CHAPTER - III

ABSORPTION SPECTRA AND STRUCTURES OF THE ORGANOTIN COMPLEXES OF 5-ARYLAZO-8-QUINOLINOLS:

IIIA. INTRODUCTION

IIIB. NATURE OF ELECTRONIC TRANSITIONS IN AZOXINES AND ITS DERIVATIVES

IIIC. RESULT AND DISCUSSION

IIID. EXPERIMENTAL

BIBLIOGRAPHY

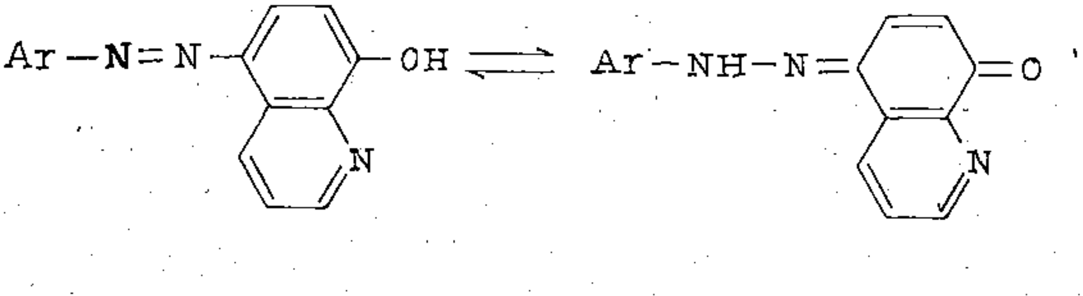
IIIA. Introduction

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 discussion[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 wave length, weak to moderate intensity band in azobenzene and related compounds ($\epsilon_{max} \approx 10^2-10^3$), is ascribed to the $n-\pi^*$ 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. MO treatment of the azobenzene[1,2] shows that the upper MO for the first $n-\pi^*$ as well as that for longest wave length $\pi-\pi^*$ transitions is the perturbed orbital originating from the antibonding π-orbital of the azo group and its energy is not very much affected by the nature of the aryl groups. The lower orbital of the first $\pi-\pi^*$ transition is the orbital arising from the perturbation of the highest 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 π-π* band in the azo compounds to such an extent that the characteristic n-π* absorption is masked by the strong absorption. Thus, in methyl red which contains -COOH and $-NMe_2$ groups in 2 and 4 positions respectively, no weak absorption band could be observed in the 440-60 nm region due to the presence of strong π-π* absorption in this region[6]. Almost all the 5-Arylazo-8-quinolinols and their derivatives investigated in the present work belong to this category and no separate band due to n- π* transition could be observed in these compound.

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 π-π* and n-π* bands[1-17]. However, the presence of -OH group in the ortho or para-position relative to the azo group often leads to a strong solvent dependent absorption spectrum due to the possibility of: (a) hydrogen bond formation by the phenolic -OH and/or (b) Azo-hydrazone tautomerism, as shown below(I).



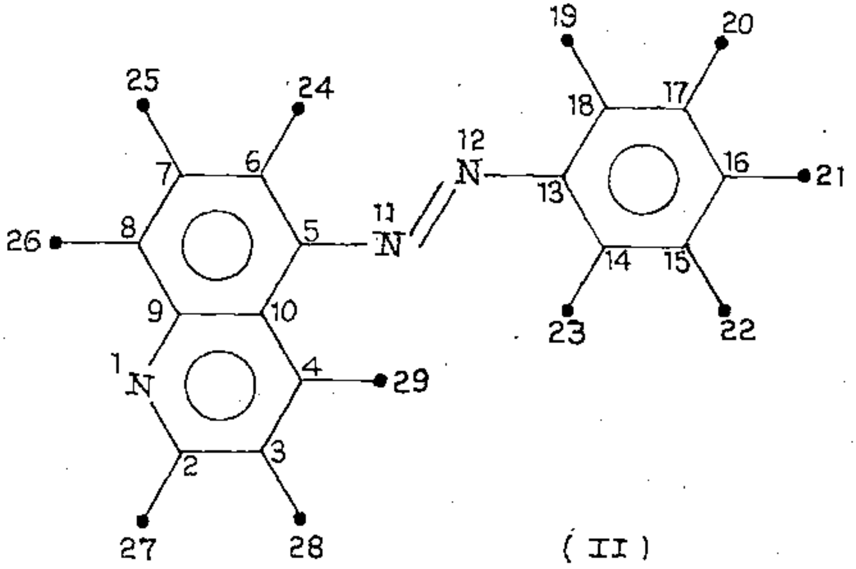
(I)

The azo-hydrazone tautomerism in hydroxy azo derivatives has been studied in great detail by several workers[3,7,9,10,18] because of its importance in determining the observed colour of azo dyes.

Although the azoxines, particularly 5-aryl azo-8-quinolinols are known for a long time[19-21] (Chapter IB), the electronic absorption spectra of this class of azo-dyes have not been studied in detail. Neither their metal complexes were subjected to such investigation. Organotin 5-phenyl azo-8-quinolinolates have only recently been prepared[22], but the authors studied their Mossbauer spectra only.

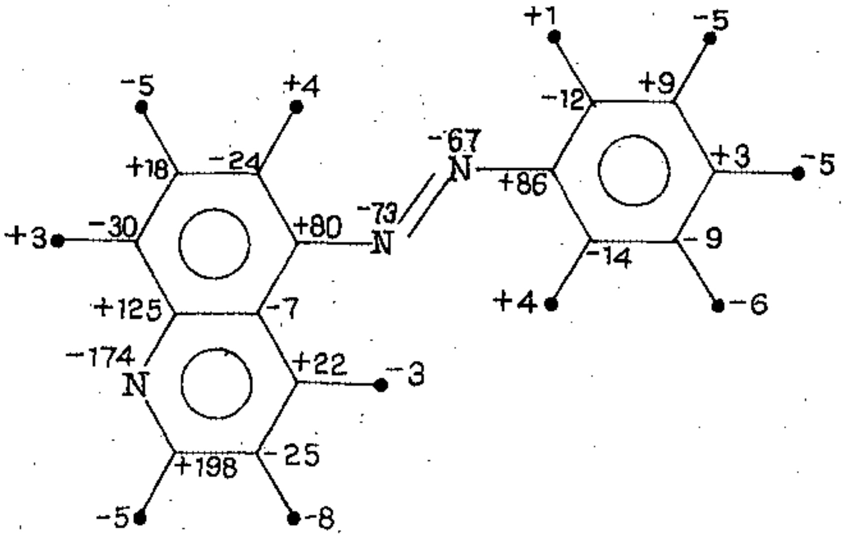
IIIB. Nature of electronic transitions in Azoxines and its derivatives:

In order to have a better understanding of the observed electronic spectra of the azoxine derivatives, we have a CNDO/2 type calculation[32-36] on molecule (II) which may be regarded as the parent molecule from which our ligands LH, L'HH' and their derivatives can be obtained by substitution at appropriate positions.



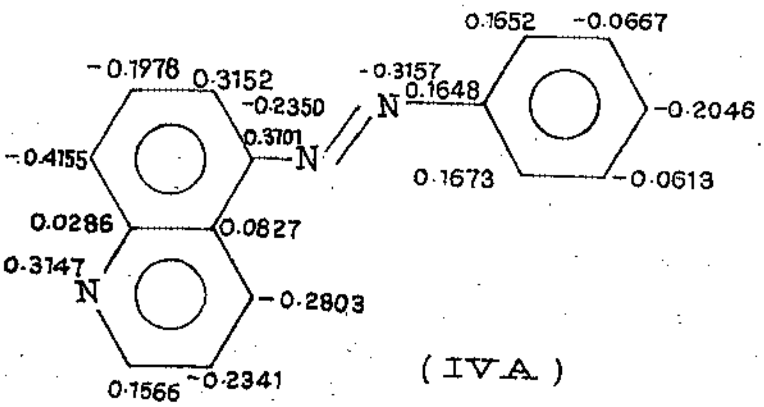
(II)

Of the 63 Molecular orbitals obtained by linear combination of the valence atomic orbitals of the atoms, 16 are of π-type. The highest occupied orbital is a π-type orbital; the lowest unoccupied one is also of the same type showing that the longest wave length intense transition in the azoxines are indeed a π-π* transition. The energy diagram of the π-type MO's are shown in Fig. 1 . The net atomic charges (σ+π) on the atoms are shown in (III) while the AO co-efficients of the highest occupied orbital (HOMO) and the lowest unoccupied orbital (LUMO) are shown in (IVA) and (IVB).



Net atomic charges (in units of 10^{-3} electron)

(III)



(IVA)

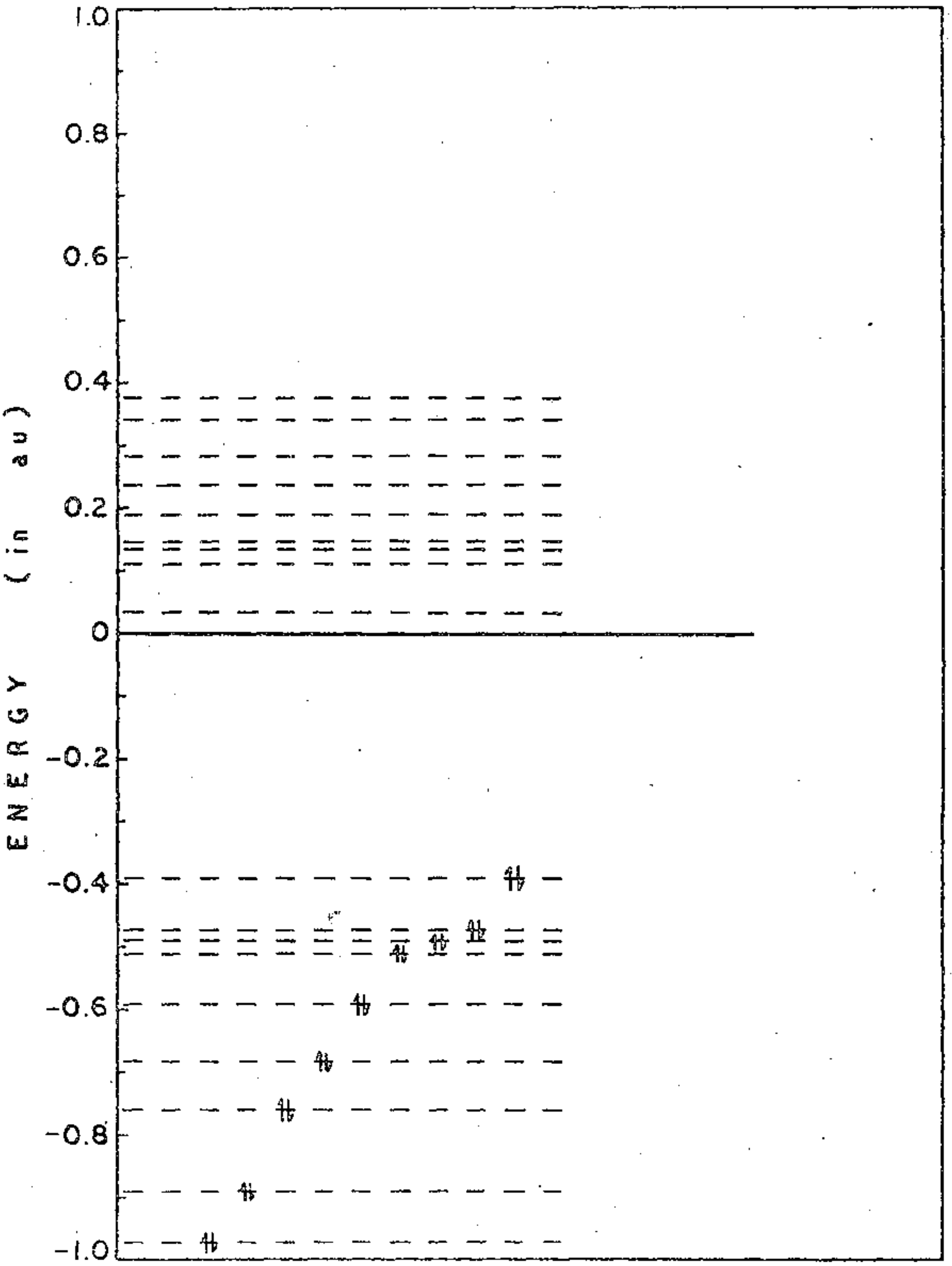
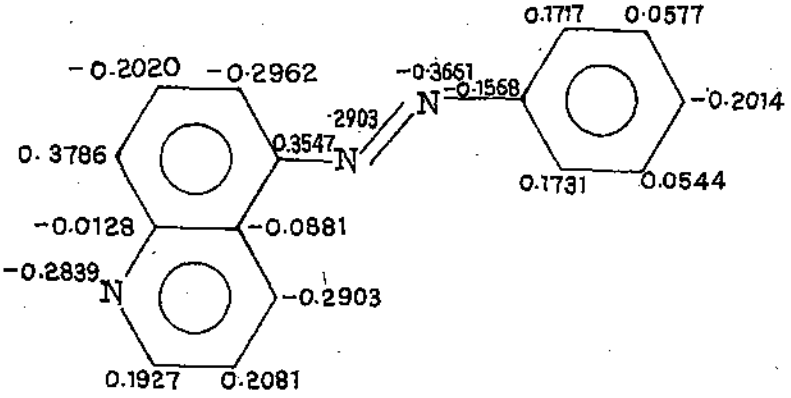
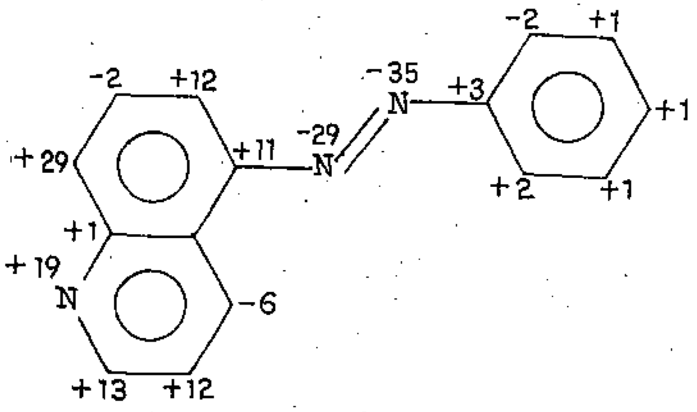


FIG. I. ENERGIES OF π - MO'S OF 5 - (PHENYL) AZO - 8 - QUINOLINE AND ELECTRON OCCUPANCIES IN THE GROUND STATE.

The transition density (charge migration) of the first π-π* transition is shown in (V) which shows that the longest wave length transition involves mostly a transfer of electron charge from the quinoline ring, more particularly the N-atom and C_8 to the azo-group, the β-N-atom getting somewhat greater share of the electron transfer during the transition.



(IVB)

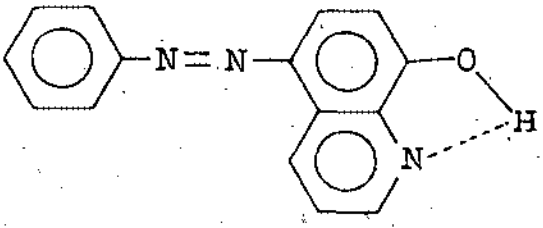


Charge migration in the lowest energy π − π* transition (in units of 10^{-3} electron, + ve sign indicates decrease of electron density on excitation and vice-versa).

(V)

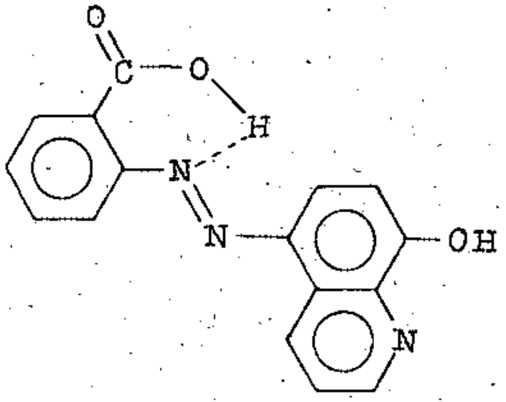
The ligands and their complexes studied in this work differs from the molecule (II) in having substituent at C_8 only (LH and its complexes) and at C_8 and $C_{8'}$ (L'HH' and its complexes). As far as the electronic spectra is concerned, these substituents can be discussed in terms of appropriate perturbations.

A substitution of H-atom at C_8 by an electron releasing substituent like -OH or -OR group would obviously lower the transition energy of the first $\pi-\pi^*$ transition because it involves a transfer of electron from the C_8 atom to the azo group. In the organotin derivatives where the O-atom is expected to have Large negative charge because of the high polarity of tin-oxygen bond[37,38] ($\overset{\delta+}{Sn} - \overset{\delta-}{O}$), the $\pi-\pi^*$ transition energy is expected to further lowered. Therefore, the organotin quinolinolato derivatives are expected to show a bathochromic shift relative to the -OMe derivatives. It must be remembered that the free ligand, i.e., phenyl azo-8-quinolinol (LH) shows not only azo-hydrazone tautomeric equilibrium in solution[23,24], but the azo form is intramolecularly H-bonded (VI). This makes any meaningful comparison difficult.

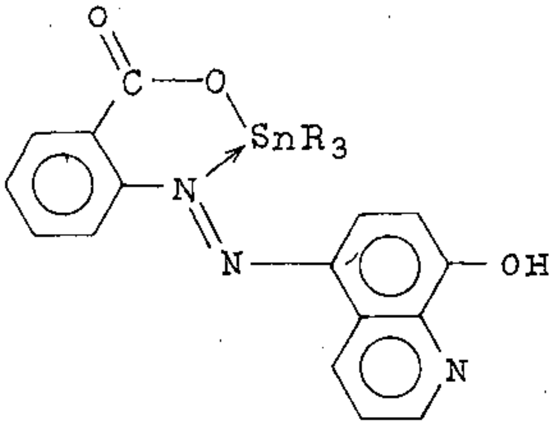


(VI)

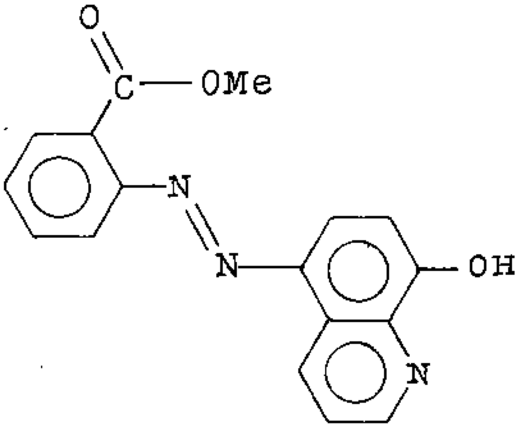
Since the 2'-position is not greatly affected in the first $\pi-\pi^*$ transition (V), a substitution at 2'-position is not going to affect this transition unless the substitution has some intra- or inter-molecular interaction with the other part of the molecule, particularly the azo group and the C_8 and quinoline N-atoms. However, any interaction with the azo-N-atoms, either through intramolecular H-bond as in L'HI' (VII) or in the organotin derivatives with N ⟶ Sn bonds (VIII) is expected to lead to a bathochromic shift relative to that in the non-interacting system, such as the ester (IX), because such an interaction would facilitate the electron flow from the quinoline ring to the azo group, thereby, lowering the transition energy.



(VII)



(VIII)



(IX)

Before we present the spectral data on the molecules studied, it must be pointed out that the discussion in this section applies to the azo form only, since the charge migration in the hydrazone form is very different (usually opposite[27]) from that in the azo form.

IIIC. Results and Discussion:

Electronic absorption spectra of the ligands and the abbreviation used for ligands are given in the preceding chapter. The spectral data for the 5-Aryl azo-8-quinolinols and their organotin derivatives are given in Table - 1. Absorption curves are also shown in Figs. 1-18. The electronic absorption spectra have been obtained in protic as well as non protic solvents. Although saturated hydrocarbon solvents, e.g., hexane etc., would have been better choice as non protic as well as non polar solvent, solubility considerations led to the choice of benzene.

Table -I

Absorption Maxima in 5-Aryl azo-8-quinolinols and their organotin derivatives.

Compound	Electronic spectra [λ_{max} nm]	
	Methanol	Benzene
A. Ligands:		
1. LH	$380, \sim 460^a$	380
2. L'HL'	435	410

Table - 1 (Contd..)

Compound	Electronic spectra $[\lambda_{max}$ nm$]$ Methanol	Benzene
3. $L'MeH$	370, ~ 450^a	370
4. $L'Me_2$	380	380
B. Organotin derivatives of the ligand:		
(i) The Organotin carboxylates:		
5. $Ph_3SnL'H$	410, 480^a	420
6. $Bu_3SnL'H$	410, 450^a	420
(ii) The Organotin quinolinolates:		
7. Ph_3SnL	410	410
8. $Ph_2Sn(L)_2$	430	430
9. $Bu_2Sn(L)_2$	430	430
10. $Oct_2Sn(L)_2$	430	430
11. $Me_2Sn(L)_2$	430	430
12. $Ph_2Sn(L'H')$	415	430, ~420^a
13. $Bu_2Sn(L'H')_2$	420	430, ~420^a
14. $Oct_2Sn(L'H')_2$	410	430, ~420^a
15. $Me_2Sn(L'H')_2$	410	430, ~420^a
16. $Ph_2Sn(L'Me)_2$	420	420
17. $Bu_2Sn(L'Me)_2$	420	420
18. $Oct_2Sn(L'Me)_2$	420	420
19. $Me_2Sn(L'Me)_2$	420	420

Table - 1 (Contd..)

Compound	Electronic spectra $[\lambda_{max}$ nm$]$	
	Methanol	Benzene
(iii) The binuclear organotin carboxylates quinolinolates:		
20. $Ph_2Sn(L'SnPh_3)_2$	420	420
21. $Bu_2Sn(L'SnPh_3)_2$	410	415
22. $Oct_2Sn(L'SnPh_3)_2$	410	415
23. $Me_2Sn(L'SnPh_3)_2$	410	410
24. $Ph_2Sn(L'SnBu_3)_2$	410	410
25. $Bu_2Sn(L'SnBu_3)_2$	410	410
26. $Oct_2Sn(L'SnBu_3)_2$	415	410
27. $Ph_3SnL'SnPh_3$	410	420

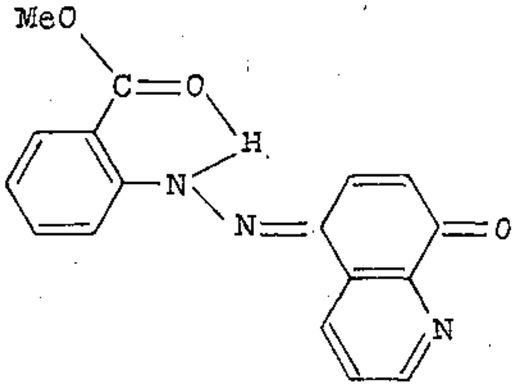
a) Inflection or shoulder

The azo-hydrazone tautomerism exhibited by the azoxines has been discussed in Chapter - I (Section IC). Like the ligands, organotin complexes in which the 8-OH group is present, show two absorption bands (Figs. 5 and 6) in the visible region at ∼ 400 nm and ~ 460-480 nm [Table -1B(i)] due to azo-hydrazone tautomerism. The lower wave length band must be assigned to the π-π* transition of the azo form since all compounds in which the -OH group is complexed with organotin group [Table -1B(ii)] and, thus, exist only in the azo form, show a single intense absorption at 400 nm. The same behaviour is observed when the 8-OH, group is methylated. For example, 5-(2'-carboxy phenyl) azo-8-methoxy quinoline, L'MeH' and 5-(2'-carbomethoxy phenyl) azo-8-methoxy quinoline, L'Me$_2$ [Table - 1A] have a single intense absorption maxima at ~ 380 nm in methanol and benzene. The longest wave length band at ~ 460-480 nm must, therefore, be attributed to the hydrazone form in agreement with earlier observations that the hydrazone form generally absorbs at a longer wave lengths[24,27]. The relative intensities of the two bands are dependent on the polarity of the solvent, intensity of the longest wave length band increasing with the solvent polarity. This is consistent with the known trends in similar molecules[23,24].

For convenience of discussion the organotin derivatives are classified into three types:

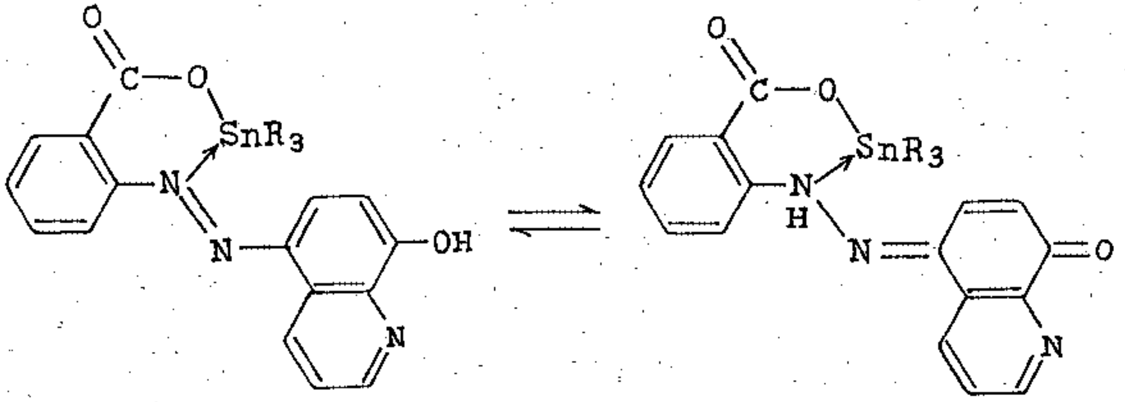
(a) The organotin carboxylates:

The relative intensities of the ~ 400 nm and ~ 460 nm band (Figs. 5 and 6) show that the azo-hydrazone equilibrium in the carboxylate derivatives is considerably shifted towards the azo form compared to that in the methyl ester L'MeH. In the latter, the hydrazone form is stabilized by the formation of a 6-membered ring[24] due to intra molecular H-bonding (X).



(X)

In the organotin complexes (XI), the presence of N → Sn coordinate bond prevents the formation of any such intra molecular H-bond in the hydrazone form. The latter form is, therefore, less favoured. As discussed in section-II, the large bathochromic shift of the $\pi-\pi^*$ transition in the azo form in $R_3SnL'H$ type complexes ($\lambda_{max} \sim 420$ nm) compared to that in the corresponding methyl ester L'MeH ($\lambda_{max} = 335$ nm) is an evidence of N → Sn coordination.



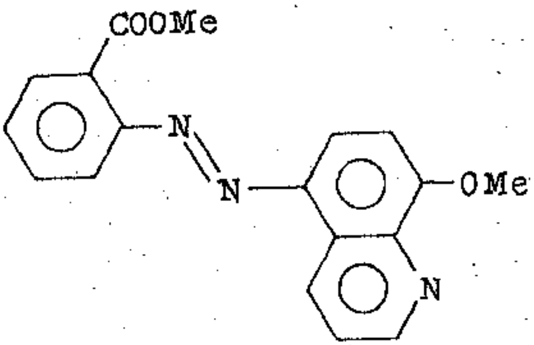
(XIA)
Azo form

(XIB)
Hydrazone form

(b) <u>The organotin quinolinolates:</u>

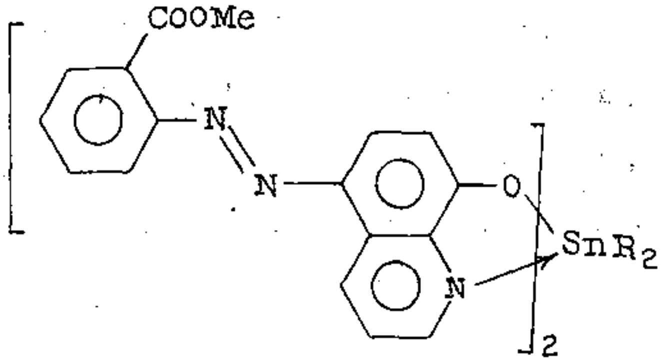
The electronic absorption spectra of the organotin-quinolinolates of the type $R_2Sn(L'H')_2$ are strongly influenced by the nature of solvent although the possibility of azo-hydrazone tautomerism is eliminated. It is, however, well known that the absorption spectra of azo benzene and substituted azobenzenes in different solvents are generally similar in nature except for some shift in the absorption maxima, the magnitude of the shift being dependent on the nature of the solvent[1,36]. A bathochromic shift of 10-15 nm is generally observed in going from non-polar to polar solvents. Any unusual solvent dependence is, therefore, indicative of some chemical equilibria in the system[26,38].

A similar behaviour is observed in case of the azoxines also. For example, the ester 5-(2'-carbomethoxy phenyl) azo-8-methoxyquinoline, L'Me$_2$ (XII), a model for the azo form, shows a single absorption maxima at 330 nm in polar as well as non-polar solvents.



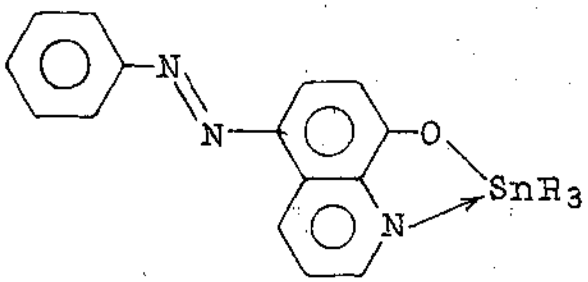
(XII)

The corresponding organotin derivatives, R$_2$Sn(L'Me)$_2$, absorb at considerably longer wave length (λ_{max} = 420 nm) and the spectra are not influenced by the nature of solvent [Table 1B(ii)]. The bathochromic shift, therefore, results from the complexation by the ligand. Such bathochromic shifts are quite well known in oxinate complexes and the organotin azoxinates are thus structurally quite similar to the organotin oxinates[26,28-31] and should be formulated as shown in (XIII).

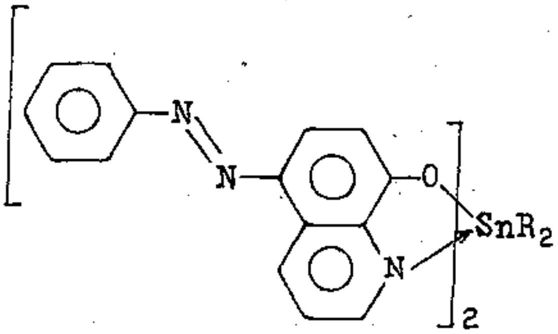


(XIII)

Similar solvent independent spectra are also shown by the organotin complexes of 5-phenyl azo-8-quinolinol (XIV) [Table - 1B(ii)].

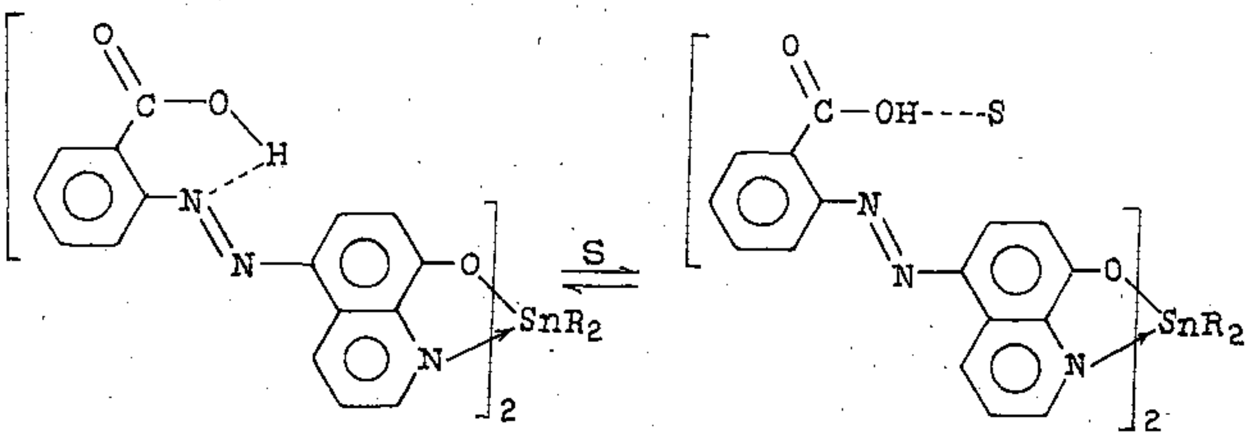


(XIV A)



(XIV B)

On the other hand, the complexes $R_2Sn(L'H')_2$ in which the carboxyl group is free, exhibit solvent-dependent spectra [Table-1B(ii)]. The compounds absorb predominantly at 415-420 nm in donor solvents like methanol, acetone, DMSO etc. and at 480 nm in non polar solvents like benzene and CCl_4. All compounds of this series in which the carboxylic proton has been replaced, e.g. $R_2Sn(L'Me)_2$ [Table -1B(ii)], $R_3SnL'H$ [Table - 1B(i)] and $R_2Sn(L'SnR'_3)_2$ [Table - 1B (iii)], have a single intense absorption at ~410 nm in all solvents mentioned above. Since, only donor solvents capable of forming strong H-bond give rise to a blue shift, we believe the following equilibrium involving a competition between the intra molecular H-bonded form (XVA) and intermolecular H-bonded species (XVB) is involved. The presence of



(XVA) (XVB)

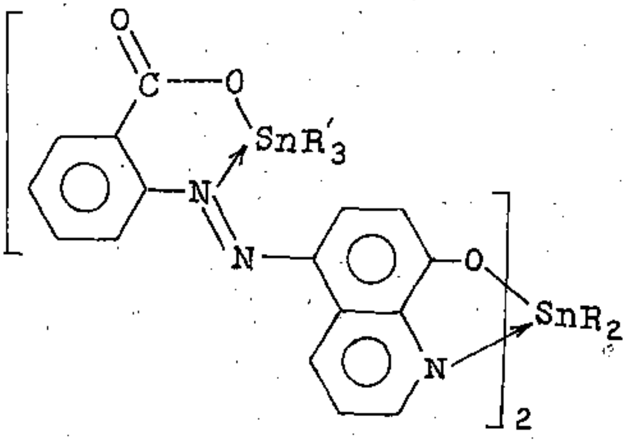
intramolecular H-bond involving the -COOH group is easily demonstrated by methylation of the -COOH group. The corresponding carbomethoxy derivatives show only a single absorption maximum.

Since the H-atom is not directly involved in the π-system, such interaction (VIB) will have little influence on the π-π^* transition and consequently, the absorption spectra closely resemble to those of the corresponding carbomethoxy compounds, $R_2Sn(L'Me)_2$. However, formation of intramolecular H-bond involving the azo-N-atom (XVA) would certainly result in a large red shift of the π-π^*transition (see Section IIIB). Such behaviour is well known in o-carboxy azo compounds. The 480 nm and ~ 410 nm absorptions should, therefore, be attributed to the species (XVA) and (XVB) respectively. Clearly, the intramolecular H-bonded form (XVA) will be the main species in aprotic solvents, while donor solvents will tend to form solvent-solute or intermolecular H-bond, thereby shifting the equilibrium towards the form (XVB).

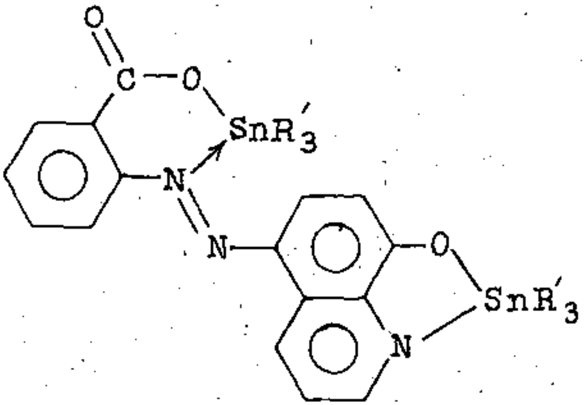
(c) The binuclear organotin carboxylate - quinolinolates:

In these organotin complexes, the possibilities of azo-hydrazone tautomerism or solvent-solute interactions through intermolecular H-bond are eliminated. Consequently, the absorption spectra are similar to the dimethoxy derivative (XII) and have a single intense absorption maxima at 410 nm in both types of solvent

[Table - 18(iii)]. The bathochromic shift as compared to $L'Me_2$ (XII) is indicative of N → Sn coordination. The compounds should thus be formulated as (XVI) and (XVII).



(XVI)



(XVII)

ELECTRONIC SPECTRA

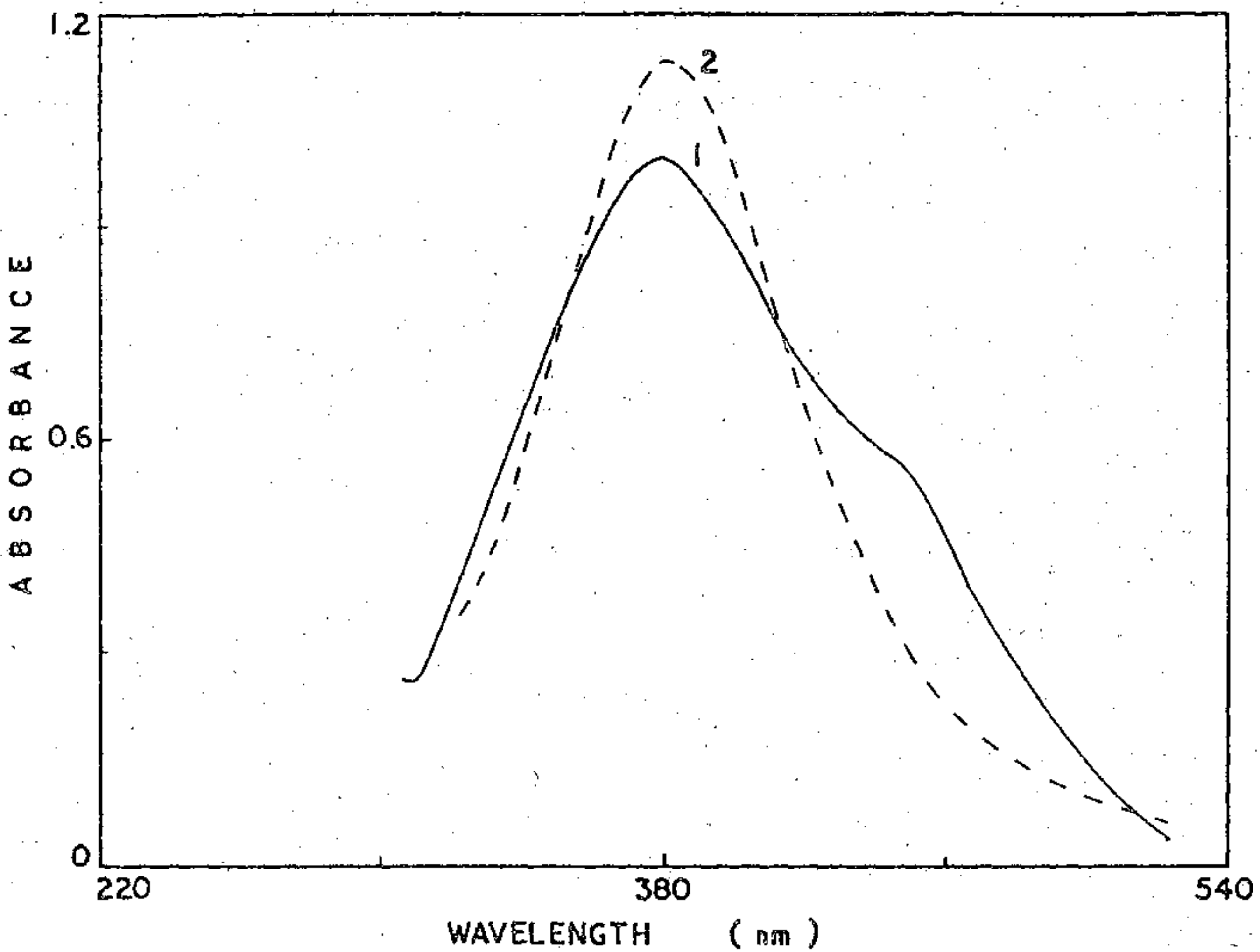


FIG. 1. ABSORPTION SPECTRA OF LH. 1. IN METHANOL AND 2. IN BENZENE.

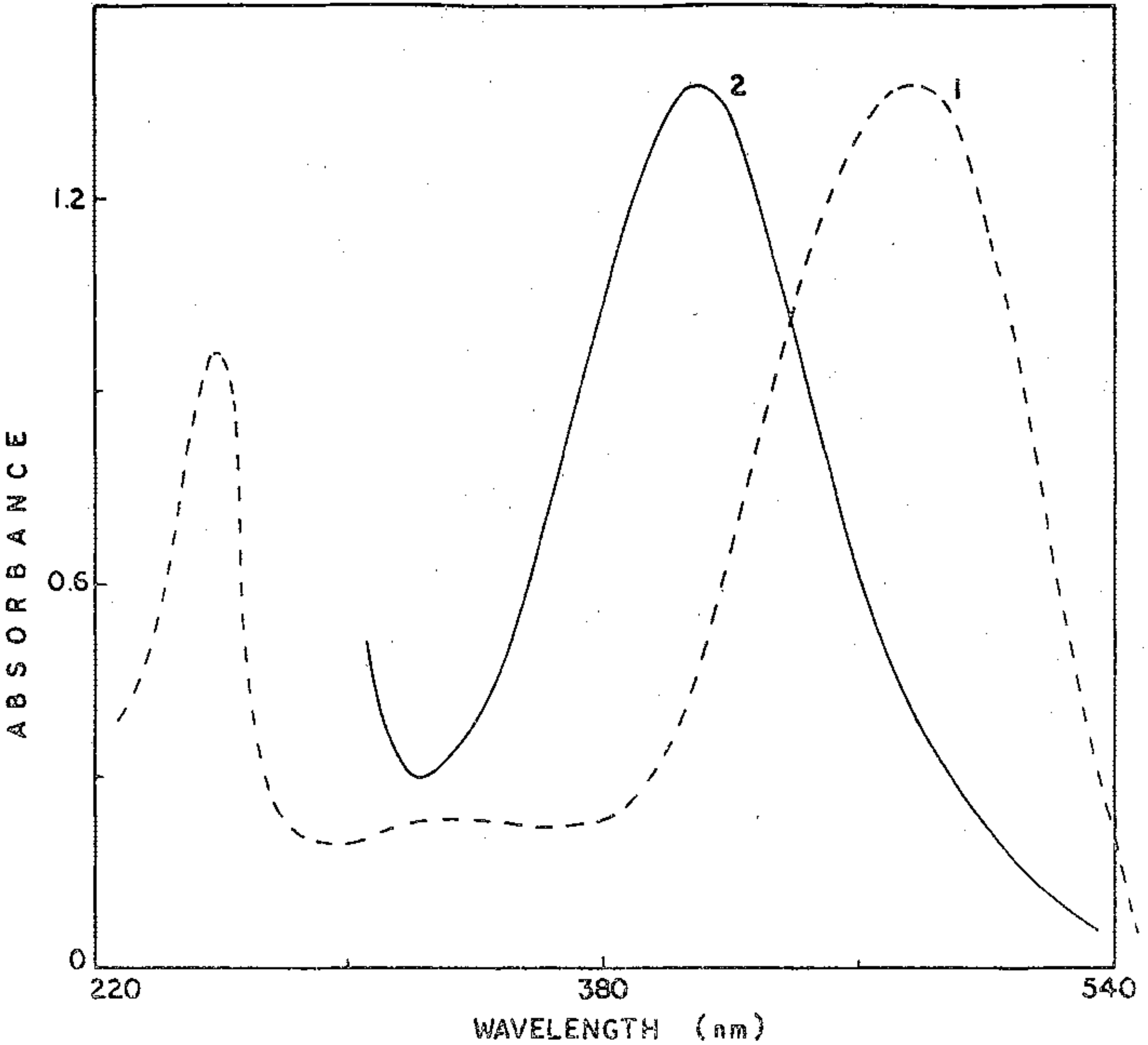


FIG.2. ABSORPTION SPECTRA OF L'HH' 1. IN METHANOL AND 2. IN BENZENE.

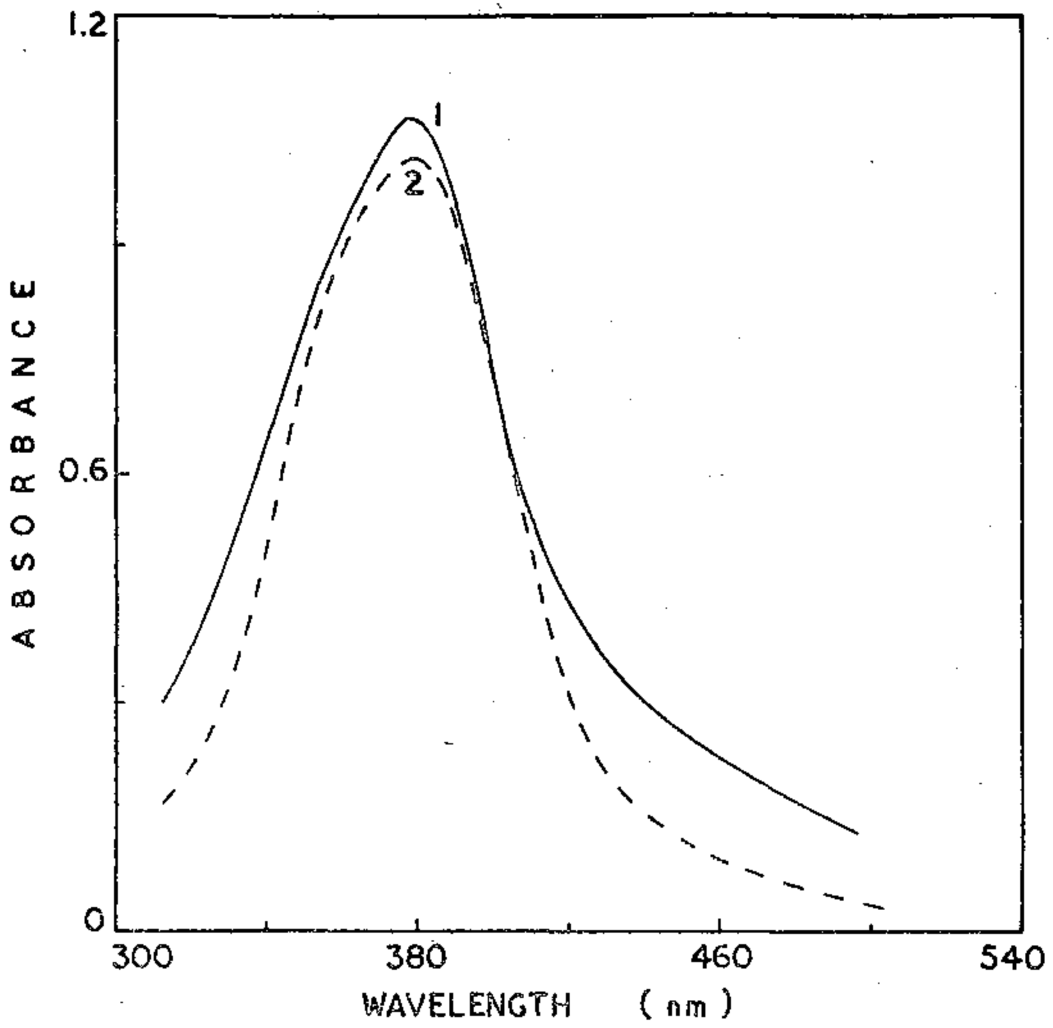


FIG. 3. ABSORPTION SPECTRA OF L'Me_2.
1. IN METHANOL AND 2. IN BENZENE.

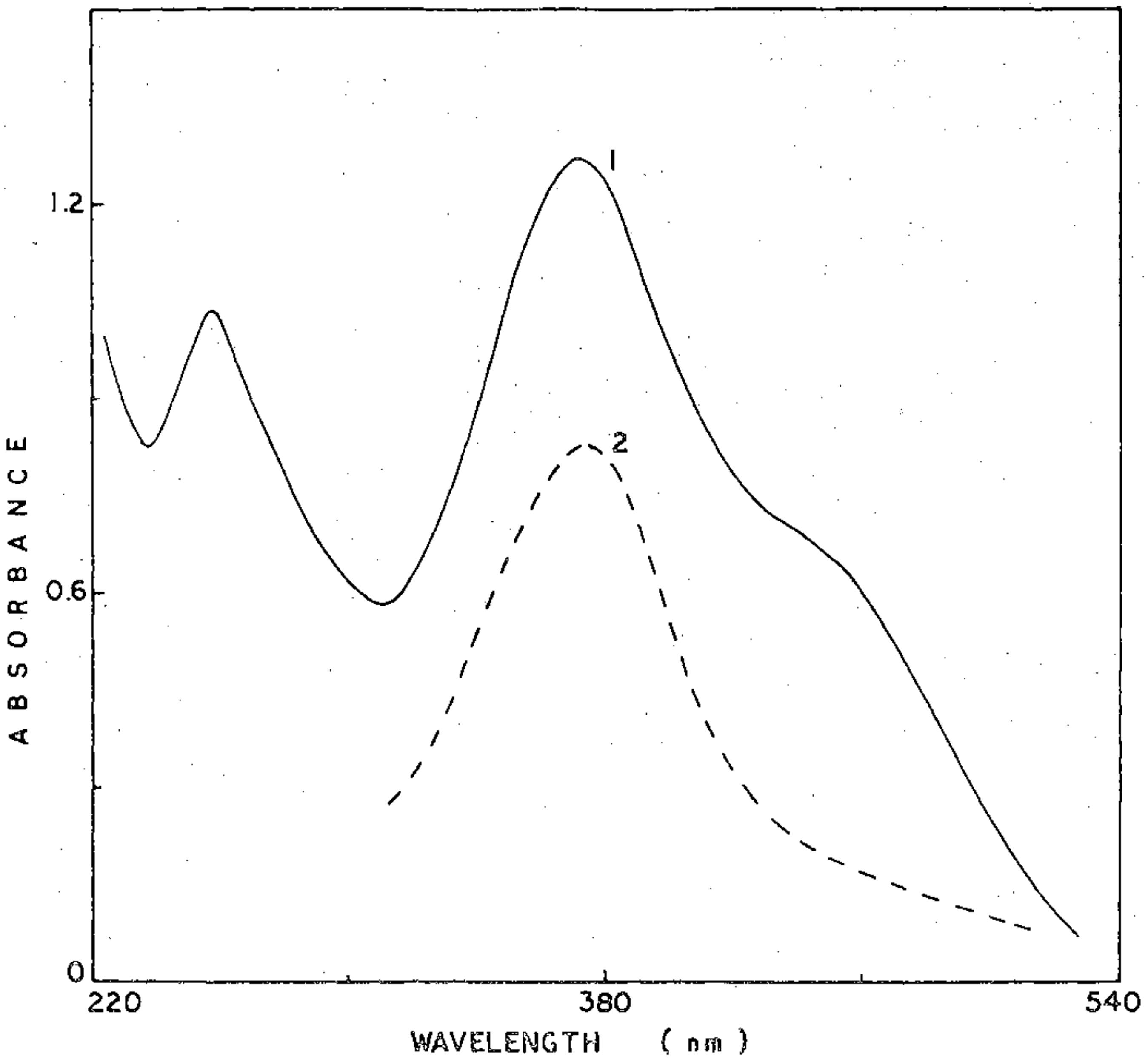


FIG. 4. ABSORPTION SPECTRA IN METHANOL OF L′MeH.
1. IN METHANOL AND 2. IN BENZENE.

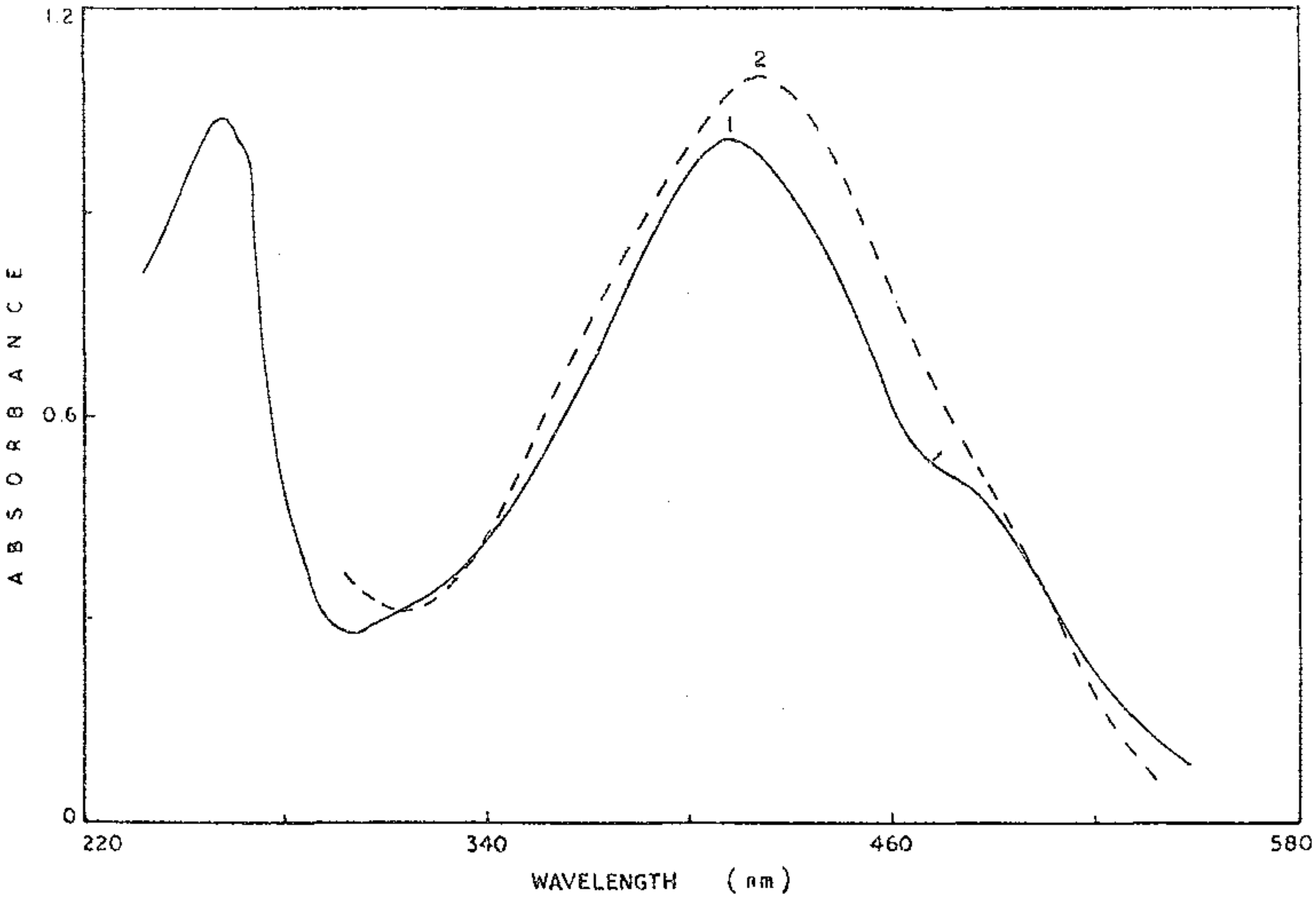


FIG. 5. ABSORPTION SPECTRA OF $Ph_3SnL'H$, 1. IN METHANOL. 2. IN BENZENE.

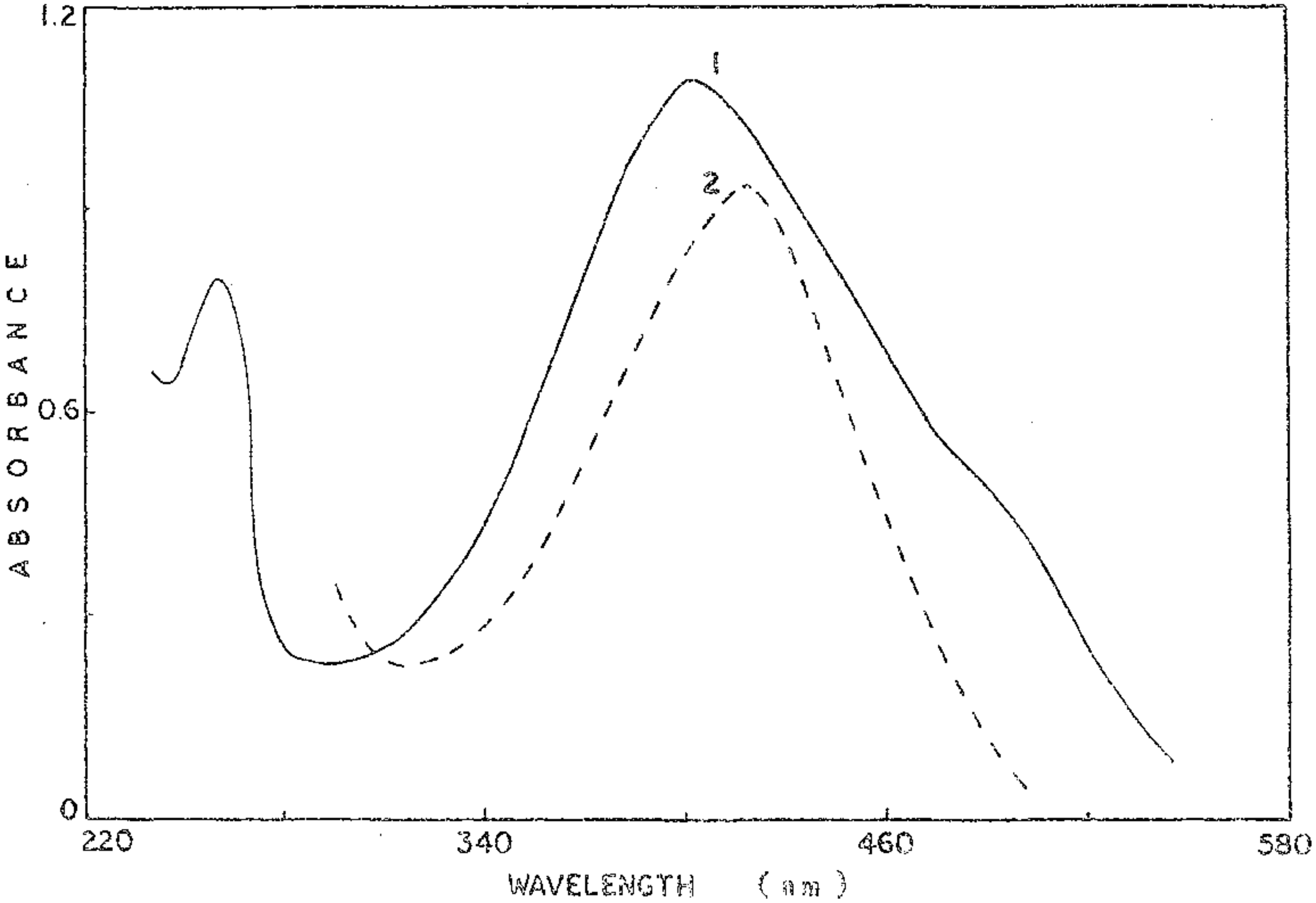


FIG. 6. ABSORPTION SPECTRA OF $Bu_3SnL'H$. 1. METHANOL, 2. BENZENE.

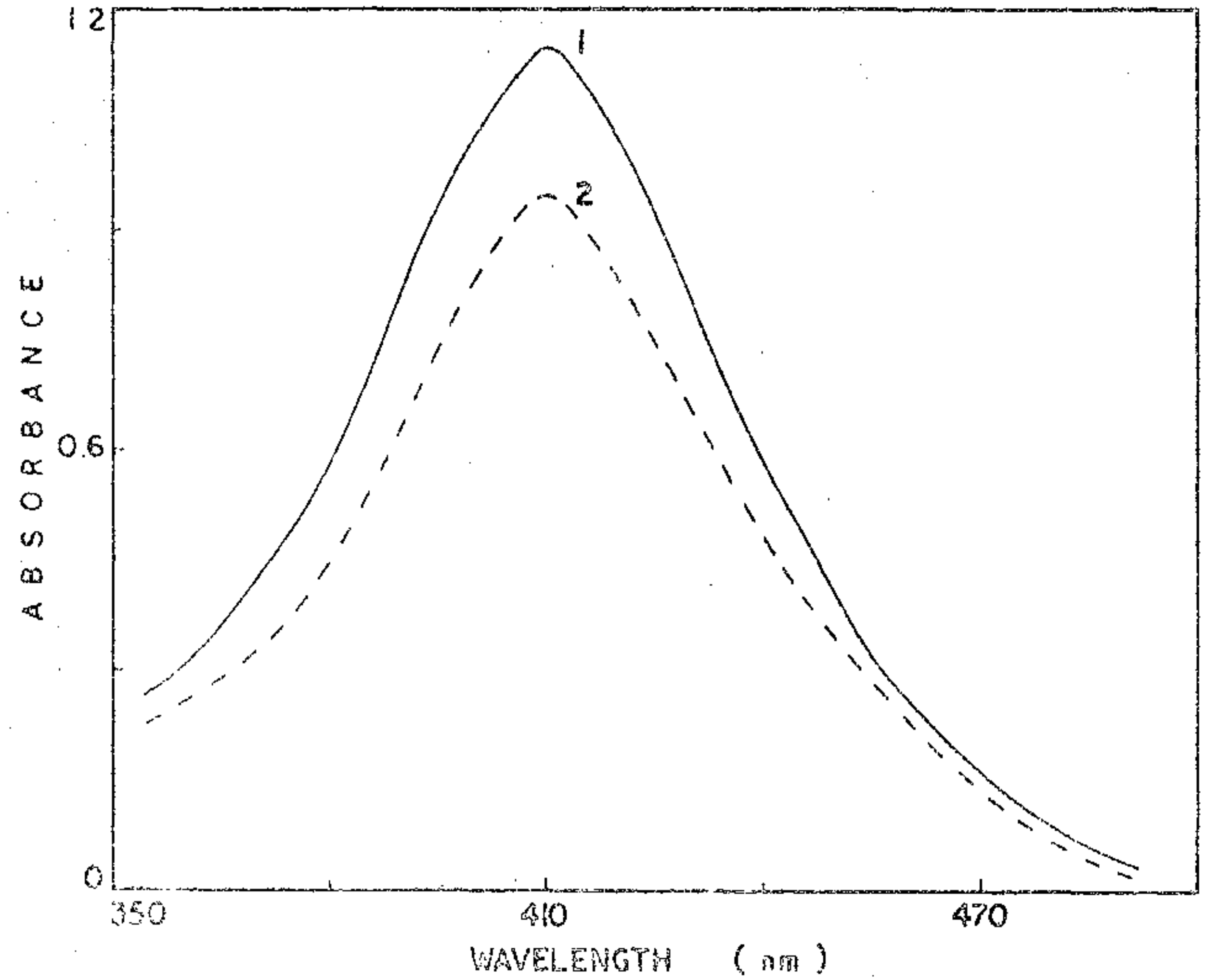
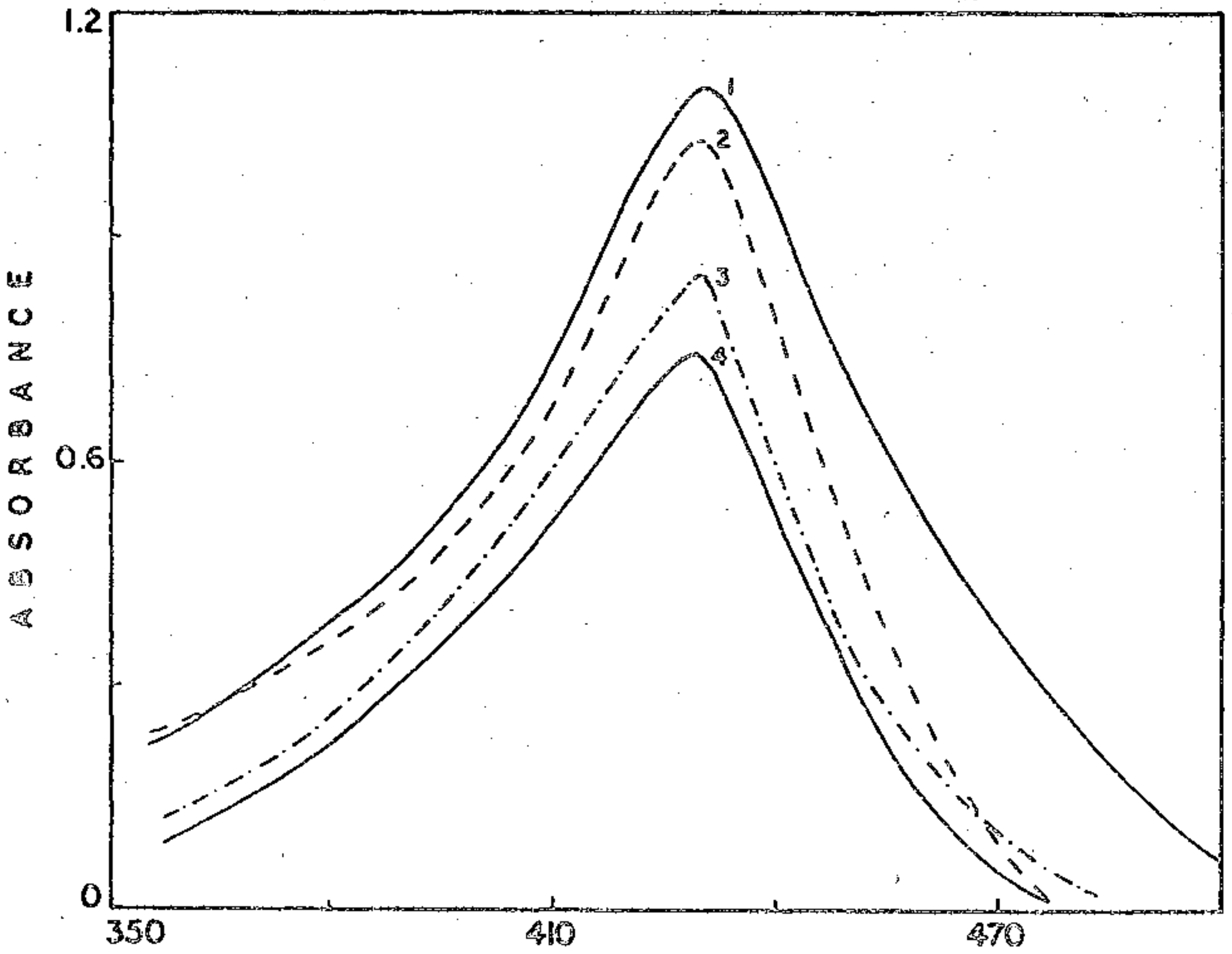


FIG. 7. ABSORPTION SPECTRA OF Ph_3SnL.
1. IN METHANOL AND 2. IN BENZENE.



WAVELENGTH (nm)

FIG. 8. ABSORPTION SPECTRA IN METHANOL OF
1. Ph_2SnL_2, 2. Bu_2SnL_2, 3. Oct_2SnL_2 AND 4. Me_2SnL_2.

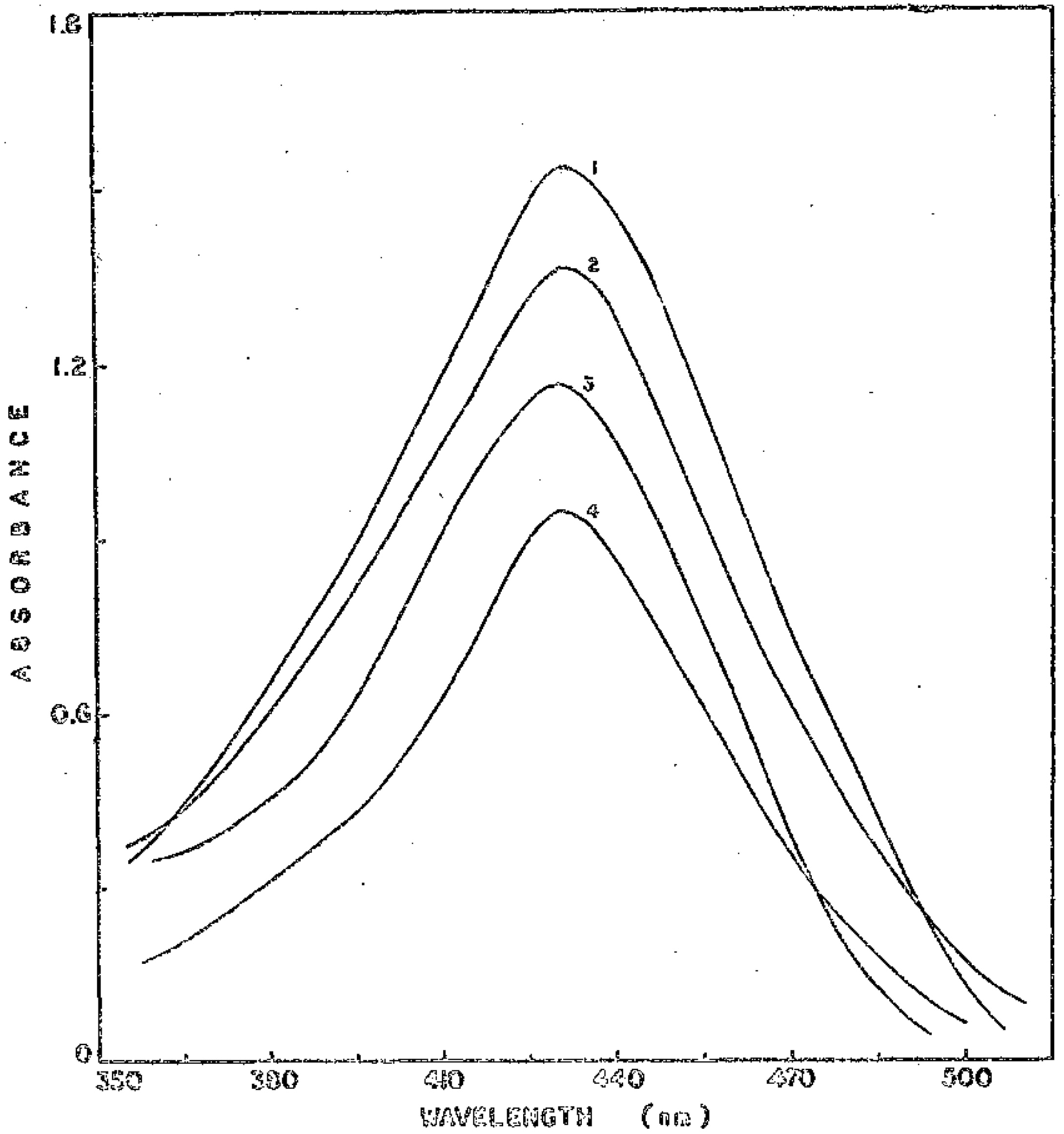


FIG. 9. ABSORPTION SPECTRA IN BENZENE OF
1. Ph_2SnL_2, 2. Bu_2SnL_2, 3. Oct_2SnL_2 AND 4. Me_2SnL_2.

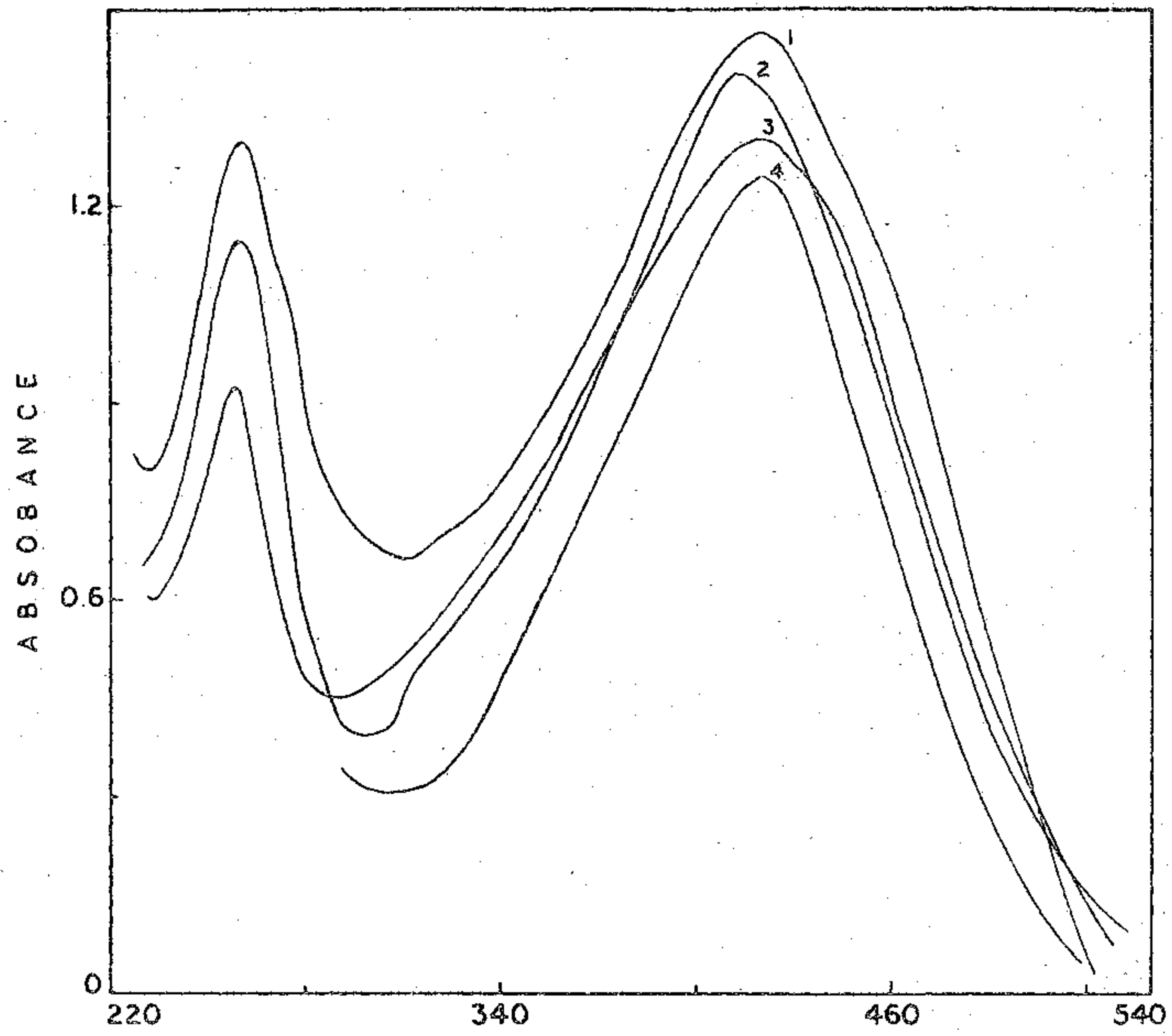


FIG. 10. ABSORPTION SPECTRA IN METHANOL OF 1. $Ph_2Sn(L'H')_2$, 2. $Bu_2Sn(L'H')_2$, 3. $Oct_2Sn(L'H')_2$ AND 4. $Me_2Sn(L'H')_2$.

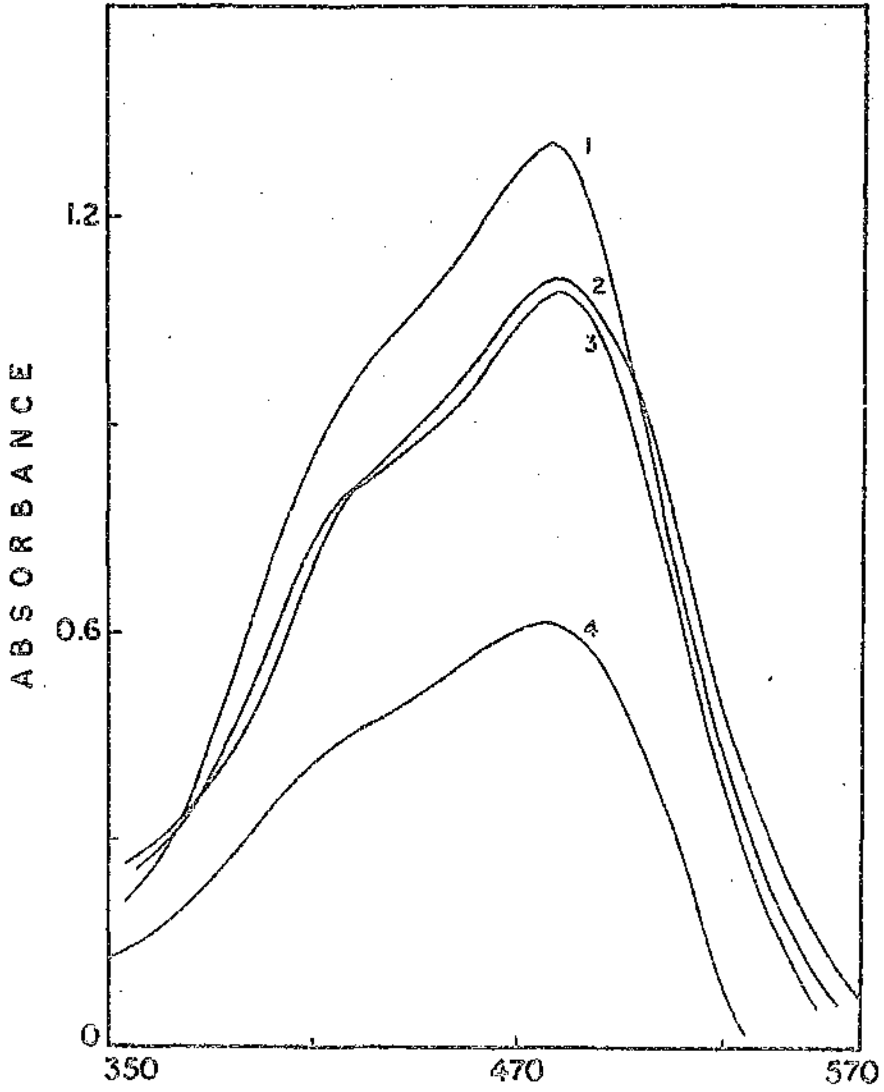


FIG. 11. ABSORPTION SPECTRA IN BENZENE OF 1. $Ph_2Sn(L'H')_2$, 2. $Bu_2Sn(L'H')_2$, 3. $Oct_2Sn(L'H')_2$, 4. $Me_2Sn(L'H')_2$.

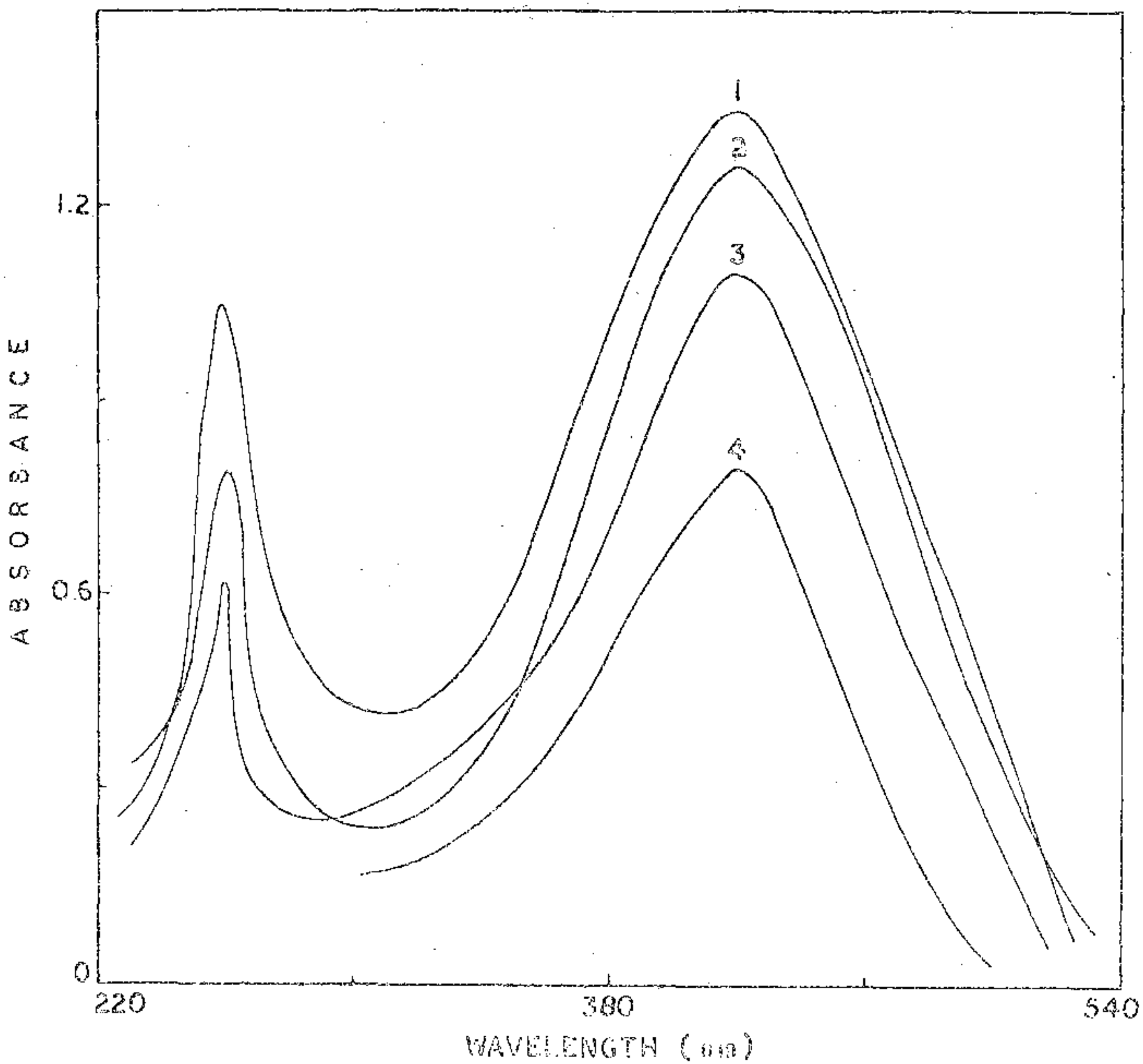


FIG.12. ABSORPTION SPECTRA IN METHANOL OF 1. $Ph_2Sn(L'Me)_2$, 2. $Bu_2Sn(L'Me)_2$, 3. $Oct_2Sn(L'Me)_2$ AND 4. $Me_2Sn(L'Me)_2$.

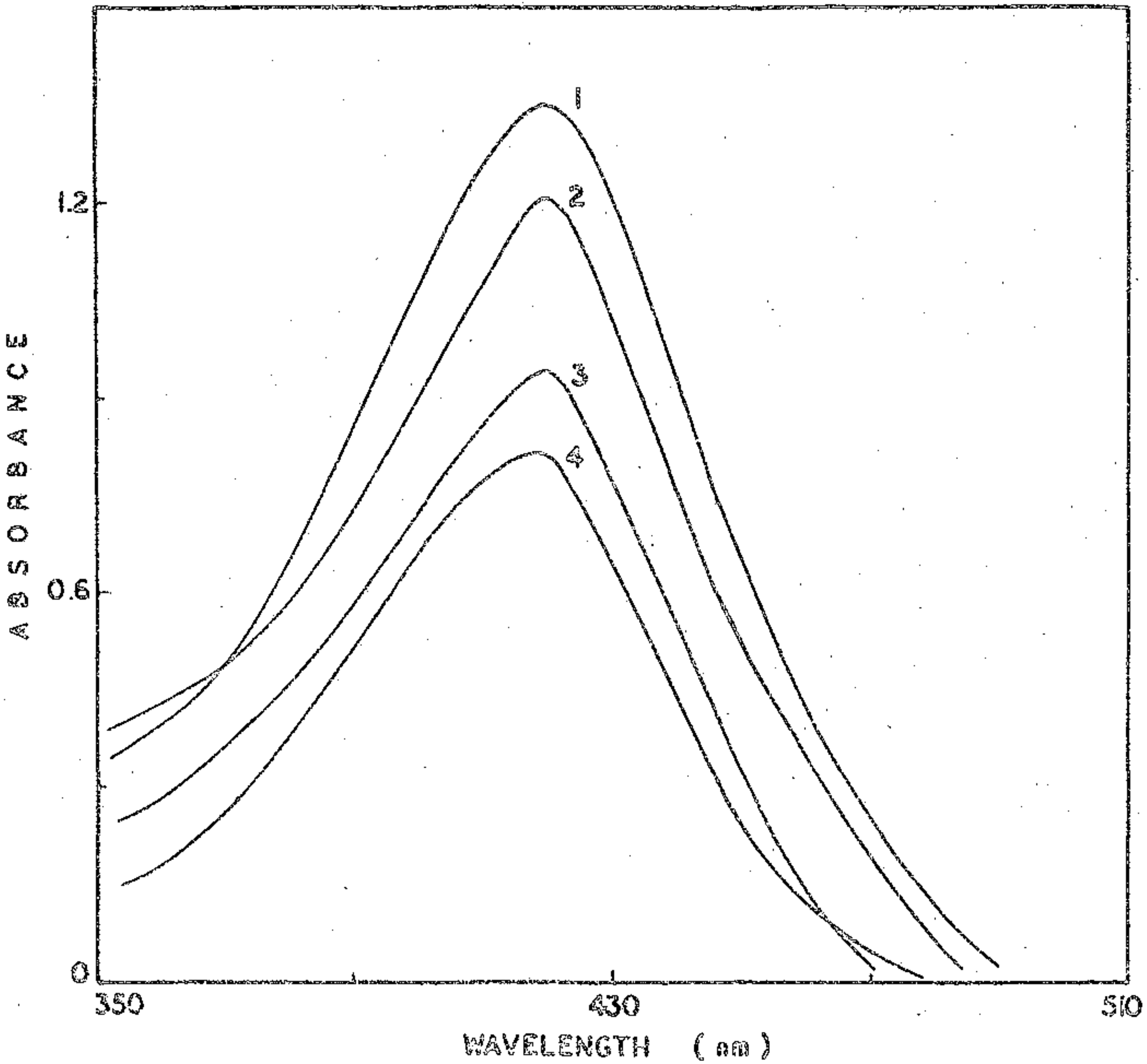


FIG. 13. ABSORPTION SPECTRA IN BENZENE OF 1. $Ph_2Sn(L'Me)_2$, 2. $Bu_2Sn(L'Me)_2$, 3. $Oct_2Sn(L'Me)_2$, 4. $Me_2Sn(L'Me)_2$.

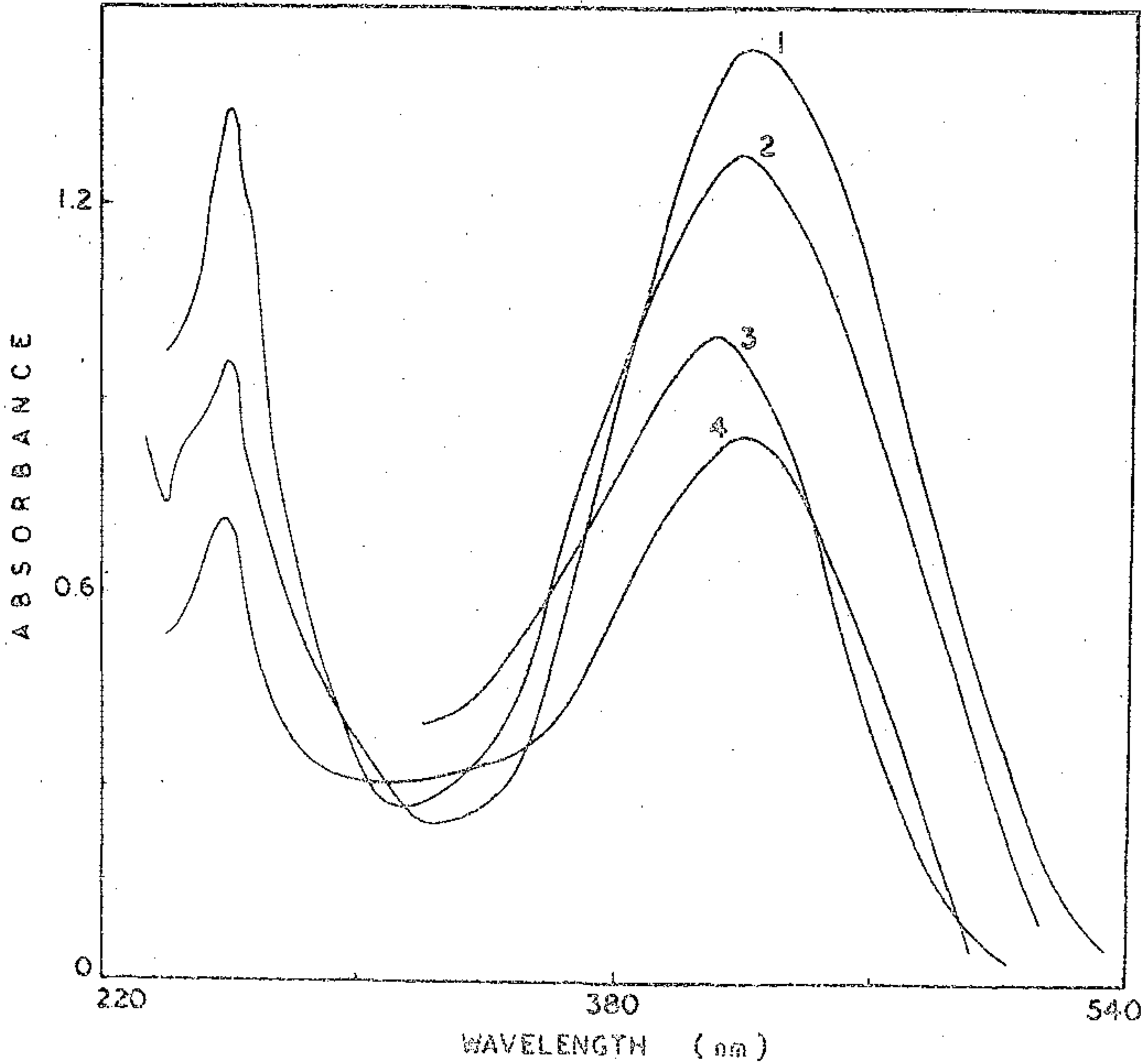


FIG. 14. ABSORPTION SPECTRA IN METHANOL OF 1. $Ph_2Sn(L'SnPh_3)_2$ 2. $Bu_2Sn(L'SnPh_3)_2$, 3. $Oct_2Sn(L'SnPh_3)_2$ AND 4. $Me_2Sn(L'SnPh_3)_2$.

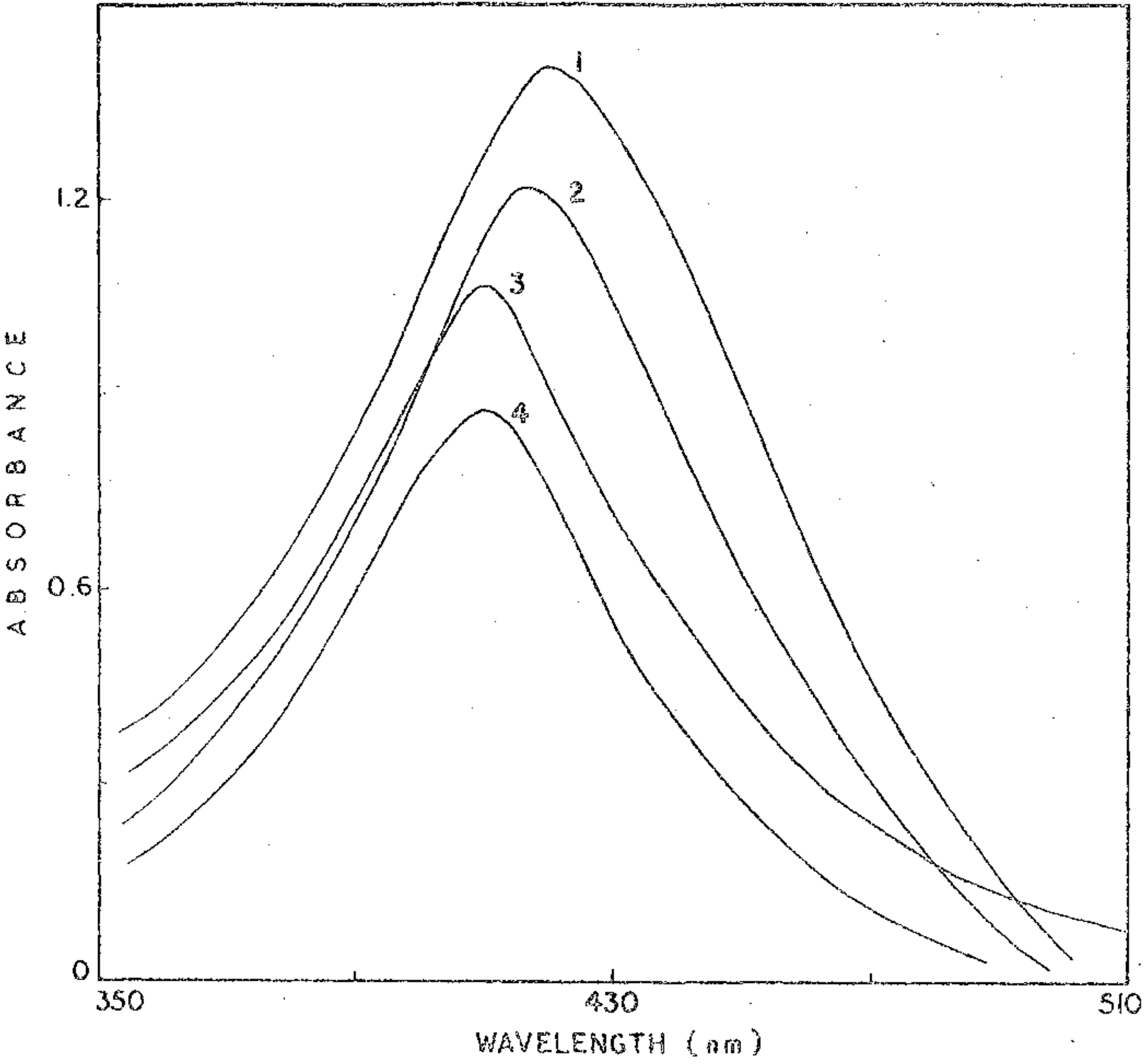


FIG. 15. ABSORPTION SPECTRA IN BENZENE OF 1. $Ph_2Sn(L'SnPh_3)_2$, 2. $Bu_2Sn(L'SnPh_3)_2$, 3. $Oct_2Sn(L'SnPh_3)_2$ AND 4. $Me_2Sn(L'SnPh_3)_2$.

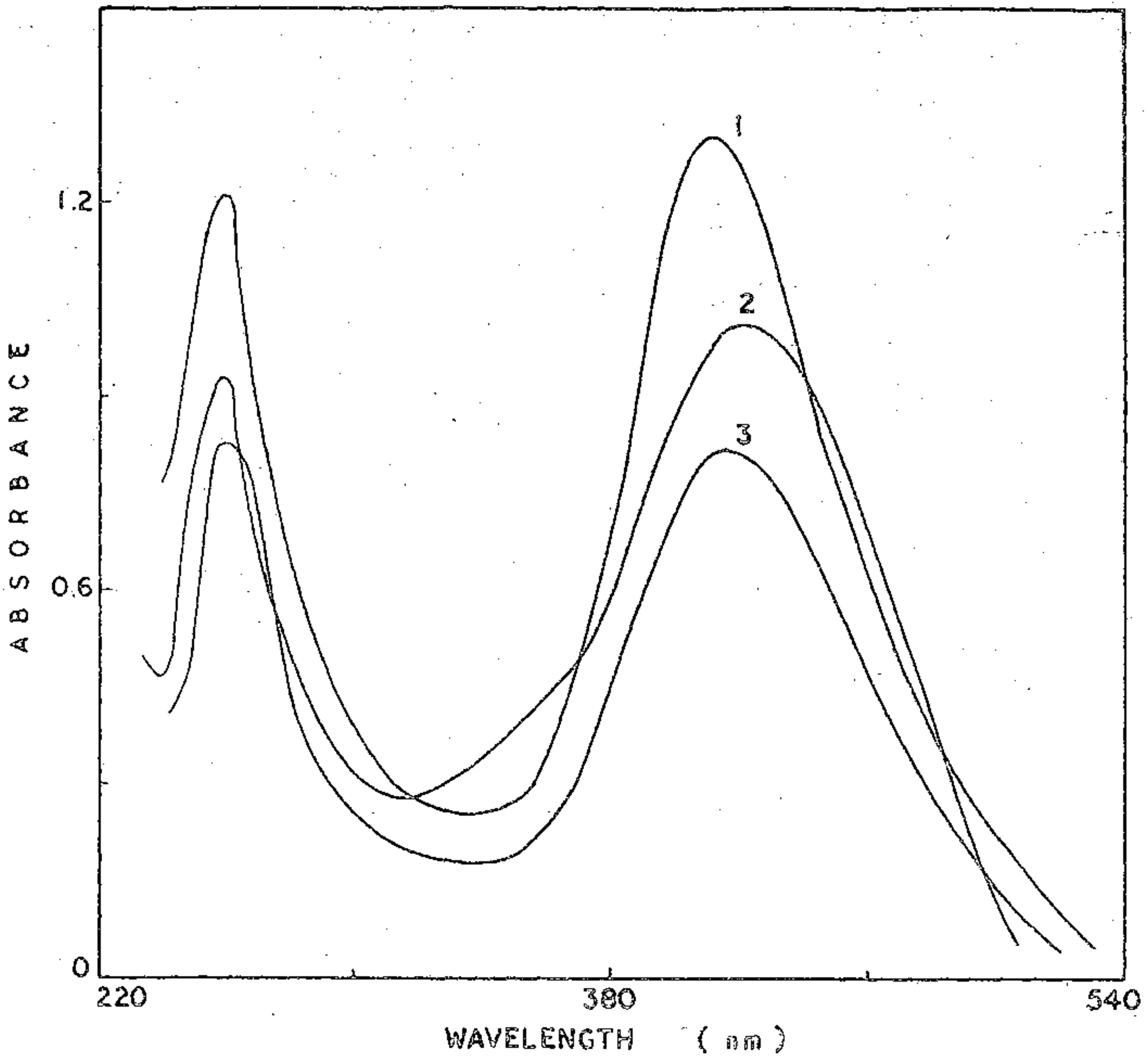


FIG. 16. ABSORPTION SPECTRA IN METHANOL OF
1. $Ph_2Sn(L'SnBu_3)_2$, 2. $Bu_2Sn(L'SnBu_3)_2$ AND 3. $Oct_2Sn(L'SnBu_3)_2$.

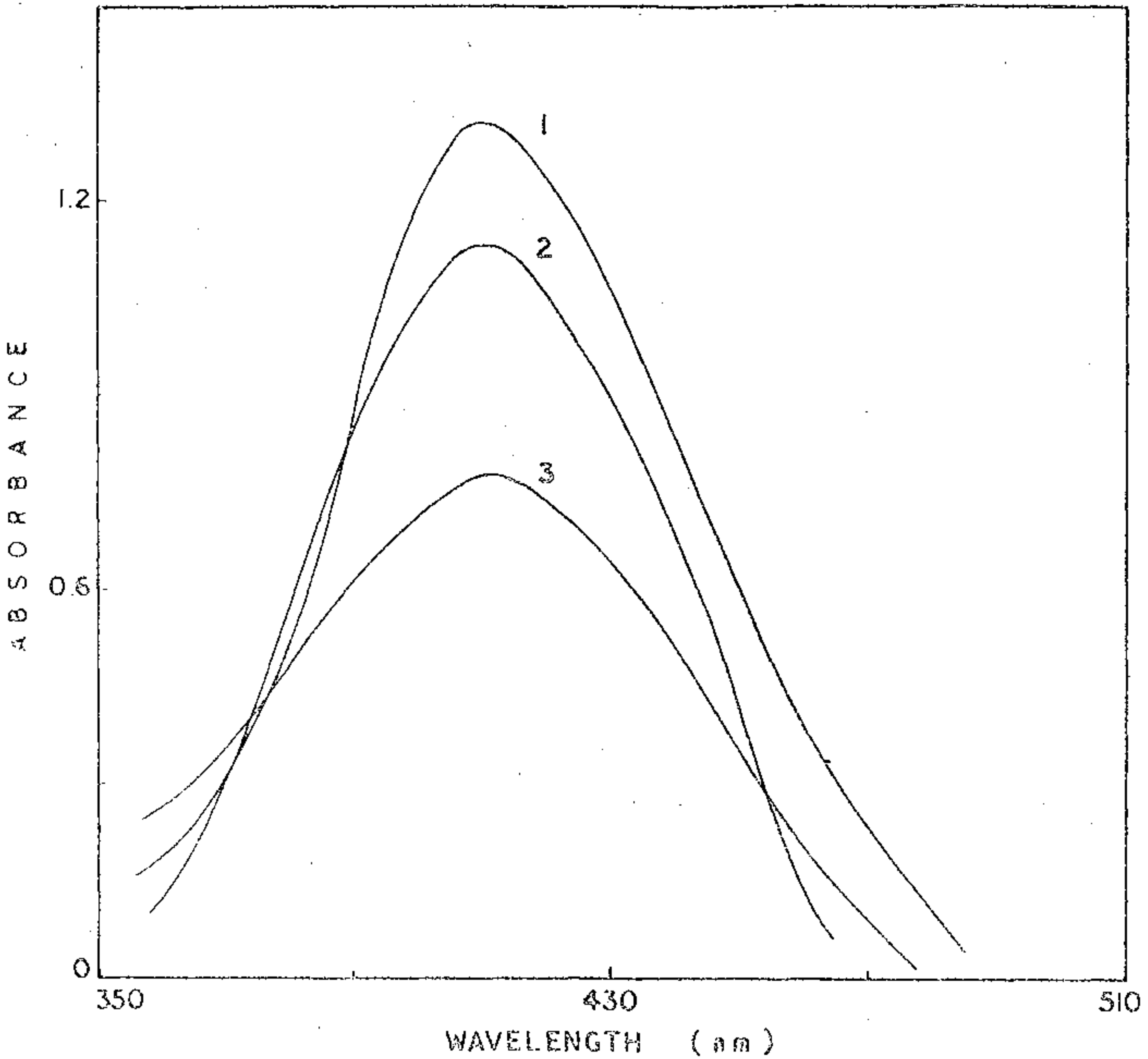


FIG. 17. ABSORPTION SPECTRA IN BENZENE OF 1. $Ph_2Sn(L'SnBu_3)_2$, 2. $Bu_2Sn(L'SnBu_3)_2$ AND 3. $Oct_2Sn(L'SnBu_3)_2$

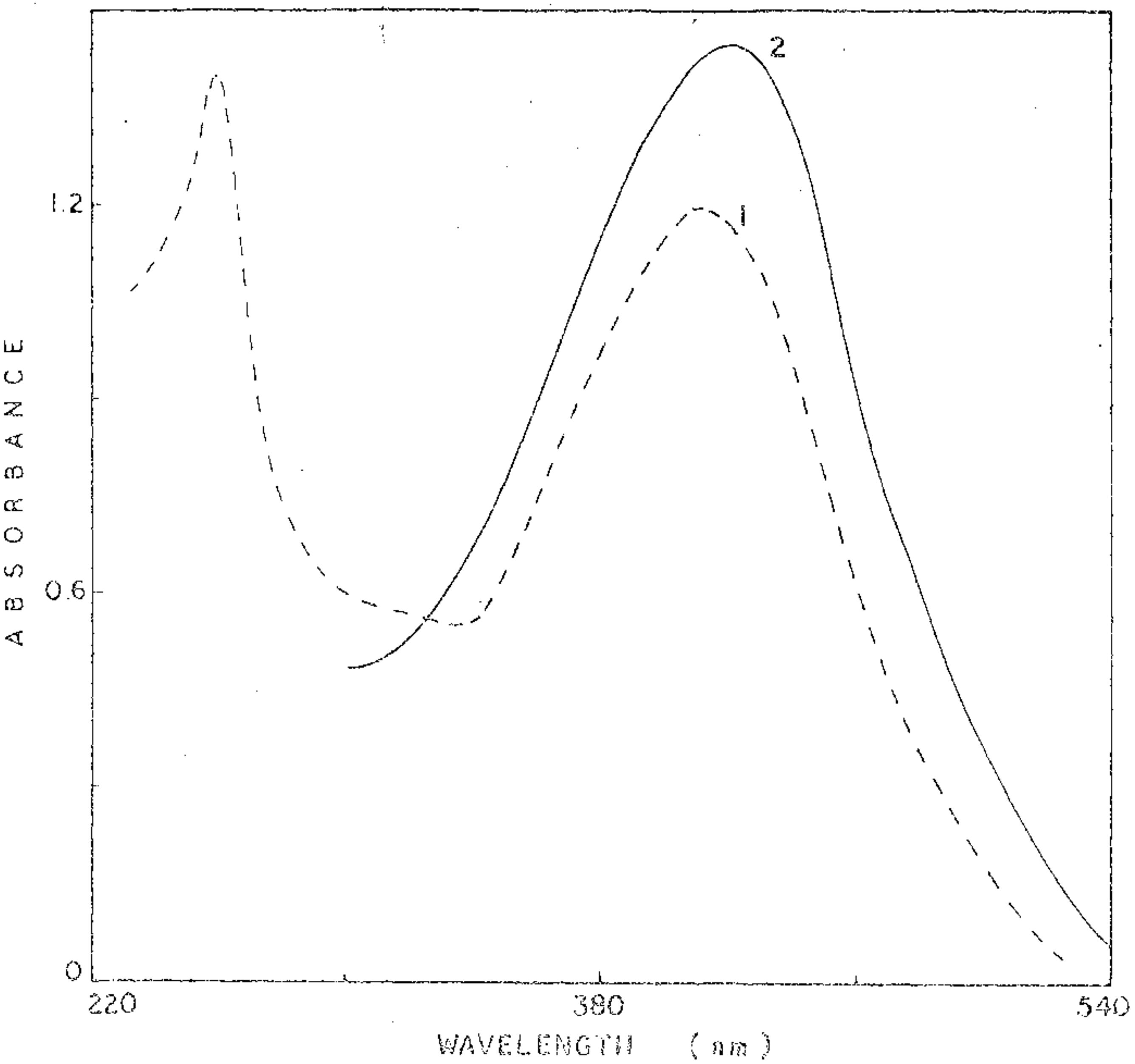


FIG. 18. ABSORPTION SPECTRA OF $Ph_3SnL'SnPh_3$
1. IN METHANOL AND 2. IN BENZENE.

IVD. Experimental

The UV-Visible spectra reported in this work were Obtained with Beckman DU-2 Spectrophotometer using 1 cm quartz cells.

All solvents used were of spectroscopic (UVASOL, E.Merck) grade.

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