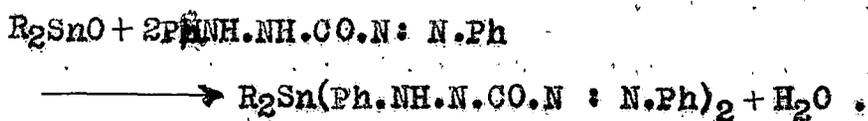
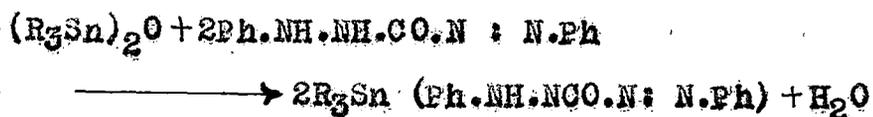


Results and discussions

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

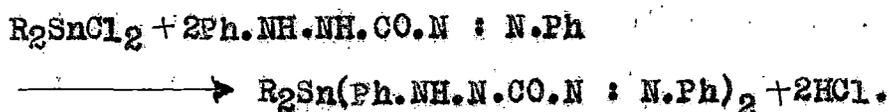
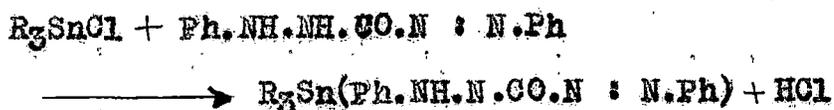
Triorganotin diphenyl carbazonates and diorganotin bis-diphenyl carbazonates have been prepared by following methods:

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



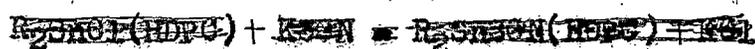
The water formed was separated by azeotropic distillation.

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

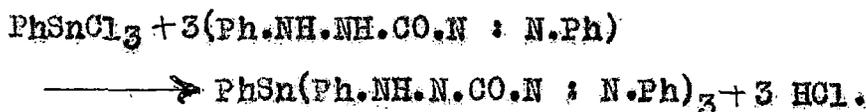


The hydrochloric acid liberated was neutralised with concentrated ammonia solution and precipitated ammonium chloride was removed by filtration.

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

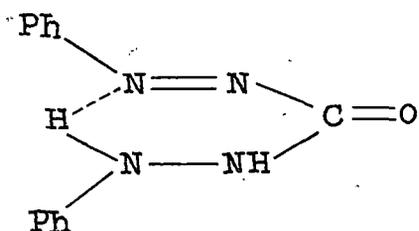


~~Potassium chloride was removed by filtration.~~ The monophenyltin tris-diphenyl carbazonate was prepared by the following method:

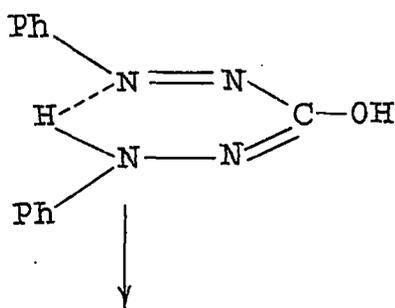


The visible spectrum of diphenyl carbazone in a polar solvent gave two absorption maxima (129). The more intense one at about 455nm and the other with much lower intensity at 565nm. In 1966 Kemula and Janowski suggested the 565 nm band due to the following

pseudo six-ring form of diphenyl carbazone.

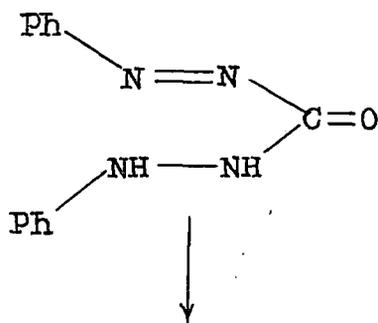


But Willems and Zeeger-Huysskens (130) attributed 565 nm band to the 'enol' form present in low concentration. The 455 nm absorption band is generally attributed to the free 'keto' form as shown below



'enol' form

$\lambda_{max} = 565 \text{ nm}$

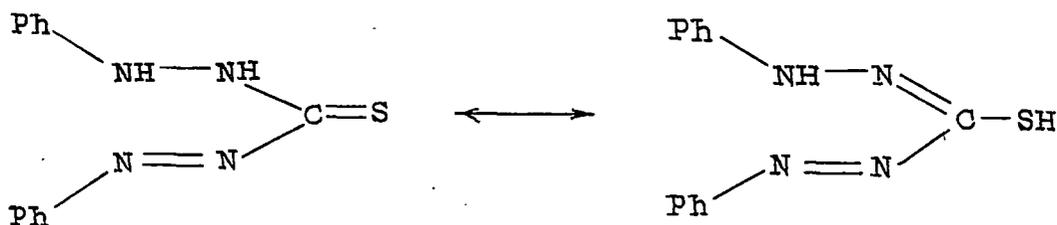


'keto' form

$\lambda_{max} = 455 \text{ nm}$

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

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



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

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

<u>Compound</u>	<u>λ_{max} (nm)</u>
$\text{Ph}_3\text{Sn}(\text{HDPC})$	548
$\text{Ph}_2\text{Sn}(\text{HDPC})_2$	550
$\text{Ph}_2\text{SnCl}(\text{HDPC})$	550
$\text{Bu}_2\text{SnCl}(\text{HDPC})$	530
$\text{Bu}_2\text{SnBr}(\text{HDPC})$	530
$\text{Me}_2\text{SnCl}(\text{HDPC})$	530

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

The IR spectral data of organotin diphenyl carbazonates gave some interesting observations. The IR spectrum of pure diphenyl carbazone in CHCl_3 or CCl_4 are reported (129) to show two absorption bands in $3000-4000\text{ cm}^{-1}$, at 3410 and 3350 cm^{-1} . The intensity of the two bands decreases and three new bands appear at 3275 , 3195 and 3075 cm^{-1} when the concentration of diphenyl carbazone increases. Kemula and Janowski ascribed the 3410 cm^{-1} band to free N-H stretching vibration of the N-H group

in the β -position to the $>C=O$ group. They assigned 3350 cm^{-1} band to free N-H stretching vibration of the N-H group in the α -position and the three new bands at 3275 , 3195 and 3075 cm^{-1} to intermolecular bonded N-H stretching vibrations. But Willems and Zeegers - Huyskens (loc. cit) assigned the 3410 cm^{-1} band to free N-H vibration and 3350 cm^{-1} band to intramolecular bonded N-H vibrations.

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

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

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

in organotin diphenyl carbazonates indicating their strong chelated nature.

In case of metallic dithizonates, δ NH bend vibrations are reported at $\sim 1520 \text{ cm}^{-1}$ by Irving (137). He also suggested that two secondary dithizonates Ag_2Dz and $\text{PdDz} \cdot 2\text{H}_2\text{O}$ have δ NH bend vibrations at 1530 and 1528 cm^{-1} respectively, which however, apparently have no such NH bond. In case of organotin dithizonates, strong absorption around 1500 cm^{-1} have been observed. Similarly we also obtained strong absorptions at $\sim 1500 \text{ cm}^{-1}$ for organotin diphenylcarbazonate. It is rather difficult to assign unequivocally the $\sim 1500 \text{ cm}^{-1}$ band due to δ NH bend vibrations, since the aromatic part of the ligand should also contribute C = C ring vibrations in the same region. Therefore, the best we can assign the $\sim 1500 \text{ cm}^{-1}$ band is probably due to coupled δ NH bend and C = C ring vibration.

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

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

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

The IR spectra of organotin diphenyl carbazonates are extremely complicated in nature, since both the organotin and

ligand moieties have large number of bands of different intensities. Hence it was not found feasible to interpret many other bands present in organotin diphenyl carbazonates.

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

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

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

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

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

Table - 1

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

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

Contd..

Table - 1 (Contd..)

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

In the pmr spectra of diphenyl carbazone, the N-H protons give a sharp singlet at 5.72 ppm and the aromatic protons appear as triplet in the region 6.7-6.96 ppm. The signals over 7.0 ppm is probably due to some impurities (CHCl₃) in the solvent. In dimethyl tin bis-diphenyl carbazonate, the methyl protons appear at 0.80 ppm as sharp singlet indicating trans methyl structure (132).

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

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

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

The alkyl protons of dibutyl tin bis-(diphenyl carbazotate) (0.6-1.9 ppm) and dibutyl bromotin diphenyl carbazotate (0.6-2.1 ppm) are found in the similar region. In comparison with these two compounds, the alkyl protons of dibutyl chlorotin

diphenyl carbazonate (0.7-2.2 ppm), are slightly deshielded. This may be due to the electron pull of the chlorine as was explained in the case of dimethyl tin derivatives of diphenyl carbazonate previously.

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

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

In case of tricyclohexyl tin diphenyl carbazonate the aromatic protons are deshielded to 6.6-7.8 ppm and cyclohexyl ring protons appeared in the region 0.7-2.3 ppm. The NH protons could be obtained in 5.63 and 9.3 ppm. The positions of alkyl

and aromatic protons are expected due to the chelated nature of the complex.

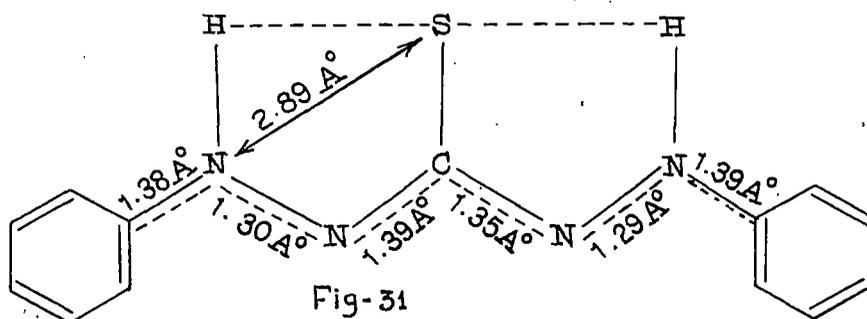
In the p.m.r. spectra of organotin derivatives of diphenyl carbazone, the position of NH protons are variable.

In diphenyl carbazone, we have noticed the NH protons to appear at 5.72 ppm. But in organotin diphenyl carbazonates, the NH protons appear in the region of 6.2-9.6 ppm. Such variation in position may be due to the nature and extent of hydrogen bonding present in such molecules. Apart from it, the position of NH is also dependent of concentration. In this connection we can cite a comparable situation in case of p.m.r. spectra of dithizone (135). "Coleman et al only observed 1.6 non aromatic protons at τ -2.03 in place of the total of 2.0 protons to 8.0 aromatic protons. Recent measurements in Leeds, using an instrument of higher resolving power (90 MHz Bruker HFX) showed that the p.m.r. spectrum of dithizone in CDCl_3 present two signals, at τ -2.61 and τ 9.03, of integrated area 3:1, and completely accounting for the two non-aromatic protons. The signal at τ 9.03 occurs in the characteristic region for the SH group in the absence of significant hydrogen bonding. Carlin^(R) had previously noted that the infrared vibration at 2590 cm^{-1} in the solid corresponded to the stretching frequency for a non-hydrogen bonded SH group. The lack of infrared absorption in region ($3100\text{-}3500 \text{ cm}^{-1}$) indicates the absence of a free : NH

group and implies its participation in strong hydrogen bonding".

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

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



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

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

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

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

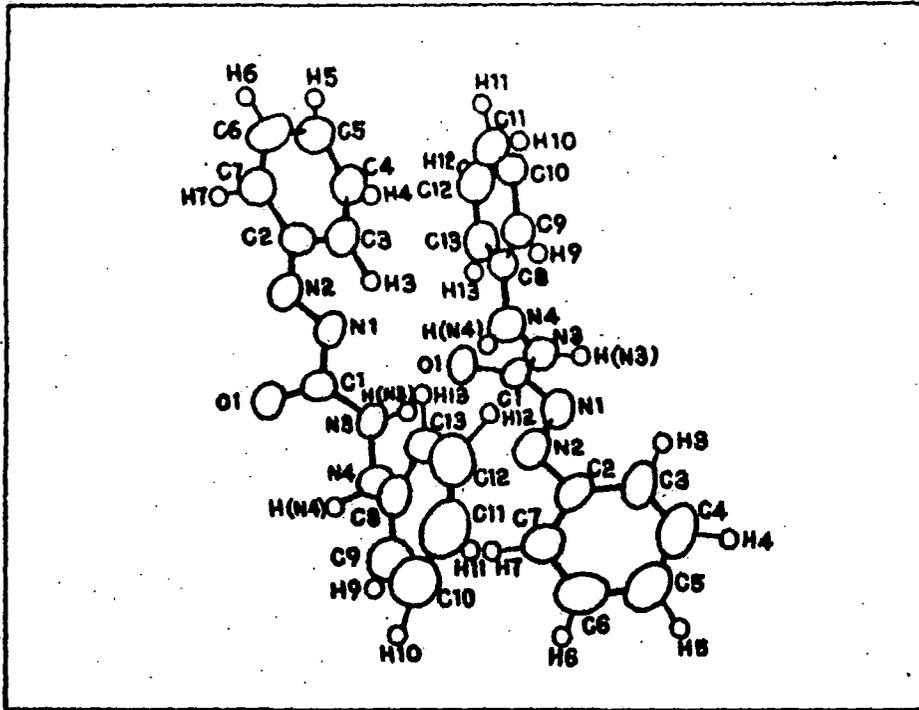


Fig.-32 X-ray crystal structure of diphenyl carbazone molecule in the asymmetric unit .

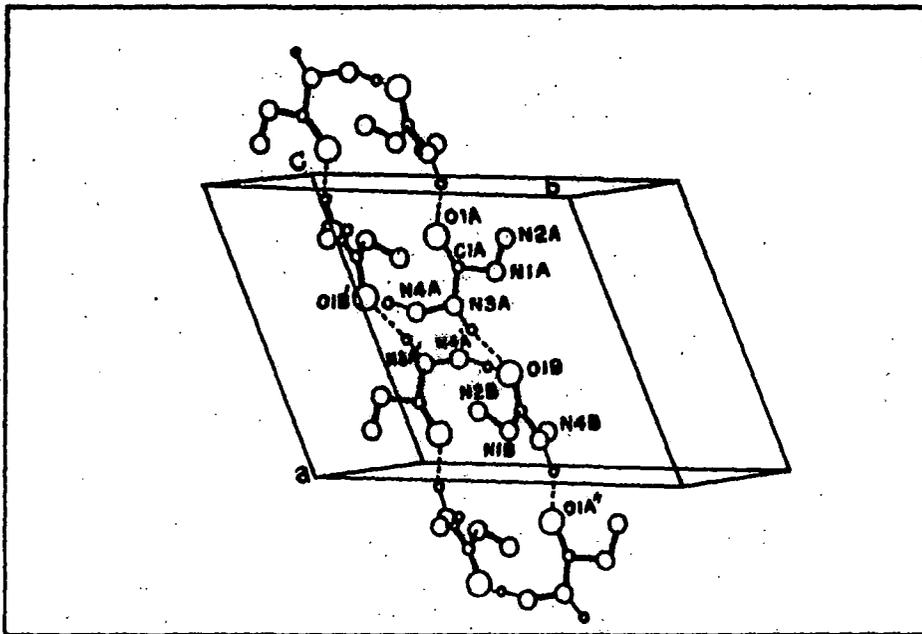
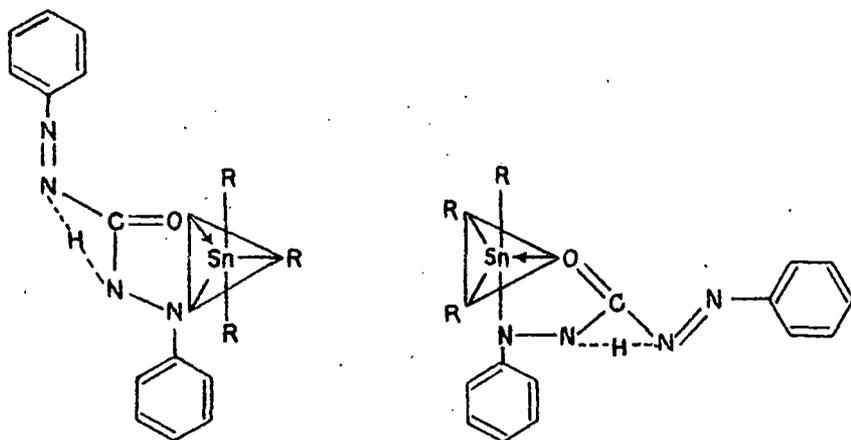


Fig-33 Packing of diphenyl carbazone molecules (hydrogen bonds are shown in dotted line and phenyl rings are omitted for clarity).

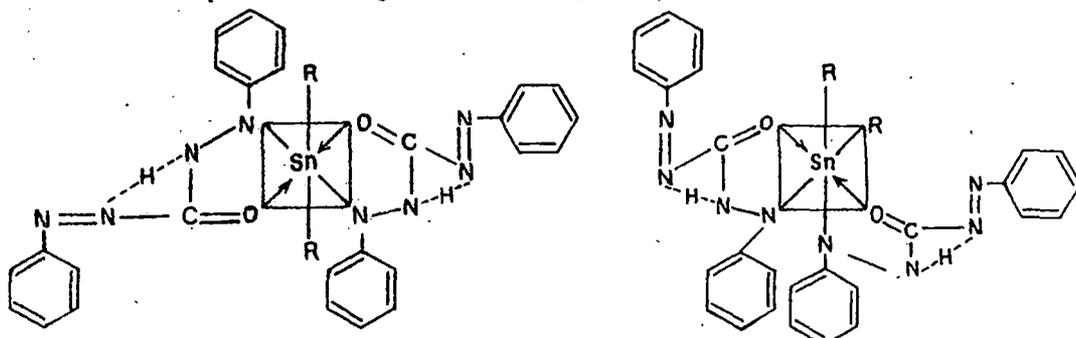
PMR spectra of many organotin diphenyl carbazone also confirm the presence of one imino proton in organotin complexes. The IR and visible spectra of organotin diphenyl carbazones clearly indicate the presence of carbonyl group in the complexes as indicated by shifting of absorption bands both in visible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

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

Possible structures of triorganotin diphenyl carbazonates



Possible structures of diorganotin bis-diphenyl carbazonates



Possible structures of diorganotin diphenyl carbazonates

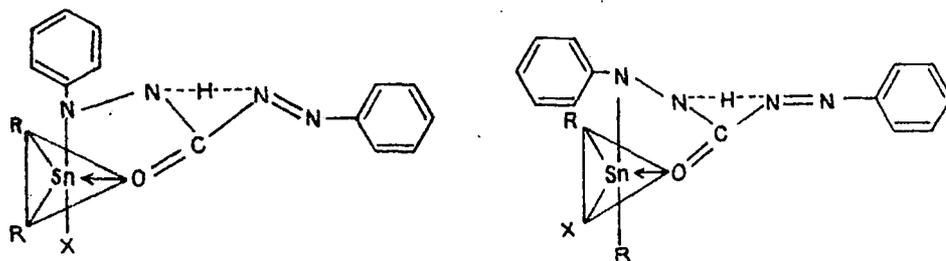
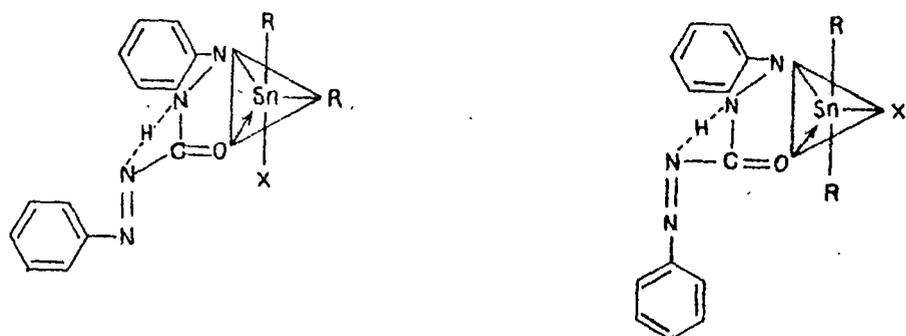


Fig-34A

Possible structures of diorganotin diphenyl carbazonates



Possible structures of monoorganotin tris diphenyl carbazonates

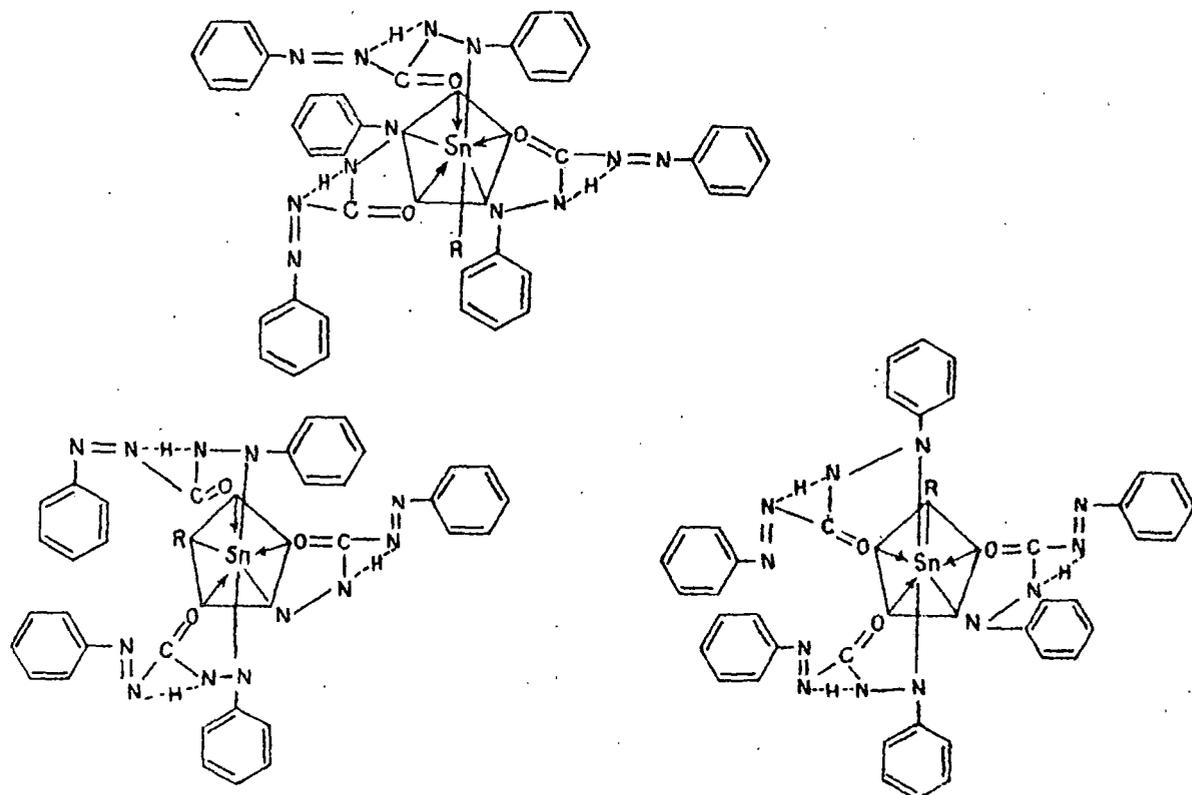


Fig-34B.