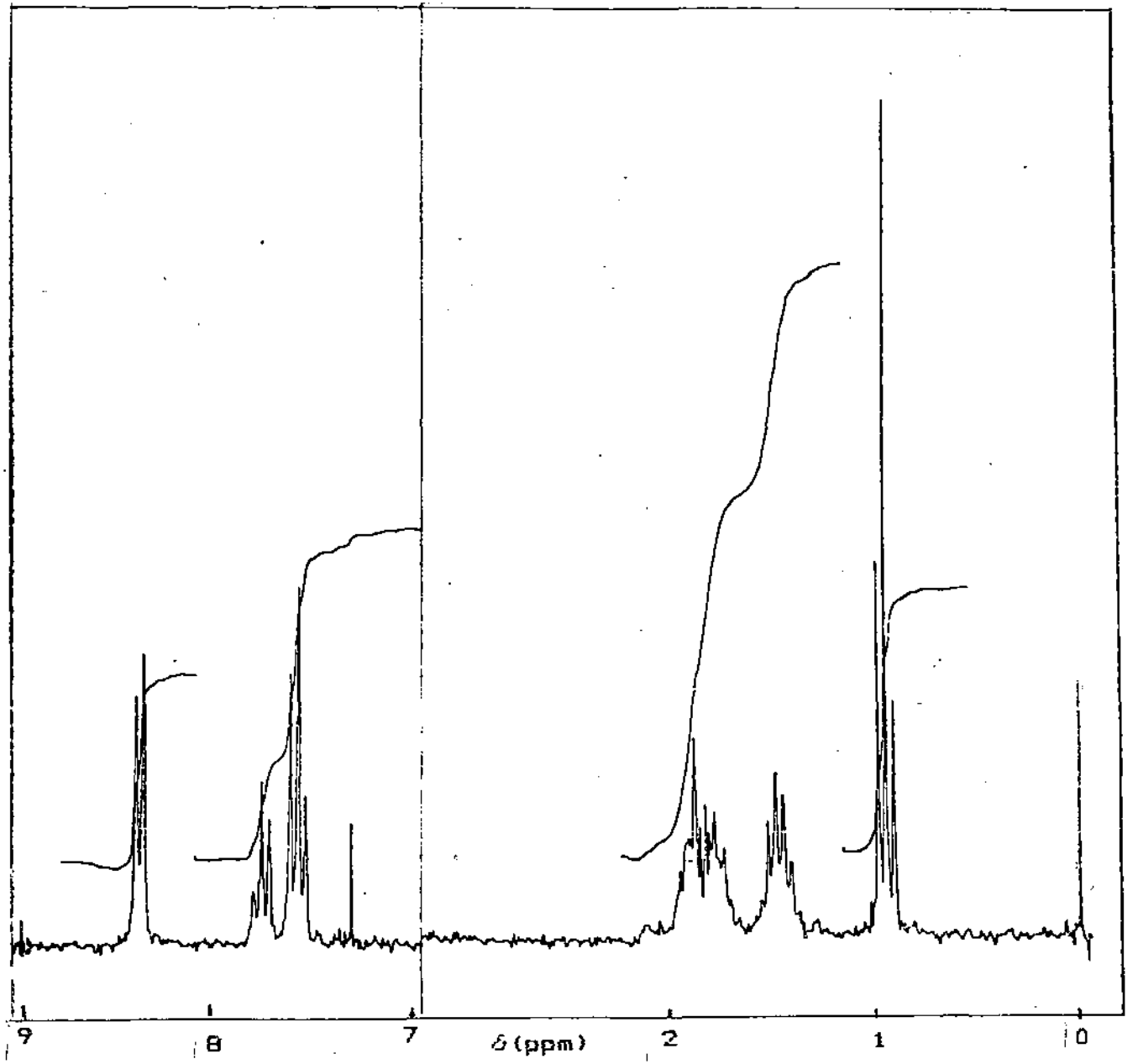


Fig.III.38. ^{1}H NMR spectrum of $Bu_2Sn(BF)_2$ in $CDCl_3$.

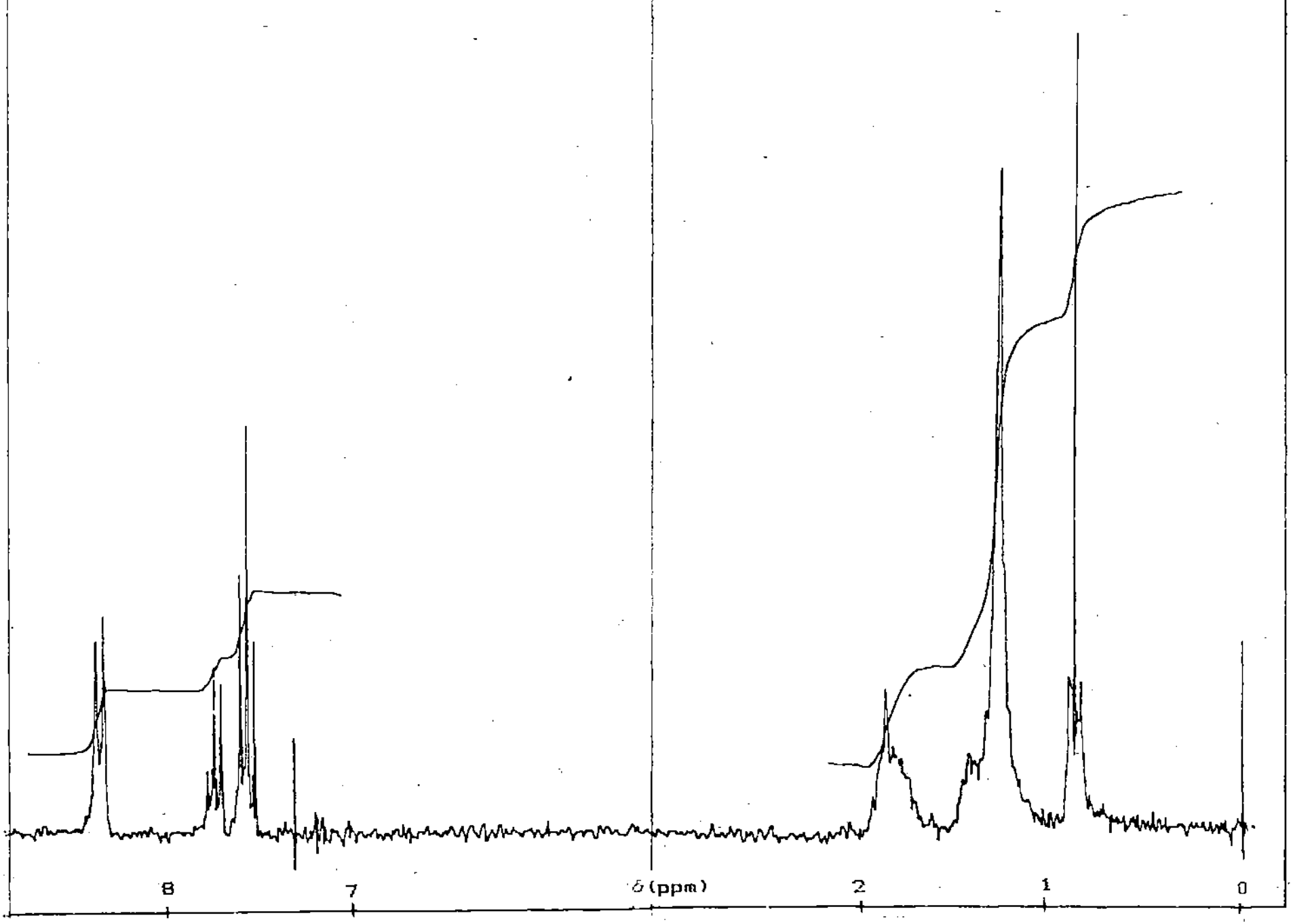


Fig.III.39. ^{1}H NMR spectrum of $Oct_2Sn(BF)_2$ in $CDCl_3$.

carboxylates[43,44].

In the derivatives of benzoyl formic acid (PhCOCOOH), due to the combined effect of the ring current and diamagnetic anisotropy of the C=O group, which remains free, the ring protons are slightly deshielded and appear as three separate groups of signals (meta, para, ortho) in the region δ 7.36-8.4 ppm.

III.3.1B. Diorganotin Di-keto carboxylates [$R_2Sn(OCOCOR')_2$] :

The diorganotin derivatives of the α-keto acids are similar to their triorganotin analogues in their solubilities, (table-III.2) melting points (table-III.1) and spectroscopic properties. For these compounds also the IR (table-III.6A) UV (table-III.10) and ^1H NMR (table-III.9) spectral data suggest intramolecular involvement of the keto group in the derivatives of PvH and PPvH, while in the derivatives of BFH the keto group remains free. Representative IR, UV and ^1H NMR spectra of these compounds are shown in figures III.10-III.14, III.27-III.33 and III.37-III.39. respectively.

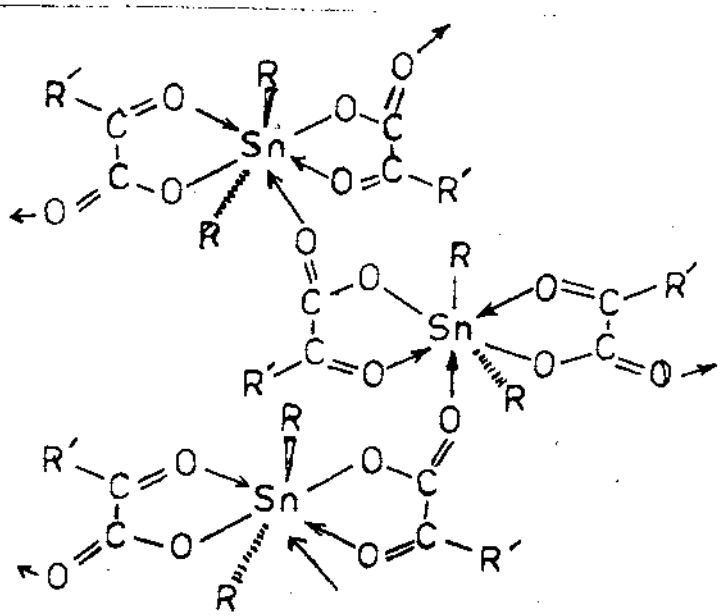
(i) IR spectra :

In the IR spectra of the diorganotin pyruvates the $\nu_{C=O}$ and ν_{asOCO} appear at around 1580 cm^{-1}, while ν_{sOCO} appears at around 1400 cm^{-1}, in the solid state. For the derivatives of PPvH the $\nu_{C=O}$ band occurs at slightly higher frequencies around 1620 cm^{-1}.

In $CHCl_3$ solution of the pyruvates the ν_{asOCO} and $\nu_{C=O}$ are raised to around 1680 and 1610 cm^{-1} respectively, while ν_{sOCO} is slightly lowered.

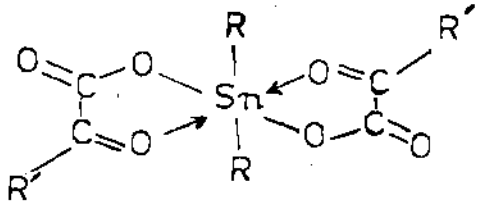
These may be interpreted in terms of the involvement of the keto group in coordination and a seven coordinate tin atom having a distorted pentagonal bipyramidal geometry in the solid state, similar to the polymeric dimethyltin dipicolinate[96].

This structure requires each molecular unit to be linked to three adjacent units through the carboxylate groups, which are most likely to function in the bridging mode, as their bite angle (—C<O O) is small (ca. 55°)[95]. Hence, the ketonic C=O group should be involved as depicted below.



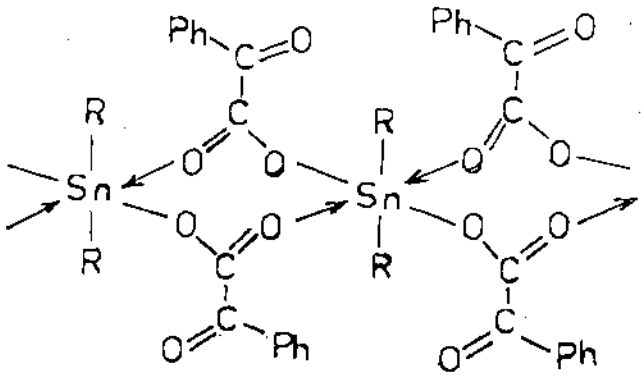
X

In solution depolymerisation is likely to occur leading to structure XI, involving monodentate carboxylate groups.



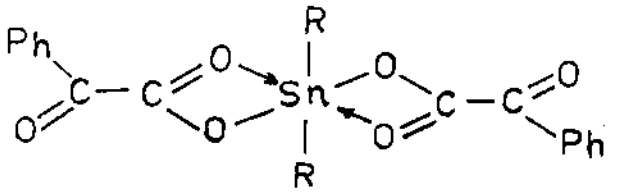
XI

In the diorganotin derivatives of BFH the $\nu_{C=O}$ frequency appears at 1686 cm^{-1}, i.e., the same as in the free acid, whereas, the ν_{asOCO} and ν_{sOCO} appear in the regions 1645-1620 cm^{-1} and 1375-1365 cm^{-1} respectively. Therefore, the keto group is not involved in coordination and this may be due to steric as well as electronic reasons as envisaged for the triorganotin benzoyl formates in section III.3.1.A. The structures of these compounds may then be represented as-



XII

In solution the ν_{asOCO} and ν_{sOCO} frequencies are only slightly changed and it is likely that chelated carboxylate groups are present, the keto group remaining free.



XIII

(ii) Electronic Absorption Spectra :

The electronic spectral data for the diorganotin esters of PvH and PPvH, shown in table-III.10, indicate that the n-π^* bands of these acids have undergone considerable blue shift on stannylation and appear in the region 300-330 nm in CCl_4 solution. As discussed for the triorganotin derivatives this shows the involvement of the keto group in coordination. Likewise, in the derivatives of BFH the n-π^* transition bands remain practically unchanged compared to the free acid, indicating the presence of non-interacting CO group.

From these observations it can be inferred that the electronic spectra further support the structures assigned to the diorganotin ketocarboxylates on the basis of IR spectra.

Table:-III.10.

Electronic spectral data of Diorganotin Keto Carboxylates:

Compounds.	$n-\pi^*$ peaks (nm) in CCl_4 Sol.	$n-\pi^*$ peaks (nm) in MeOH Sol.
PvH	370, 350, 335(sh)	330
$Bu_2Sn(Pv)_2$	340[b]	280
PPvH	385, 368, 306	345, 330, 300
$Bu_2Sn(PPv)_2$	320, 310, 296	305, 294(sh), 234
$Oct_2Sn(PPv)_2$	320, 290	278
BFH	393, 375, 360	346, 336, 292(sh)
$Bu_2Sn(BF)_2$	393, 375, 360	360, 280(sh)
$Oct_2Sn(BF)_2$	,,	,,
$Me_2Sn(BF)_2$	,,	344, 280(sh)
$Ph_2Sn(BF)_2$	,,	,,

sh-shoulder.

III.3.1.C. Carboxylato Diorganotin Hydroxides [$R_2Sn(OCOCOR')OH$] :

This group of compounds consists of organotin derivatives of PvH and PPvH, which are hydrolysates of diorganotin dicarboxylates. These highly polymeric products are obtained by heating, in benzene or solvent ether, stoichiometric amounts (1:1) of diorganotin oxide and acid for a few minutes to several hours. When oxide and acid are taken in 1:2 ratio these products are obtained along with the dicarboxylates.

On the basis of analytical data (table-III.2) these compounds can be formulated as $R_2Sn(OCOCOR')OH$. Only a few of

these compounds have well defined melting points, others decompose at high temperature. They are soluble in polar solvents like acetone or alcohol and therefore, are highly polar in nature.

Their IR spectra (table-III.6B) are characterised by the presence of broad bands below 3420 cm^{-1}, which are well below similar bands in the free acids. This bands should be attributed to OH groups which are either strongly hydrogen bonded or involved in intermolecular coordination. (Some typical IR spectra are given in figures III.40-III.44.).

Table:-III.6B.

Characteristic IR freguencies (Cm^{-1}) of some Keto Carboxylato Organotin Hydroxides (in Nujol/KBr).

Sl. no.	Compound	ν_{OH}	$\nu_{C=O}$	ν_{asOCO}	ν_{sOCO}
1.	$Bu_2Sn(Pv)OH$	3420-3380	1770	1605[b]	1412
2.	$Oct_2Sn(Fv)OH$	,,	1775	1604[b]	1412
3.	$Me_2Sn(Fv)OH$	3400-3300	1780	1660[b]	1385
4.	$Ph_2Sn(Fv)OH$	,,	1770	1600[b]	1452
5.	$Bu_2Sn(FPv)OH$	3260[b]	1684	1652 1630	1432
6.	$Oct_2Sn(FPv)OH$	3254[b]	1700	1653 1585	1400
7.	$Me_2Sn(PPv)OH$	3260[b]	1745[b]	1670 1605	1405
8.	$Ph_2Sn(PFv)OH$	3375[b]	1676	1612	1408

b-broad.

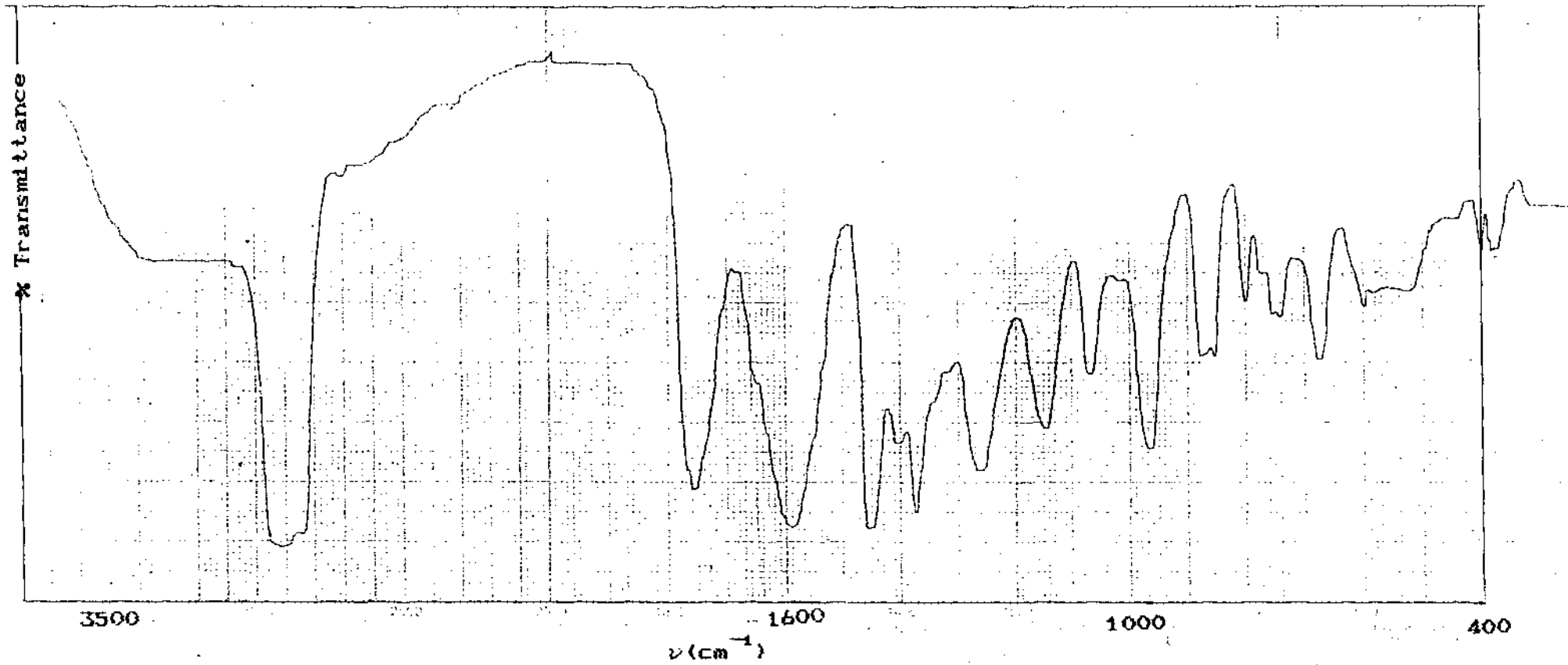


Fig.III.40. IR Spectrum of $Bu_2Sn(Pv)OH$ in Nujol.

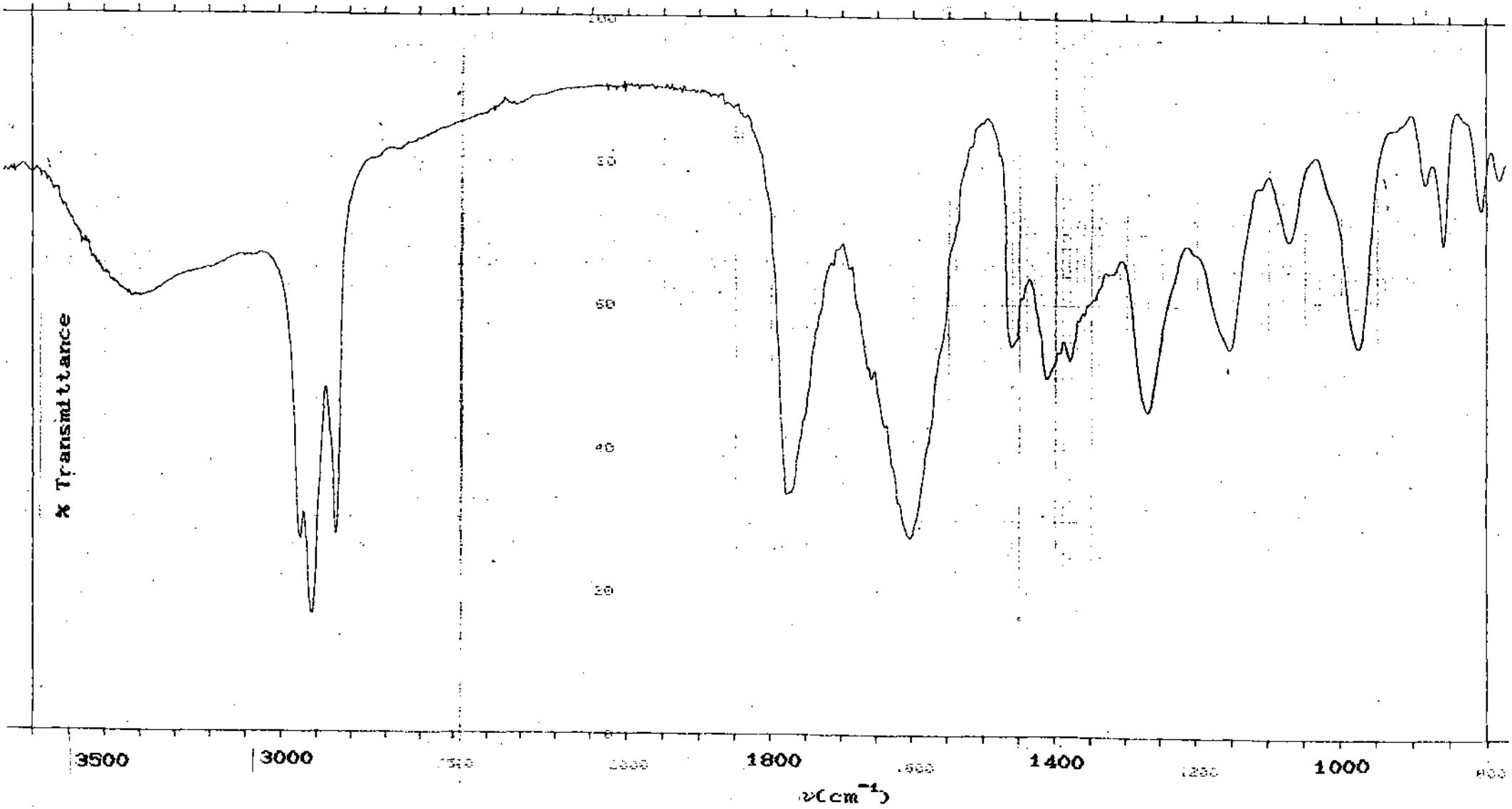


Fig.III.41. IR Spectrum of $Oct_2Sn(Pv)OH$ in KBr.

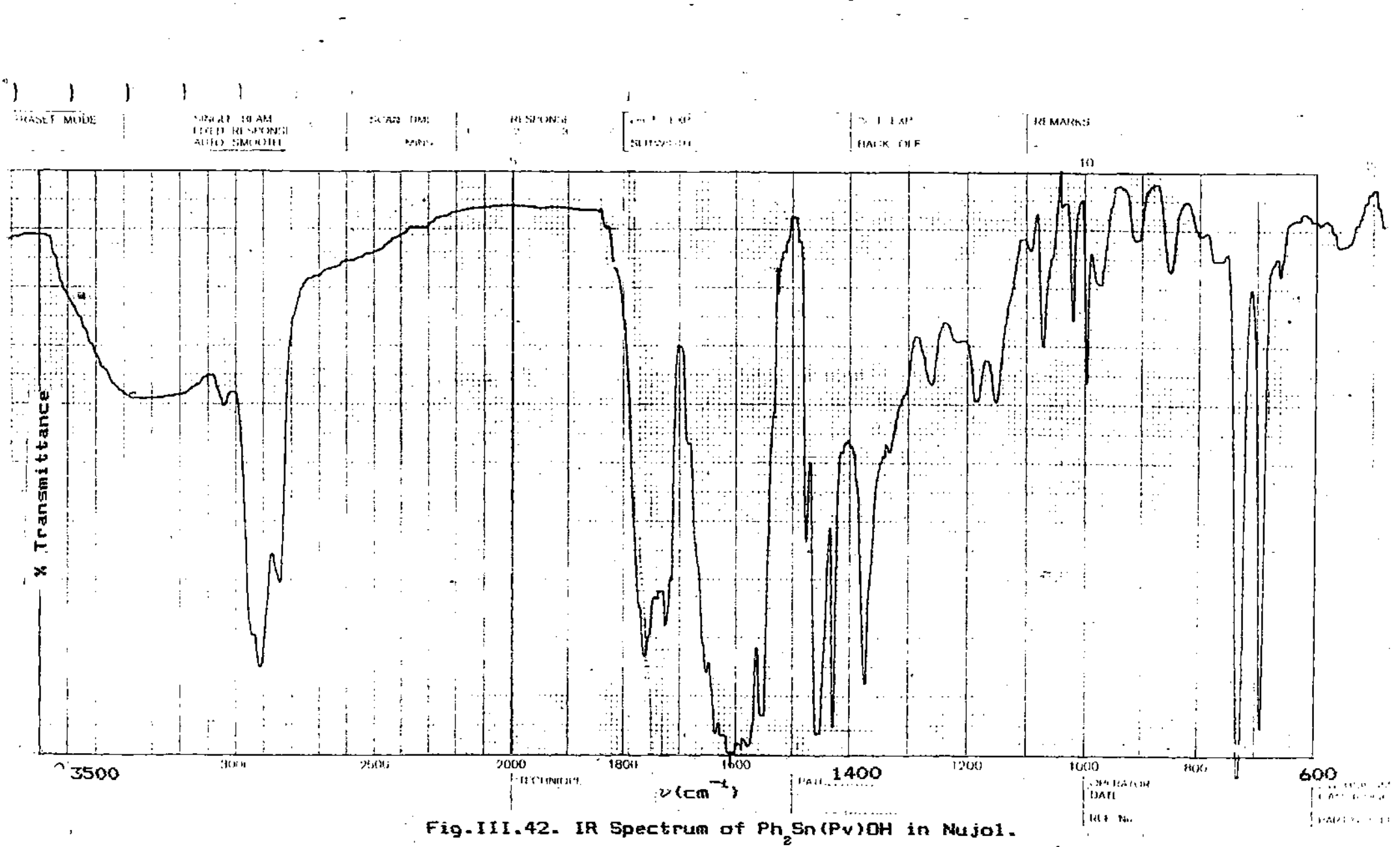


Fig.III.42. IR Spectrum of $Ph_2Sn(Pv)OH$ in Nujol.

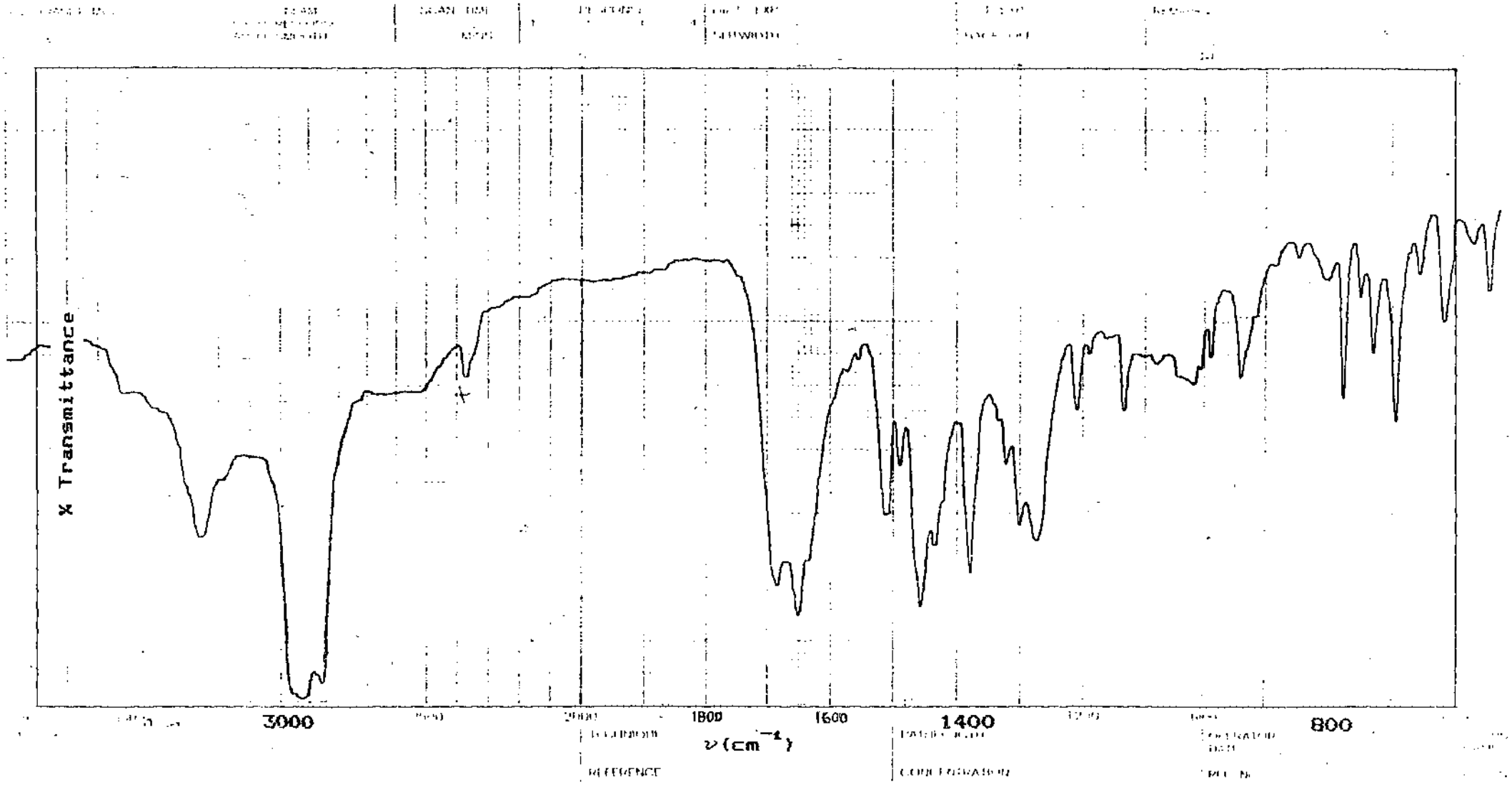


Fig.III.43. IR Spectrum of $Bu_2Sn(PPv)OH$ in Nujol.

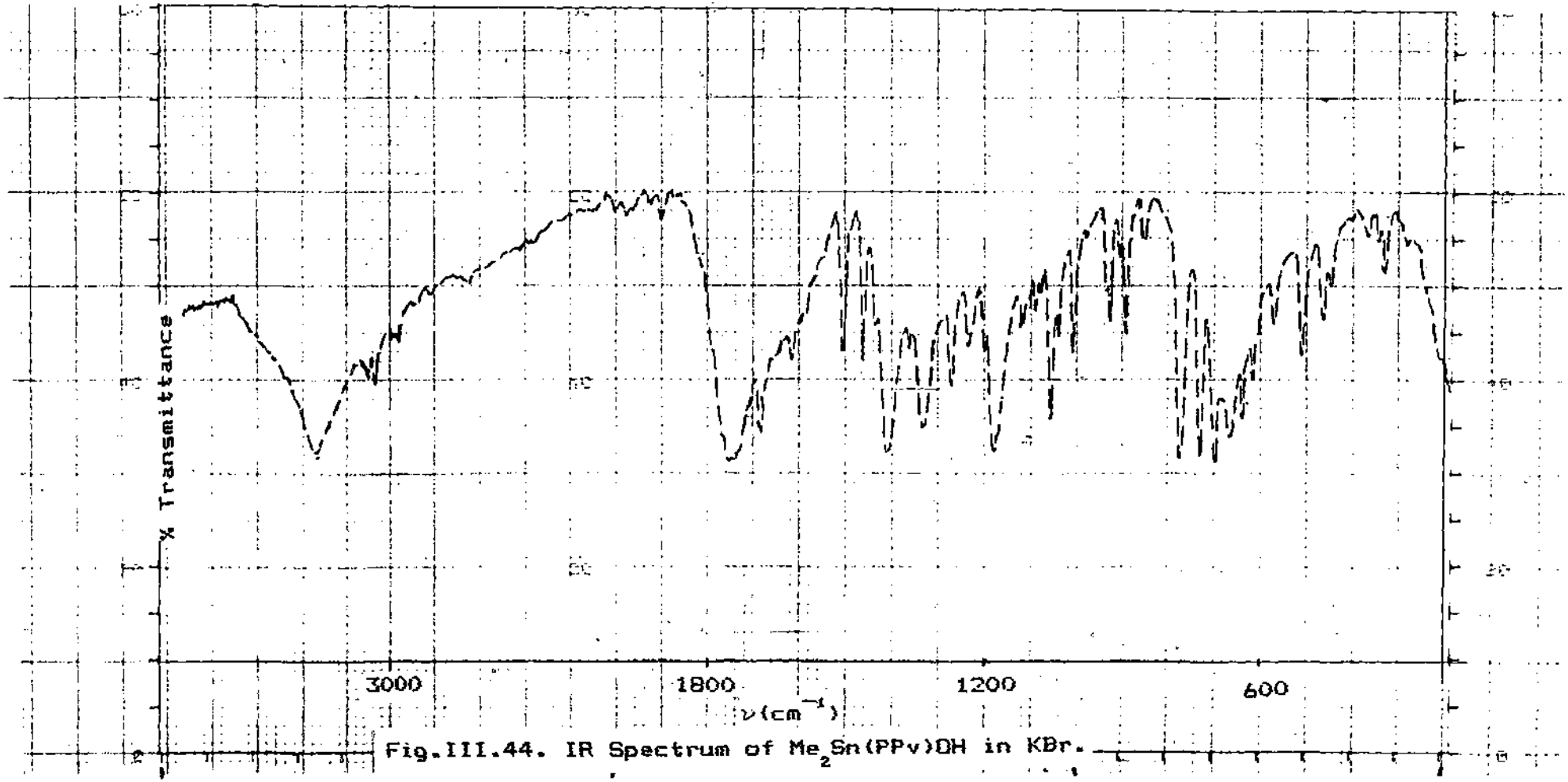
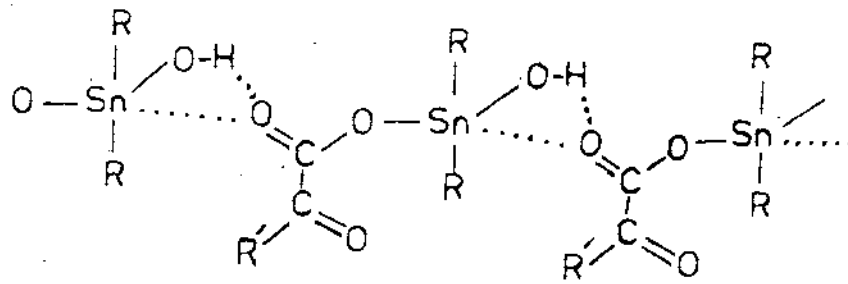
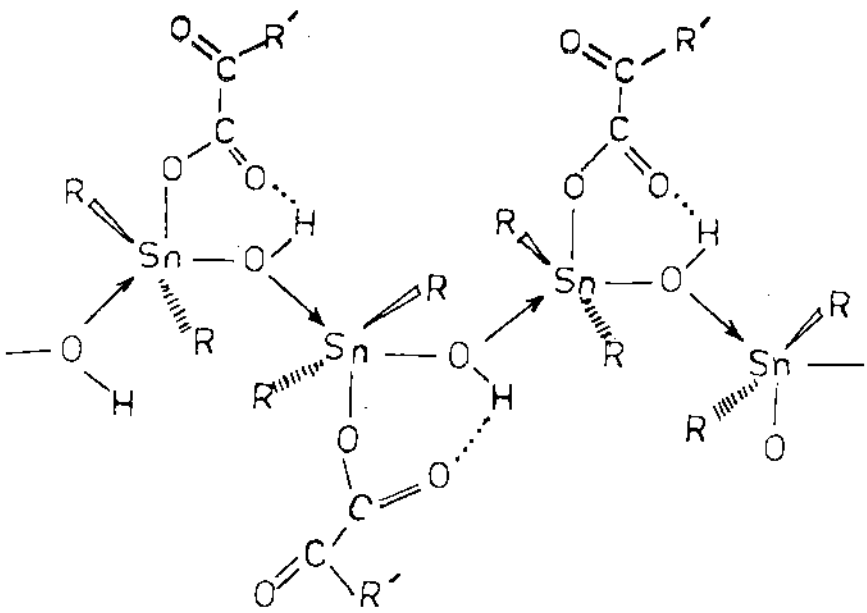


Fig.III.44. IR Spectrum of $Me_2Sn(PPv)OH$ in KBr.

Another peculiarity of these compounds is the occurrence of the $\nu_{C=O}$ bands at much elevated frequency compared to the free acids, viz., around 1770 cm^{-1} and 1700 cm^{-1} for the derivatives of PvH and PPvH respectively. These indicate the presence of free keto group comparable to the triorganotin derivatives of γ-keto carboxylic acids investigated by KumarDas et.al.[40]. The asymmetric and symmetric carboxyl stretching bands of these compounds appear in the region 1660-1600 cm^{-1} and 1430-1400 cm^{-1} respectively, in the solid state. These can be interpreted by assuming the presence of either, (a) hydrogen bonded carboxylate groups, involving trigonal bipyramidal tin atom geometry having the R groups above and below the equatorial plane of three O atoms as shown in structure XIV/XV below- or, (b) a bidentate carboxylate group involving 6-coordinate tin atoms as shown in structure XVI below, with the R groups occupying meridional positions as in the H-bonded structure XV.

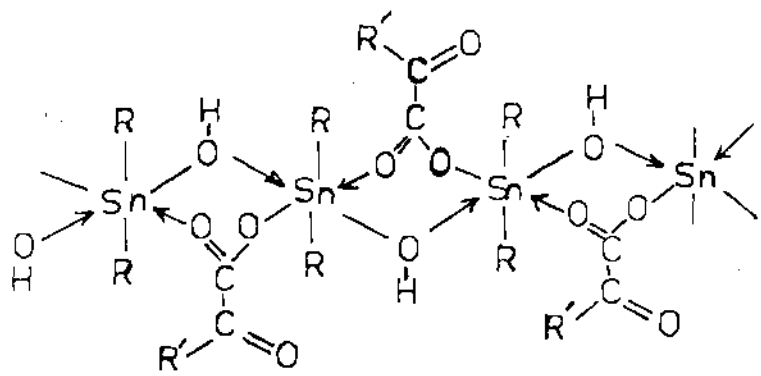


XIV



XV

The structures XV and XVI differ only slightly because one can be easily converted into the other by the simple rotation of the carboxylate moiety through 180° about the Sn—O (ester) bond.



XVI

The probable course of the reaction between diorganotin oxides and keto acids leading to the formation of the carboxylato diorganotin hydroxides may be represented as follows:

$$2\ R_2SnO + 4\ HOCOCOR' \xrightarrow{-2HOH} 2\ R_2Sn(OCOCOR')_2 \xrightarrow[-2\ R'COCOOH]{+HOH}$$

$$(R'COCOO)R_2SnOSnR_2(OCOCOR') \underset{-HOH}{\overset{+HOH}{\rightleftharpoons}} 2\ R_2Sn(OCOCOR')OH$$

It is also possible that the oxide and acid react directly to produce $R_2Sn(OCOCOR')OH$

$$R_2SnO + HOCOCOR' \longrightarrow R_2Sn(OCOCOR')OH$$

Apart from their reactions with Ph_2SnO, the keto acids produced $Ph_2(OCOCOR')OH$ from their reaction with $(Ph_3Sn)_2O$ also, probably through the cleavage of Ph-Sn bond, to be discussed in the next chapter.

III.3.2. *Conclusion :*

On the basis of spectroscopic evidences it can be inferred that the course of reaction between the α-keto acids and organostannoxanes is determined primarily by the nature of the $R'COCOO^-$ moiety and depending on the R' group, intra molecularly coordinated organotin carboxylate derivatives may be formed in some cases.

Spectroscopic data suggest that, in some of the keto carboxylates, the tin atom has apparently attained a coordination number of six through involvement of the carboxyl moiety in both inter and intra molecular coordination.

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