CHAPTER - IV

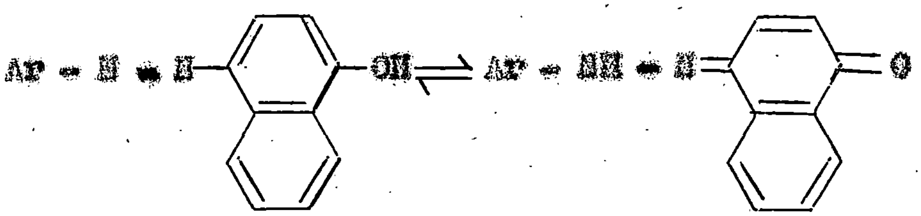
ABSORPTION SPECTRA AND STRUCTURE OF THE ORGANOTIN (ARYL AZO) PHENOXY ACETATES.

IVA. Introduction

The electronic spectra of azobenzene and related compounds have been studied extensively by several workers (1-14) and have been interpreted in terms of molecular orbital description (1,2,15,16). On the basis of these studies, the absorption bands in the UV - Visible region, which are generally, three to four in number, may be divided into two types. The longest wavelength, weak to moderate intensity band in azo benzene and related compounds ($\epsilon_{max} \approx 10^2 - 10^3$), is ascribed to the ~~n~~ $n-\pi^*$ transition and the other more intense absorption bands ($\epsilon_{max} \approx 10^4$) are ascribed to $\pi-\pi^*$ transitions. While the position of the first $\pi-\pi^*$ band varies considerably from compound to compound, the position of the $n-\pi^*$ band is almost unaffected by the aryl groups and occurs at about 440 - 460 nm. This is easily explained in terms of MO treatment of the azo benzene system. The upper MO for the first $n-\pi^*$ and $\pi-\pi^*$ transitions is the perturbed orbital originating from the antibonding π orbital of the azo group and its energy is almost independent of the nature of the aryl groups. The lower orbital of the first $\pi-\pi^*$ transition is the orbital arising from the perturbation of the higher bonding π orbitals of the aryl groups and hence its energy largely depends on the aryl groups. On the other hand, the lower orbital of the $n-\pi^*$ transition being a non-bonding orbital of the azo group its energy is unaffected by the aryl groups.

Substituents like $-NH_2$, $-NMe_2$, $-OH$, $-COOH$ etc. which are capable of producing large bathochromic shift of the $\pi-\pi^*$ transitions by extending the conjugation, may often shift the first $\pi-\pi^*$ band in the azo compounds to such an extent that the characteristic $n-\pi^*$ absorption is masked by the strong absorption. Thus methyl red which contains $-COOH$ and $-NMe_2$ groups in 2 and 4 positions respectively, no weak absorption band could be observed in the 440 - 460 nm region due to the presence of strong $\pi-\pi^*$ absorption in this region (6). All the acetic acids and their derivatives investigated in the present work belong to this category and no separate band due to $n-\pi^*$ transition could be observed in these compounds.

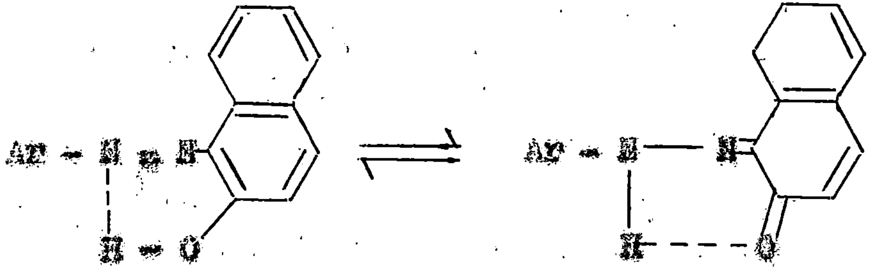
In the absence of specific solvent - solute interactions the electronic absorption spectra of the azo compounds do not show any strong solvent dependence apart from a small red shift of both the $\pi-\pi^*$ and $n-\pi^*$ bands (1,17). However, the presence of $-OH$ group in the aryl part of the azo compounds often leads to a strongly solvent dependent absorption spectrum due to the possibility of (a) hydrogen bond formation by the phenolic - OH group and/or (b) azo -hydrazone tautomerism as shown below (1).



I

The azo-hydrazone tautomerism in hydroxy azo derivatives has been studied in great detail by several workers (3,7, 9,10,18). It has been found that the azo-hydrazone tautomeric equilibria, e.g., I, is important only in the azo napthol series while no indication of the presence of hydrazone form could be found in the hydroxy azo-benzenes and phenyl azonapthols (3,19, 20).

In phenyl azonapthols, the presence of an isosbestic point in the visible absorption curves measured in a variety of solvents has been given as an evidence for the presence of the equilibrium I in phenyl azonapthols (7). Both the azo and hydrazone forms may be stabilised in suitable donor solvents by external hydrogen bonds formed by the -OH and -NH group respectively. However, with a given solvent, the phenolic hydrogen generally forms stronger bonds than the -NH group and the concentration of azo form increases in the order : hexane $<$ ethyl alcohol $<$ benzene $<$ chloroform $<$ 50% ethyl alcohol $<$ acetic acid, in contrast to observation in aryl azo 2-napthol series. This effect is considerably enhanced by ortho substituents which sterically inhibit the formation of the external hydrogen bonds in the hydrazone tautomer and thus, unexpectedly low concentration of the phenyl hydrazone form is present in the ortho substituted 1-aryl azo-4-napthols (9). On the other hand, both the tautomers in 1-aryl azo-2-napthols (IIa, IIb) are unable to form external hydrogen bonds and the concentration of the more polar Ketonic structure increases in the order of solvents:

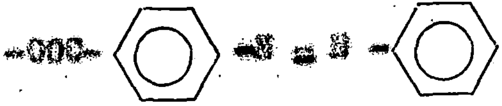


IIa IIb

hexane < benzene < ethyl alcohol < chloroform < acetic ~~and~~ acid < water, approximately in line with increasing dielectric constants (9).

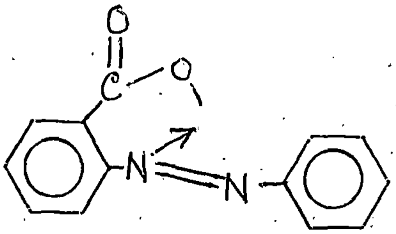
Though a large number of metal complexes, particularly those of chromium, nickel, cobalts and copper, of hydroxy and O-carboxy azo compounds have been prepared because of their importance in the dye industry, comparatively little attention has been paid to the study of the electronic spectra of the metal derivatives (5,21-25). No detailed general account of the effect of co-ordination on the electronic spectra of the azo compounds is so far available. In the early work by Ernsberger and Brode (21), a comparison of the absorption spectra of a series of phenyl azo p-cresol, β-napthol and β-napthylamine derivatives with those of the copper, nickel and cobalt compounds has been made. The metal derivatives were found to exhibit a new band in the visible region together with the absorption bands corresponding to those found in the parent azo dye. The new bands in the metal complexes occur at the same position for a given metal, regardless of the dye with which it is combined and may therefore be ascribed to an electronic transition within the metal atom only.

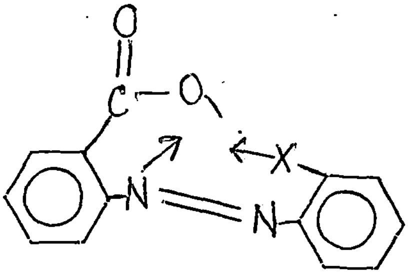
Absorption spectra of organotin derivatives of (aryl azo) benzoic acids have been reported by Majee and Banerjee (26) where it is shown that organotin (aryl azo) benzoates may be classified into three categories, viz., (i) derivatives of O-(aryl azo) benzoic acids where the coupling components has no donor groups (e.g., $-NH_2$, -OH, OMe etc.) at the ortho position, (ii) derivatives of O-(aryl azo) benzoic acids where the coupling components have a donor group at the ortho position and (iii) derivatives of the p-(aryl azo) benzoic acids. This classification actually corresponds to ligating ability of the compounds. Thus the first group of compounds represent the derivatives of the ligands which are potentially bidentate, the second group represent potentially terdentate ligands while the p-carboxy ligands are only monodentate (III-V).



Monodentate

III





Bidentate

(X = $-NH_2$, $-OH$, $-OMe$)

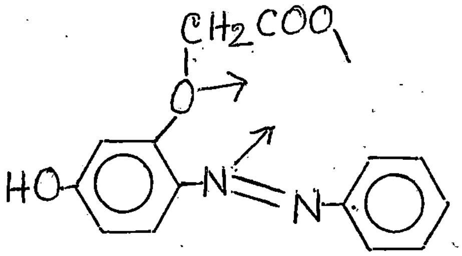
Terdentate

IV

V

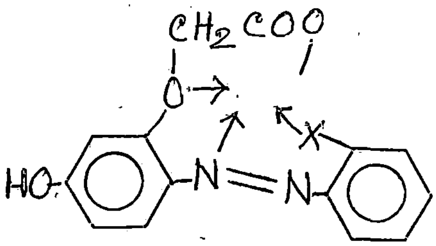
Because the stability of the complexes generally increase with the number of annelated chelate rings, complexes derived from V are usually more stable than those formed by IV, which in turn, is more stable than the p-(aryl azo) benzoates where N(azo)→M co-ordination is not possible. This is reflected in the solvent sensitivity of the absorption spectra of organotin complexes (26).

Although some of the aryloxy acetic acids used in the present investigation are terdentate (type VI), the O-substituted derivatives (type VII) are potentially tetradentate.



Terdentate

(VI)



Tetradentate

$X = OH, OCH_3, F, Cl$ etc.

(VII)

Another interesting possibility is the azo-hydrazone tautomeric equilibrium of the following type.

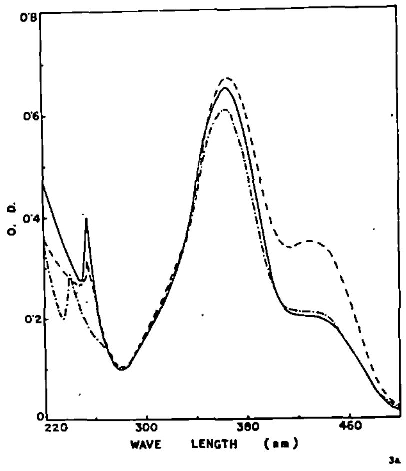


Fig. 1 Absorption spectra in methanol of

1. L$_1$H (3.6 x 10^{-5} M, — • — • —)

2. Ph$_3$SnL$_1$ (4.1 x 10^{-5} M, ————)

3. Bu$_3$SnL (3.7 x 10^{-5} M , — — — —)

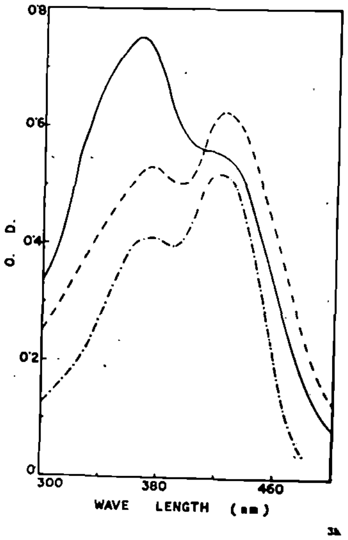
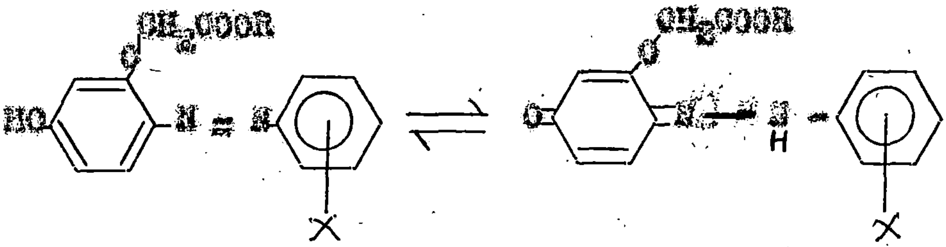


Fig. 2 Absorption spectra in benzene of

1. L$_1$H (————)

2. Ph$_3$SnL$_1$ (2.8 x 10^{-5} M, — • — • —)

3. Bu$_3$SnL$_1$ (3.76 x 10^{-5} M, — — — —)



VIII

We shall now present electronic absorption spectral data which support the formation of 7-coordinated triorganotin chelates in some cases.

IVB. Electronic Absorption spectra of the ligands and the abbreviation used for ligands are given in the preceding chapter. The spectral data for the aryloxy acetic acids and their organotin derivatives are given in Table 1. Absorption curves are also shown in figs. 1-24.

Table -1

Absorption Maxima in (Aryl azo) phenoxy acetic acids and their organotin derivatives.

Compound	Solvent	λ_{max}(nm)	(log ϵ)	
1. L_1H	Methanol	240 (3.09)	365 (4.23)	430^a
	Benzene		368	420
2. Ph_3Sn-L_1	Methanol	268 (3.1)	365 (1.19)	150^a
	Benzene		370 (4.16)	480 (4.28)

Contd..

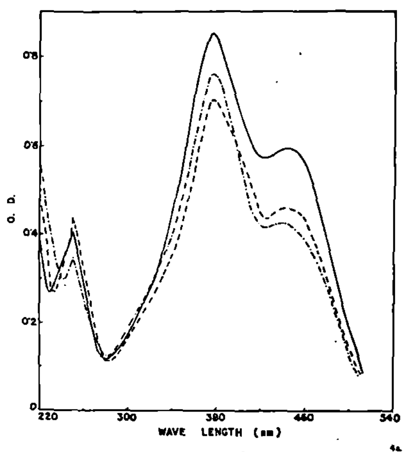


Fig. 3 Absorption spectra in methanol of
1. L_3H (3.63 x 10^{-5} M, — — — —)
2. Ph_3SnL_3 (3 x 10^{-5} M, — · — · —)
3. Bu_3SnL_3(3.26 x 10^{-5} M, ————)

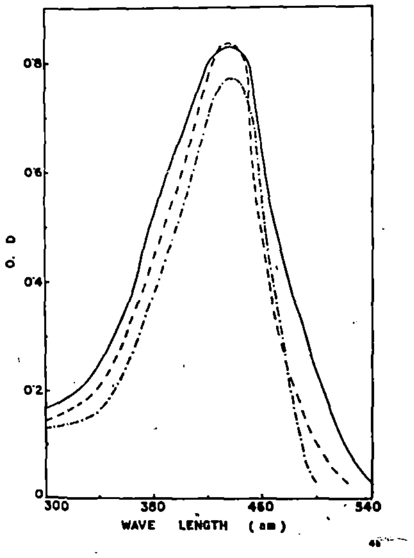


Fig. 4 Absorption spectra in benzene of
1. L_3H (————)
2. Ph_3SnL_3 (3.7 x 10^{-5} M, — — — —)
3. Bu_3SnL_3 (4 x 10^{-5} M, — · — · —)

Table - 1 (Contd..)

Compound	Solvent	λ_{max}(nm)	(logϵ)	
3. Bu_3Sn-L_1	Methanol	255 (4.03)	365 (4.25)	450^a
	Benzene		372 (4.14)	422 (4.22)
4. L_2H	Methanol	270 (4.00)		450 (4.03)
	Benzene		378 (4.14)	423 (4.23)
5. $(Ph_3Sn)_2L_2$	Methanol	274 (4.03)	375 (3.06)	530 (4.3)
			387 (3.09)	560 (4.31)
6. $(Bu_3Sn)_2L_2$	Methanol	270 (4.30)	390 (4.2)	525 (4.36)
			385 (4.2)	560 (4.32)
7. L_3H	Methanol	230 (3.02)	374 (4.31)	437 (4.03)
			435	
8. Ph_3SnL_3	Methanol	250 (4.14)	375 (4.36)	437 (4.17)
	Benzene			435 (4.34)
9. Bu_3SnL_3	Methanol	250 (4.03)	375 (4.41)	440 (4.25)
	Benzene			435 (4.23)

Contd..

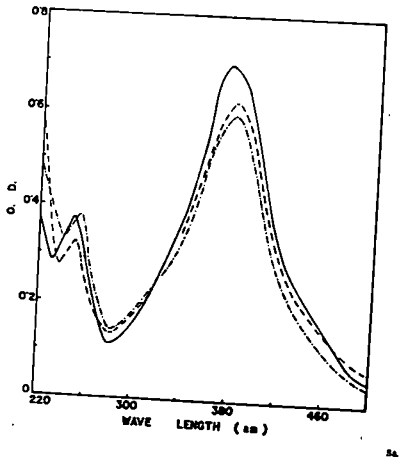


Fig. 5 Absorption spectra in methanol of

1. L_4H (3.53×10^{-5} M, ————)
2. Ph_3SnL_4 (3.3×10^{-5} M, —·—·—)
3. Bu_3SnL_4 (3.9×10^{-5} M, - - - -)

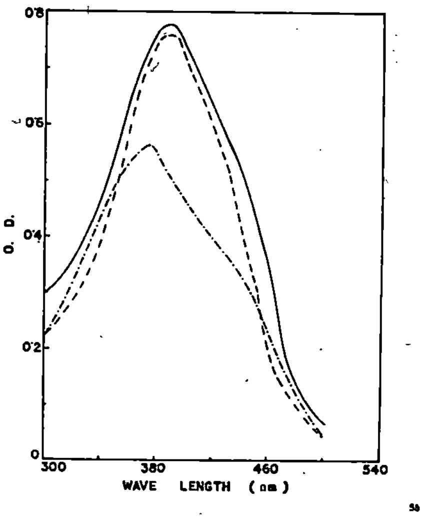


Fig. 6 Absorption spectra in benzene of

1. L_4H (—·—·—)
2. Ph_3SnL_4 (4.7×10^{-5} M, - - - -)
3. Bu_3SnL_4 (4.1×10^{-5} M, ————)

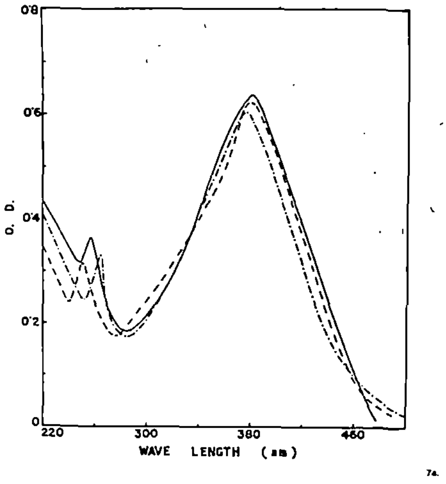


Fig. 7 Absorption spectra in methanol of

1. L_5H (4.8×10^{-5} M, — · — · —)
2. Ph_3SnL_5 (3.9×10^{-5} M, — — — —)
3. Bu_3SnL_5 (4.6×10^{-5} M, ————)

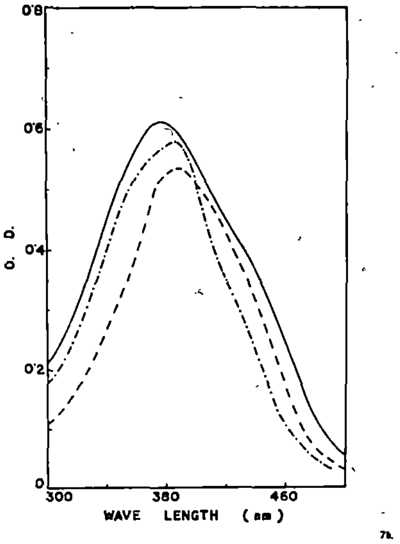


Fig. 8 Absorption spectra in benzene of

1. L_5H (————)
2. Ph_3SnL_5 (3.2×10^{-5} M, — · — · —)
3. Bu_3SnL_5 (3.1×10^{-5} M, — — — —)

Table - 1 (Contd..)

Compound	Solvent	λ_{max}(nm)	(log ϵ)	
10. L_4H	Methanol	250(4.02)	377(4.3)	
	Benzene	375		430^a
11. Ph_3SnL_4	Methanol	254(4.06)	380(4.25)	
			397(4.2)	430^a
12. Bu_3SnL_4	Methanol	250(3.09)	380(4.2)	
			397(4.28)	440^a
13. L_5H	Methanol	265(3.15)	375(4.09)	
		375		440^a
14. Ph_3SnL_5	Methanol	250(3.09)	380(4.2)	
			397(4.26)	435^a
15. Bu_3SnL_5	Methanol	253(3.1)	380(4.14)	
			397(4.25)	440^a
16. L_6H	Methanol	260(3.22)		435 (4.25)
	Benzene			415
17. Ph_3SnL_6	Methanol	270(3.39)		435 (4.19)
	Benzene			440 (4.32)
18. Bu_3SnL_6	Methanol	270(3.36)		434 (4.24)
	Benzene			440 (4.37)

Contd..

Table – 1 (Contd..)

Compound	Solvent	λ_{max} (nm)	(log ϵ)	
19. L_7H	Methanol	250(4.04)	370(4.24)	450^a
	Benzene		370	450^a
20. Ph_3SnL_7	Methanol	253(4.2)	370(4.26)	450^a
	Benzene		370(4.26)	450^a
21. Bu_3SnL_7	Methanol	256(4.13)	370(4.22)	450^a
	Benzene		370(4.3)	450^a
22. L_8H	Methanol	280(3.09)	370(4.14)	435 (4.00)
23. Ph_3SnL_8	Methanol	250(4.08)	370(4.26)	435 (4.04)
	Benzene		370^a	425 (4.33)
24. Bu_3SnL_8	Methanol	250(4.05)	370(4.24)	435 (4.01)
	Benzene		375^a	425 (4.36)
25. L_9H	Methanol	250(4.02)	372(4.33)	
	Benzene		370(4.11)	
26. Ph_3SnL_9	Methanol	250(3.06)	372(4.22)	
	Benzene		372(4.08)	

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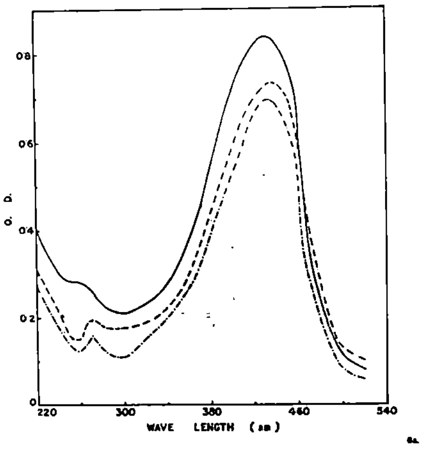


Fig. 9 Absorption spectra in methanol of

1. L_6H (4.4×10^{-5}M, ———)
2. Ph_3SnL_6 (4.7×10^{-5}M, — — — —)
3. Bu_3SnL_6 (3.9×10^{-5}M, — · — · —)

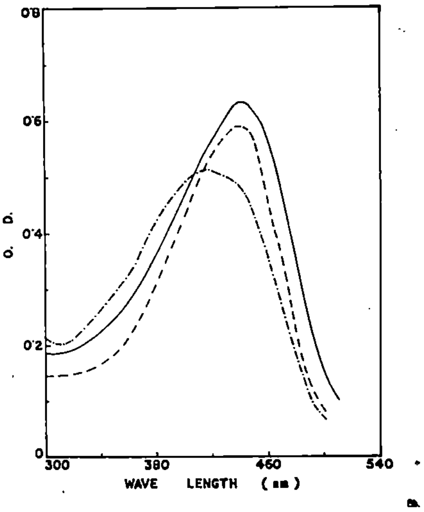


Fig. 10 Absorption spectra in benzene of

1. L_6H (— · — · —)
2. Ph_3SnL_6 (2.8×10^{-5}M, — — —)
3. Bu_3SnL_6 (2.78×10^{-5}M, ———)

Table - 1 (Contd..)

Compound	Solvent	λ_{max}(nm)	(log ϵ)	
27. L_{10}	Methanol	258	375	
	Benzene		376	440^a
28. Ph_3SnL_{10}	Methanol	260(4.15)	375(4.36)	
	Benzene		375(4.40)	
29. L_{11}	Methanol	260	375	445
	Benzene			440
30. Ph_3SnL_{11}	Methanol	260(3.92)	375(4.28)	
	Benzene		375(4.24)	

a) Inflection or shoulder.

The electronic absorption spectra of almost all the compounds are characterised by the presence of three absorption bands in the UV - visible region. The lowest wave length peak in the 250-270 nm region undoubtedly originates from perturbed local excitation in the aryl groups, while the absorption in the visible region is associated with the $\pi - \pi^*$(azo) transition.

An examination of the data given in Table 1 shows that the absorption characteristic of the organotin derivatives are generally very similar to that of the free ligands

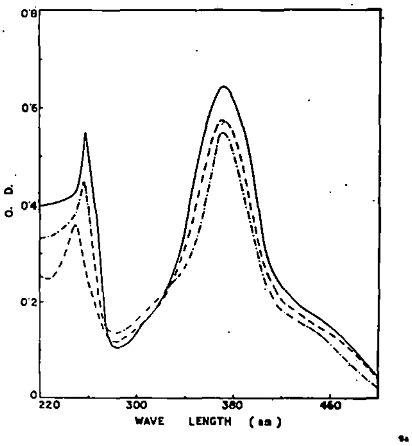


Fig. 11 Absorption spectra in methanol of

1. L_7H (3.26×10^{-5} M, — — — —)

2. Ph_3SnL_7 (3.3×10^{-5} M, ———)

3. Bu_3SnL_7 (3.3×10^{-5} M, — · — · —)

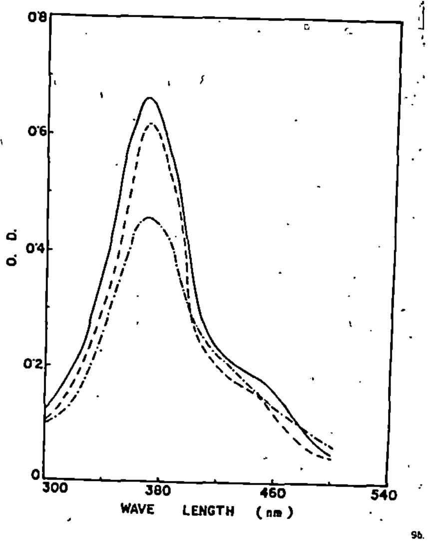


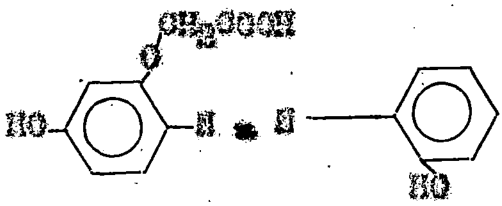
Fig. 12 Absorption spectra in benzene of

1. L_7H (— · — · —)

2. Ph_3SnL_7 (3.6×10^{-5} M, ———)

3. Bu_3SnL_7 (3.3×10^{-5} M, — — —)

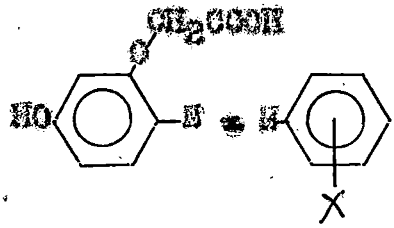
except where the ligand is a hydroxyl group at ortho position in the diazo moiety as in IX.



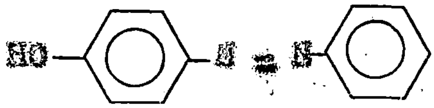
IX

A general feature of the absorption spectra of almost all the compounds is two absorption maxima in the visible region which suggests the presence of tautomeric equilibrium in solution.

In the absence of any tautomeric or solvent - solute equilibria, the absorption spectrum of the (2-benzene azo). 5-hydroxy phenoxy acetates (X) is expected to be closely similar to that of the 4-hydroxy azo benzene (XI) except for a small bathochromic shift that may arise due to the substituents in the aryl moiety of (X)



(X)



(XI)

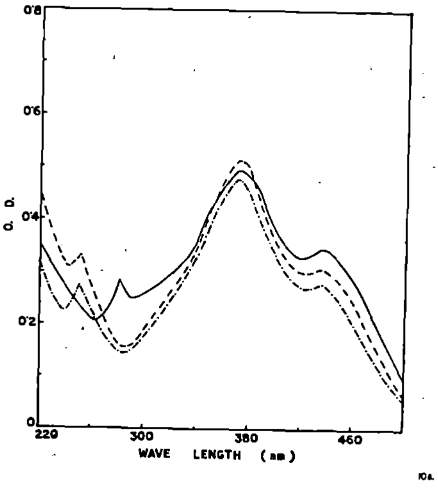


Fig. 13 Absorption spectra in methanol of

1. L_2H (2.5 x 10^{-5}M, ———)

2. Ph_2SnL_2 (2.8 x 10^{-5}M, — — —)

3. Bu_2SnL_2 (2.7 x 10^{-5}M, — . — . —)

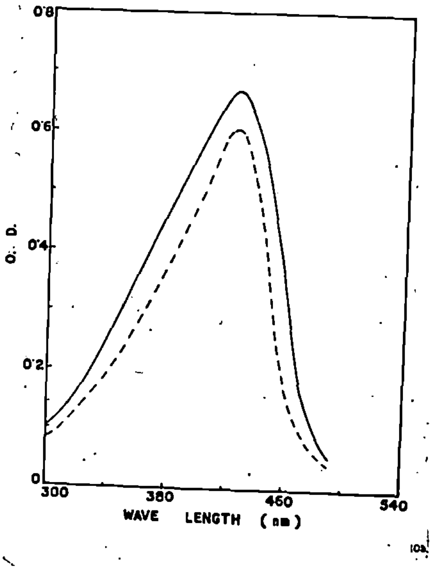


Fig. 14 Absorption spectra in benzene of

1. Ph_2SnL_2 (3.1 x 10^{-5}M, ———)

2. Bu_2SnL_2 (2.6 x 10^{-5}M, — — —)

The absorption spectrum of XI shows the presence of only one strong transition around 350 nm due to $\pi - \pi^*$ transition with a weak band at 436 nm due to $n - \pi^*$ transition.(1) All substituted derivatives of XI also show the presence of a single strong absorption band which occur in the range 350-390 nm depending on the substituent. Since compound (X) differs from the substituted 4-hydroxy azo benzene only by an acetoxy group which is not expected to show absorption in the same region if it exists in the azo form like the 4-hydroxy azo benzenes. In fact, almost all the compounds show an intense absorption in 360 - 390 nm. Obviously, this absorption is associated with $\pi - \pi^*$ transition in the azo form. The additional band at much longer wave length should be attributed to the presence of the hydrazone form in equilibrium with the azo form. This is consistent with known behaviour of the hydrazone form which always absorb at longer wave length compared to the corresponding azo form(23).

That azo-hydrazone equilibrium is responsible for the presence of two absorption bands in the visible region in the present compounds is conclusively demonstrated by the following observations.

Replacement of the H atom of the hydroxyl group by a methyl or stannyl group as shown in (XII) which eliminates the possibility of azo-hydrazone tautomerism results in a

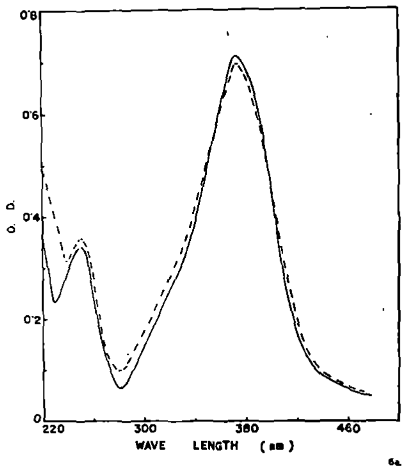


Fig. 15 Absorption spectra in methanol of
1. L_3H (5.3×10^{-5} M, ———)
2. Ph_3SnL_3 (4.2×10^{-5} M, – – – –)

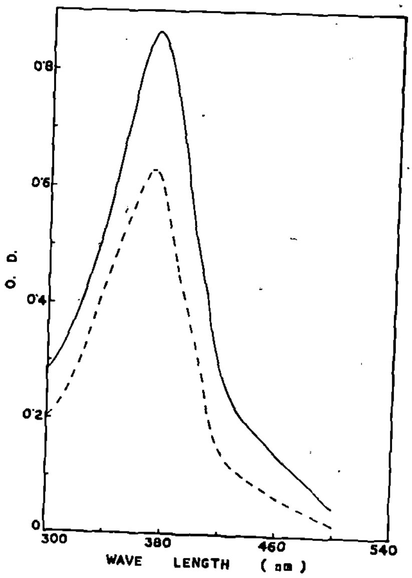
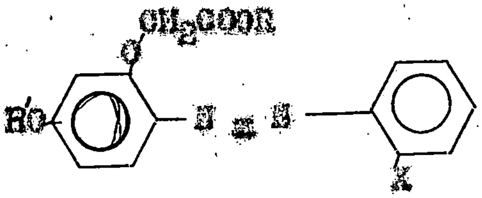


Fig. 16 Absorption spectra in benzene of
1. L_3H (4.8×10^{-5} M, – – – –)
2. Ph_3SnL_3 (3.6×10^{-5} M, ———)

single absorption band at 370 nm.



R = H, Ph$_3$Sn ; R' = CH$_3$Ph$_3$Sn

and X = Cl, OCH$_3$

(XII)

The long wave length absorption around 430 nm is, thus eliminated whenever the possibility hydrazone form is eliminated clearly, the longest wave length absorption band around 420 – 450 nm region, when present, must be attributed to the presence of the hydrazone form. The data given in Table – 2 demonstrates this.

Table – 2

Visible absorption maxima in compounds of type XII.

Sl. No.	R	R'	X	Solvent	λ_{max}(nm)	Tautomer(s) present in solution
1.	H	H	Cl	Benzene	375,430^a	Azo & Hydrazone
				Methanol	377	Azo

Contd..

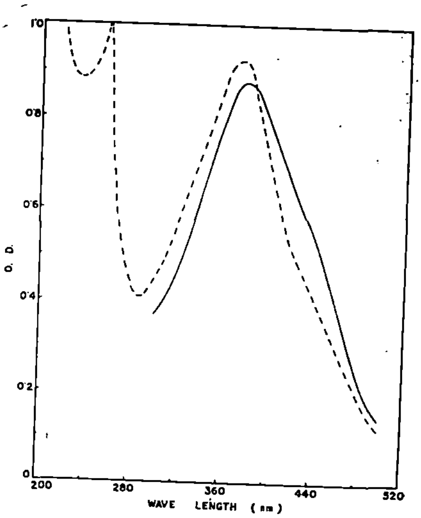


Fig. 17 Absorption spectra of

1. L_{10} in methanol (– – – –)
2. L_{10} in benzene (———)

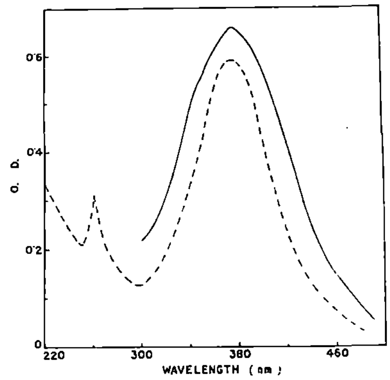


Fig. 18 Absorption spectra of

1. Ph_3SnL_{10} in methanol (2.6×10^{-5} M, — — —)
2. Ph_3SnL_{10} in benzene (4.1×10^{-5} M, ———)

Table - 2 (Contd..)

Sl. No.	R	R'	X	Solvent	λ_{max} (nm)	Tautomer(s) present in solution
2.	Ph_3Sn	H	Cl	Benzene	367,438[a]	Azo & Hydrazone
				Methanol	360	Azo
3.	Bu_3Sn	H	Cl	Benzene	367,440[a]	Azo & Hydrazone
				Methanol	360	Azo
4.	H	CH_3	Cl	Benzene	370	Azo
				Methanol	370	Azo
5.	Ph_3Sn	CH_3	Cl	Benzene	372	Azo
				Methanol	372	Azo
6.	CH_3	Ph_3Sn	Cl	Benzene	375	Azo
				Methanol	375	Azo
7.	H	H	OCH_3	Benzene	435	Hydrazone
				Methanol	374,437	Azo & Hydrazone
8.	CH_3	H	OCH_3	Benzene	440	Hydrazone
				Methanol	375,445	Azo & Hydrazone
9.	CH_3	Ph_3Sn	OCH_3	Benzene	375	Azo
				Methanol	375	Azo

a = Inflexion or shoulder.

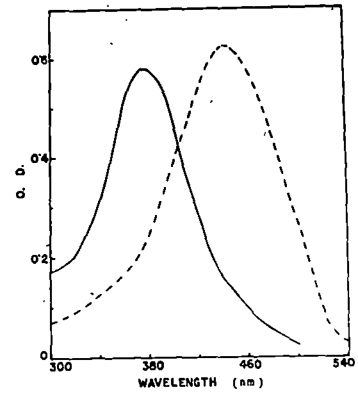


Fig. 19 Absorption spectra in benzene of

1. L_{11} (— — — —)

2. Ph_3SnL_{11} (3.5×10^{-5} M, ———)

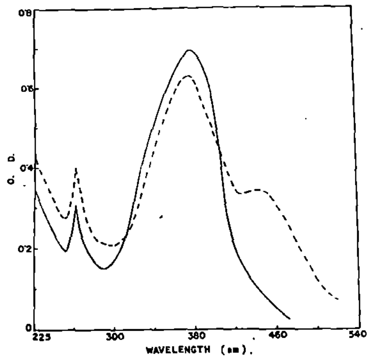


Fig. 20 Absorption spectra in methanol of

1. L_{11} (— — — —)

2. Ph_3SnL_{11} (3.77×10^{-5} M, ———)

The data given in table - 2, clearly shows that presence of azo-hydrazone tautomeric equilibria in solution, the hydrazone form being favoured in the non polar solvent benzene. A quantitative study of this equilibrium is discussed in the next section.

IVC. Quantitative study of the Azo-hydrazone tautomeric equilibria in 2-(benzene azo) 5-hydroxy phenoxy acetic acids and their organotin derivatives.

It is of interest to make a quantitative study of the azo-hydrazone tautomeric equilibria in the 2-(benzene azo) 5-hydroxy phenoxy acetic acid, related molecules and their organotin derivatives in order to determine how this equilibrium is affected by the organotin group.

Let us represent the equilibrium as

$$A \underset{}{\overset{K_T}{\rightleftharpoons}} H \qquad \ldots (1)$$

where the tautomeric equilibrium constant K_T is given by

$$K_T = [H] / [A] \qquad \ldots (2)$$

$[H]$ and $[A]$ respectively, denote the equilibrium concentration of the hydrazone form, H and the azo form, A.

Spectrophotometric estimation of the equilibrium constant is quite simple in principle provided the molar extinction co-efficients of each form is known at suitable wave lengths, preferably at the absorption maximum of the azo form or that of the hydrazone form.

Assuming the validity of Beer's law, the optical density, D_λ at any wave length λ, of a solution having a molar concentration C, is given by

$$D_\lambda = \left\{ \epsilon_\lambda^A \, [A] + \epsilon_\lambda^H \, [H] \right\} \cdot l \qquad \ldots (3)$$

where ϵ_λ^A and ϵ_λ^H are the molar extinction of the azo and the hydrazone form respectively, l is the path length of the cell.

The total concentration of the solute is given by

$$C = [A] + [H] \qquad \ldots (4)$$

Combining equation (3) and (4) we obtain

$$[A] = [D_\lambda/l - \epsilon_\lambda^H \cdot C] \,/\, [\epsilon_\lambda^A - \epsilon_\lambda^H] \qquad \ldots (5)$$

and

$$[H] = [C \cdot \epsilon_\lambda^A - D_\lambda/l] \; [\epsilon_\lambda^A - \epsilon_\lambda^H] \qquad \ldots (6)$$

Substituting in equation (2), we get

$$K_T = (C \cdot \epsilon_\lambda^A - D_\lambda/l) / (D_\lambda/l - \epsilon_\lambda^H \cdot C) \quad .. (7)$$

Thus the equilibrium constant can be easily determined from a single spectrophotometric measurement provided the molar extinction co-efficient of each form is separately known.

The problem is, however, complicated by the fact that the solution in any solvent contains both the forms in equilibrium making it difficult to determine the molar extinction co-efficient of each form separately without a knowledge of the equilibrium constant. Further, the equilibrium cannot be shifted almost completely in any direction except by changing the solvent often the change in solvent not only introduces drastic change in absorption maxima and molar extinction co-efficient, it is not always possible to find a solvent in which only one form exists.

In order to overcome this difficulty the following approach has been adopted in the present work.

It is well known that the integrated molar absorption is not only theoretically significant (1,27), but is a more reliable experimental measure of absorption than the molar extinction co-efficient which is affected by a variety of parameters. Unlike molar extinction, the integrated molar absorption of a compound is not strongly affected by change of solvent though the band maximum may undergo considerable shift. Experimental determination of integrated absorption is, however, more difficult. Fortunately, the absorption bands of most compounds may be closely approximated by gaussian curve of the following type

$$A_{\nu} = A_{max}.\ \mathrm{Exp} \left[-b \left\{ (\nu - \nu_{max}) / \Delta\nu_{1/2} \right\}^{2} \right] \qquad \ldots (8)$$

where

A_{ν} = absorbance at the frequency

A_{max} = absorbance at the band maximum

ν_{max} = frequency of the band maximum

$\Delta\nu_{1/2}$ = band half width

and $b = \log e^{2} = 2.772$

The advantage of expressing the experimental band shape in terms of analytical functions, such as equation (8), lies in the calculation of integrated absorbance (A) which is given by,

$$A = \int_{band} A_{\nu}\, d_{\nu} = 1.065.\ \epsilon_{max}\ .\ \Delta\nu_{1/2} \qquad \ldots (9)$$

The absorbance data over the visible region of the spectrum were fitted to gaussian curve given by equation (8) by least square method. It was observed that the absorbance data of compounds showing only a single absorption peak in this region (without any inflexion or marked band) can be expressed by equation (8). In case of compounds showing evidence of azo-hydrazone tautomerism, the optical data can be fitted by a linear combination of two such curves, one corresponding to the azo form and the other corresponding to the hydrazone form. The integrated absorbance corresponding to each band can then be taken to be proportional to the concentration of each tautomer in the solution. That such an assumption is experimentally justified may be seen from the data given in Table 3. The data clearly shows that total integrated absorption of a given ligand or its organotin derivatives remain nearly constant although the intensity of the two bands vary widely due to variation in the relative concentrations of the azo and the hydrazone form which vary from compound to compound and also from solvent to solvent. The constancy of the total integrated intensity, therefore, shows that the integrated molar absorbance of the two forms are equal.

Table - 3

Integrated molar absorbance of the visible absorption band of 2-(benzene azo) 5-hydroxy phenoxy acid, related compounds and their organotin derivatives.

Compound	Solvent	λ_{max}(nm)	Total integrated molar absorbance x 10^{8} (litre mole^{-1} cm^{-1} sec^{-1})
1. Ph_3SnL_1	Benzene	370,420	1.3
2. Bu_3SnL_1	Methanol	368,430	1.3
3. Ph_3SnL_4	Benzene	367,430	1.1
4. L_5H	Benzene	370	1.00
5. Ph_3SnL_5	Benzene	372	1.00
	Methanol	372	1.1
6. L_7H	Methanol	370,460	1.12
7. Ph_3SnL_7	Methanol	370,450	1.16
	Benzene	370,450	1.12
8. Bu_3SnL_7	Benzene	373,450	1.06
9. Ph_3SnL_8	Methanol	370,435	1.44
	Benzene	370,425	1.43
10. Bu_3SnL_8	Methanol	370,435	1.6
11. Ph_3SnL_{10}	Methanol	375	1.38
	Benzene	375	1.47
12. Ph_3SnL_{11}	Methanol	375	1.29
	Benzene	375	1.13

It is, therefore, reasonable to use the following relations:

$$K_T = [H] \;/\; [A] \;=\; A_h / A_a \qquad \ldots (10)$$

where [H] and [A] are the equilibrium concentrations of the hydrazone and the azo form respectively and A_h and A_a are the corresponding integrated absorbance in a given solution.

Using a computer programme which fits the absorbance data over the visible region of spectrum in terms of two superimposed gaussian bands such that the square of the residual is minimum, the integrated absorbance as well as their ratio which is equal to the equilibrium constant K_T were determined. These are given in Table 4. The calculated absorption maxima of the azo and the hydrazone forms are also included in table 4.

Table - 4

Integrated absorbance and azo-hydrazone tautomeric equilibrium constant in 2-(benzene azo) 5-hydroxy phenoxy acetic acid, related compounds and their organotin derivatives.

Compound	Solvent	Azo form λ^{*}_{max} (nm)	$A_a \times 10^3$	Hydrazone form λ^{*}_{max} (nm)	$A_h \times 10^3$	K_T
1. L_4H	Methanol	358	3.79	440	0.30	0.08
	Benzene	347	3.53	426	1.30	0.37

Contd..

Table - 4 (Contd..)

Compound	Solvent	Azo form a* λ_{max} (nm)	$A_a x10^3$	Hydrazone form a* λ_{max} (nm)	$A_h x10^3$	K_T
2. Ph_3SnL_1	Methanol	358	3.83	454	0.44	0.11
	Benzene	380	2.31	420	1.52	0.66
3. Bu_3SnL_1	Methanol	363	4.26	445	0.54	0.13
	Benzene	346	3.24	423	2.62	0.81
4. L_3H	Methanol	372	5.04	461	0.73	0.14
5. Ph_3SnL_3	Methanol	376	4.97	400	0.65	0.13
6. Bu_3SnL_3	Methanol	376	5.96	460	0.94	0.16
7. L_4H	Benzene	365	5.07	434	0.32	0.04
8. Ph_3SnL_4	Benzene	334	4.97	430	0.21	0.04
9. Bu_3SnL_4	Benzene	346	5.40	440	0.23	0.04
10. L_5H	Benzene	369	5.37	437	0.14	0.03
11. Ph_3SnL_5	Benzene	373	4.40	424	0.25	0.05
12. Bu_3SnL_5	Benzene	373	3.52	429	0.39	0.11
13. L_7H	Methanol	367	3.46	469	0.21	0.06
	Benzene	368	2.79	469	0.31	0.11
14. Ph_3SnL_7	Methanol	367	3.76	463	0.26	0.07
	Benzene	365	3.76	459	0.30	0.08
15. Bu_3SnL_7	Methanol	366	2.91	437	0.23	0.08
	Benzene	363	3.13	452	0.27	0.08

Contd..

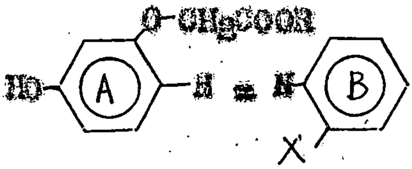
Table - 4 (Contd..)

Compound	Solvent	Azo form a* λ_{max} (nm)	$A_a \times 10^3$	Hydrazone form a* λ_{max} (nm)	$A_h \times 10^3$	K_T
16. L_8H	Methanol	371	3.77	457	0.52	0.13
17. Ph_3SnL_8	Benzene	385	1.67	430	2.77	1.6
18. Bu_3SnL_8	Methanol	264	3.30	430	0.23	0.06
	Benzene	376	1.64	426	1.62	1.00
19. L_9H	Methanol	366	4.33	-	-	-
	Benzene	360	4.30	-	-	-
20. Ph_3SnL_9	Methanol	366	4.53	-	-	-
	Benzene	365	3.3	-	-	-
21. L_{10}	Methanol	362	9.2	-	-	-
	Benzene	371	8.4	4.23	0.20	0.02
22. Ph_3SnL_{10}	Methanol	371	3.6	-	-	-
	Benzene	372	6.1	-	-	-

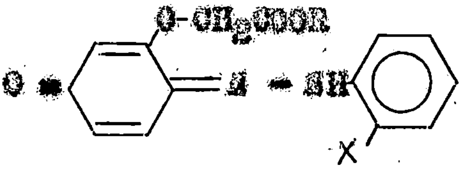
a* = The absorption maxima given in this table were obtained by least square fit of the optical density data in the visible region in terms of gaussian functions [eqn.^{n} (8)]

Data given in table 4 shows the following trends:

(i) The azo form predominates over the hydrazone form both in polar and non-polar solvents in compounds where the Diazo moiety (ring B) contains a substituent in the ortho position as shown below:



(XIII A)



(XIII B)

$R = H, CH_3, Bu_3Sn –, Ph_3Sn –$

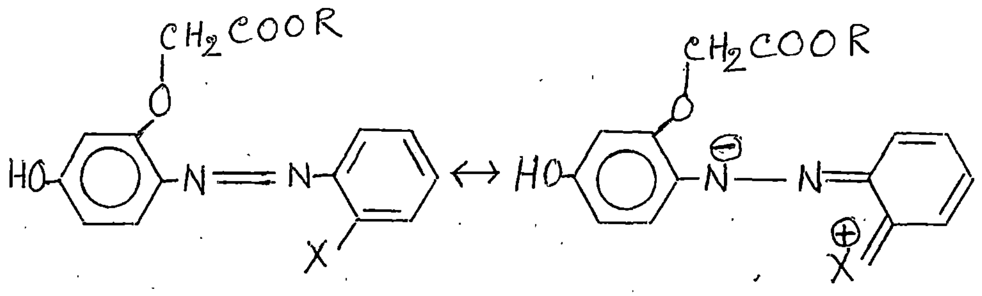
$X = Cl, F, OCH_3$

(ii) The absence of O-substituent (X = H in XIII) shifts the equilibrium markedly, in favour of the hydrazone form in the organotin derivatives (compounds Nos. 2,3,17, 18, Table 4).

(iii) As expected non polar solvent like benzene stabilizes the hydrazone form compared to that in methanol as shown by the marked increase in the equilibrium constant.

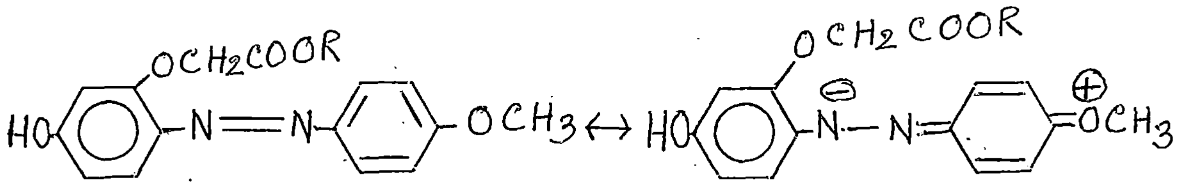
The predominance of the azo form in O-substituted compounds in other series have been attributed to steric factors (9). While steric factors may have some role, another more likely reason for the increased stability of the azo -

form compared to the hydrazone form in O - substituted compounds is the possibility of resonating structure of the type XIVB.



(XIV A) (XIV B)

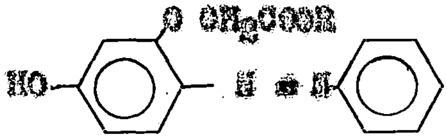
Since resonance structure of type XIVB is not possible in the hydrazone form, this would tend to destabilize the hydrazone form compared to the azo form. That this is contributing factor is shown by p-substituted compounds where the azo form again predominates



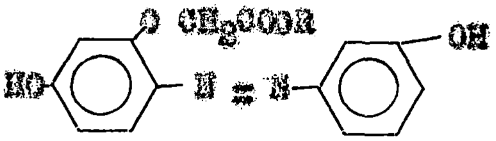
(XV A) (XV B)

$R = H, Ph_3Sn -, Bu_3Sn -$

For example, the equilibrium constant of the p-methoxy derivatives (compounds nos. 13,14,15) and o-methoxy derivatives (compound nos. 4,5,6) are nearly equal. In fact, calculated equilibrium constants are somewhat lower in the p-methoxy derivatives. Since steric factors cannot be involved in the p-methoxy compounds, the effect must be attributed to resonance shown in (XIV) and (XV). The equilibrium constants of XVI) and (XVII) lend further support to this



(XVI)



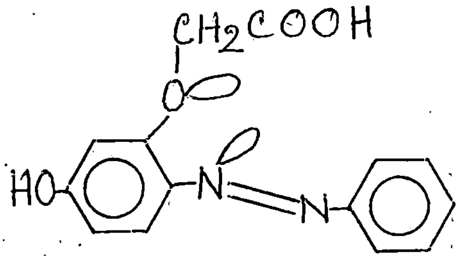
(XVII)

The equilibrium constants of (XVI) and (XVII) respectively, in methanol are 0.09, 0.13 (R = H); 0.11, 0.12 ($R = Ph_3Sn$ -) and 0.13, 0.06 ($R = Bu_3Sn$ -). Thus, the meta substituent, in contrast to ortho - or para substituent, has no effect on the azo - hydrazone tautomeric equilibrium. This, however, is not surprising since resonance of the type shown in (XIV) and (XV) are not possible in the m-substituted derivatives.

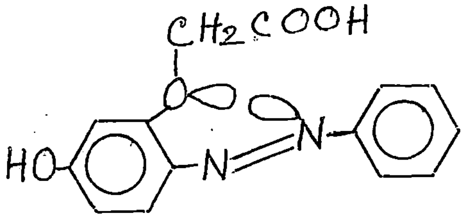
IVD. Electronic spectra of the organotin derivatives and probable structure.

Excepting the organotin derivatives of ligand (IX) which will be separately discussed because of the many interesting features associated with them, the spectra of the organotin derivatives are very similar to that of the ligand in the position of the absorption maxima except for some modification in the azo-hydrazone equilibria as discussed in the preceding section.

The steric effects of ortho substituents in the mono azo dyes and their preferred geometry has been discussed by Griffiths (28). The same considerations show that to minimise steric interaction between the nitrogen lone pair electrons and the ortho acetoxy group (the oxygen atom has also lone pairs) structure (XVIII) will be preferred to (XIX) since a very strong lone pair lone pair interaction is expected in the later.



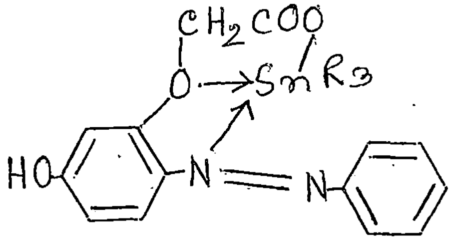
(XVIII)



(XIX)

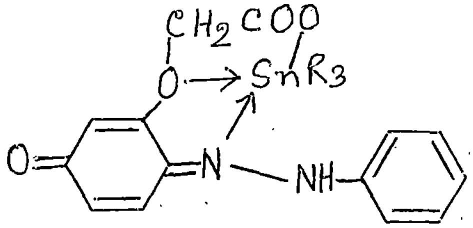
The possible conformation of the ligands showing lone pair lone pair interaction.

For steric reasons, the organotin derivatives are therefore likely to have structure (XX) in the azo form and (XXI) in the hydrazone form.



(XX)

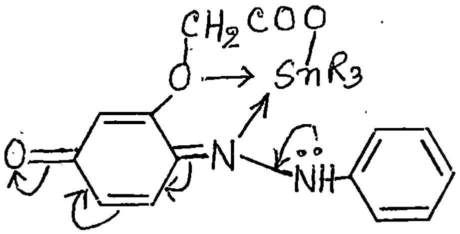
Probable structure of the azo form of the organotin derivatives.



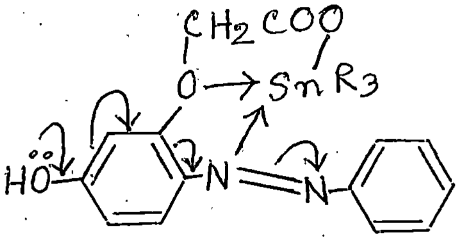
(XXI)

Probable structure of the hydrazone form of the organotin derivatives.

As shown in (XXII), the visible transition in the hydrazone form is typically a donor - acceptor transition, the amino group being the donor and the carboxyl group, the acceptor (28). The direction of charge migration is opposite to that in the azo form (XXIII).



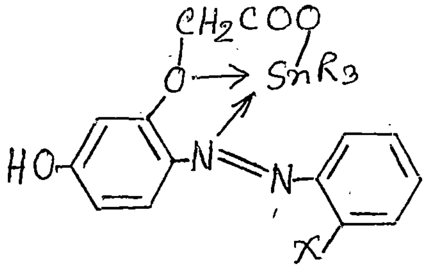
(XXII)



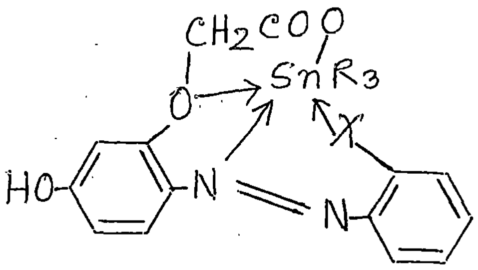
(XXIII)

In both the case N-atom co-ordinated to the organotin group is not directly involved in the charge migration and the co-ordination by the organotin group is therefore likely to have very little effect on the visible spectrum, a fact amply borne out by the experimental data given in Table -1.

In the presence of a donor substituent in the ortho position to the azo group in the other benzene ring (diazo moiety), the organotin derivatives may have two possible structures (XXIV) and (XXV) (only the azo form is shown), the tin atom is 6-co-ordinated in the former and 7-co-ordinated in the later.



(XXIV)



(XXV)

Structure (XXIV) being similar to (XXIII), the visible spectrum of the organotin derivative is expected to be almost similar to that of the free ligand in line with the other compounds where the substituent X is absent. However, co-ordination by the group/atom X which renders the tin atom 7-co-ordinated as in (XXV) is expected result in a bathochromic shift because of the expected formal positive charge on the donor on co-ordination. This would facilitate electron migration from the hydroxyl group to the azo group as shown in (XXIII) resulting in a bathochromic shift. Examination of the absorption data given in Table 1 show such bathochromic shift in ortho fluoro- and ortho-chloro compounds (No. 11,12,14,15), although no such shift is observed in the ortho methoxy compound. This is not surprising as an examination of a model shows steric over crowding in a structure of type (XXV) when X = OCH_3, but not with X = F or Cl. Thus, the chloro and fluoro substituted organotin derivatives are to be regarded as 7-co-ordinated while that of the methoxy derivative is most likely a 6-co-ordinated compound of type (XXII) or (XXIII).

IVB. Absorption spectra and probable structure of Bis-(triorganotin) derivatives of 2-(2'-hydroxy benzene azo), 5-hydroxy phenoxy acetic acid (IX).

As mentioned in Chapter III, 2-(2'-hydroxy benzene azo), 5-hydroxy phenoxy acetic acid always furnished a bis (triorganotin) derivative which may be formulated as follows:

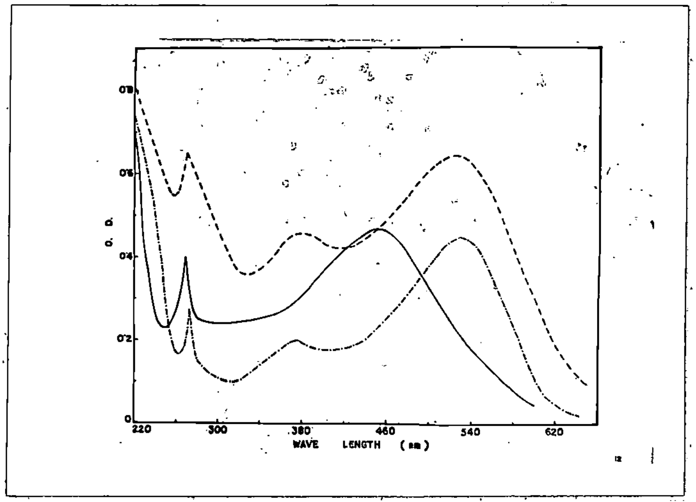


Fig. 21 Absorption spectra in methanol of
1. L_2H (5.9×10^{-5} M, ———)
2. $(Ph_3Sn)_2L_2$ (2.24×10^{-5} M, — · — ·)
3. $(Bu_3Sn)_2L_2$ (2.8×10^{-5} M, - - - -)

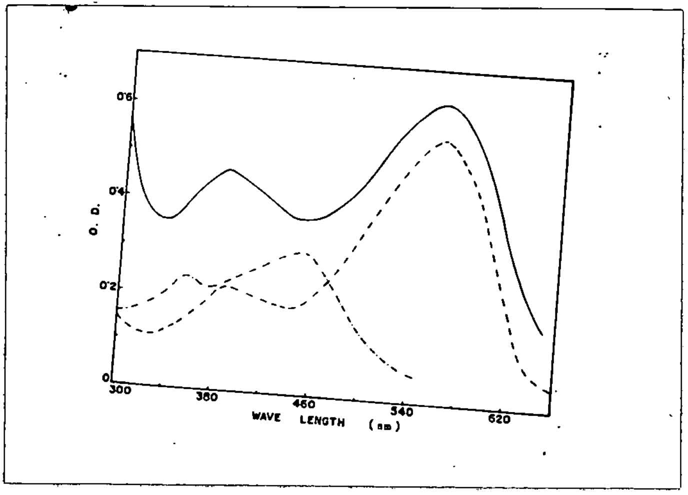
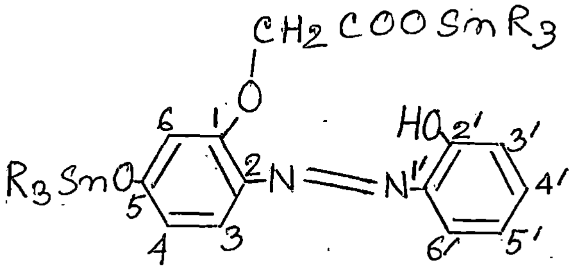


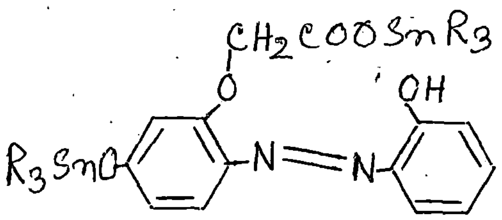
Fig. 22 Absorption spectra in benzene of
1. L_2H (— · — · —)
2. $(Ph_3Sn)_2L_2$ (2.73×10^{-5} M, - - - -)
3. $(Bu_3Sn)_2L_2$ (3×10^{-5} M, ———)



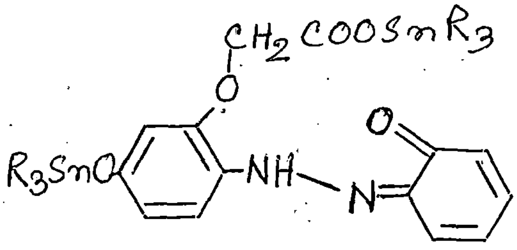
(XXVI)

These derivatives are characterised by a extremely large bathochromic shift of the longest wave length visible absorption maxima in the free ligand (figs. 21,22). For example, the longest wave length absorption in the ligand occurs at 450 nm in benzene while the absorption maxima occurs at 560 nm in the same solvent in the Bis (tributyl tin) or Bis (triphenyl tin) derivatives.

The ligand as well as the organotin derivatives shows two absorption maxima in the visible region. In view of our discussion, this is to be expected because of the presence of azo-hydrazone equilibrium as shown below:



(XXVII A)



(XXVII B)

It should be noted that it is the -OH group in the diazo component that takes part in azo-hydrazone tautomerism in contrast to other compounds so far discussed where the -OH group is present on the coupler component. The hydrazone form in these compounds may be regarded as ortho quinone derivatives (XXVIIB) in contrast to (XXI) which may be regarded as para quinone derivatives.

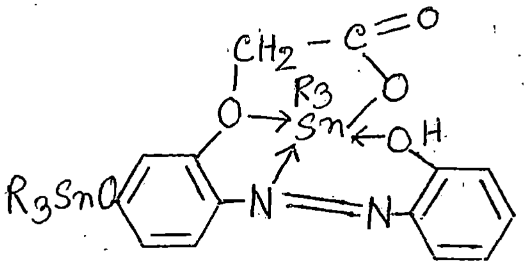
A summary of the absorption data is shown in Table 1 and the equilibrium constant for the tautomeric equilibrium calculated according to the method discussed in Sec. IVC is given in Table 5.

Table - 5

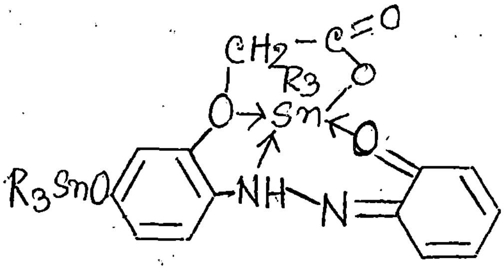
Visible absorption maxima and tautomeric forms of the ligand and organotin derivatives of type XXVI.

Compound	Solvent	Azo form		Hydrazono form		K_T
		$A_a x 10^3$	λ_{max}(nm)	$A_h x 10^3$	λ_{max}(nm)	
1. Ligand (IX)						
	Methanol	-	-	2.55	450	-
(L_2H)	Benzene	1.58	355	2.15	450	1.36
2. $(Bu_2Sn)_2L_2$	Methanol	1.55	330	2.14	526	1.37
	Benzene	1.43	365	2.60	560	1.81
3. $(Ph_2Sn)_2L_2$	Methanol	1.35	375	1.84	550	1.36
	Benzene	1.33	387	2.37	560	1.78

Considerable bathochromic shift of the absorption maxima both in the azo form and the hydrazono form suggests strong co-ordination with 7-co-ordinated structure as shown below:



Azo form



Hydrazone form

A strong co-ordinate bond by the ketonic oxygen atom in the hydrazone form would increase its acceptor strength thereby facilitating the charge migration during the transition depicted in (XXII). This explains the large bathochromic shift observed in the organotin compounds.

IVF. Effect of alkali on the absorption spectra of organotin derivatives.

It has been shown by Majee and Banerjee (29) by spectrophotometric titration of organotin (aryl azo) benzoates that the ease of cleavage of the Sn-O bond by $OH^{(-)}$ represented by the eqn. (11) is related to the co-ordination no. of the tin atom.

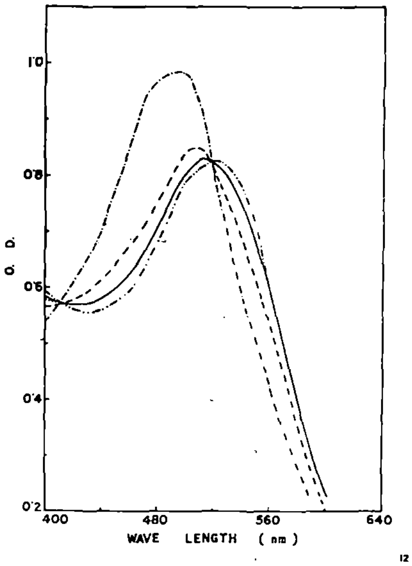
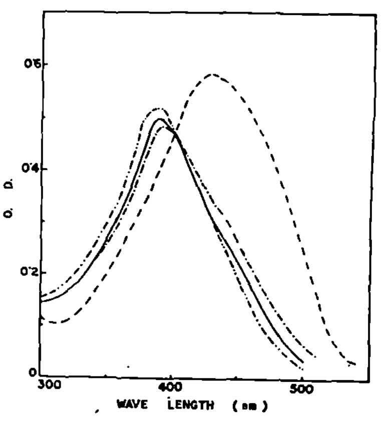


Fig. 23 Absorption spectra in methanol of

1. $(Ph_3Sn)_2L_2$ (3.8×10^{-5} M, —··—··)
2. " 0.5 equivalent NaOH (————)
3. " 1 " " (————)
4. " 2 " " (— — — —)
5. " 10 " " (—·—·—)

Fig. 24 Absorption spectra in methanol of

1. Ph_3SnL_2 (2.9×10^{-5} M, —··—··—)
2. " 1 equivalent NaOH (————)
3. " 10 " " (—·—·—)
4. " 20 " " (— — — — —)

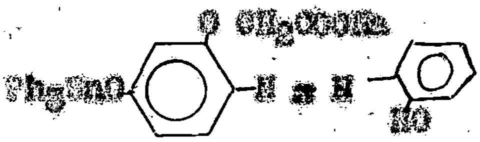


4

$$R_3SnO - X + OH^{(-)} \longrightarrow R_3SnOH + X^{(-)} \qquad \ldots (11)$$

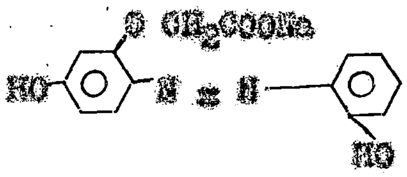
For examples, the penta co-ordinated derivatives were found to cleave almost quantitatively by equivalent amount alkali whereas the 6-co-ordinated compounds were very stable towards alkali. It is therefore expected that the 7-co-ordinated compounds, if formed should be more resistant to cleavage by alkali.

The effect of methanolic NaOH on Bis (triphenyl) tin derivative is shown in fig. 23. The presence of isobestic point implies an equilibrium involving two absorbing species. Use of even tenfold excess of NaOH does not, however, change the spectrum into that of the ligand under same alkali concentration. Obviously both the triphenyl tin groups are not cleaved by alkali. The cleavage of the Ph_3Sn group bound to the carboxyl group as in XXVIII should result in a spectrum similar to that of the Na salt of the dye (XXIX)



λ max = 405 nm

(XXVIII)



λ max = 450 nm

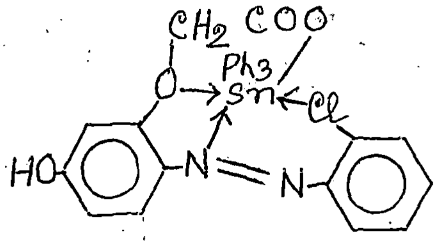
(XXIX)

The large difference in the absorption maxima clearly indicates the Ph_3Sn group bond to the -COO group is not cleaved, instead Phenoxy - $SnPh_3$ bond is cleaved. This is to be expected in view of facile of Sn - O bonds. Thus the action of $OH^{(-)}$ on $(Ph_3Sn)_2L_2$ (L_2H = ligand IX) can be represented as

$$(Ph_3Sn)_2L_2 + OH^{(-)} \rightleftharpoons Ph_3SnL^{(-)} + Ph_3SnOH$$

The bis (tributyl tin) derivative also shows the same behaviour.

The effect of alkali on compound (XXX) is shown in fig. 24. Again, it can be seen that very large excess of $OH^{(-)}$ is required to hydrolyse the stannyl group indicating a strong co-ordination. Even an 80 fold excess of alkali have only slight effect on the spectrum.



(XXX)

XVI. Conclusion

On the bais of electronic absorption spectra of the organotin derivatives of the 2-(aryl azo) 5-hydroxy phenoxy acetic acids studied in the present work it may be concluded:

(i) In the absence of a donor group (Cl, F, OH) in the ortho position of diazo component of the ligand, it behaves as terdentate forming 6-co-ordinated triorganotin chelates.

(ii) The presence of Cl, F or -OH in the ortho position of diazo component makes the ligand tetradentate leading to the formation of 7-co-ordinated triorganotin chelates. It may be pointed out that the present examples constitute the first examples of 7-co-ordinated triorganotin chelates.

(iii) In solution, the ligands as well as the organotin complexes exist generally as a equilibrium mixture of the azo and the hydrazone tautomers.

IVII. Experimental

1. Synthesis : The synthesis of (benzene azo) phenoxy acetic acids and their organotin derivatives used in the present spectrophotometry study are given in Chapter-III.

2. UV - visible spectra: The UV - visible spectra were recorded with Beckman DU-2 spectrophotometer using 1 cm quartz cells.

All solvents used were of Uvasol (E.Merck, West Germany) grade.

3. Computation of Integrated Absorbance and equilibrium constants: Integrated absorbance and constants were computed according to the standard least square technique using DCM Microsystem - 1121.

BIBLIOGRAPHY

1. H.Suzuki	Electronic absorption spectra and geometry of organic molecules, Academic Press, New York. Ch. 23 (1967), and references therein.
2. H.H.Jaffe and M. Orchin	Theory and applications of ultra-violet spectroscopy, John Willey and Sons (1962) and references therein.
3. R.Price (K.Venkataraman ed.)	The Chemistry of synthetic dyes, Academic Press, Vol. 3 (1970) 303.
4. J.Schulze, F.Gerson, J.N.Murrell and E. Heilbronner	Helv. Chim. Acta 44 (1961) 428.
5. P.Grammaticakis	Bull. Soc. Chem. France (5) 18 (1951) 951.
6. B.Majee and S.K. Chakravarti	Z.Phy. Chem. 57 (1968) 89.
7. A.Burawoy, A.G.Salem and A.R.Thompson	J.Chem. Soc. (1952) 4793.
8. P.J.Mitchell and L.Phillips	J.Chem. Soc., Perkin II (1974) 109.
9. A.Burawoy and A.R. Thompson	J.Chem. Soc., (1955) 1443.
10. E.Fischer and Mrs. Y.Frei	J.Chem. Soc. (1959) 3159.
11. W.R.Brode and L.E. Cheyney	J.Org. Chem., 6 (1941) 341.
12. W.R.Brode and L.E. Herdle	J.Org. Chem., 6 (1941) 713.
13. W.R.Brode	Ber. 61 (1928) 1722.
14. W.R.Brode	J.Am.Chem.Soc., 51 (1929) 1204.

15. H.H.Jaffe and S.J. Yeh and R.W.Gardner	J. Mol. 2 (1958) 120.
16. P.P.Birnbaum	J.H.Linford and D.W.G.Style, Trans. Faraday. Soc., 49 (1953) 735.
17. H.Suzuki	Bull. Chem. Soc., Japan 33 (1960) 381.
18. K.J.Morgan	J.Chem. Soc., (1961) 2151.
19. J.B.Sepeson	Acta. Chem. Scand. 5 (1951) 491.
20. A.Burawoy and J.T. Chamberlain	J.Chem. Soc., (1952) 3734.
21. M.L.Ensberger and W.R.Brode	J.Org. Chem. 6 (1941) 331.
22. K.Venkataraman	The Chemistry of synthetic dyes, Academic Press, Vol. 1 (1952) and references therein.
23. C.F.Callis, N.C. Nielson and J.C. Bailar	J.Am.Chem.Soc., 74 (1952) 3401, 6018.
24. H.D.K. Drew and J.K.Landquist	J.Chem. Soc., (1938) 292.
25. H.D.K.Drew and R.E. Fairbairn	J.Chem. Soc., (1939) 823.
26. B.Majee and S. Banerjee	J.Organometal. Chem. 140 (1977) 151.
27. C.N.Banwell	Introduction to Molecular spectroscopy, McGraw Hill, New York (1966), Ch. 4
28. J.Griffiths	Colour and Constitution of Organic Molecules, Academic Press (1976), London, New York, San Francisco, p. 187, 191 and references therein.
29. B.Majee and S. Banerjee	J.Organometal. Chem. 139 (1977) 39-46.

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