Results and discussions

Triorganotin dithizonates and diorganotin bis-dithizonates have been prepared by the following two methods:

(a) by refluxing a mixture of organotin oxide and dithizone in 1:2 molar ratio in chloroform:

$$(R_3Sn)_2O + Ph.NH.NH.\overset{S}{\overset{\|}{C}}.N{:}N.Ph \longrightarrow R_3Sn(Ph.NH.NCSN{:}N.Ph) + H_2O$$

$$R_2SnO + Ph.NH.NH.\overset{S}{\overset{\|}{C}}.N{:}N.Ph \longrightarrow R_2Sn(Ph.NH.NCSN{:}N.Ph)_2 + H_2O$$

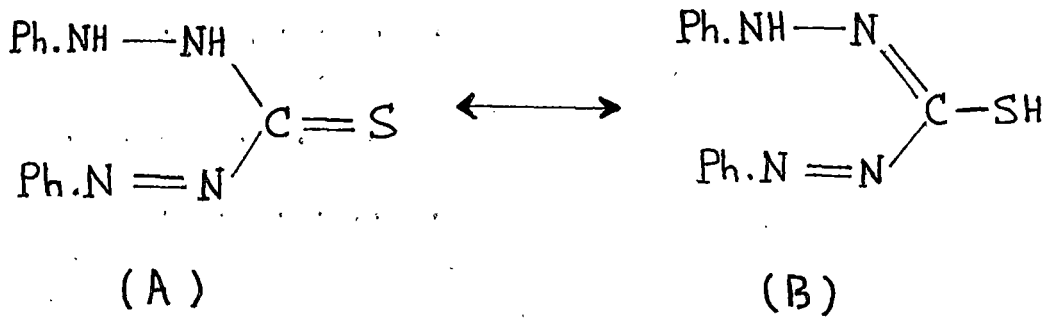
and(b) reaction of one mole of organotin chloride with one or two moles of dithizone:

$$R_3SnCl + Ph.NH.NH.\overset{S}{\overset{\|}{C}}.N : N.Ph \longrightarrow R_3Sn(Ph.NH.NCSN : N.Ph) + HCl$$

$$R_2SnCl_2 + Ph.NH.NH.\overset{S}{\overset{\|}{C}}.N : N.Ph \longrightarrow R_2Sn(Ph.NH.NCSN : N.Ph)_2 + HCl$$

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

Dithizone is a diabasic acid, it contains two labile hydrogen per molecule, one of which attacks the oxygen or chlorine of the organotin oxide or chloride in equillibrium reaction to give water or hydrochloric acid respectively along with the formation of the organotin derivatives of dithizone. Solid dithizone exists mainly in the thioketone form (A) (226) but in solution it undergoes rapid tautomeric equilibrium with the thiol form (B) (fig. 11) (195)



(A) (B)

Fig. - 11

There is no evidence of dithizone losing a second proton to form Dz^{-2} in aqueous solution. Geiger and Sandell (223) showed

that the absorption spectrum of dithizone in 1.5M-NaOH did not differ from that in weaker solution. But in 10M-KOH a colour change to red-violet occurred which might have been due to the formation of Dz^{2-}, although it could also have been due to the presence of silver, from the alkali, which might have remained uncomplexed by the added cyanide. The authors also concluded that the pK_2 of dithizone is greater than 15.

While many authors have tended to ignore the possibility of the removal of a second proton from dithizone, it is certainly labilized when the first is replaced by a metal. This is shown by the formation of mixed silver-mercury dithizonates (229) and silver phenyl mercury dithizonates, but most convincingly by the behaviour of the yellow primary phenyl mercury (II) dithizonate, which gives rise to a magenta coloured anion:

$$\text{(yellow) } PhHg(HDz) \rightleftharpoons \text{(magenta) } PhHgDz^- + H^+$$

and for which the value of pK = 11.46 could be determined by spectrophotometry in 52.8% (v/v) ethanol-water mixture (230). A solution of mercury dithizonate, $Hg(HDz)_2$, in an organic solvent undergoes 99% N-deuteriation to $Hg(DDz)_2$ simply by shaking with D_2O (231). When the dissociation of the thiol-proton is blocked by alkylation, it is quite easy to detach the remaining imino proton. Thus S-methyl dithizone (MeHDz) forms a series of chelated metal complexes such as $Ni(MeDz)_2$, PhHg(MeDz), and (MeDz)CuCl (232).

Thus, Fischer (233) realised that two types of metal-dithizone complexes could be obtained and he termed these complexes as keto-and enol-complexes; the former formed preferentially in acid or neutral solution, the latter in basic solution or with a deficiency of dithizone. In keto-complexes, he assumed that it was the hydrogen of the imino-group of dithizone that was replaced by metal and he proposed formulae (Fig. 12a) and (Fig. 12b) where M^{I} and M^{II} are metals giving Uni- or bivalent

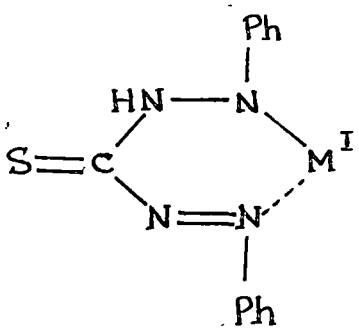


Fig. - 12(a)

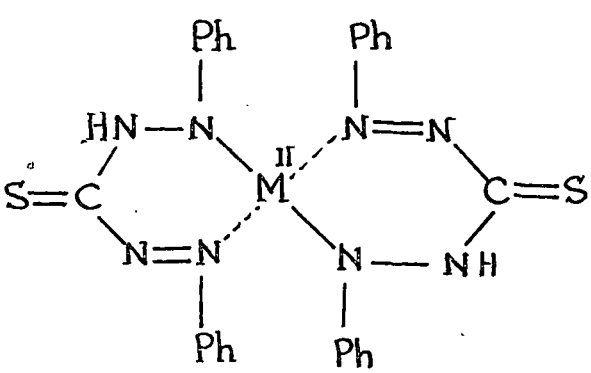


Fig. - 12(b)

cations. Since this was equivalent to assuming a reaction of the reagent in the thioketone form (Fig. 12a and 12b), Fischer termed the product keto-dithizonates and the enol-complexes was formulated by him as (Fig. 12c) or (Fig. 12d).

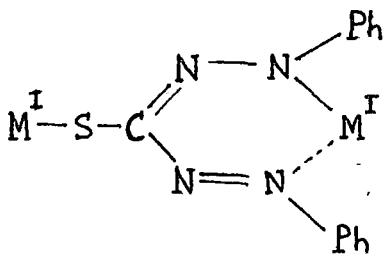


Fig. - 12(c)

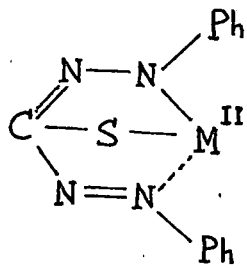
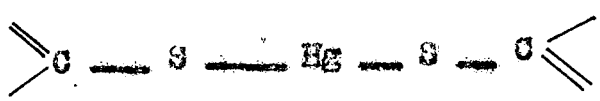


Fig. - 12(d)

Sandell rejected this "loaded" nomenclature of Keto-and enol-dithizonates and referred to these compounds as primary and secondary dithizonates respectively which have been accepted widely.

Fischer's formulation of metal dithizonates (Fig. 12a) and (Fig. 12b), can be criticised on many grounds. First of all, since metals which most readily form primary dithizonates (i.e. Ag, Hg, Cu, Co, Ni, Cd, Tl, Bi, Sn, In) are precisely those which are most readily separated as sulphides in qualitative analysis. It seems more probable that their dithizone complexes would contain metal-sulphur bonds (234, 235) and they could be derived from the thiol tautomer of dithizone. This suggestion is supported by the failure of S-methyl dithizone to form metal complexes under condition where dithizone reacts readily, and more decisively (234) and by the result of an X-ray crystallographic study of mercury dithizonate (236) which establishes unambiguously the presence of the grouping



A further argument against Fisher's formulation (Fig. 12b) can be based on steric consideration (235). Examination of model shows that steric hindrance to co-ordination due to the proximity of the four bulky phenyl groups would be least with metals such as mercury, zinc and cadmium, which favour tetrahedral bond orbitals, but would be so large as to inhibit complex formation completely with metal such as copper and nickel which adopt square

planar configurations in their inner chelate complex (unless gross distortion from coplanarity would occur). In fact there appears to be no great difference between the ease of formation of dithizone complexes with those different metals, and the absorption spectra of the corresponding complexes present no distinguishing features. That di-napthyl thio carbazone forms metal complexes as readily as dithizone, despite the enormously increased steric hindrance to co-ordination that would result if imino hydrogen atoms were involved, appears to be a cogent argument against Fischer's view.

About the structure (Fig. 12c) and (Fig. 12d) of Fischer it may be observed that the four valency bonds of carbon can not be forced to adopt the configuration implied by (Fig. 12d) and formula such as (Fig. 12c) pay little regard to the normal co-ordination number and stereo chemistry of the metal concerned (237).

Later on, X-ray crystallographic studies of metal dithizonates showed a common pattern for the structure of solid primary dithizonates of dipositive cation like (Fig. 13a) (237).

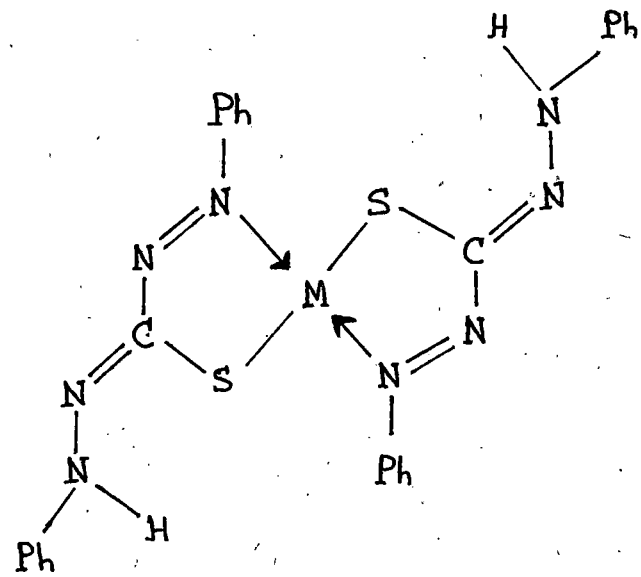


Fig. - 13 (a)

The structure of secondary dithizonates was suggested by Alsop in 1969. Later Komula and Ganko (238, 239) from the molecular weight, magnetic property, infrared and X-ray analysis of the

secondary dithizonates of bivalent cation, proposed the structure (Fig. 13b)

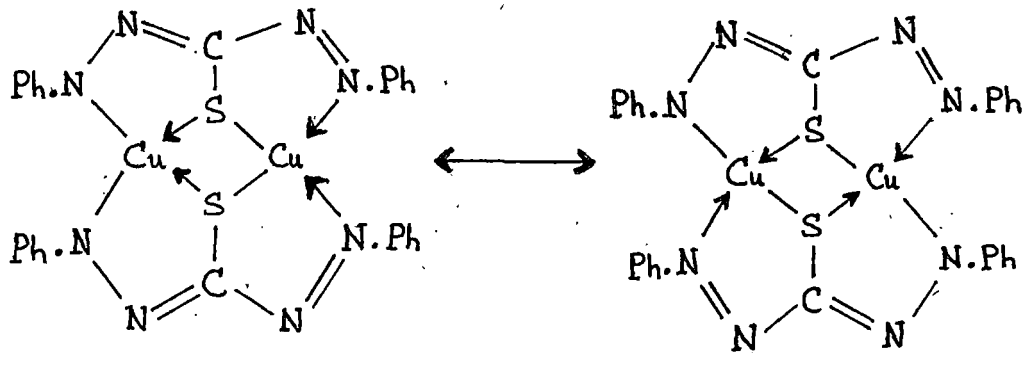


Fig. - 13 (b)

and for monovalent cation they proposed the structure of secondary dithizonate as Fig. 13c.

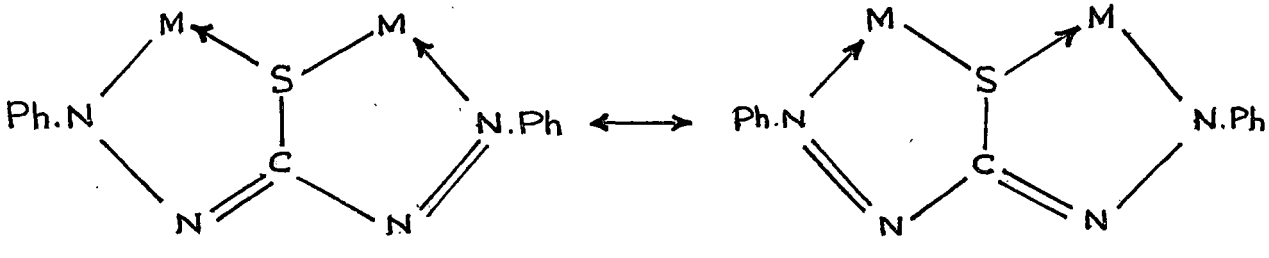


Fig. - 13 (c)

Thus from the above discussionsit may be expected that two types of organotin dithizonates could be obtained like the metallic dithizonates. Now the organotin dithizonates so far have been synthesised by us, all show an absorption band due to stretching of an N-H bond in the I.R. spectrum in the region of 3200 cm^{-1} and PMR of organotin dithizonates also show >NH peak at $\tau = 0.62 - 0.65$ corresponding to a single proton. Thus the possibility of organotin dithizonates prepared by us to have a bonding like secondary dithizonates in which both the hydrogen of dithizone are replaced by metal ion is ruled out. So, the organotin dithizonates so far have been synthesised by us are suggested to be primary dithizonates, in which only one hydrogen atom of dithizone has been used in bonding with organotin moiety.

Irving and Cox (195) in their studies of dithizone with organometallic compounds, suggested the formation of $R_3Sn(HDz)$ and $R_2Sn(HDz)_2$ in solution by studying the absorption spectra. But they did not isolate any solid compound. They suggested in complex $R_3Sn(HDz)$ and $R_2Sn(HDz)_2$ the metal atom can achieve its maximum co-ordination of four by forming respectively one or two metal sulphur bonds (Fig. 14a). Further co-ordination is unlikely and chelation by dithizone residue can not take place (as in Fig. 14b).

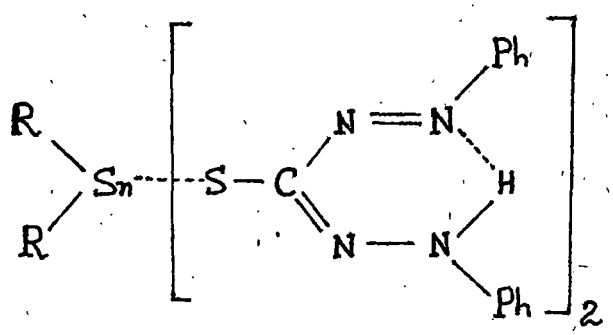


Fig.- 14 (a)

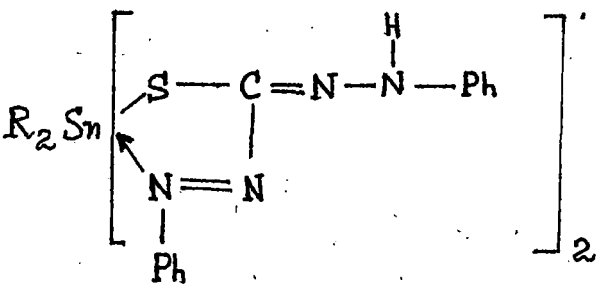


Fig.- 14 (b)

According to them such complexes must be formulated as (Fig. 14a) or as some variant in which the hydrogen bond is broker and the group attached to the carbon atom adopts one or other of several possible configurations which must be in labile equilibri

They ruled out an alternative formulation (Fig. 14b) where a five membered chelate ring would occupy two cis-co-ordination of the metal atom. But X-ray crystallographic studies support the formulation (Fig. 14b) for solid mercury dithizonate (236).

In view of recent structural studies of organotin complex compounds, it seems highly probable that solid organotin dithizonates should be penta or hexa co-ordinated tin compounds. In our opinion, the tetra co-ordinated organotin dithizonates are rather unlikely in view of the following observations.

The visible absorption spectrum of dithizone in an organic solvent exhibits two well-defined bands at 450 and 620 nm assumed to be originated from the thione-thiol tautomers (195) (Fig. 11). But the organotin dithizonates possess a single absorption band in the region 450-510 nm. Since, there is commonly a bathochromic shift when chelating agents such as acetylacetonate, 8-hydroxy-quinoline and N-phenyl benzohydroxamic acid 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.

The chelated nature of organotin dithizonates is also supported by the PMR spectra of dibutyl tin bis-dithizonate. In general, on complex formation the alkyl group attached to tin in

chelate exhibits shielding which is due to the increased electron density on the tin via ligand donation which is observed in dibutyl tin bis-dithizonate [for uncomplexed dibutyl tin dichloride τ_{CH_3} = 9.04 (triplet), τ_{CH_2} = 8.19 (complex pattern) (227); for dibutyl tin bis-dithizonate τ_{CH_3} = 9.34 (triplet) and τ_{CH_2} = 8.38 (complex pattern)].

From the I.R. spectral data done by us so far, we have noticed that all these compounds show N-H stretching frequency in the region 3100-3250 cm^{-1}. Duncan and Thomas (240) reported that N-H bond not involved in hydrogen bonding has stretching frequency at 3326 cm^{-1} in diazo amino benzene, Ph-N = N-NH.Ph, which is somewhat analogous with the dithizone structure. Thus the presence of N-H stretching frequency at 3100-3250 cm^{-1} indicates intramolecular hydrogen bonding in organotin dithizonates.

On the basis of existence of intra molecular hydrogen bonding and chelated nature of organotin dithizonates, triorganotin dithizonates may have one of the following possible structures.

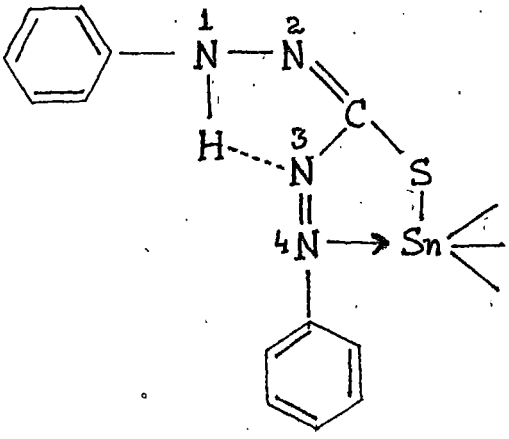


Fig-15(a)

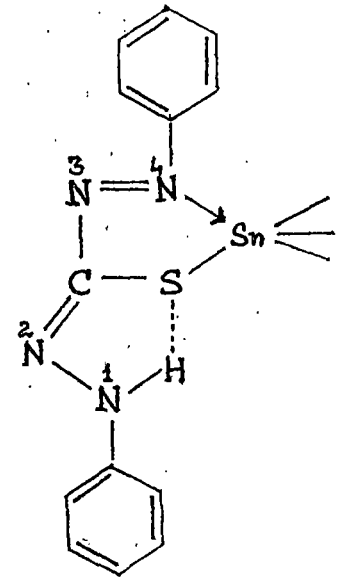


Fig.- 15 (b)

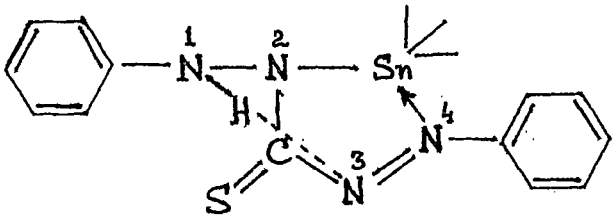


Fig.-15(c)

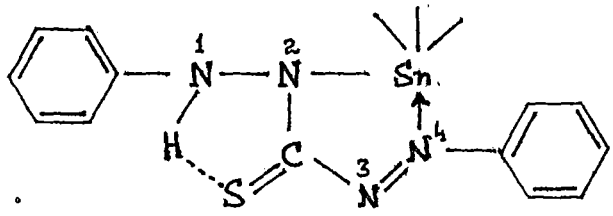


Fig.- 15 (d)

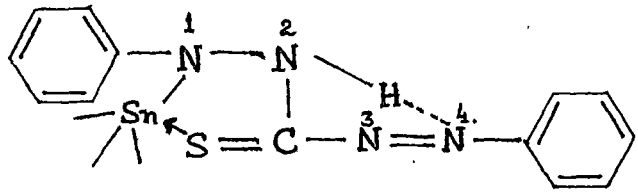


Fig.- 15(e).

Of these structures, (Fig. 15a) and (Fig. 15b) would appear to be more likely for the following reasons:

Since metals which most readily form primary dithizonates (i.e.,Ag, Hg, Cu, Co, Ni, Cd, Tl, Bi, Zn, In) are precisely those which are most readily separated as sulphides in qualitative analysis it seems rather more probable that their dithizone complexes would contain metal-sulphur bond which was supported by X-ray analysis of primary metallic dithizonates (236) and the I.R. spectra of tri organotin dithizonates are very similar to those of metallic dithizonates, the possibility of structures (Fig. 15c) and (Fig. 15d) are rather unlikely.

Structure (Fig. 15e) for triorganotin dithizonates is also rather unlikely on the ground that the hydrogen atom attached to 2-N atom in dithizone would be expected to be more acidic than that attached to the 1-N atom due to the proximity of the sulphur atom.

Bellamy (241), however, has suggested that ν (C = S) frequency would be found in this region of 1050-1234 cm^{-1}. On the basis of the above assignment, we can assign the band at 1220 cm^{-1} in free dithizone as due to the ν (C = S) and the shifting of this band to 1205 - 1172 cm^{-1} in organotin dithizonates, however, favours structure (Fig. 15e); but in view of the following observations it seems to be rather unlikely.

Alsop (226) has determined the crystal structure of dithizone by X-ray method and concluded that in the solid state it crystallises in the space group $P2_1/n$, with a = 11.95, b = 22.24, c = 4.69A^0 and β = 91.6^0. The molecule is effectively coplanar, the C-S bond distance being 1.74A^0 which suggests a thioketone structure (Fig. 11) rather than a thiol structure for dithizone. It is very difficult to obtain a single crystal of dithizone because it is very susceptible to twinning, it crystallises as a thin and fragile lathe, elecngated along one axis. Unfortunately, Alsop's crystal was twinned, so that the β -angle could not be determined accurately and the precision of the intensity measurements was also adversely affected. Recently Laing (242) redetermined the crystal structure of dithizone by X-ray method with a relatively good single crystal which was obtained by chance from chloroform solution. He found β = 82.0^0, a = 4.70, b = 22.53, c = 11.95A^0. The molecule (Fig. 16) is nearly planar, with the C-S bond lying on the intersection of two mirror 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 π -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 (Fig. 16) which are equivalent.

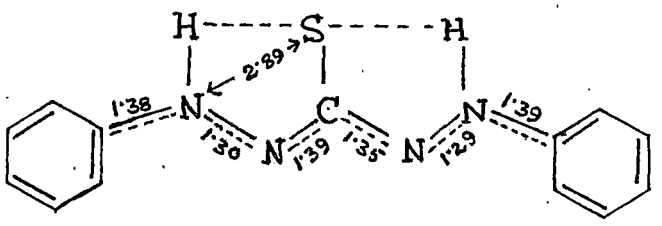


Fig. - 16

Thus from the above discussions it is clear that dithizone in the solid state does not contain $>C=S$ group, so the assignment of band at 1220 cm^{-1} in dithizone for ν ($>C=S$) is inconsistent with the structure of dithizone. Thus structure (Fig. 15e) for triorganotin dithizonates seems to be rather unlikely.

Meriwether et al.(231) Ashizawa (243), Dyferman (244), Ramkrishna (245) and Komula and Ganko (238) have suggested for metallic dithizonates the band at 3180-3350 cm^{-1} for NH stretch, band at 1515 - 1545 cm^{-1} for δ NH bend, the band at 1257-1375 cm^{-1} for N-phenyl and a group of bands in the region of 1130-1238 cm^{-1} for coupled N-C-S bond vibrations. All the triorganotin dithizonat

studied here show absorptions at 3210-3246 cm^{-1} and 1508-1512 cm^{-1} which have been assigned for : NH stretching and bending vibrations respectively. A group of bands between 1130-1182 cm^{-1} have been assigned for the coupled N-C-S bond vibrations and the band at 1342-1360 cm^{-1} has been assigned for N-phenyl vibration. Since all the triorganotin dithizonates studied here show absorption bands between 1130-1182 cm^{-1} indicating the presence of N-C-S group, all these compounds can then be suggested to have the structure (Fig. 15a) or (Fig. 15b), in which the tin atom is penta co-ordinated, the arrangement of the groups around tin atom possibly being in trigonal bipyramidal one, like other triorganotin chelate compounds, fig. 17.

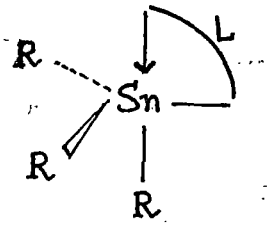


Fig. - 17.

The structure of organotin dithizonates which has been proposed can also be explained nicely on the basis of visible absorption spectra. As pointed out earlier the visible absorption spectrum of dithizone in an organic solvent exhibits two well defined bands at 440-460 nm and 590-640 nm (246) that have been assumed to originate from the thione and thiol tautomers (195). Since formazans of the general formula (Fig. 18a; X = Cl or alkyl) have their main absorption band at ~ 420 nm and the dithizonate ion (X = S⁻) absorbs at 470 nm and thiobenzophenone

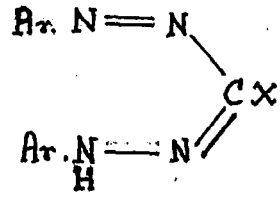


Fig. 18(a)

and other thioketones have absorption band near 600 nm, it was suggested that lower absorption band of dithizone was due to the thiol tautomer and higher absorption band was ascribed to the

thione tautomer. But Carlin (247) in the light of optical, infrared and NMR spectroscopy concluded that solution of dithizone contained a thione dimer (Fig. 18b) and a thiol form (Fig. 18c).

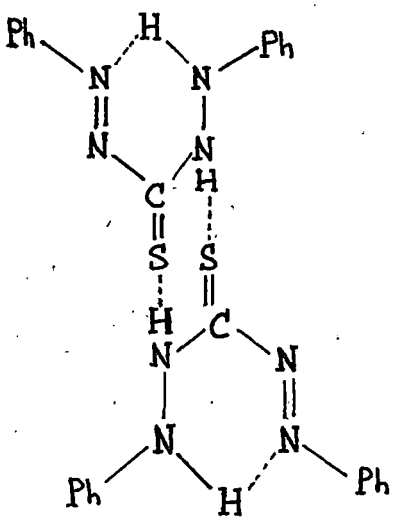


Fig. - 18(b)

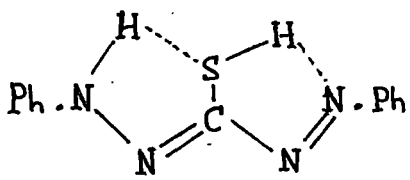


Fig. - 18(c).

Although there is no evidence of dimerisation in solution or in the solid state, it should be noted that the long wave length band is now ascribed to the thiol form whereas the short wave length band is ascribed to thione dimer (247).

More recently, Coleman, Foster, Kazan and Mason were unable to obtain the N.M.R. spectrum of dithizone due to its low solubility but by using 1,5-(O-diethyl phenyl) thiocarbazone in $CDCl_3$, they observed $\tau = -2.03$ (1.6 protons), 1.9 and 2.67 (8 aromatic protons), 7.0 (4-methylene protons) and 8.6 (6 methyl protons) (248). The signal at $\tau = -2.03$ showed no evidence of spliting over the range 50 to -45°c in $CHCl_3$ but became narrower. They interpreted their data as favouring a single structure (Fig. 18d) with protons equivalent and suggested (Fig. 18e) as the structure

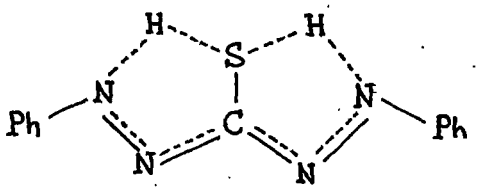


Fig. - 18 (d)

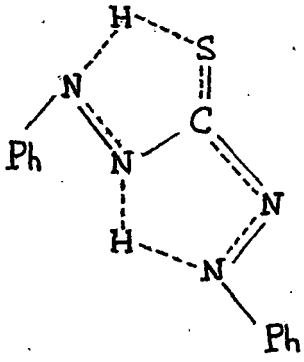


Fig. - 18 (e)

of red metastable form (λ_{max} = 550 nm) which they observed when a green solution of chloroform in a dry non polar solvent was subjected to intense irradiation with the near infrared tungsten lamp of a Cary-14 spectrophotometer. They discarded the idea of thiol-thione equilibrium in solution of dithizone.

It should be noted that Coleman et al.only observed 1.6 non-aromatic protons at τ = -2.03 in place of 2.0 protons to 9.0 aromatic protons. Recent measurements in Leeds (249), using an instrument of higher resolving power showed that the NMR spectrum of dithizone in $CDCl_3$ presented two signals at τ = -2.61 and τ = 9.03 of integrated area 3:1 and completely accounting for 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 (250). Carlin 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 (247). The lack of infrared absorption in the region 3100-3500 cm^{-1} indicates the absence of free : NH group and implies its participation in strong hydrogen-bonding. But the most recent measurements (249), which have included studies of several homologues of dithizone and both isomeric forms of the corresponding S-methyl derivatives, the conclusion is that the thiol form (comprising about 25% of the total in $CDCl_3$) has the (resonating)

structure (Fig. 18f) or less likely (Fig. 18g) whereas the thione form could be (Fig. 18d) or (Fig. 18e).

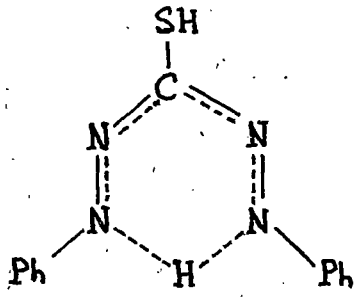


Fig. -18(f)

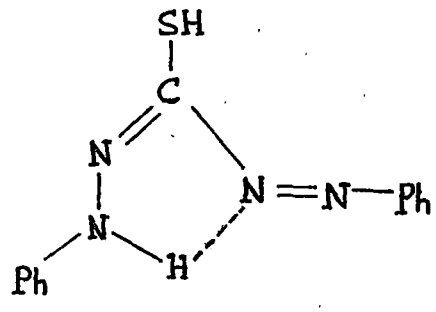
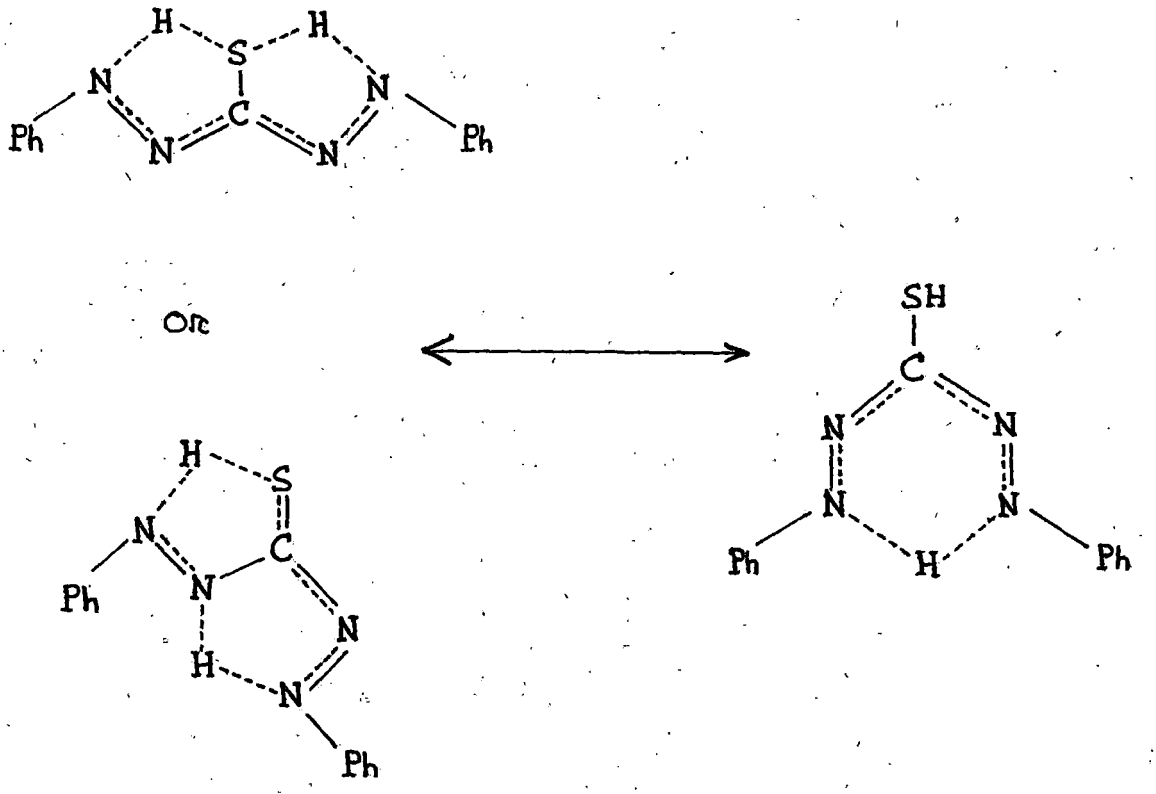


Fig. -18 (g)

So from the above discussion, at present, according to the modern view, the allocation of bond and tautomeric equilibrium of dithizone in an organic solvent may be represented as follows:



Thione form ($\lambda_{max.}$ 440-450nm) Thiol form ($\lambda_{max.}$ 596-640 nm).

Fig. - 18 (h)

Since, in organotin dithiocarbonates, there is only a single visible absorption band at 470-500 nm (except in triphenyl tin dithiocarbonate which absorbs at 450 nm) (Table I-IV) the change in spectrum on forming a metal complex can be explained by the

disappearance of thiol band at ~ 600 nm and a bathochromic shift of the thione band from ~ 450 nm. Thus the thione form interacts with the organotin chloride or oxide in the following way to form organotin dithiocarbamates and attain structure (Fig. 19a) or (Fig. 19b).

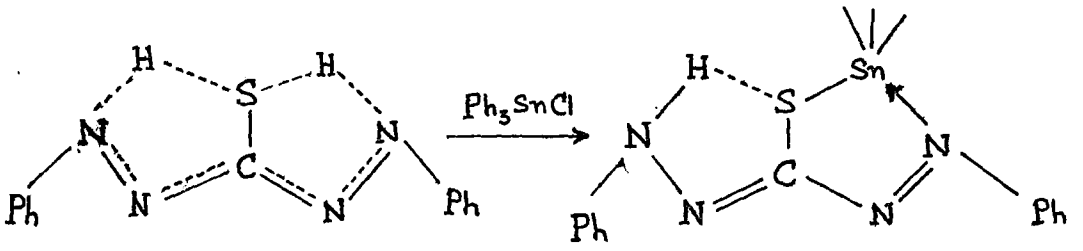


Fig. - 19 (a)

or

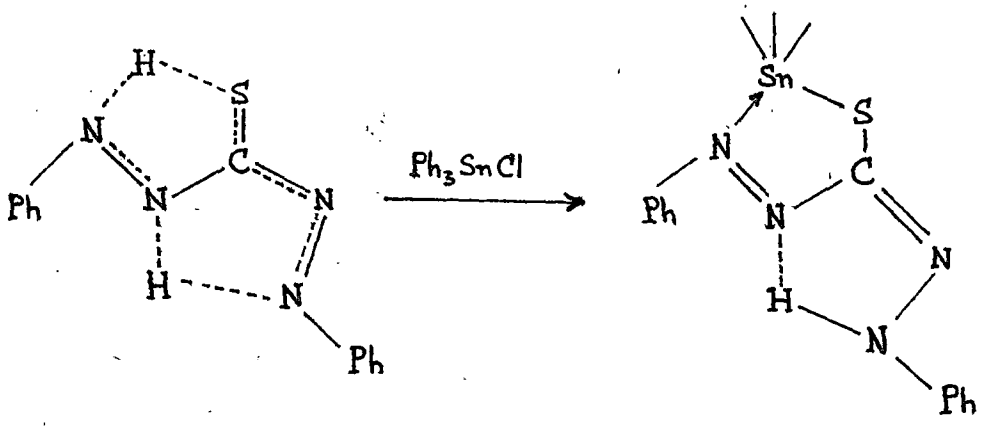


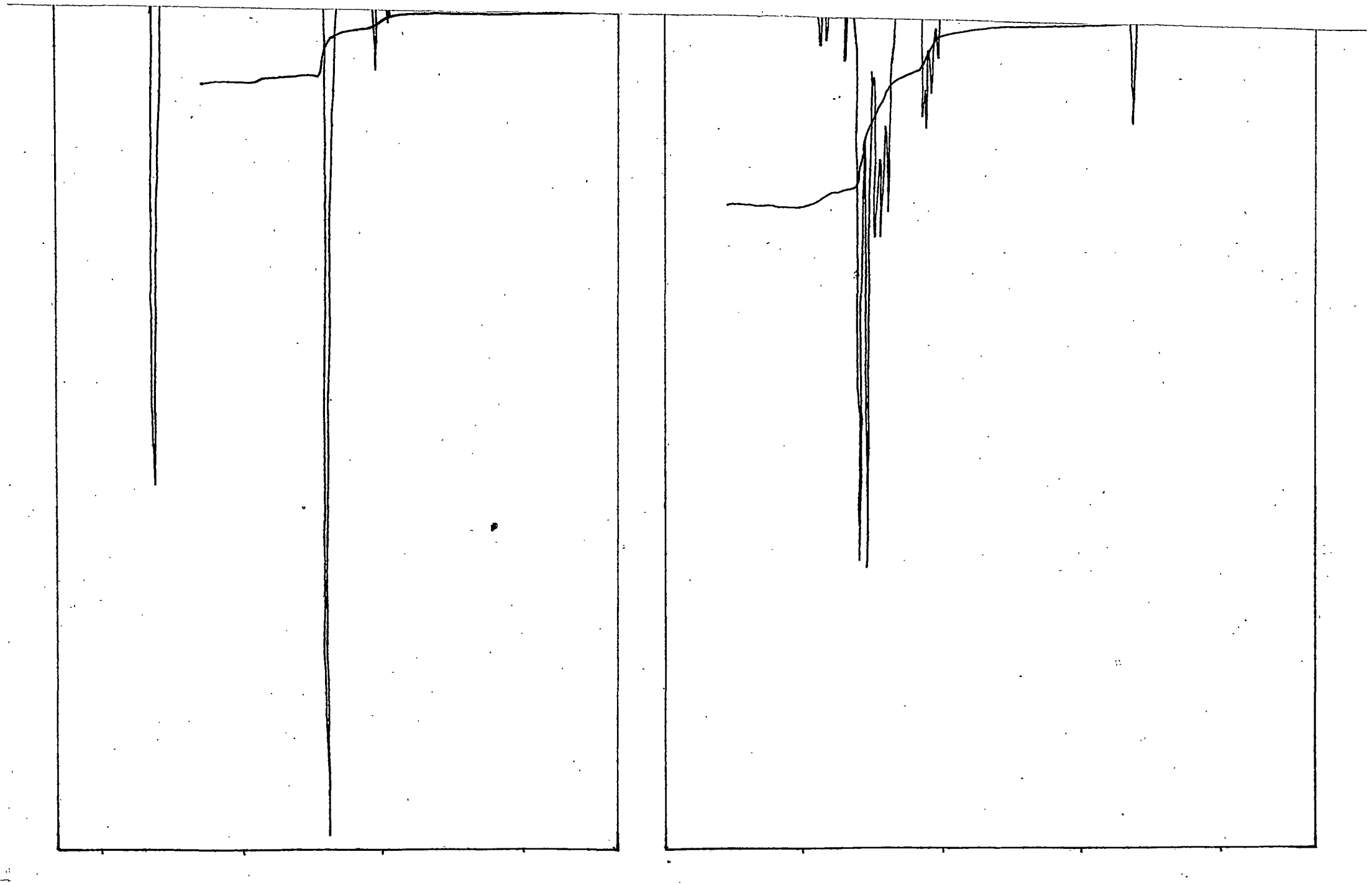
Fig. - 19 (b)

These two structures are identical with the structures (Fig. 15a) and (Fig. 15b) which were proposed for triorganotin dithizonates from I.R. data.

For diorganotin bis-dithizonates the weak absorption band at 3210-3242 cm^{-1} has been assigned for : NH stretching vibrations. A strong absorption band at 1510-1520 cm^{-1} has been assigned to : NH bend. The absorption band at 1345-1370 cm^{-1} has been assigned for N-phenyl vibration. Another group of absorption bands between 1130-1195 cm^{-1} have been assigned for coupled N-C-S bond vibrations. The diorganotin bis-dithizonates show similar I.R. spectra as triorganotin dithizonates. So it may be assumed that the nature of bonding of diorganotin moities with dithizone is similar to that of triorganotin dithizonates.

The proton nuclear resonance spectra (90 MHz) of dimethyl tin bis dithizonate and dibutyl tin bis-dithizonate were recorded in $CDCl_3$. The dimethyl tin bis-dithizonate showed a singlet for the alkyl groups at τ=8.72. The other peaks at τ= 0.65 and in the region τ=2.05 to 2.72 have been assigned for imino proton and phenyl protons respectively. From the integration of the curve, the ratio of the iminoproton, phenyl protons and methyl protons have been found to be 1:10:3, which is consistent with the composition of the complex.

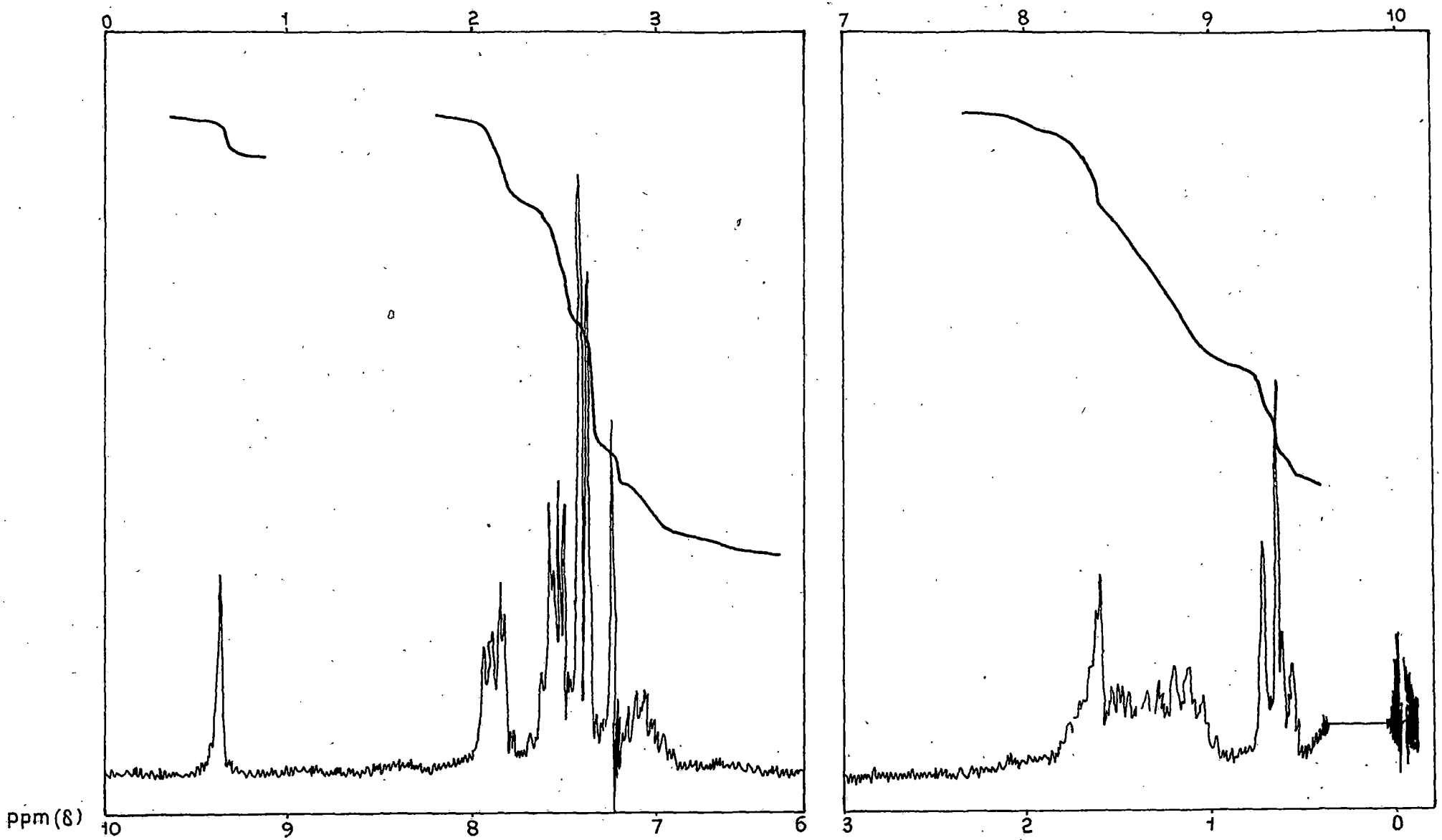
The resonance pattern of alkyl groups in dibutyl tin bis-dithizonate exhibit resonance associated with methyl and methylene



groups. Methyl groups show a triplet having τ= 9.26, 9.34 and 9.42 and methylene groups give a characteristic complex pattern in the region τ=8.33 to 8.93. The other peaks at τ=0.62 and in the region τ=2.08 to 2.76 have been assigned for imino proton and phenyl protons. From the integration of the curve, it has been observed that the ratio of the imino proton, phenyl protons and butyl protons are 1:10:9 which is also in consistence with the composition of the complex.

The uncomplexed dimethyl tin dichloride has resonance for methyl groups at τ= 8.3 in carbon tetrachloride and τ= 8.77 in trifluoroacetic acid (110) and the uncomplexed dibutyl tin dichloride exhibits resonance at τ_{CH_3} = 9.04 (triplet) and τ_{CH_2} = 8.19 (complex pattern) in carbon tetrachloride.

In general, on complex formation, the alkyl group attached to the tin in chelate exhibits shielding which is due to the increased electron density on the tin via ligand donation which has been observed in dibutyl tin bis-dithizonate. Thus it may be inferred that dibutyl tin bis-dithizonate is a chelate complex. On the other hand the marked deshielding observed in the chelate dimethyl tin bis-dithizonate, may be explained by assuming a trans R-arrangement which is necessarily perpendicular to the dithizone ring. Free rotation would allow the methyl group on the end of alkyl chains and the intermediate methylene groups to reside above the cloud of heterocycle producing shielding, while a group



PMR Spectrum of dibutyl tin bis dithizonate

Fig--- 20 (b)

directly attached to the tin would be in a deshielding area (227). In addition, the normal inductive effect of the co-ordinating ligand and the magnetic influence of the tin atom also combine to govern the alkyl resonance position. The PMR spectra of dimethyl tin bis dithizonate showed a single methyl signal, indicating a trans alignment of methyl groups in an octahedral structure.

Sn^{119} and Sn^{117} satellites appeared at τ = 8.32 and 9.12 and $J(Sn^{119}-C-H)$ and $J(Sn^{117}-C-H)$ are 42 and 39 cps respectively for dimethyl tin bis dithizonate. The signal at τ 8.40 may be due to some impurities.

A number of diorganotin bis-chelates have been isolated (57, 103, 109, 166-71) and found to contain hexa co-ordinated tin atom. McGrady and Tobias suggested a trans octahedral configuration for the diorganotin bis-oximate from their I.R., Raman and NMR studies. From three dimensional X-ray studies of dimethyl tin bis-oximate, Schlemper (172) showed a highly distorted octahedral structure. The bond angle in the octahedron range from 73.4° to 110.7° . Though the tin atom in dimethyl tin bis-oximate is six co-ordinated, $\hat{C}-Sn-C$ angle is nearly tetrahedral. Diphenyl tin bis (N-N'-diethyl dithiocarbamate) possesses a distorted octahedral geometry (175). The angle subtended at the tin atom by the group is $101.4(6)^{\circ}$, with the two Sn-C bond distances equal. Harrison et al.(101) have determined the crystal structure of

$Me_2Sn(MeCO.NOMe)_2$ by X-ray method. The compound has also been shown to be a distorted octahedral, the two N-acyl hydroxyl amine residue function as a bidentate ligand where the Me-Sn-Me group is not linear, the C-$\widehat{Sn}$-C angle being 145.8°. Thus a distorted octahedral structure may be a general feature of six coordinated organotin chelate compounds. So, in the light of the above discussion, it seems probable that diorganotin bis-dithizonates may also be six co-ordinated complex with a distorted octahedral geometry where the term cis-or trans-configuration is of less significance.

Diorganotin halide dithizonates, $R_2SnX(HDz)$ (R = Ph, Me, Bu, P-tolyl, Bz; X = Cl, Br, I, SCN) have been prepared. While $R_2SnX(HDz)$ (X = Cl, Br), $Bu_2Sn(SCN)(HDz)$ and $Ph_2SnI(HDz)$ have been prepared by the reaction:

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

$R_2SnX(HDz)$ (X = SCN, I) [except $Bu_2Sn(SCN)(HDz)$ and $Ph_2SnI(HDz)$] have been prepared by the replacement of chloride from the corresponding complexes.

$$R_2SnX(HDz) + KSCN \longrightarrow R_2Sn(SCN)(HDz) + KX$$

$$R_2SnX(HDz) + KI \longrightarrow R_2SnI(HDz) + KX$$

Since the Sn-X (X = Cl, Br, I) modes are known to appear at lower frequency (below 325 cm^{-1}) in most cases, the spectra of $R_2SnX(HDz)$ above this range are very similar. For all the compounds of this series the weak band at 3160-3265 cm^{-1} has been assigned to ν NH stretch and another band at 1495-1520 cm^{-1} has been assigned to δNH bend. The band at 1320-1345 cm^{-1} has been assigned to N-phenyl and a group of strong bands between 1140-1220 cm^{-1} have been assigned for coupled N-C-S bond vibrations, similar to triorgano tin dithizonates.

The proton nuclear resonance spectrum of dimethyl chlorotin dithizonate taken in $CDCl_3$ shows peaks at τ= 0.63, 2.18-2.6 and 8.78 for imino proton, phenyl protons and methyl protons. From the integration of the curve, the ratio of imino proton, phenyl protons and methyl protons has been found to be approximately 1:10:6 which is consistent with the composition of the complex. As the PMR spectrum of the complex, $Me_2SnCl(HDz)$ shows only a singlet for methyl groups at τ= 8.78, a trans alligament of methyl groups, in a pentagonal bipyramidal structure, has been suggested for the complex. Sn^{119} and Sn^{117} satellites appear at τ= 8.38 and τ= 9.18 and $J(Sn^{119}-C-H)$ and $J(Sn^{117}-C-H)$ are 59 and 57.5 cps respectively. The signals at τ= 7.8 and τ=8.45 may be due to some impurities.

The I.R. spectra of thiocyanate complexes $R_2Sn(SCN)(HDz)$ are exactly identical with those of the corresponding halide

complexes except [illegible] a very strong intense absorption band [illegible] at 2020-2040 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 (251) have suggested the following criteria to distinguish between these two types of co-ordination:

	M-N≡C-S	M-S-C≡N
ν(C≡N)	below 2100 cm^{-1} (broad)	2100 cm^{-1} (sharp)
ν (C-S)	860-760 cm^{-1}	690-720 cm^{-1}
ν (NCS)	490-450 cm^{-1}	440-400 cm^{-1}

Though the C-S stretching frequency is more useful in distinguishing these two isomers (251, 252, 253) the ligand i.e. dithizone has so many absorption bands in this region that they may obscure the C-S stretching band. Hence on the basis of C≡N stretching frequency the thiocyanate group in organotin dithizonates may be considered to be linked to tin atom through the nitrogen atom as all of them show absorption band at 2020-2040 cm^{-1}, though the band in some cases appears to be rather sharp.

Mullins and Curran (160) have shown that $Ph_2Sn(SCN)(OX)$ does not contain any -NCS- bridging in the solid since absorption

by this compound is at 2025 cm^{-1} in KBr compared to 2033 cm^{-1} in benzene solution and they have suggested a penta co-ordinated tin in $Ph_2Sn(SCN)(OX)$. They have also suggested from dipole moment measurement a cis-arrangement of hydrocarbon groups for this compound. From Mossbaur spectra $Ph_2SnX(OX)$ (X = SCN, Cl) have been shown to have a preferable penta co-ordinated structure (254). The strong band at 2020-2040 cm^{-1} in $R_2Sn(SCN)(HDz)$ which is due to the C≡N stretching frequency shows no change in the position of absorption band in chloroform solution indicating the absence of -NCS- bridging in these complexes and suggests a penta co-ordinated trigonal bipyramidal structure for these compounds like other diphenyl tin halo oxinates.

The ligand dithizone ~~which~~ has a large number of absorption bands particularly in the region of 490-800 cm^{-1}. The presence of so many bands in this region has made the assignment for Sn-O, Sn-N rather difficult in the organotin dithizonates. Moreover, the unreliability of assignment below 400 cm^{-1} due to the experimental inadequacy has made the assignment of Sn-X (X = Cl, Br, I), Sn-S and Sn-N bands not feasible. The far infrared measurement could provide a better picture for such assignments but the lack of proper facilities have restricted us to investigate further in this area for the time being. However, the medium intensity bands at 502-530 cm^{-1} and 530-558 cm^{-1} in organotin dithizonates can be assigned due to Sn-O mode, since Sn-O mode is known to appear

in many organotin compounds at 470-554 cm^{-1} and 525-580 cm^{-1} (21).

$Me_2Sn(NO_3)(Ox)$ (where HOx = oxine) was prepared from the reaction of $Me_2Sn(Ox)_2$ and silver nitrate in methanol (107). The reaction scheme is as follows:

$$R_2Sn(Ox)_2 + AgNO_3 \xrightarrow{\text{in } CH_3OH} R_2Sn(NO_3)(Ox) + AgOx.$$

Attempts were made to prepare corresponding dithizonates.

When quantitative amount of dimethyl tin bis-dithizonate and silver nitrate were taken in chloroform in 1:1 molar ratio and refluxed for three hours, silver dithizonate was separated out and the other product isolated was dimethyl tin bis-dithizonate which was confirmed by infrared spectra and mixed melting point with an authentic sample of dimethyl tin bis-dithizonate. No other product could however be isolated in pure state. Since there is evidence that $Me_2Sn(NO_3)(Ox)$ disproportionates in presence of donor solvents like water and pyridine to form more stable hexa co-ordinated $Me_2Sn(Ox)_2$, it seems probable that in this case the compound $Me_2Sn(NO_3)(HDz)$ is formed as an intermediate which then disproportionates rapidly to the more stable hexa co-ordinated $Me_2Sn(HDz)_2$ and $Me_2Sn(NO_3)_2$, although we could not isolate the latter compound. Thus the probable reaction is as follows:

$$Me_2Sn(HDz)_2 + AgNO_3 \xrightarrow{\text{in } CHCl_3} Me_2Sn(NO_3)(HDz) + Ag(HDz)$$

$$\downarrow$$

$$Me_2Sn(HDz)_2 + Me_2Sn(NO_3)_2$$

Attempt to synthesise the compound $Ph_2Sn(CH_3COO)(HDz)$ from the reaction of corresponding chloro derivative with sodium acetate resulted the separation of sodium chloride and the formation of organotin dithizonate having m.p. 166-167°C. However this compound could not be characterised.

It has been shown by Datta, Majee and Ghosh (119) that the penta co-ordinated compound triphenyl tin oximate, $Ph_3Sn(Ox)$ reacts readily with mercuric halides at room temperature to produce phenyl tin halide dioximate, $PhSnX(Ox)_2$, phenyl mercuric halide, $PhHgX$ and triphenyl tin halide, Ph_3SnX. Similar reaction has also been found to occur with diphenyl tin bis-oximate, but under drastic condition, to produce phenyl tin halide dioximate and phenyl mercuric halide. Similar reaction has also been found to occur in the case of triphenyl tin N-phenyl benzo hydroxamate and diphenyl tin bis-N-phenyl benzohydroxamate (156). On the other hand, $(Ph_3Sn)_2S$ reacts with mercuric chloride to form mercuric sulphide and triphenyl tin chloride, Ph_3SnCl (112). The reaction of triphenyl tin dithizonate and diphenyl tin bis-dithizonate with mercuric chloride resulted the formation of mercury dithizonate

and triphenyl tin chloride, diphenyl tin dichloride respectively. The reaction is as follows:

$$2Ph_3Sn(HDz) + HgCl_2 \longrightarrow 2Ph_3SnCl + Hg(HDz)_2$$

$$Ph_2Sn(HDz)_2 + HgCl_2 \longrightarrow Ph_2SnCl_2 + Hg(HDz)_2$$

From the above results it seems that migration of phenyl group from tin to mercury occurs only when tin is directly bonded to oxygen as in the case of $Ph_3Sn(Ox)$, $Ph_2Sn(Ox)_2$, $Ph_3Sn(PBHA)$ and $Ph_2Sn(PBHA)_2$ (where HOx = oxine and HPBHA = N-phenyl benzo hydroxamic acid) but fails to do so when tin is bonded to sulphur as in the case of $(Ph_3Sn)_2S$ and $Ph_3Sn(HDz)$ and $Ph_2Sn(HDz)_2$.

Pradhan and Ghosh (100) have synthesised a novel compound $PhSn(OCH_3)XL$ (HL = N-phenyl benzohydroxamic acid, X = Cl, Br, I, SCN) which have a dimeric structure like (Fig. 21).

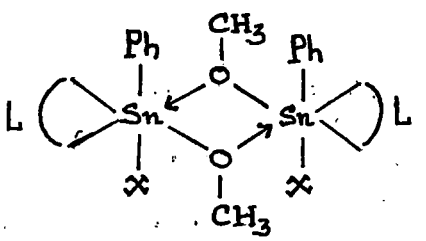


Fig. - 21

Since organotin alkoxides are sensitive to wide range of protic species and polar organic compounds to undergo substitution reaction (255) attempts have been made to synthesise organotin mixed chelates through the substitution reaction of $PhSn(OCH_3)XL$ with different monodentate and bidentate ligands to form $PhSnXLL'$ (L' = monodentate or bidentate ligands).

Thus in an attempt to prepare mono-organo-halo-carboxylate tin N-phenyl benzohydroxamate, phenyl chloro methoxy tin N-phenyl benzohydroxamate was refluxed in acetic acid and trifluoro acetic acid separately. In both the cases we got compounds having m.p. 256-258°C and 173-75°C respectively. Both these compounds gave similar type of I.R. spectra but it has not been so far possible to characterise them.

Furthermore, attempts were made to prepare mixed chelates through the reaction of $PhSn(OCH_3)Cl_2$ with pyridine and picoline. Phenyl chloro methoxy tin N-phenyl benzo hydroxamate reacted with pyridine and picoline at room temperature to give solids of m.p. 118-20°C and 127-28°C respectively. Here again we failed to characterise them. The substitution by monodentate ligands did not produce any definite desired product.

Then attempts were made to substitute $-OCH_3$ group of $PhSn(OCH_3)X_2$ by bidentate chelating agents like oxine and dithizone. Here we were ~~been~~ successful in isolating few organotin mixed ligand complexes and believe that many more complexes of this

type would be possible to isolate in future by this route. The mixed ligand complexes isolated so far are of the type $PhSnXLL'$ (X = Cl, Br, HL = N-phenyl benzohydroxamic acid, HL' = oxine and dithizone). Although many organotin chelates have been well studied, there are only a few reports on mixed chelates in which two kinds of ligands co-ordinate to one tin atom. The mixed chelates which have been reported are only of the type R_2SnLL' (110,131,132) (where HL = oxine and HL' = tropolone, kojic acid, β-diketones) but no mixed chelate of the type $RSnXLL'$ has been reported so far. Perhaps, it is the first example of organotin mixed chelates of the type $RSnXLL'$ (X = halogen, L and L' are bidentate chelating agents).

$$PhSnX(OCH_3)L \quad + \quad HL' \longrightarrow \quad PhSnXLL' + CH_3OH$$

(A) (B) (C)

HL = N-phenyl benzohydroxamic acid

HL' = oxine or dithizone; X = Cl and I.

The infrared spectrum in Nujol, the U.V. and visible absorption spectra in chloroform solution and sharp melting point of (C) are quite different from those of (A) and (B). Thus it may be concluded that (C) is not a mixture of (A) and (B) in the solid state. The I.R. spectra of phenyl halo methoxy tin N-phenyl benzohydroxamates show an intense broad absorption band at 430-90 cm^{-1} which has been assigned to $\overline{OSnOSn}$ ring system in the

methoxy compounds by Pradhan and Ghosh (100). But no such band in the region 480-90 cm^{-1} has been found in the complexes (C), indicating the absence of methoxy bridge in these complexes. A group of bands in the region of 1220-1140 cm^{-1} in free dithizone has been assigned for coupled N-C-S bond vibrations and the shifting of these bands to lower frequencies in between 1200-1130 cm^{-1} for all the organotin dithizonates has been observed which indicates the complexation of organotin moities with dithizone. In the present complexes (C) where L' = dithizone, a group of bands between 1200-1160 cm^{-1} has also been observed which was absent in (A), suggesting complexation of dithizone with organotin moities. Presence of N-phenyl benzohydroxamate residue to (C) is indicated by a strong absorption band in the I.R. spectra at 935 cm^{-1} which has been assigned to ν(N-O) mode. Similar band absorption occured at 940 cm^{-1} in the complex phenyl halo methoxy tin N-phenyl benzohydroxamate and at 920 cm^{-1} in free N-substituted benzohydroxamic acids (156). This suggest strongly the presence of N-substituted benzohydroxamic acid as a co-ordinated ligand in (C). Phenyl halo methoxy tin N-substituted benzohydroxamates absorb strongly at 1520-40 cm^{-1} and these bands have been assigned to ν(C = O) in these complexes by Pradhan and Ghosh (156) and all organotin dithizonates absorb at 1510-1520 cm^{-1} which have been assigned to N-H band. But in the complexes (C) where L' = Dithizone, a broad band at 1500-1530 cm^{-1} has been observed, which may be due

to the close presence of ν (C = O) and ν (-NH) bend. Thus from the above discussion it is clear that I.R. data of (C) [L'] where L' = dithizone] suggest strongly the possibility of co-ordination of the ligands to tin atom resulting hexa co-ordinated octahedral structures. Again for the complex (C) [L' where L' = oxine], the co-ordination of oxine to tin atom is however difficult to interpret from I.R. data because ν (Sn-O) and ν (Sn-N) occur at lower wave lengths. But the co-ordination of N-phenyl benzohydroxamic acid is easy to understand from the absorption bands at 932-935 cm^{-1} and 1520-1530 cm^{-1} since most of the organotin N-phenyl benzo hydroxamate complexes absorbed around 940 cm^{-1} and 1520-1540 cm^{-1} (156) for ν (N-O) and ν (C = O) vibration respectively.

The co-ordination of both the ligands in (C) may also be supported from the electronic spectra. $Ph_3SnX(Ox)L$ (where X = Cl, I and Ox = oxine and L = N-phenyl benzohydroxamic acid) show absorptions at 259-61 nm and 330-35 nm. The bands at 259-61 nm and 360-65 nm may be assigned to N-phenyl benzohydroxamate and oxinate groups respectively since organotin N-phenyl benzohydroxamate complexes absorb in the U.V. region at 252-293 nm (156) and the organotin oxinates absorb at 360-380 nm in the visible region and at ~ 260 nm in the U.V. region (113). Thus the band at 330 nm in $Ph_3SnX(Ox)L$ is certainly due to the oxine group but the band at 259-61 nm may be due to either N-phenyl benzohydroxamic

acid or oxine residues or for the both.

$Ph_3SnX(HDz)L'$ (where X = Cl, I, HgDz = Dithizone and HL = N-phenyl benzohydroxamic acid) show two absorption bands at 265-70 nm and at 500 nm. The band at 500 nm is definitely due to the presence of dithizone in the complexes, since all the organotin dithizonates so far studied by us absorb in the region 450-500 nm. The band at 265-70 nm may be due to either ~~or both the~~ dithizone or N-phenyl benzohydroxamic acid or for the both because both of them absorb in this region.

Electronic spectral measurements indicate that for the triorganotin dithizonates in carbon tetrachloride the change in absorption maxima depends on the nature of the organic groups as is evident from the table I. But in the series $R_2Sn(HDz)_2$, the position of the absorption maxima changes with the nature of organic groups in few cases only. Here diphenyl-, dibutyl-, and dipropyl tin bis-dithizonates absorb at the same wave length whereas the corresponding dimethyl tin derivative absorbs at lower wave length and the corresponding dibenzyl and di-para-tolyl derivatives absorb comparatively at higher wave length (Table I).

In the case of diorgano chloro/thiocyanato tin dithizonates, there is practically no change in the position of the absorption maxima with the nature of organic groups except in the case of

methyl derivative which absorbs at slightly lower wave length (Table II and IV). Although it is not quite discernible whether the position of maxima is really dependent on the nature of the halogen atoms but it is observed that the thiocyanato compounds always absorb at slightly higher wave length. All the iodo compounds absorb at slightly different wave length from each other which is shown in table III.

The stability of all these three types of compounds $R_3Sn(HDz)$, $R_2Sn(HDz)_2$ and $R_2SnX(HDz)$ can roughly be compared following the shifting of absorption band at 450 nm to higher wave lengths.

Sone and his co-workers (256,257) have studied a number of metal chelate compounds and have shown that the ligand absorption band is shifted to longer wave length due to chelate formation and the extent of this shift parallels the stability of chelate complex. Kawakami and Okawara (102) have shown that the organotin oximates are chelated compounds in solution since the peak of oxine in the U.V. region shifts to longer wave length in the complexes. And the sequence of stability constants of these oximates have been drawn from the band shifts in non polar solvents.

As shown in table 1 to IV , all the three series of organotin dithizonates mentioned above show strong absorption at 450-500 nm and the absorption maxima of free ligand at 450 nm show

bathochromic shift in non polar solvent carbon tetrachloride. Thus all these organotin dithizonates are chelated compounds in solution and if the relationship between the band shift and the stability of the chelates are applicable here, then the sequence of stability of these complexes would be

$$R_2SnX(HDz) > R_2Sn(HDz)_2 > R_3Sn(HDz).$$

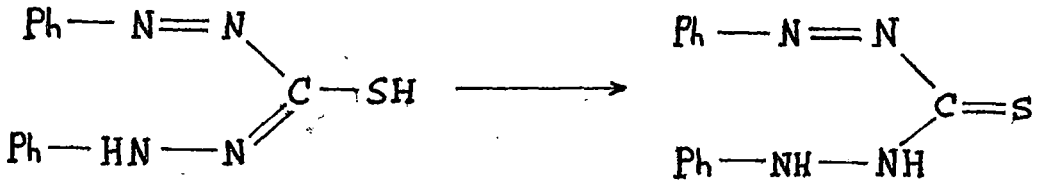
It has been observed in almost all triorgano tin dithizonates and di-organotin bis-dithizonates a weak absorption band at 610 nm in carbon tetrachloride solution. This absorption band may be explained by the partial photochemical decomposition of organotin dithizonates while taking spectra in the visible region, since it has been observed that organotin dithizonates are phtosensitive in solution. The absence of any absorption band at 610 nm in carbon tetrachloride for diorganohaletin dithizonates indicate their greater stability towards light which is quite consistent with the idea that the order of stability of organotin dithizonates are :

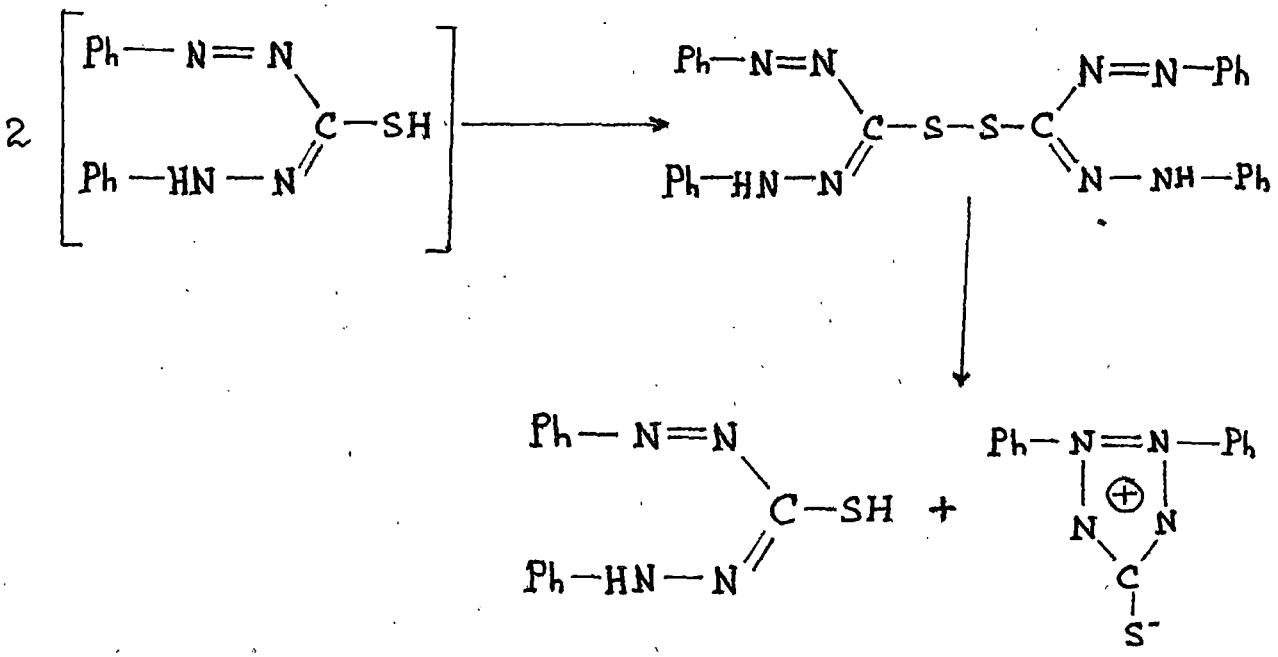
$$R_2SnX(HDz) > R_2Sn(HDz)_2 > R_3Sn(HDz)$$

It is notoriously difficult to prepare and preserve pure solid samples of dithizone and the deterioration of its stock solution in organic solvents such as chloroform and carbon tetrachloride has plagued the analyst since this reagent has introduced in 1925. Careful purification of the organic solvent reduces the rate of deterioration which is certainly accelerated by traces of heavy metals, by light and air, by alkali and oxidants, and by rise of temperature (258).

The deterioration of a solution of dithizone in organic solvents was reviewed and shown to be due to a multiplicity of photochemical and oxidative reaction (259). Bis 1,5 diphenyl formazan-3-yl disulphide has been isolated and characterised as a product of the action (inter alia) of aqueous iodine upon dithizone or silver dithizonate (259). Its spontaneous thermal cleavage to give an equimolar mixture of a mesoionic compound 2, 3 diphenyl-2, 3-dihydro tetrazolium-5-thiolate and dithizone is shown to explain the partial regeneration of deteriorated solution of dithizone when treated with reducing agents. The identity of Fischer's diphenyl thiocarbazide, Bamberger's tetrazolium betaine and ogilive and Corwin's dehydro dithizone with the orange mesoionic compound obtained from dithizone by using such oxidants as hydrogen peroxide, potassium permanganate, iodobenzene dichloride and iron (III) and thallium (III) was established by elemental analysis and visible and infrared spectrophotometry (259). Thus

the possible reaction during deterioration are:





The spectra of a freshly prepared solution of dithizone in methanol and the spectrum of this solution taken after different interval of time is shown in fig (22a). Here we see that dithizone absorbs strongly in the visible region at 470-480 nm and in the U.V. region at 272 nm. But the intensity of absorption band at 470-80 nm decreases gradually with time and after 113 hours there is no absorption maximum at 470-80 nm, but a new peak is developed at 420 nm and after 28 hours a new peak is found at 230 nm, which vanished after 65 hours. Besides this, a new peak is also developed at 254 nm. Thus from this observation it is clear that the concentration of dithizone in the solution gradually decreases with time and after 113 hours, there is no dithizone in the solution, since the characteristic absorption of dithizone at 480 nm disappeared from the visible absorption spectrum. H.M.N.H. Irving et al (259) have shown that Bis-1, 5-diphenyl formazan-3-yl disulphide in methanol has two absorption maxima one at 420 nm and the other at 254 nm. So from our studies, we also suggest the formation of disulphide during deterioration in the solution. However, the new absorption band at 230 nm can not be accounted for. In fact, the deterioration of solution of dithizone in organic solvents are due to a multiplicity of photochemical and oxidative reaction and there may be various products formed during deterioration as observed earlier.

The spectra of freshly prepared solution of triphenyl tin dithizonate in methanol and the spectrum of this solution taken

Spectrum of Dithizone in Methanol

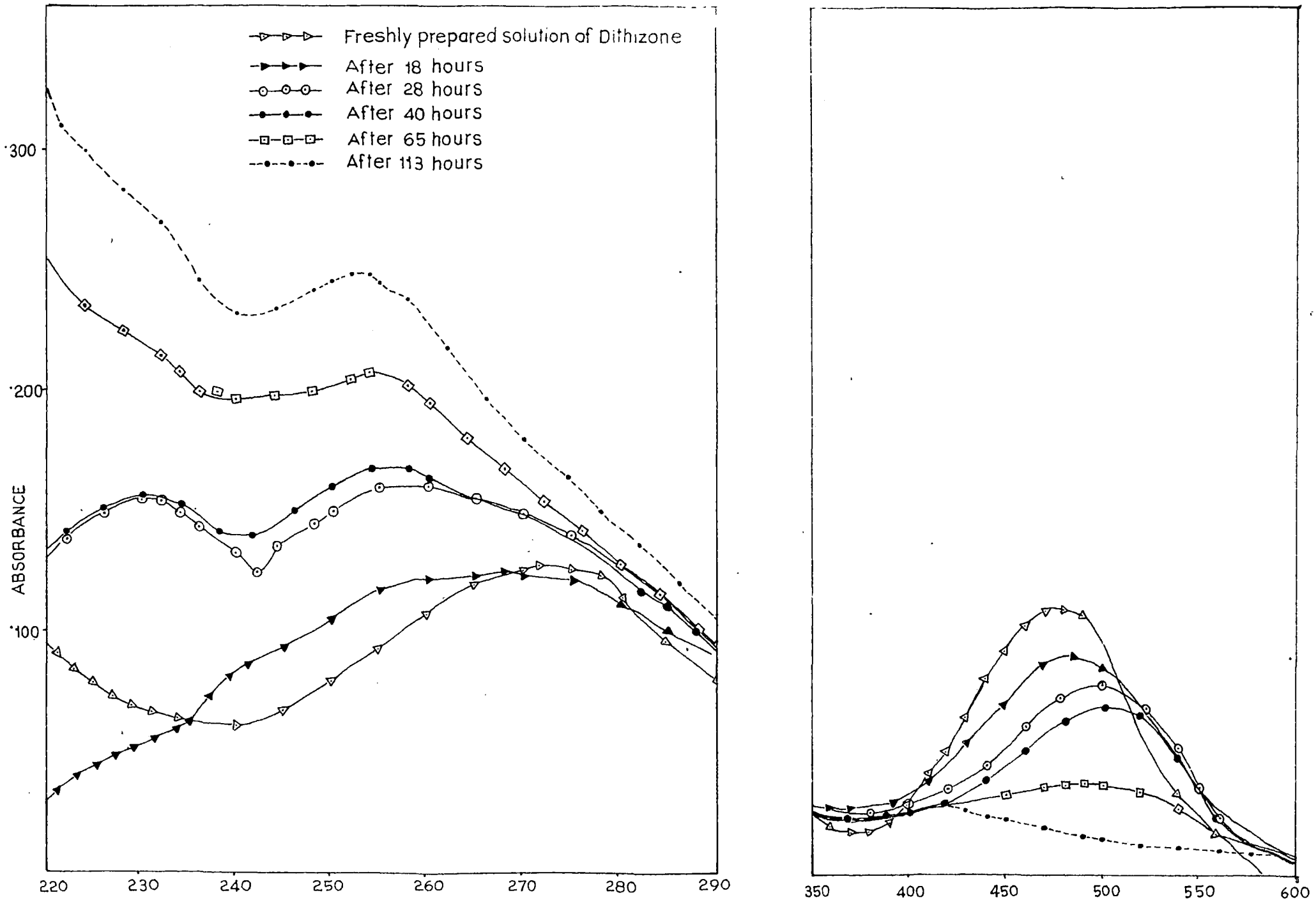


Fig--- 22 (a)

Spectrum of Triphenyl tin Dithizonate in Methanol

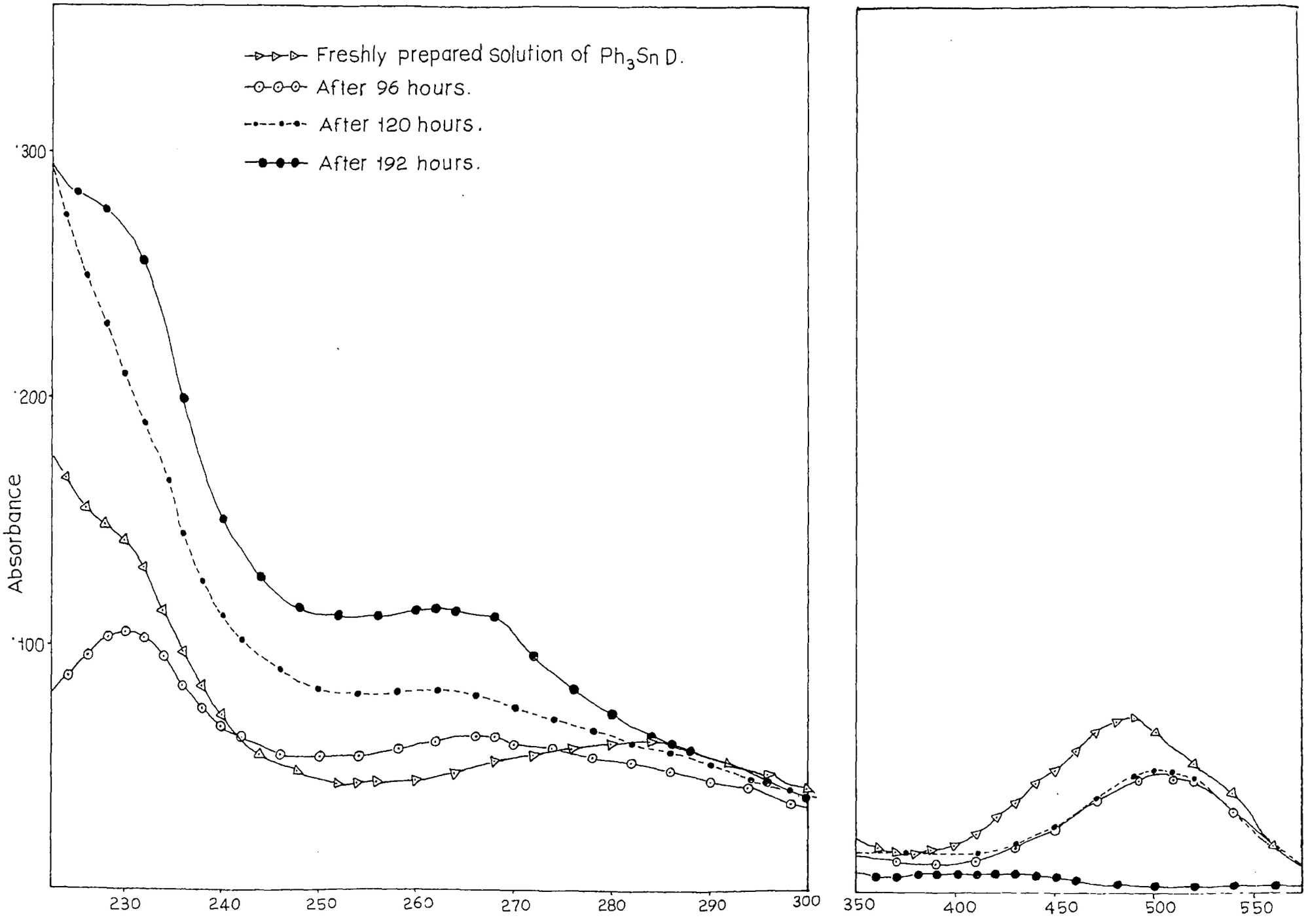


Fig--- 22 (b)

after different interval of time is shown in fig (22b). Here again we see that triphenyl tin dithizonate in methanol solution absorbs strongly in the visible region at 490 nm and on standing the solution, the intensity of absorption at 490 nm gradually decreases and ultimately the maxima vanishes and developed a new very low absorption maxima at 420 nm. In the U.V. region after 96 hours a new peak is developed which disappeared after 120 hours. After 120 hours a new peak is also developed at 254 nm. These two absorption maxima one at 254 nm and the other at 420 nm may be accounted for the formation of disulphide in the solution. Similar absorption band is also found in the deteriorated solution of diphenyl tin bis dithizonate and diphenyl tin bromo dithizonate (fig. 22c) and (fig. 22d) after 151 hours and 174 hours respectively. Here in these cases also the formation of disulphide may be suggested in the deteriorated solution to account for the two absorption bands at 254 nm and 420 nm. The organotin dithizonate solution also deteriorates in other non polar solvent like carbon tetra chloride but such deterioration is appreciably slower in comparison with polar solvents like methanol since the decrease in intensity of absorption maxima occurs very slowly for one or two days.

It has also been observed that triphenyl tin dithizonate solution in cyclohexane undergo rapid photochemical decomposition (fig. 22e). Triphenyl tin dithizonate solution in cyclohexane

Spectrum of Diphenyl tin bis dithizonate in Methanol

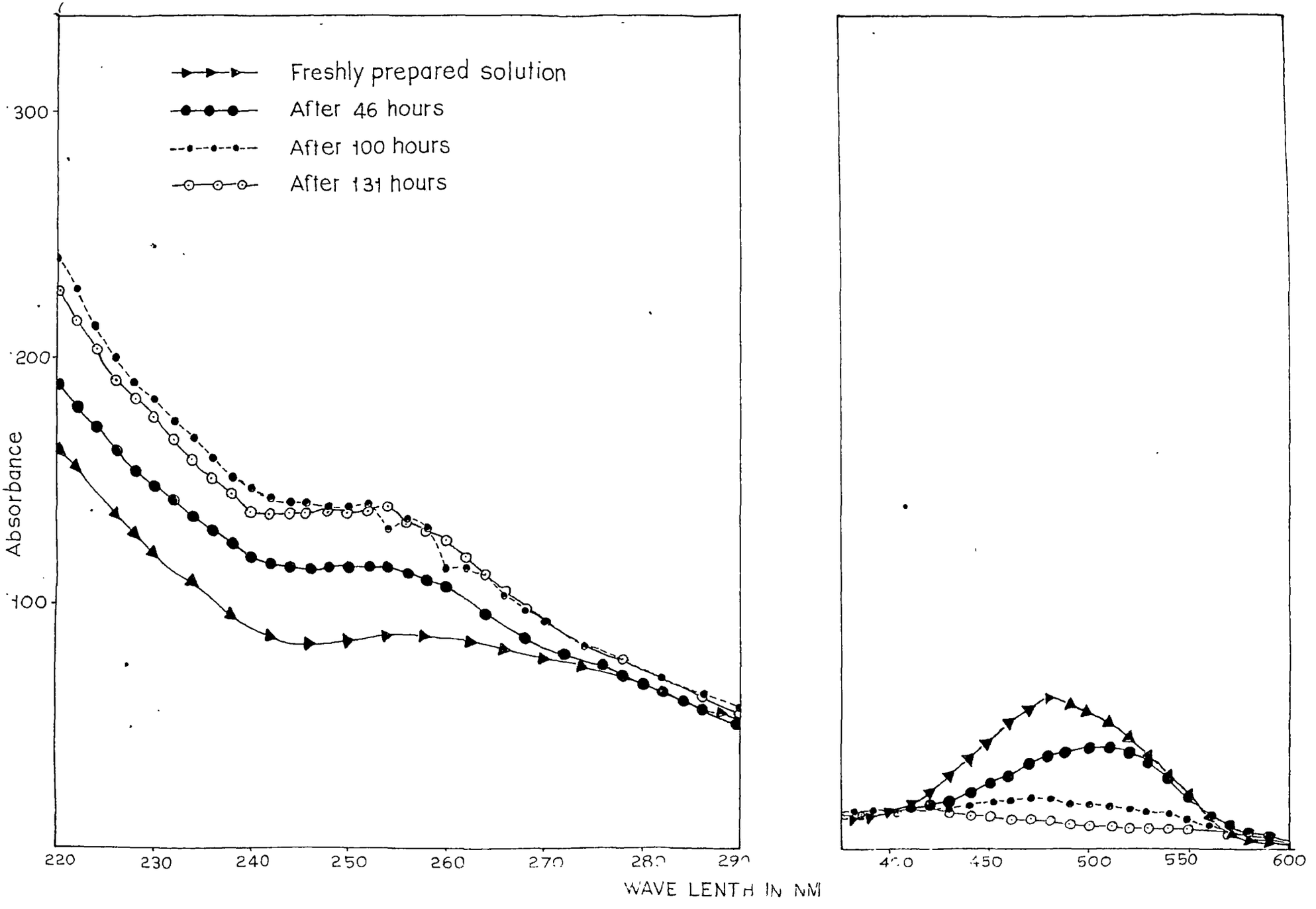


Fig--- 22 (c)

Spectrum of diphenyl bromo tin dithizonate in methanol

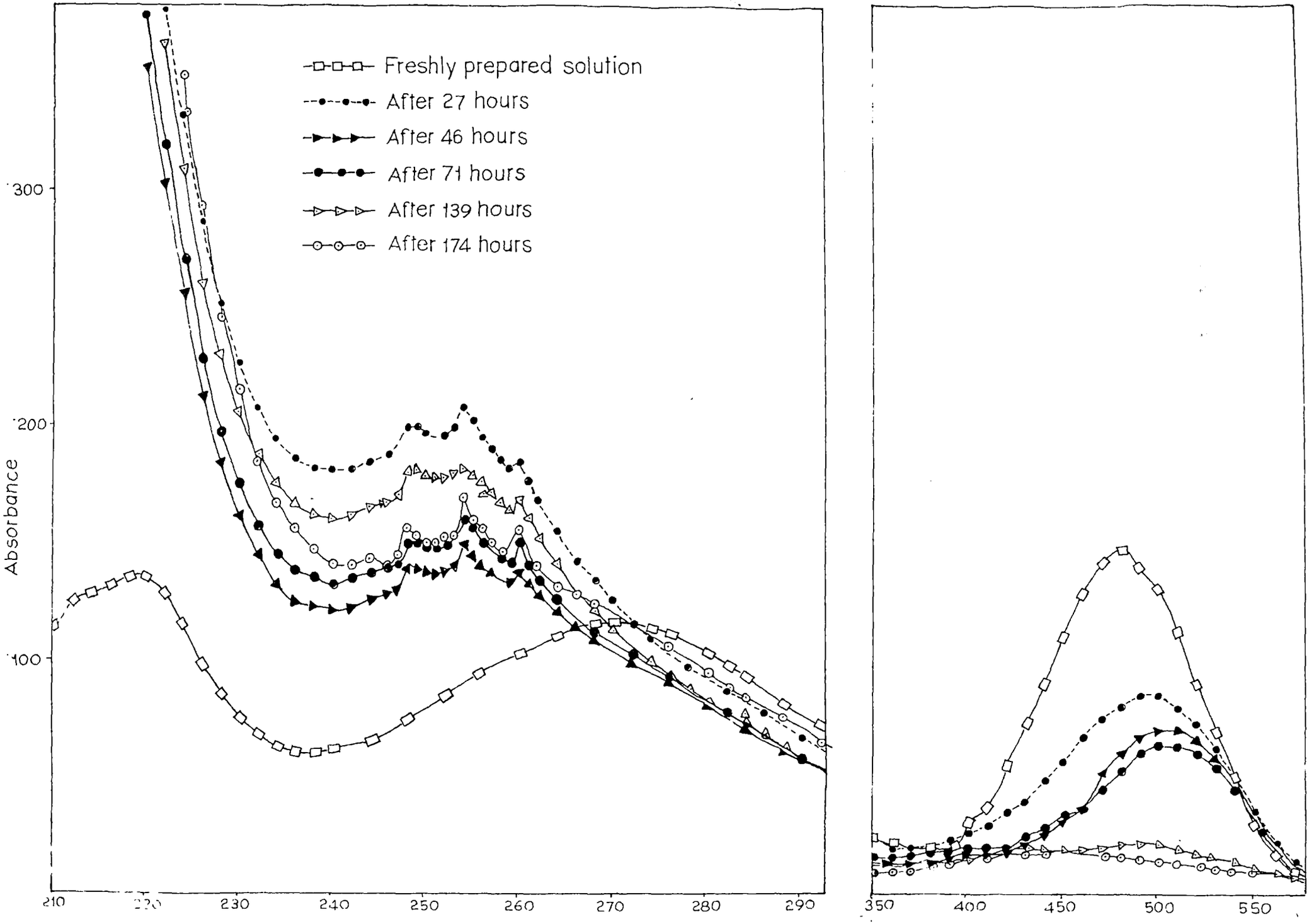


Fig--- 22 (d)

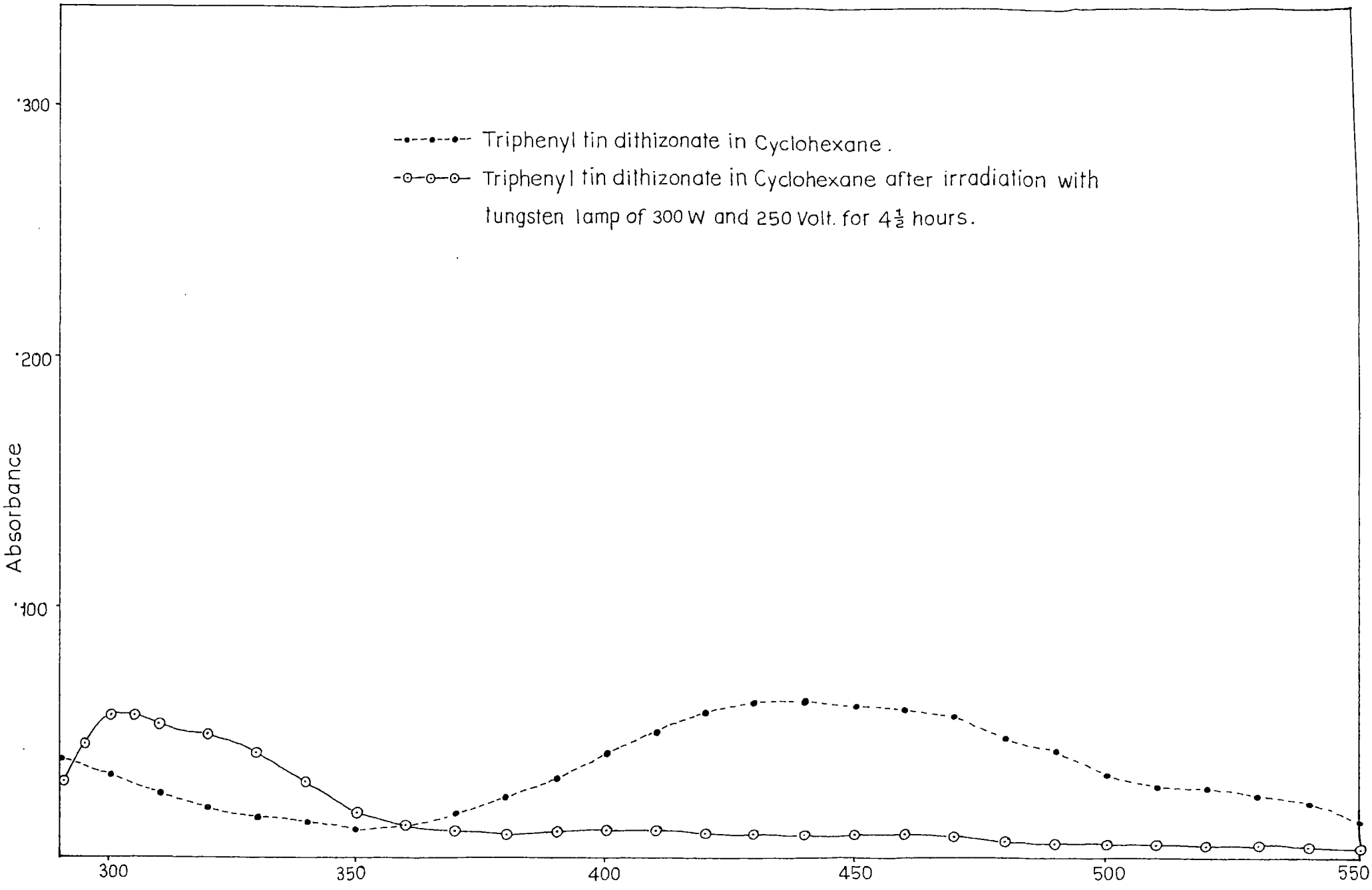

·300
·200
·100
Absorbance
Triphenyl tin dithizonate in Cyclohexane.
Triphenyl tin dithizonate in Cyclohexane after irradiation with tungsten lamp of 300 W and 250 Volt. for 4½ hours.
300
350
400
450
500
550
Wave length in nm.

Fig--- 22 (e)

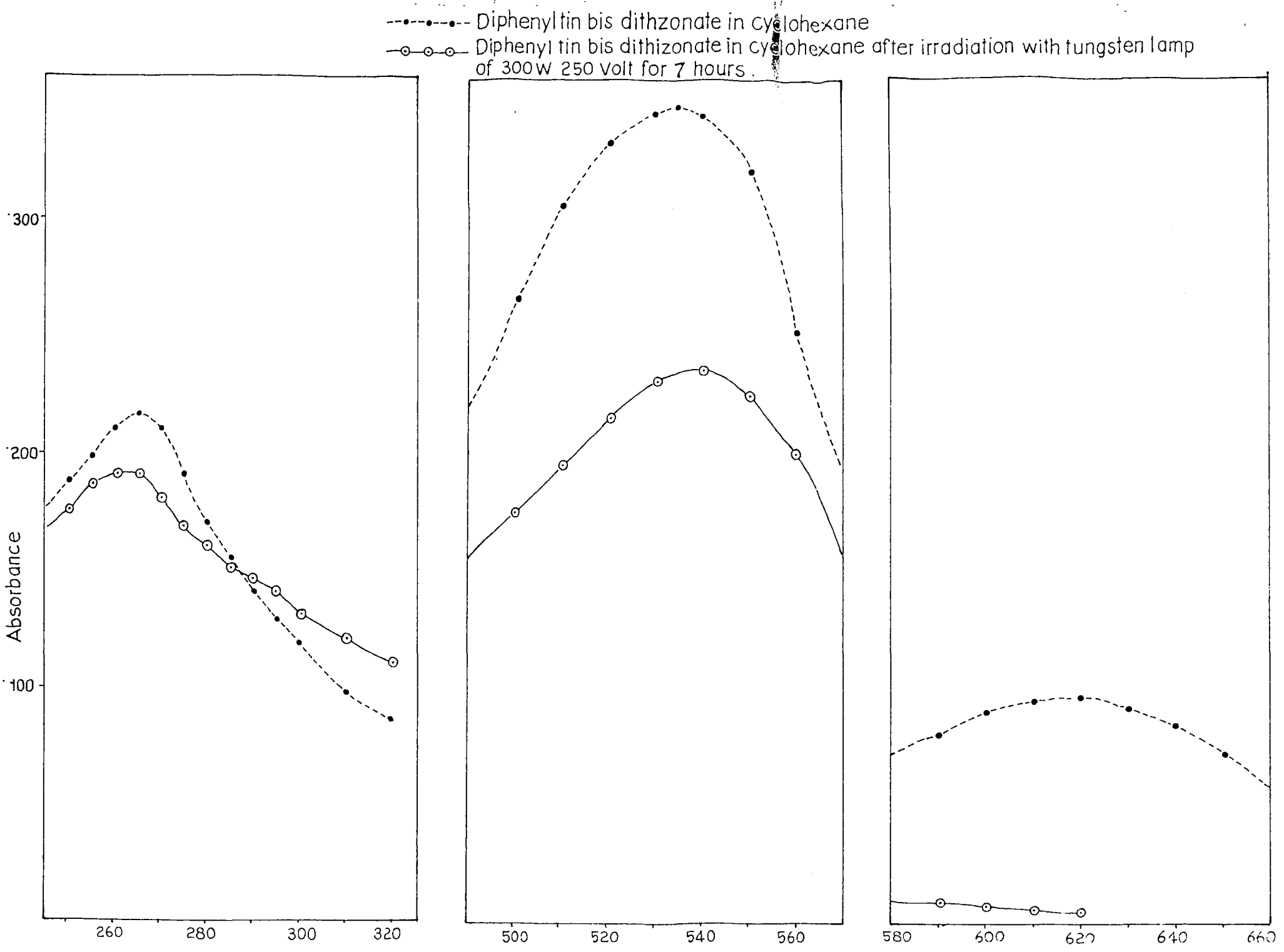

Diphenyl tin bis dithzonate in cyclohexane
Diphenyl tin bis dithizonate in cyclohexane after irradiation with tungsten lamp of 300 W 250 Volt for 7 hours.
Absorbance
300
200
100
260
280
300
320
500
520
540
560
580
600
620
640
660
Wave length in nm.

Fig--- 22 (f)

--•--•--•-- Diphenyl bromo tin dithizonate in cyclohexane

—⊙—⊙—⊙— Diphenyl bromo tin dithizonate in cyclohexane after irradiation with tungsten lamp of 300 w 250 volt for 7 hours.

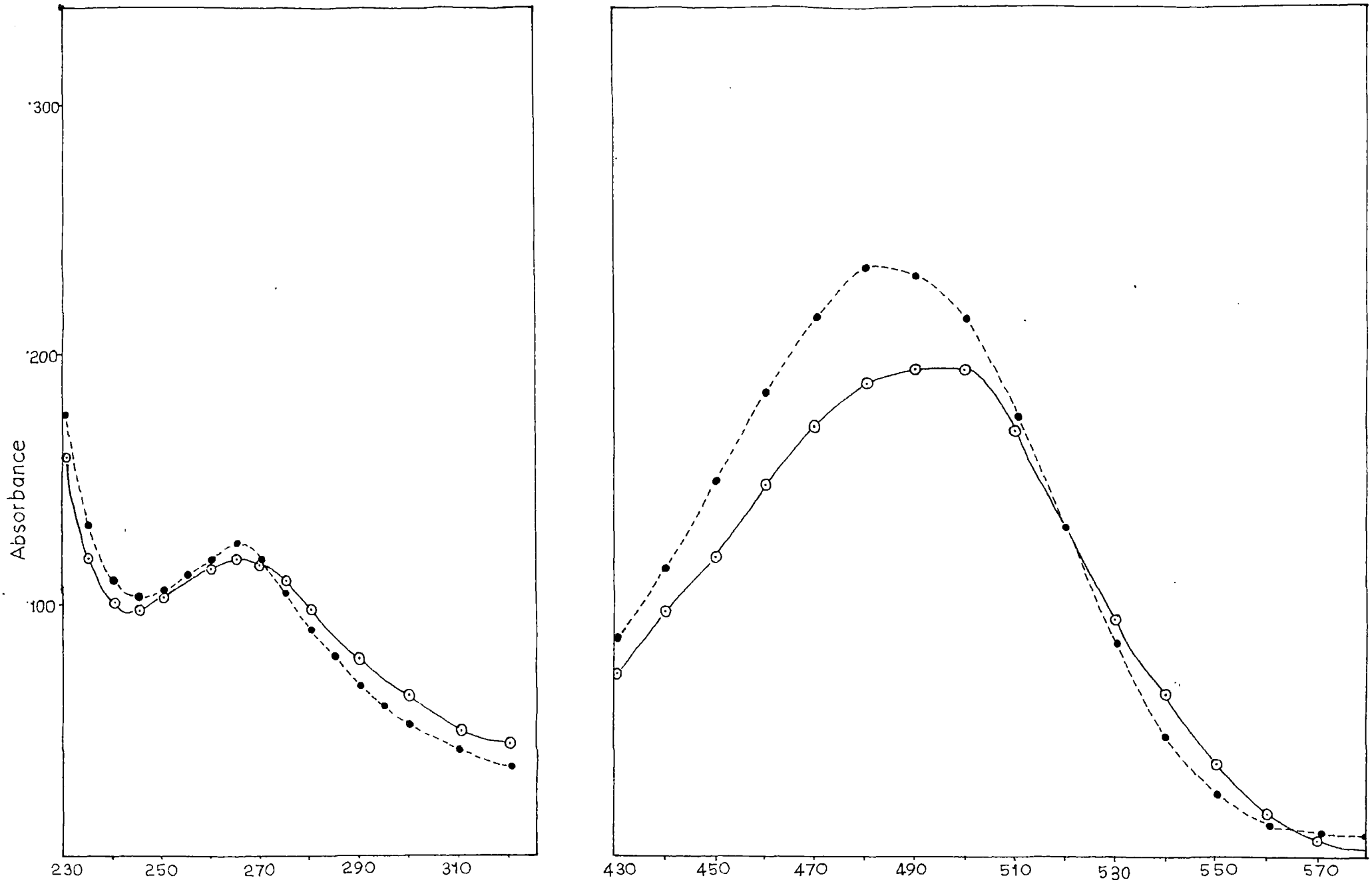


Fig--- 22 (g)

absorbs strongly at 440 nm and after irradiation with tungsten lamp for seven hours, it has been observed that there is no absorption band at 490 nm, and instead of this, a new band has appeared at 300 nm. H.M.N.H. Irving has shown that Bis-1, 5-diphenyl formasan 3-yl disulphide absorbs at 415 nm and 303 nm. But here we have observed only a single absorption at 303 nm. Thus the appearance of the band at 300 nm can not definitely be said due to disulphide. Di-phenyl bromotin dithizonate and diphenyl tin bis dithizonate also undergo photochemical decomposition which is evident from the fact that the intensity of absorption maxima is lowered on irradiation with tungsten lamp for seven hours.

Thus the deterioration of organotin dithizonates in methanol may be due to photochemical decomposition or solvolysis or for the both liberating free dithizone which gradually undergo deterioration to form disulphide that may further be changed to some unidentified products. But in non hydroxylic solvent there is little chance of solvolysis. In such a case the deterioration must be resulted from the photochemical decomposition of the complex.