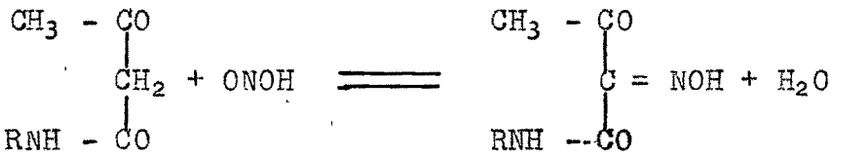
RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

1. Monoximes : N-aryl 2,3-dioxobutyramide 2-oxime :

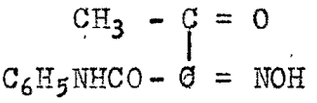
1.(a) Structures of vic-oxime-ketones :

N-aryl acetoacetamide(where aryl amide may be anilide, o-toluidide, o-chloranilide or methyl anilide) was treated with nitrous acid to obtain the corresponding N-aryl 2,3-dioxobutyramide 2-oxime.

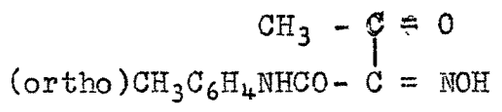


As a result, the products of the following structures are formed :

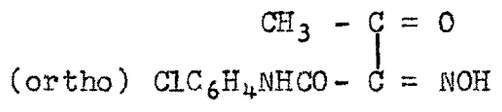
(I)



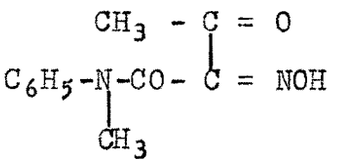
(II)



(III)



(IV)

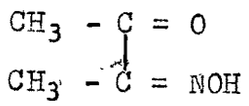


These structures are in accord with the suggestions of Meyer (164,165), Knorr (184),

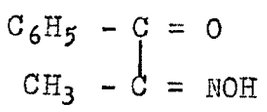
Naik et al. (185) and Dave and Talati (186).

For the purpose of comparison the following vic-oxime-ketones of known structures were also prepared by the methods suggested in the experimental part.

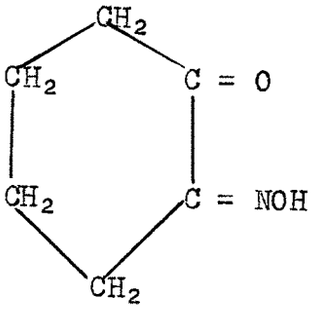
(V)



(VI)

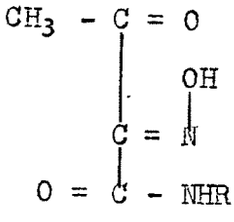


(VII)

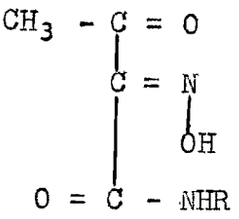


1. (b) Stereoisomerism of vic-oxime-ketones :

The unsymmetrical vic-oxime-ketones would exhibit stereoisomerism. Thus, the stereoisomers that might be obtained in the present case may be represented as



(i)
Anti-amide structure



(ii)
Syn-amide structure

where R is an aryl group. However, attempts to separate isomers of any of these have failed ; only one form is obtained in all cases. To account for the absence of isomerism in these cases the following evidence from literature is cited :

(i) Whiteley (88) obtained only one compound by the action of nitrosyl chloride on ethyl acetoacetate ;

(ii) Naik et al. (185) obtained only one isomer of N-aryl 2,3-dioxobutyramide 2-oxime by the action of nitrosyl chloride on the respective N-aryl 2,3-dioxobutyramide ;

(iii) Knorr (184) obtained only one derivative of 2,3-dioxobutyranilide 2-oxime by the action of nitrous acid on acetoacetanilide ;

(iv) Dave and Talati (186) obtained only one isomer when N-aryl 2,3-dioxobutyramide was treated with nitrous acid ;

(v) Zanetti (206) observed that 2,4-pentanedione by the action of nitrous acid, yields only one derivative ;

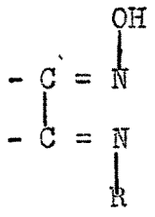
(vi) According to Hantzsch (207) only one isomeric form is obtained because of the relative instability of the other.

The following evidence may be considered for deciding its isomeric nature :

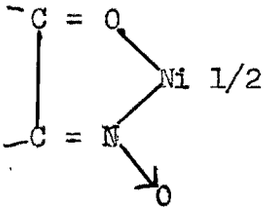
(i) Ethyl 2,3-dioxobutyrate 2-oxime gives reactions with metal ions which are similar to those of 2,3-dioxobutyranilide 2-oxime (82,197). This

indicates that NH of - $CONH_2$ group may not be involved in the chelate ring formation through oxime-hydrogen.

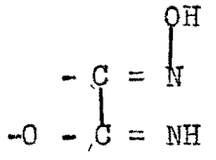
(ii) Pfeiffer (141) showed that anti-oxime-imines having the structural group



form red complexes with nickel in the same manner as with anti-dioximes. It is observed that the compounds under investigation do not exhibit this characteristic property. Desai et al.(208, also 197) found that the metal chelates of nickel with N-aryl 2,3-dioxobutyramide.wereygreenuTheg formulated them as

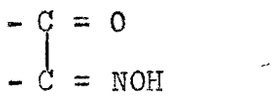


Hence it can be suggested that anti-imide structure



is not likely in the compounds.

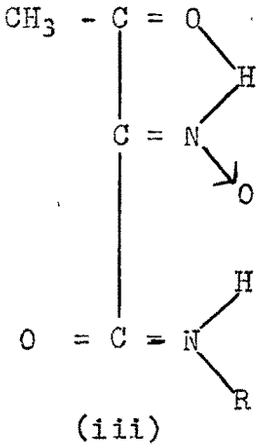
(iii) Whiteley (88) and Feigl (89) observed that the compounds containing the group



gave a characteristic reaction with ferrous salts known as the iron-blue reaction. The compounds under investigation give this characteristic reaction. Further the iron-blue reaction has been given by compounds which do not contain the amido group. Hence it may be assumed that carbonyl group (and not carboxyl group) would be involved in the reaction.

(iv) Taylor (209) suggested that ethyl 2,3-dioxobutyrate 2-oxime has anti-acetyl configuration.

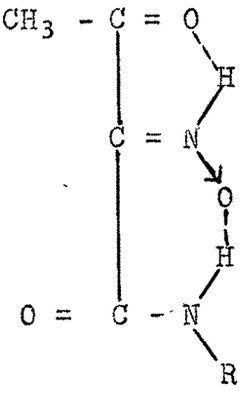
(v) Talati (187) suggested that N-aryl 2,3-dioxo-butyramide 2-oxime have Syn-amide configuration, the oxime hydrogen forming chelate ring with acetyl carbonyl.



(iii)

Desai (188) observed that stability of the N-aryl 2,3-dioxobutyramide 2-oxime is greater than that

of ethyl 2,3-dioxobutyrate 2-oxime and proposed that the amide NH may be involved in H-bonding with oxime O.



(iv)

We find that the stability of 2,3-dioxo-butyranilide 2-oxime is greater than that of N-methyl 2,3-dioxobutyranilide 2-oxime. The decreased stability may be attributed to the non-formation of chelate ring involving anilide NH group and to the steric effect of the methyl group.

1.(c) Absorption spectra of vic-oxime-ketones :

The absorption spectra of N-methyl 2,3-dioxo-butyranilide 2-oxime are investigated in different solvents in the ultra-violet region.(vide table IX) (The absorption spectra of 2,3-dioxobutyranilide 2-oxime in different solvents are known ; ref. 187, 188). These are presented in fig.1 and the wave-length maxima (λ max) and the corresponding molar extinction coefficients (E_m) for the above substances are given in table XXVII. (Values of λmax and E_m from ref. 187,188 are given in brackets.)

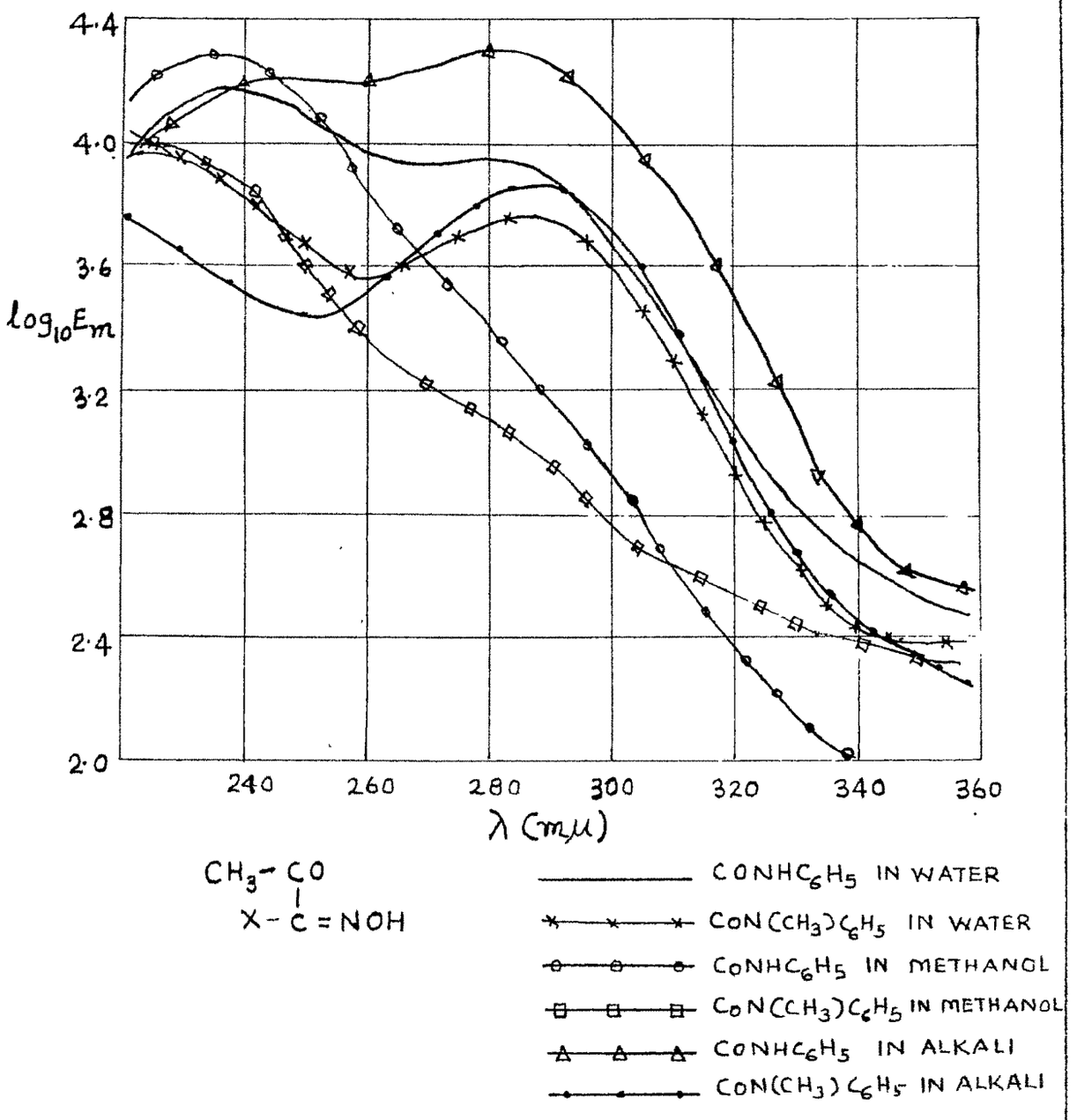
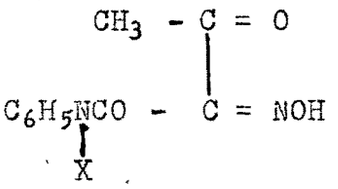


FIG 1 ULTRA-VIOLET ABSORPTION SPECTRA OF N-ARYL 2,3-DIOXOBUTYRAMIDE 2-OXIME IN DIFFERENT SOLVENTS.

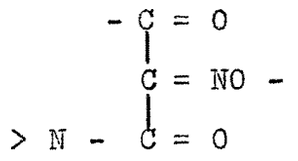
TABLE XXVII

Ultra-violet absorption spectra of N-substituted 2,3-dioxobutyranilide 2-oxime.



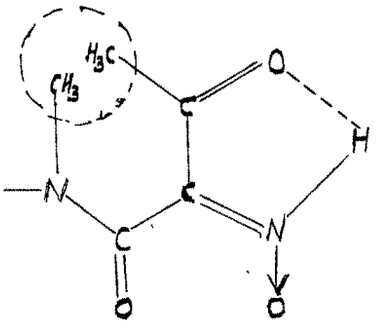
No.	Substance X =	in water λ(max) (mμ)	E_m	in methanol λ(max) (mμ)	E_m	in alkali λ(max) (mμ)	E_m
1.	H.	(233-39	14570)	(236-38	18940)	(245-47	15940)
		(280-81	9040)	-	-	(280-82	19310)
2.	CH_3	284-87	5800	-	-	286-88	7190

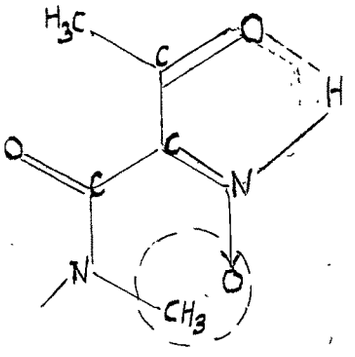
The intense absorption band (K) at 236-39 mμ in aqueous and alcoholic solutions has been attributed by Dave and Talati (186) and Desai (188) to the crossed conjugated system.



The K-band is missing in the spectra of N-methyl

2,3-dioxobutyranilide 2-oxime in the above solvents. It may be assumed that a large blue shift has taken place such that the maximum is shifted beyond the working range of the instrument. The shift may be attributed to the opening up of the chelate ring involving anilide NH group. Similar results have been obtained with naphthol-AS (210). It was observed that in relation to the absorption spectrum of naphthol -AS, that of its N-methyl derivative showed a marked hypsochromic shift and was attributed to its non-formation of the chelate ring. This favours the chelation of anilide group. The methyl group may also introduce steric effect as shown below :





The steric effect of the methyl group would also cause a blue shift of the band.

The second band (X) observed at 280-81 mμ in the spectrum of 2,3-dioxobutyranilide 2-oxime in aqueous solution has been attributed by Desai (188) to its ionic tautomer. The X-band is comparable to that of the sodium salt of the oxime (6) and was attributed to the ionic form of the crossed conjugated system with the oxime having isomeric imine-oxide structure.

The band is observed at 284-87 mμ in the spectrum of N-methyl 2,3-dioxobutyranilide 2-oxime in aqueous solution. The bathochromic shift, in this case, is accompanied by hypochromic shift.

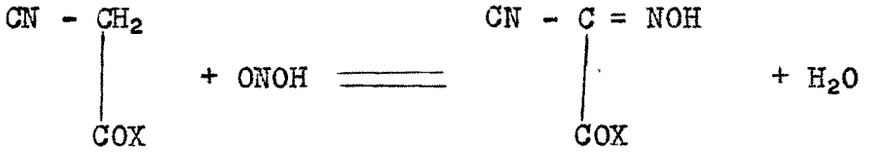
The X-band is observed in aqueous solution but not in alcoholic solution. It is suggested that the oxime and its ionic tautomer are in equilibrium in aqueous solution and that the ionisation of the oxime group is suppressed in alcoholic solution.

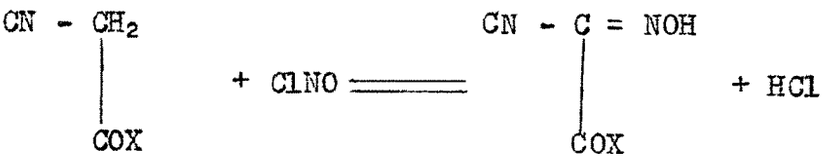
The hyperchromic shift of the X-band is observed in alkali solution and may be attributed to the increased ionisation of the(tautomeric) oxime group and less probably of the enolised ketone.

2. Monoximes and dioximes (derivatives of the oxime of 2-cyano glyoxylic acid) :

2.(a) Structures of monoximes :

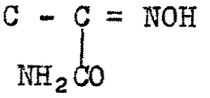
Ethyl cyanoacetate was converted into cyano-acetamide, cyanoacetanilide, N-methyl cyanoacetanilide and N,N'-ethylene bis(cyanoacetamide) by the methods suggested in the experimental part. These were converted into oximino- derivatives by the action of nitrous acid, or nitrosyl chloride.



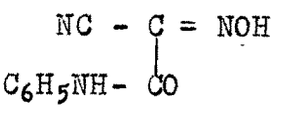


As a result, the products of the following structures are formed :

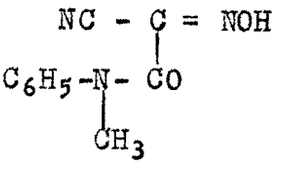
(VIII)



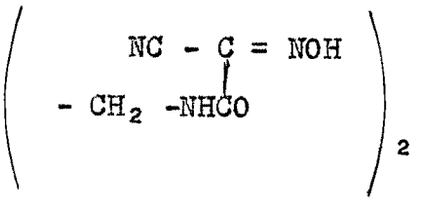
(IX)



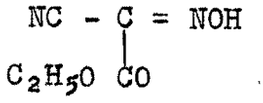
(X)



(XI)



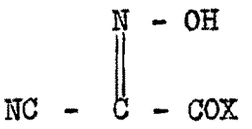
(XII)



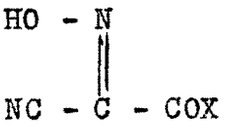
These structures are in accord with the suggestions of Muller (147), De Paolini and Imberti(151), Conrad and Schulze (152), etc.

2.(b) Stereoisomerism of monoximes :

The stereoisomers that can be obtained in the case of above compounds may be represented as



(vii)



(viii)

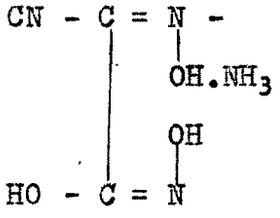
(Anti-nitrile structure (Syn-amide structure)

Syn-nitrile structure (. Anti-amide structure)

Attempts to separate isomers of any of these have failed ; only one isomer is obtained in each case. (The oxime of 2-cyano glyoxylanilide is known in two crystal forms.) The following evidence may be considered for deciding their isomeric nature.

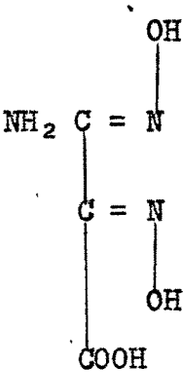
(i) N-aryl 2,3-dioxobutyramide 2-oxime is shown to have syn-amide structure.

(ii) Ulpiani (150) showed that the ammonium salt of the oxime of 2-cyano glyoxylo hydroxamic acid has syn structure



suggesting anti-nitrile structure for the oxime of 2-cyano glyoxylic acid.

(iii) De Paolini and Imberti(151) showed that the oxime of 2(hydroxy-amidino) glyoxylic acid has anti structure

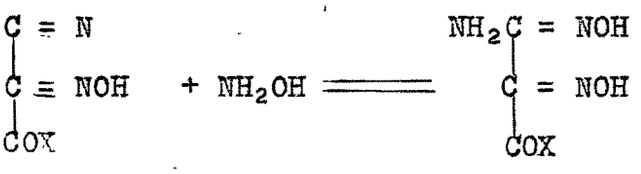


suggesting that the oxime of 2-cyano glyoxylic acid would have syn-acid structure.

Hence it may be suggested that the oxime of 2-cyano glyoxylic acid derivatives has anti-nitrile or syn-acid structure (vii).

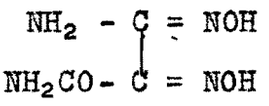
2.(c) Structure and stereoisomerism of dioximes :

Attempts were made to convert the oximes of 2-cyano glyoxylic acid derivatives (namely ethyl ester, amide,anilide and N-methyl anilide) into the corresponding oximes of 2-(hydroxyamidino) glyoxylic acid derivatives by the action of hydroxyl amine :



However, only the oxime of 2-(hydroxyamidino) glyoxyl amide could be obtained. Its structure may be represented as

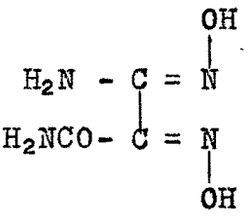
(XIII)



Its stereoisomeric nature may be decided on the basis of the following evidence :

(i) Ulpiani (150) and Wieland and Baumann (163) showed that it has anti-dioxime structure.

(ii) It gives a reaction with nickel which is similar to that of anti-dioxime with nickel. Hence it may be considered to have anti-dioxime structure as :



(ix)

Anti-dioxime

2.(d) Absorption spectra of monoximes :

The absorption spectra of the oximes of 2-cyano glyoxylic acid derivatives were investigated in different solvents in the ultraviolet region (vide table X). These are presented in figs. 2, 3 and 4; the wave-length maxima (λ_{max}) and the corresponding molar extinction coefficients (E_m) for them are presented in table XXVIII.

The intense absorption band (K) at 228-34 mμ observed in case of aqueous and alcoholic solutions of the oximes of 2-cyano glyoxylic acid derivatives is considered to be a $\pi \longleftrightarrow \pi^*$ transition and is attributed to the crossed conjugated system

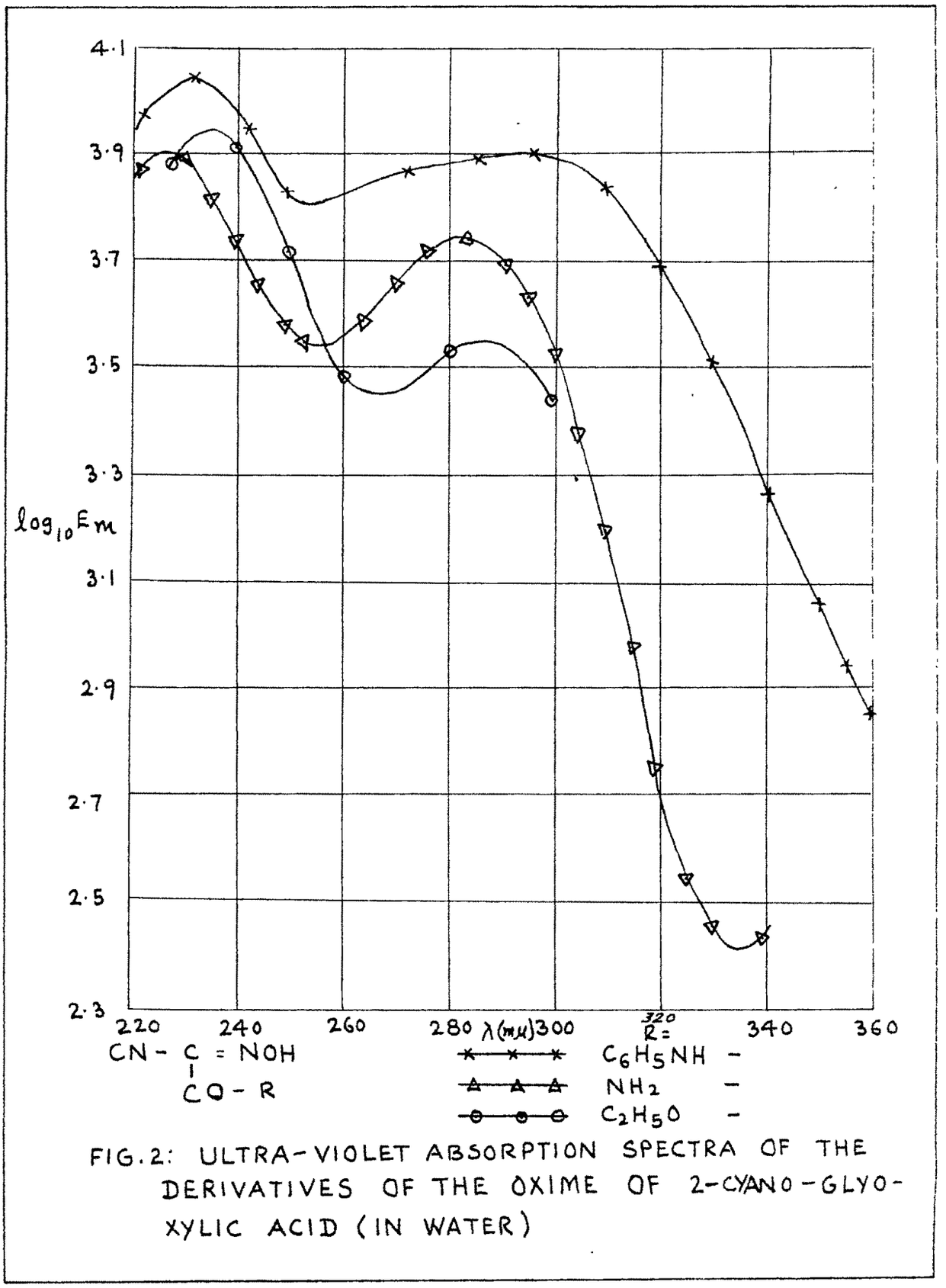


FIG. 2: ULTRA-VIOLET ABSORPTION SPECTRA OF THE DERIVATIVES OF THE OXIME OF 2-CYANO-GLYOXYLIC ACID (IN WATER)

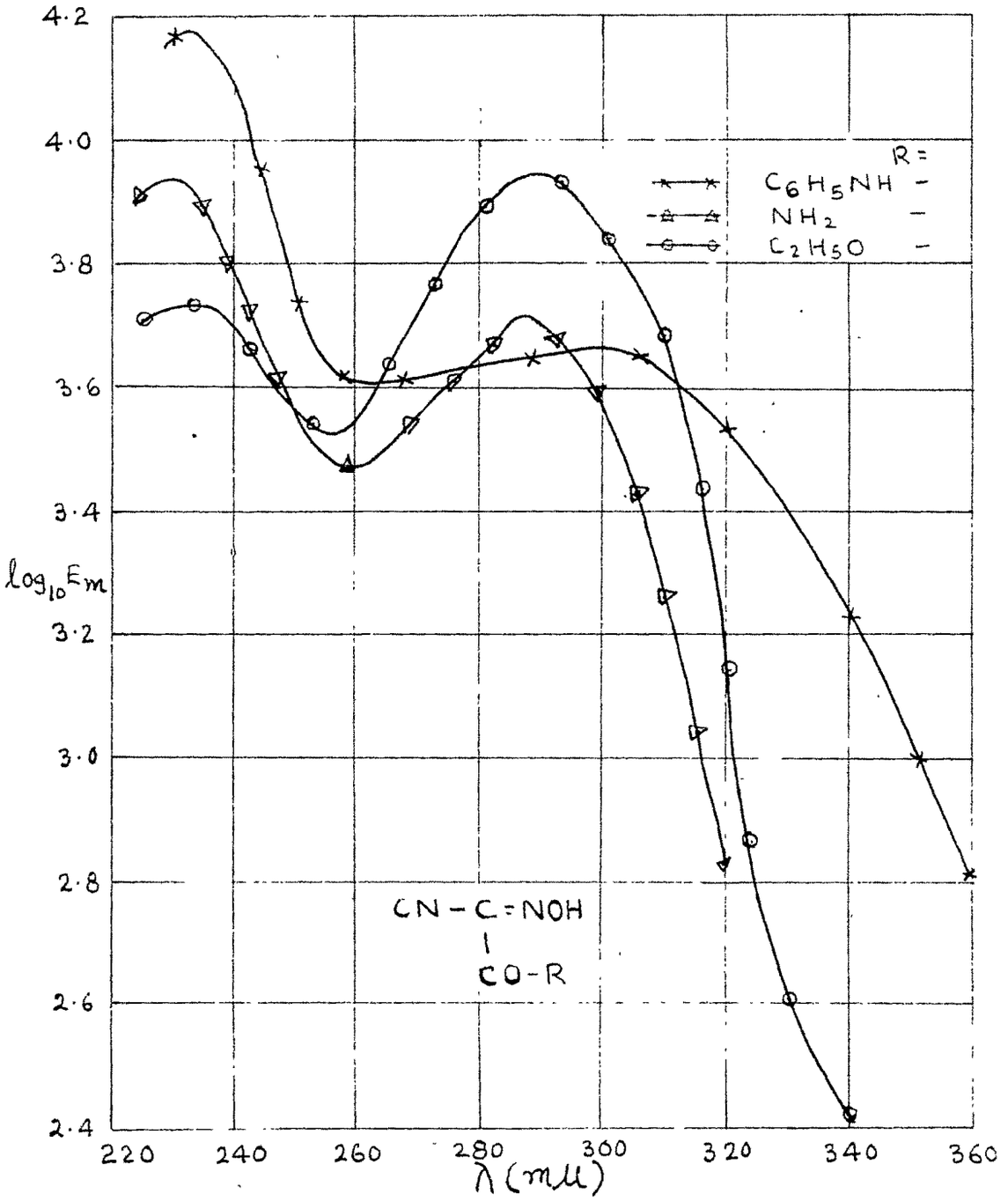
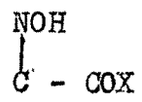


FIG. 3: ULTRA-VIOLET ABSORPTION SPECTRA OF THE DERIVATIVES OF THE OXIME OF 2-CYANO GLYOXYLIC ACID (IN METHANOL)

TABLE XXVIII

Ultra-violet absorption spectra of the oximes of 2-cyano glyoxylic acid derivatives



No.	Substance X =	in water λmax (mμ)	E_m	in water λmax (mμ)	E_m	in methanol λmax (mμ)	E_m	in methanol λmax (mμ)	E_m
1.	NHC_6H_5	231-32	11685	294-98	8590	233-34	22970	298-99	4710
2.	NH_2	228	7400	283-85	6850	229-30	8560	284-86	5100
3.	OC_2H_5	232-34	3500	284-85	12150	232-33	5080	288-90	10800

$$\begin{array}{l} C \equiv N \\ | \\ C = NO - \\ | \\ -C = O \end{array}$$

The absorption bands of 2,3-butane dione dioxime and 2,3-dioxobutyranilide dioxime in methanolic solutions are at 227 mμ and 236-38 mμ respectively. Since the absorption band of the oxime of 2-cyano glyoxylanilide in alcohol is at 233-34 mμ, it is considered that extension of the conjugated system is weaker in oxime-nitrile than in dioxime. It may be attributed to (i) the partial localisation of π -election system of C ≡ N group, (ii) differences in the hybrid orbitals used and the π -bond formation in the case of nitrile and oxime groups and / or (iii) steric differences in the length of the chromophoric system.

No shift is observed when the absorption band of the oxime of 2-cyano glyoxylamide is compared with that of 2,3-butanedione monoxime. Hence it may be considered that the conjugative effect of carbonyl group in 2,3-butanedione monoxime is similar to that of the nitrile and amide groups in the oxime of 2-cyano glyoxylanilide. Further the bands of the oximes of ethyl 2-cyano-glyoxylate and of 2-cyano glyoxylanilide show red shift when compared with the band of the oxime of 2-cyano glyoxylamide and may be considered to indicate increase in conjugation in those systems.

When we compare the absorption bands of the oximes of 2-cyano glyoxylic acid derivatives in methanol with those in water, we find that the band undergoes a slight blue shift as the polarity of the solvent is increased. This is largely indicative of the absence of solute-solvent interaction.

The second band (X) observed in the spectra of 2-oximes of 2,3-dioxobutyric acid derivatives is also observed in the spectra of the oximes of 2-cyano glyoxylic acid derivatives. The band is observed at 283-99 mμ in aqueous and alcoholic solution, and may be attributed to their ionic tautomers.

The band is less intense in methanolic solution than in aqueous solution. This might result from the decrease in ionisation of the oxime group in alcoholic solution and the shift of the equilibrium.

2.(e) Reactions with metal ions :

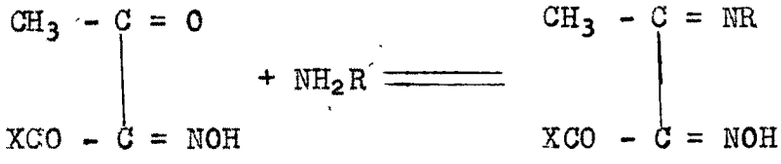
The oximes of 2-cyano glyoxylic acid derivatives gave characteristic reactions with iron (II), cobalt (II), nickel (II), copper (II), etc. It was observed that 2-oximes of 2,3-dioxo-butyric acid derivatives give greenish precipitates with nickel (II) (197,208). It is now observed that the oximes of 2-cyano glyoxylic acid derivatives give yellowish colouration or precipitates. It is further observed that the oxime of "mono-derivatives" give colourations only with various metal ions whereas the oxime of "bis-derivative" gives precipitates with

most of these metal ions. This may be attributed to the decreased solubility of the oxime of " bis-derivative " and its polymeric metal complexes. These reactions were not investigated further. The preparation of metal complexes of the oxime of N,N'-ethylene bis(cyanoacetamide) and of the oxime of 2-(hydroxyamidino) glyoxylamide was attempted; the products obtained were, however, unsatisfactory and need further investigation. Incomplete work on the complexes is not recorded in the experimental part.

3. vic-Oxime-imines :

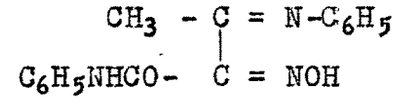
3.(a) Structures of vic-oxime-imines :

vic-Oxime ketones (I to III) prepared earlier were converted into vic-oxime-imines by treating them with primary amines. The reaction is

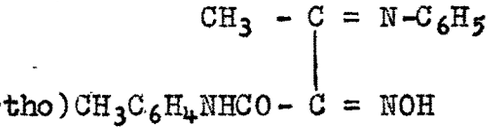


As a result, the products of the following structures are formed :

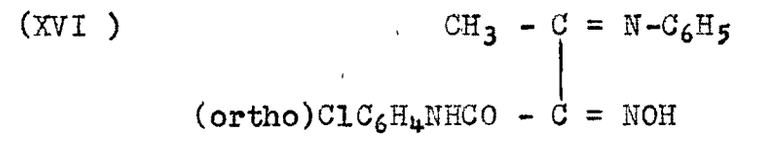
(XIV)



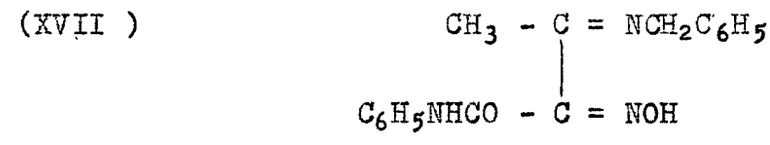
(XV)



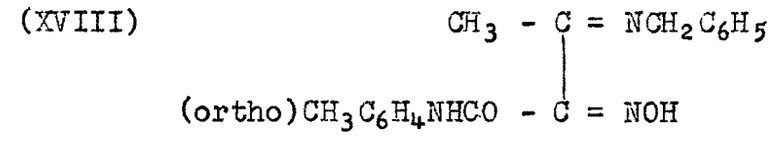
(XVI)



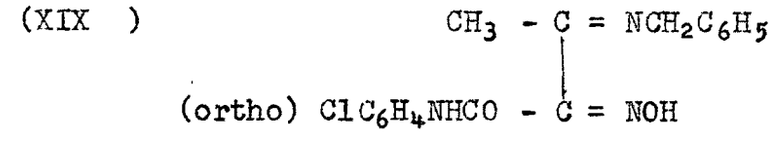
(XVII)



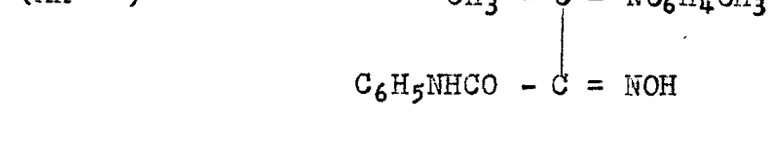
(XVIII)



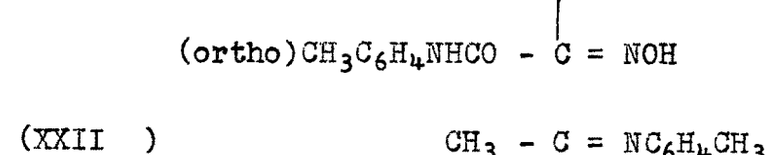
(XIX)



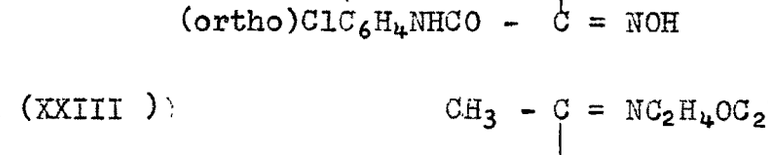
(XX)



(XXI)



(XXII)



(XXIII)

(XXIV) $CH_3 - C = NC_6H_4OC_2H_5$ (para)

(ortho)$CH_3C_6H_4NHCO - C = NOH$

(XXV) $CH_3 - C = NC_6H_4OC_2H_5$ (para)

(ortho)$ClC_6H_4NHCO - C = NOH$

These structures are in accord with analysis and eliminate the possible formation of

$CH_3 - C(NHR)_2$

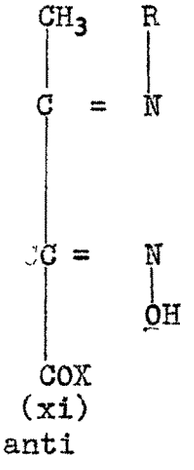
$XCO - C = NOH$

(x)

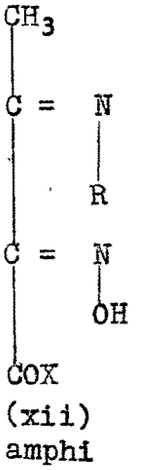
It may be noted that all attempts to prepare the Schiff bases from N-methyl 2,3-dioxobutyranilide 2-oxime failed.

3.(b) Stereoisomerism of vic-oxime-imines :

Since vic-oxime-ketones under investigation are shown to have anti-ketone (syn-amide) structure, their Schiff bases could have the following isomeric forms :



(xi)
anti



(xii)
amphi

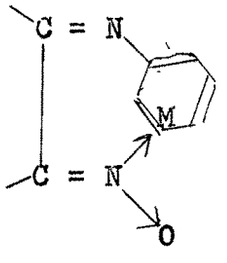
Anti-configuration is atrributed to the products on the basis of the following considerations :

(i) Oximes of the vic-oxime-ketones under investigations are shown to have anti-configuration (187) ;

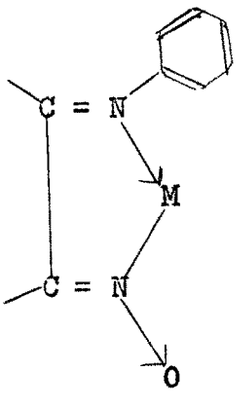
(ii) Phenyl and phenyl methyl hydrazones of the vic-oxime-ketones (I to III) are found to have anti-configuration (188) ;

(iii) It has been shown (141,194,195) that when one of the oxime group in a vic-dioxime is replaced by an imino group, the resulting compound would form complexes with metal ions in the same manner as vic-dioximes and may be assumed to have same isomeric nature ;

(iv) Amphi structure would not form metal complexes with transition metal ions due to the steric effect as shown below :



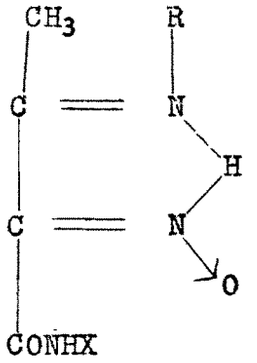
Anti-structure, however, can form the complexes



The ligands under investigation form complexes with transition metal ions and may be assumed to have anti-configuration.

Hence the Schiff bases from N-aryl 2,3-dioxo-butyramide 2-oxime may be represented as having anti-structure (xi).

Oxime group is shown to be hydrogen-bonded in vic-oxime-ketones. It is assumed that it is chelated in these compounds also. Hence they may be better represented as



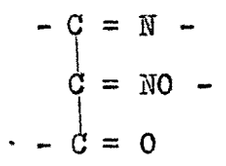
(xiii)

3.(c) Ultra-violet absorption spectra of vic-oxime-imines:

The ultra-violet absorption spectra of vic-oxime imines in methanol and alkali solutions are investigated (table-XI). The absorption spectra of these compounds are presented in figs 4 to 9 and the wave-length maxima (λ max) and their corresponding molar extinction coefficients (E_m) are given in table XXIX.

In figs. 4 to 6, the curves for the Schiff bases from benzyl amine are markedly different from those of Schiff bases from aniline, p-toluidine and p-phenetidine. The difference may be attributed mainly to the presence of CH_2 group in between the conjugated system and the phenyl ring in the Schiff bases from benzyl amine. Thus the CH_2 group insulates the phenyl ring from the rest of the conjugated system (OC - C = C -) in the Schiff bases from benzyl amine. It may be noted here that the Schiff bases from benzyl amine are distinctly coloured in comparison to the Schiff bases from aniline, p-toluidine and p-phenetidine.

The intense absorption band (K) at 223-36 mμ observed in case of the Schiff bases from N-aryl 2,3-dioxo-butyramide 2-oxime in methanol is considered to be a $\pi \longleftrightarrow \pi^*$ transition and is attributed to the crossed conjugated system.



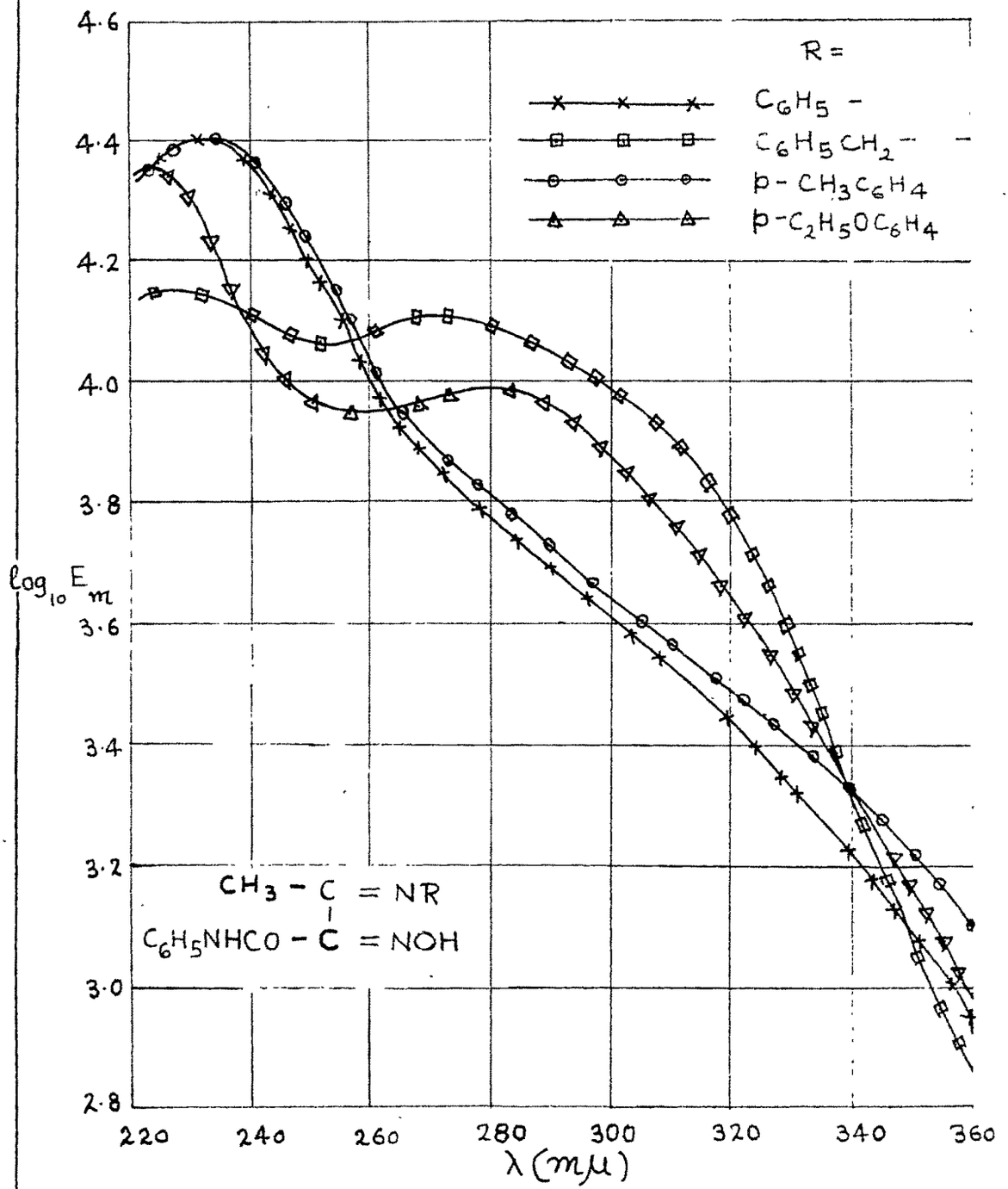


FIG. 4: ULTRA-VIOLET ABSORPTION SPECTRA OF THE SCHIFF BASES FROM 2,3-DIOXO-BUTYRANILIDE 2-OXIME (IN METHANOL)

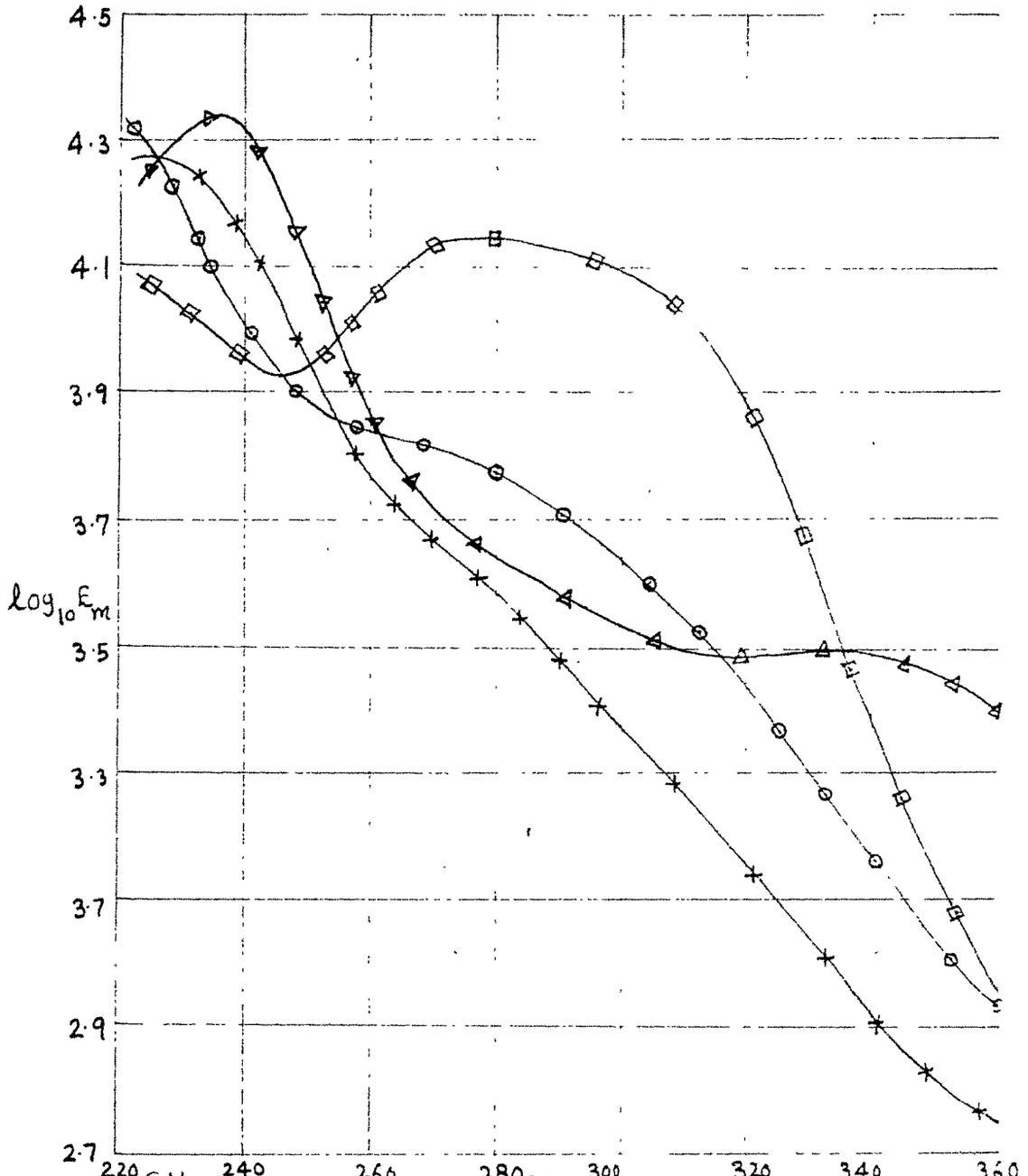
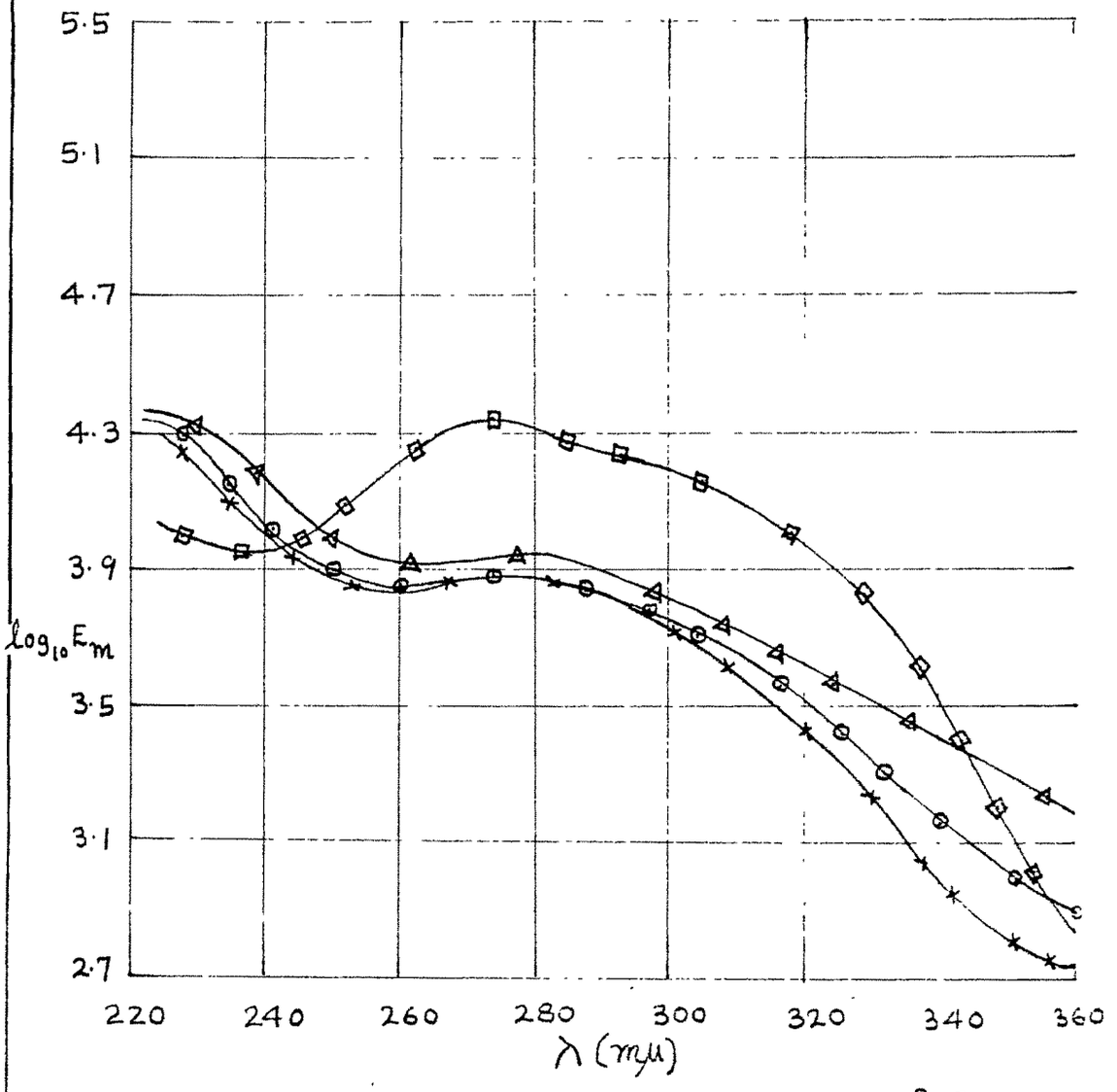


FIG. 5: ULTRA-VIOLET ABSORPTION SPECTRA OF THE SCHIFF BASES FROM 2,3-DIOXO-o-BUTYROTOLUIDIDE 2-OXIME (IN METHANOL)



$CH_3 - C = NR$
$o\text{-}ClC_6H_4NHCO - C = NOH$

R =
C_6H_5 –
$C_6H_5CH_2$ –
$p\text{-}CH_3C_6H_4$ –
$p\text{-}C_2H_5OC_6H_4$ –

FIG: 6 : ULTRA-VIOLET ABSORPTION SPECTRA OF THE SCHIFF BASES FROM 2'-CHLORO 2,3-DIOXO-BUTYRANILIDE 2-OXIME (IN METHANOL)

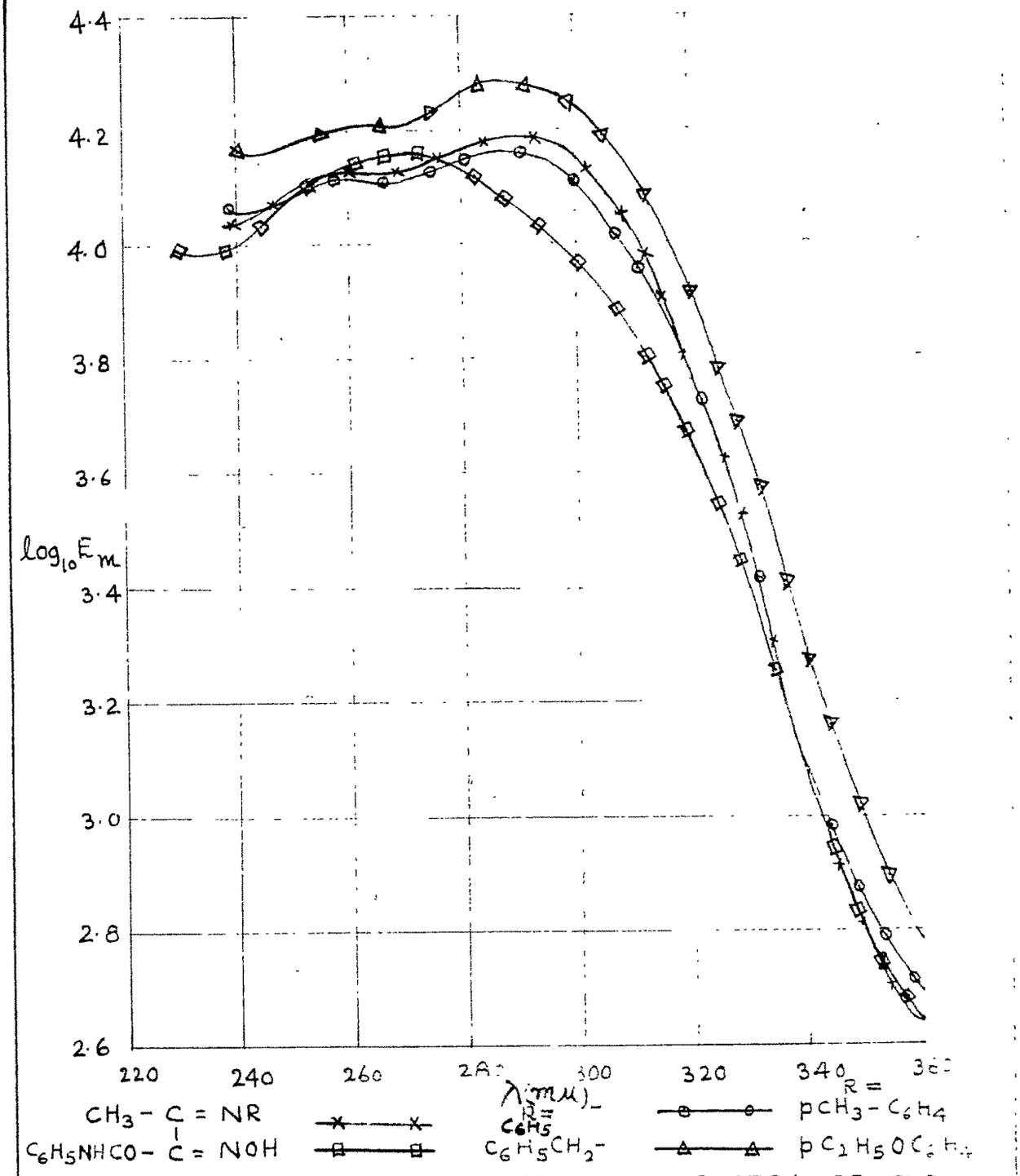


FIG. 7: ULTRA-VIOLET ABSORPTION SPECTRA OF THE SCHIFF BASES FROM 2, 3 - DIOXO - BUTYRANILIDE 2- OXIME (IN ALKALI SOLUTION)

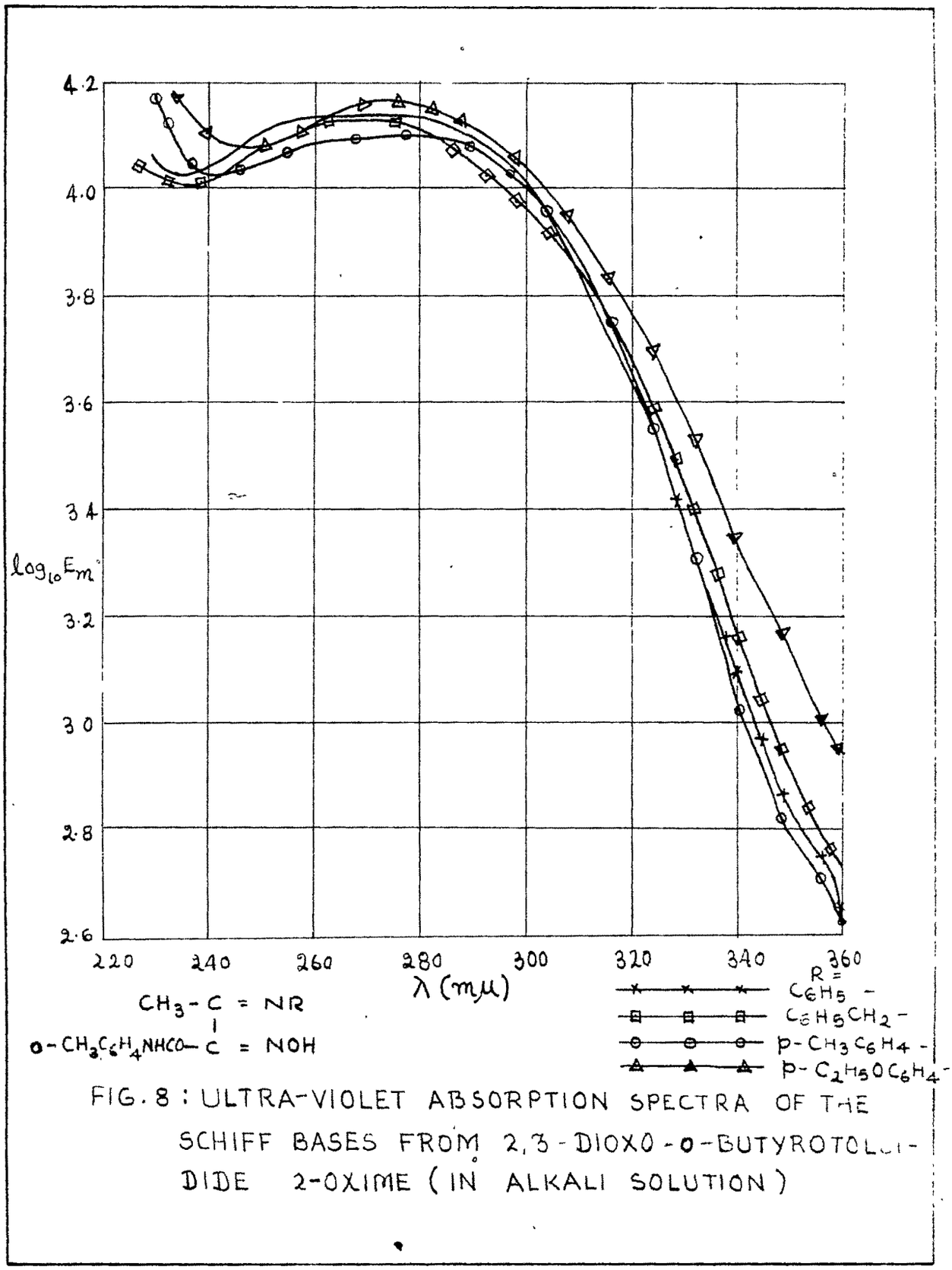
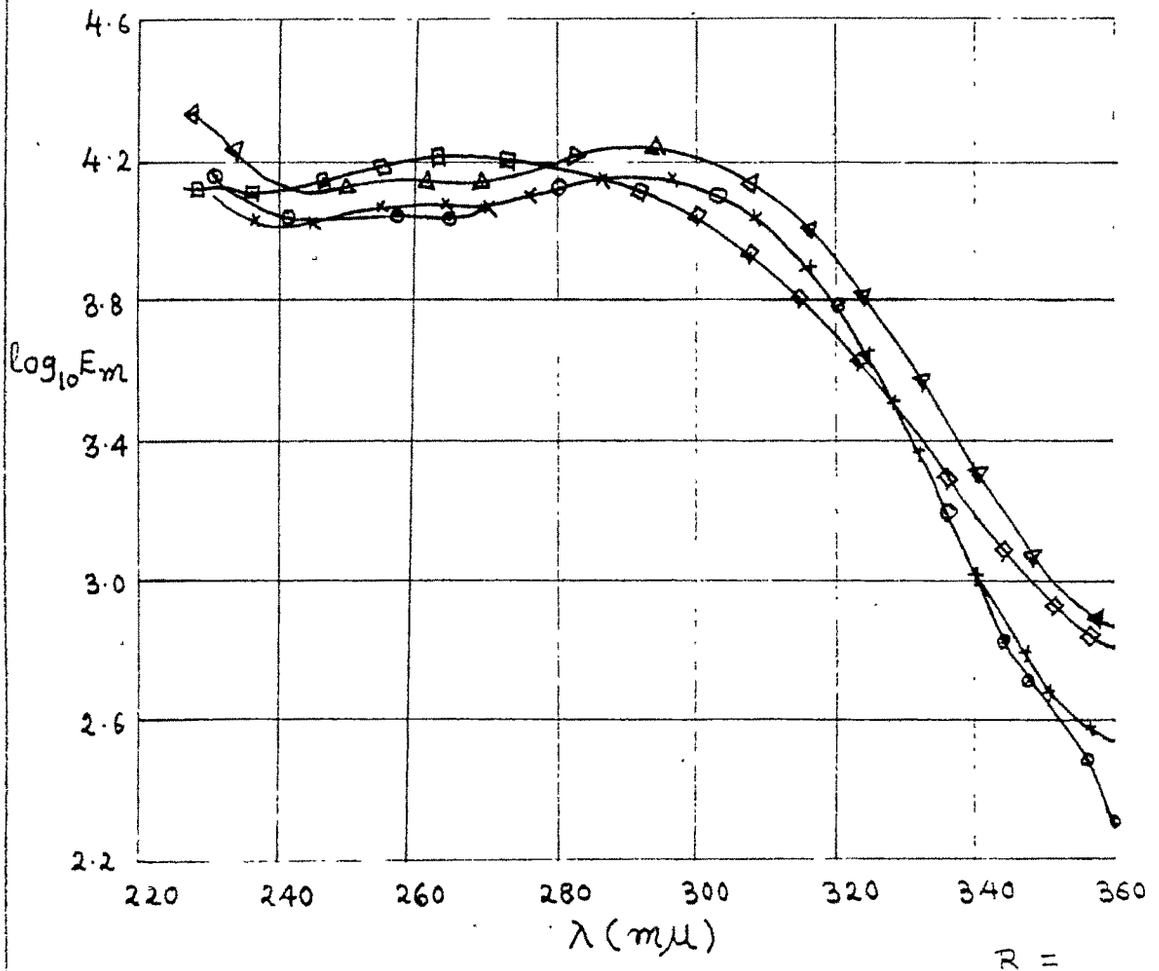


FIG. 8 : ULTRA-VIOLET ABSORPTION SPECTRA OF THE SCHIFF BASES FROM 2,3-DIOXO-O-BUTYROTOLUI-DIDE 2-OXIME (IN ALKALI SOLUTION)



$CH_3-C(=NR)-C(=NOH)-CONHC_6H_4Cl$-o

R =

- C_6H_5
- $C_6H_5CH_2$
- p-$CH_3C_6H_4$
- p-$C_2H_5OC_6H_4$

FIG. 9 : ULTRA-VIOLET ABSORPTION SPECTRA OF SCHIFF BASES FROM 2-CHLORO 2,3-DIOXO-BUTYRANILIDE 2-OXIME (IN ALKALI SOLUTION)

TABLE XXIX

Ultra-violet absorption spectra of vic-oxime-imines

$CH_3 - C = N - R$

$XNHCO - C = NOH$

No	Substance R =	X	in methanol λ_{max} (mμ)	E_m	in methanol λ_{max} (mμ)	E_m	in alkali λ_{max} (mμ)	E_m	in alkali λ_{max} (mμ)	E_m
(1)	(2)		(3)		(4)		(5)		(6)	
1.	C_6H_5	C_6H_5	231-32	24450			258	11720	290-92	13520
2.	C_6H_5	o-$CH_3C_6H_4$	223	18970			256	13530	276	13770
3.	C_6H_5	o-ClC_6H_4			274-78	7630	256	13500	290	15720
4.	$C_6H_5CH_2$	C_6H_5	226	14660	270-72	12560			268-70	14690
5.	$C_6H_5CH_2$	o-$CH_3C_6H_4$			272-74	14410			270	14180

1	2	3		4		5		6	
6.	$C_6H_5CH_2$	o-ClC_6H_4		276	21750			270	16570
7.	p-$CH_3C_6H_4$	C_6H_5	232-33	25310		256-62	13050	286-88	14730
8.	p-$CH_3C_6H_4$	o-$CH_3C_6H_4$						280	12920
9.	p-$CH_3C_6H_4$	o-ClC_6H_4		277	7870	258-60	11960	290	15020
10.	p-$C_2H_5OC_6H_4$	C_6H_5	224	21220	280-81	8740	264	16250	286	19490
11.	p-$C_2H_5OC_6H_4$	o-$CH_3C_6H_4$	234-36	3250	324	21830			272	14750
12.	p-$C_2H_5OC_6H_4$	o-ClC_6H_4			276-79	8890	258	15090	290	18150

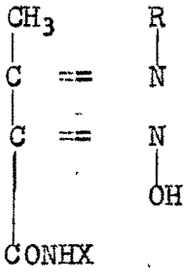
Since the absorption band of 2,3-dioxobutyranilide 2-oxime in alcohol is at 236-38 mμ, the replacement of the oxime group by the imine group causes a blue shift of about 10-12 mμ. Thus the OH group appears to have considerable auxochromic effect. It has been observed by Desai (188) that K-bands of the monoxime and dioxime of 2,3-butane dione and also those of 2,3-dioxobutyranilide 2-oxime and 2,3-dioxime in alcohol had almost the same value of wave-length for each pair. It indicates the similarity of the two chromophores. Hence it is suggested that the replacement of conjugated C = O by C = N weakens conjugation. If the phenyl group extends the conjugation of the crossed conjugated system rather than being insulated, the band is shifted 5-6 mμ to the red. The shift is smaller, however, in comparison to that due to the introduction of OH or NHPh to the - C = N - , and may indicate that the phenyl ring is not coplanar with the remaining conjugated system.

Dave and Talati (186) observed a blue shift on the introduction of ortho substitutents (Cl, CH_3) in the anilide ring system and attributed it to the "side-chain" effect on the absorbing system in the dioxime of N-aryl 2,3-dioxobutyramide in solution. A similar shift has been observed in the spectra of the Schiff bases from N-aryl 2,3-dioxobutyramide 2-oxime and may be attributed to the "side chain" effect on the absorbing system. It may be noted here that the spectrum of the Schiff base from

2,3-dioxo o-butyr)-o-toluidide 2-oxime and aniline has a different nature.

The introduction of a para substituent in the phenyl ring system attached to the imine group would normally extend the conjugation if the ring is coplanar with the remaining conjugated system. Such extension of conjugation is not observed in these spectra and hence it may be assumed that the phenyl ring attached to the imine group is not coplanar with the absorbing system suggested earlier.

The second band (X) is observed at 270 - 81 mμ in some of these spectra. A similar band was observed in the spectra of vic-oxime-ketones and was attributed by Desai (188) to the existence of the ionic tautomer of the conjugated oxime. In the case of the Schiff bases, cis-trans isomers would also cause a difference in the spectra. It may be noted here that some of the Schiff bases were investigated for their phototropic properties and were found to be non-phototropic. Hence the Schiff bases may be considered to have a stable trans configuration



Hence the band may be attributed to the ionic tautomer of the conjugated oxime in these compounds also.

In the alkali solution X-band is observed in 268-92 mμ region. In case of Schiff bases from benzyl - amine a blue shift is observed for the band in alkali solution in relation to one in alcohol solution. On the other hand a red shift or a new band is observed in the spectra of Schiff bases from aniline,p-toluidine or p-phenetidine in alkali solution in relation to those in methanol solution. It is also observed that red shift is associated with increased intensity of the band and may be attributed to the increased ionisation of the system.

In the alkali solution K-band is not observed in the region 223-36 mμ ; instead a new band is observed in the 254-64 mμ region. It has about half the intensity of the corresponding K-band observed in methanol solution.

3(d) Infra-red spectra of vic-oxime-imines :

Since the work on infra-red spectra was carried out at another place (Bombay) all compounds could not be investigated. The infra-red spectra of Schiff bases from 2,3-dioxo-butyranilide 2-oxime and aniline(and benzylamine) were investigated by potassium bromide pellet technique (vide Tables XV and XVI). The two compounds exhibit wide differences in their spectra. The Schiff base from 2,3-dioxobutyranilide and aniline exhibits two bands at about 3.10 and 3.14 μwhich may be attributed to the anilide NH st.frequencies. The double bands may be attributed to the intermolecular H-bonding (association)

involving anilide group. Further, the broad band observed at about 3.07 μ is attributed to the H-bonded oxime OH group. This is in accord with earlier observations. Borello and Henri (100) and Sadler (25) observed a band at about 3.12 μ for the oxime OH. Palm and Werbin (23) also observed a band at about 3.08 μ and attributed it to the associated oxime OH. The Schiff base from 2,3-dioxo-butyranilide and benzylamine exhibits a band at about 3.10 μ and is attributed to the anilide NH. st.frequency. The oxime band is not observed in the pellect-spectrum. It is suggested that the oxime group in this compound is strongly H-bonded.

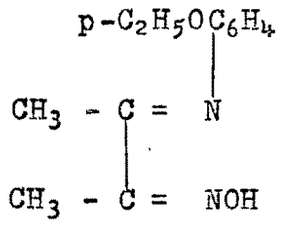
3(e) Reactions with metal ions :

The vic-oxime imines under investigations give characteristic reactions with Fe(II), Co(II), Ni(II), Cu(II), Pd(II) and Co(III). These reactions are similar to those of the corresponding vic-dioximes investigated by Talati (187) and of the corresponding vic-oxime-hydrazones investigated by Desai (188). These reactions were investigated in details ; the products were isolated in most cases and studied to elucidate their nature.

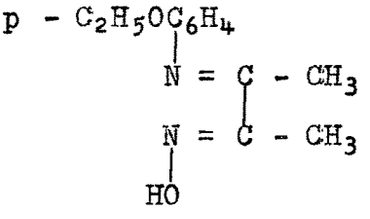
3(f) Schiff base from 2,3-butane dione oxime :

For the purpose of comparative studies, an attempt was made to prepare similar ligands by treating 2,3-butane dione oxime with aromatic amines. As a result the following Schiff base was prepared :

(XXVI)



Since the oxime and phenyl hydrazone of 2,3-butane dione oxime are shown to have anticonfiguration (187 ; 188) it is considered that the Schiff base may also have a similar anticonfiguration. Hence it may be represented as



Its ultra-violet absorption spectrum was investigated in methanol and in alkali solutions (table XIV). The absorption spectra are presented in Fig. 10. Its wave-length maxima and the corresponding molar extinction coefficients are

in methanol		in alkali solution	
λ max (mμ)	E_m	λ max (mμ)	E_m
236-37	23060	232-34	13750
290-92	3260	272	16680
326-28	2948	312**	4700

** inflection

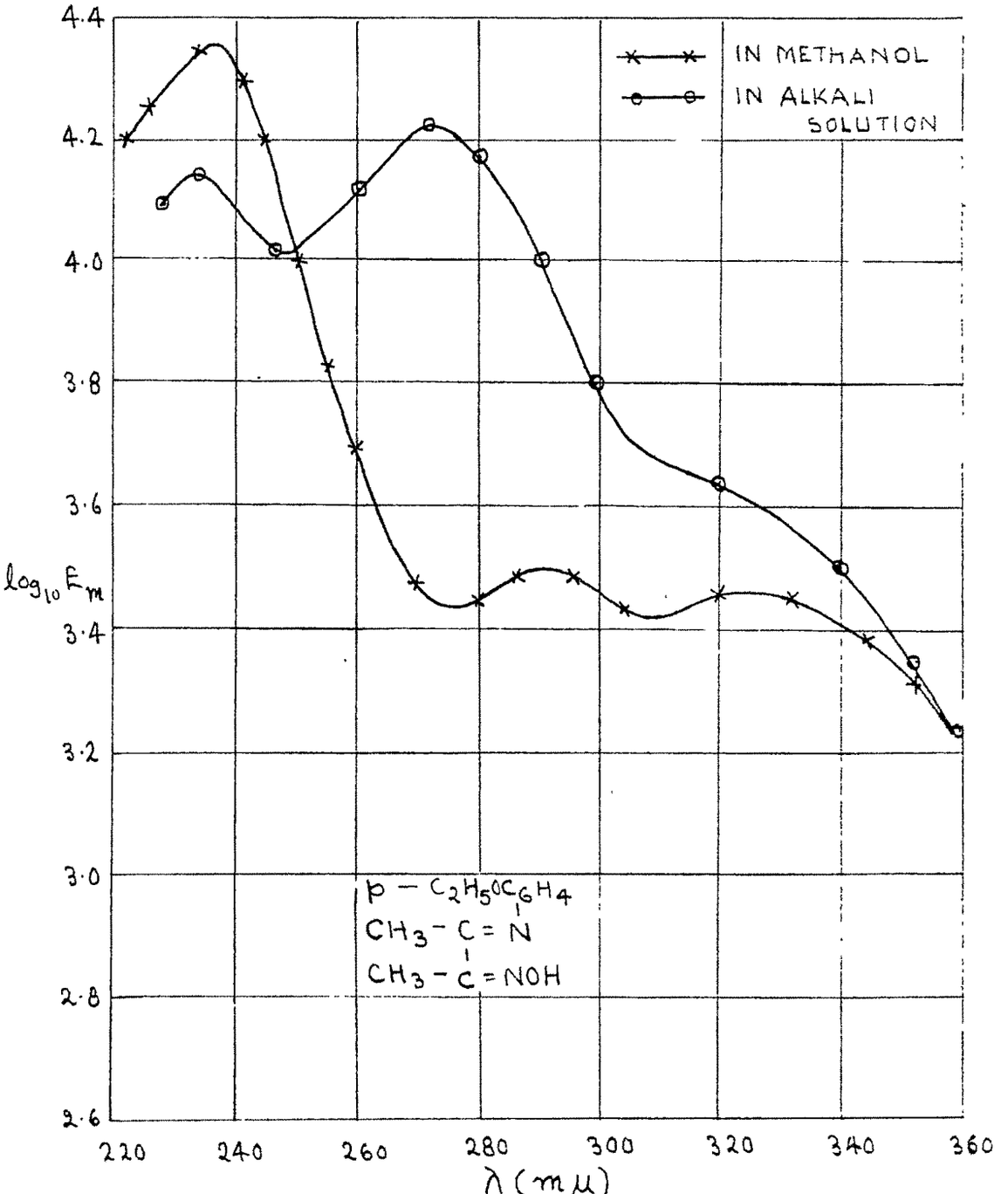


FIG. 10 ULTRA-VIOLET ABSORPTION SPECTRA OF THE SCHIFF BASE FROM 2,3-BUTANE DIONE MONOXIME AND p-PHENETIDINE IN METHANOL AND ALKALI SOLUTION

The intense absorption band at 236-37 mμ in methanol solution is considered to be a $\pi \longleftrightarrow \pi^*$ transition and is attributed to the conjugated system

$$\begin{array}{l} -C=N- \\ -C=NO- \end{array}$$

It is suggested earlier that the replacement of conjugated C = O by C = N weakens conjugation and that the attachment of the phenyl ring to N causes a weak extension of the conjugation, shifting the band 5-6 mμ to the red. The red shift observed in the present case is about 9-10 mμ from the band of 2,3-butane dione oxime at 227 mμ.

The X-band is split into two weak bands at 290-92 and 326-28 mμ in methanol solution. This band structure is intensified in alkali solution and may be attributed to the ionic tautomer of the conjugated oxime.

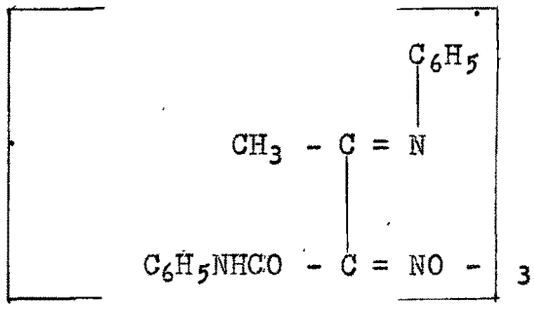
Its reactions with transition metal ions were investigated. Characteristic colourations were obtained with Co(II) and Ni(II), and precipitates were obtained with Cu(II) and Fe(II). The complexes with Cu(II) and Fe(II) were prepared and studied.

4. Complexes of nickel with vic-oxime-imines:

4(a) Complexes of nickel (formed in absence of ammonia) :

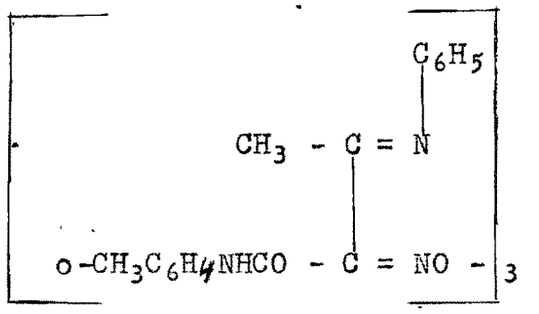
The products obtained by treating nickel chloride with the Schiff bases from N-aryl 2,3-dioxobutyramide 2-oxime are formulated, on the basis of analysis, as follows :

(XXVII)



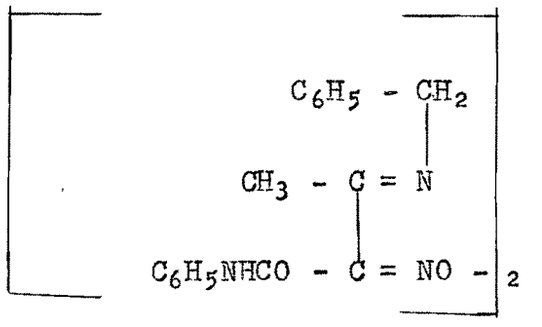
$Ni_2(OH)(H_2O)_3$

(XXVIII)



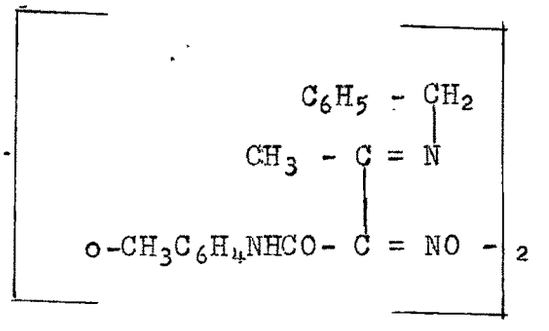
$Ni_2(OH)(H_2O)_3$

(XXXIX)



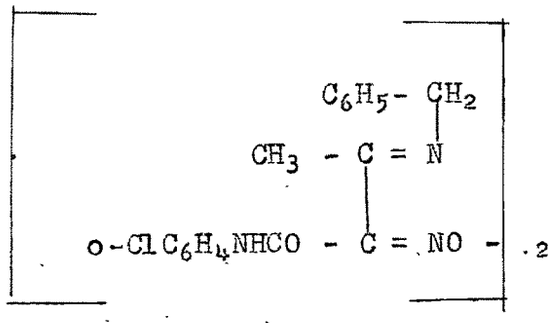
Ni

(XXX)



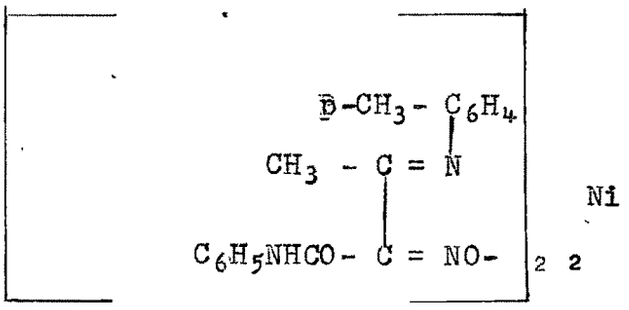
Ni

(XXXI)

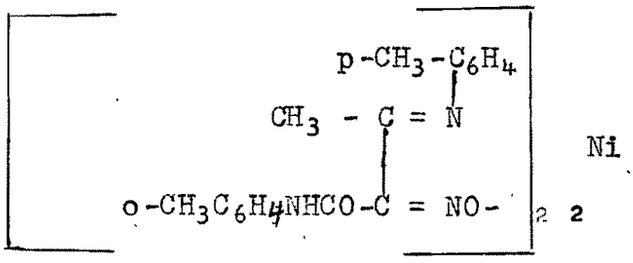


Ni

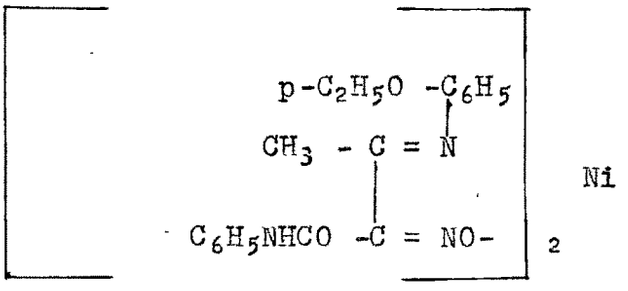
(XXXII)



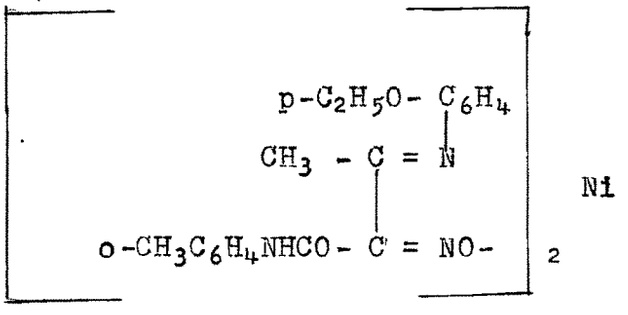
(XXXIII)



(XXXIV)

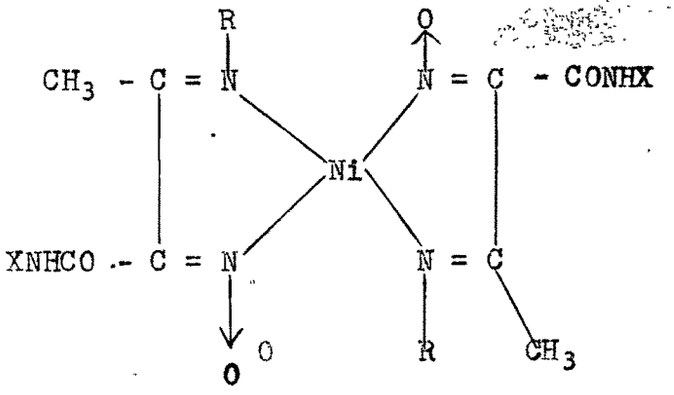


(XXXV)

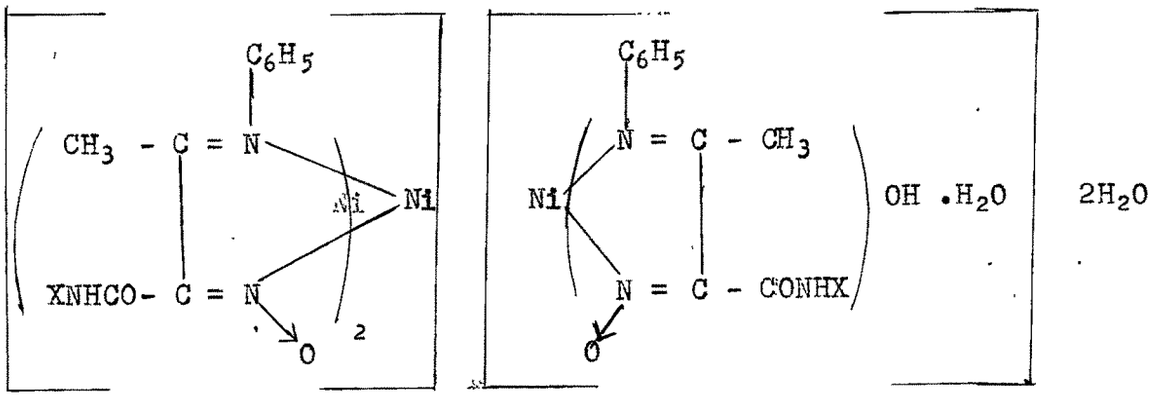


They are soluble in alcohol, acetone, ether, carbon tetrachloride, etc. It is suggested that they are complex compounds or chelates rather than salts. Electrical conductivity of nickel complexes of the Schiff bases from 2,3-dioxobutyranilide 2-oxime and aniline or benzylamine in methanol was investigated (vide table- XVIII).

It was observed that they are non-ionic in solution. Hence the products may be represented as



R =	X =
$C_6H_5CH_2$-	C_6H_5-, o-$CH_3C_6H_4$-, o-ClC_6H_4-
p-$CH_3C_6H_4$-	C_6H_5-, o-$CH_3C_6H_4$-
p-$C_2H_5OC_6H_4$-	C_6H_5-, o-$CH_3C_6H_4$-



X = C_6H_5-; o-$CH_3C_6H_4$-

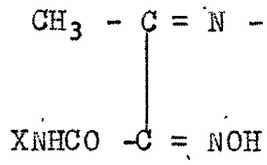
The ultra-violet absorption spectra of the nickel complexes were investigated. However, it was not possible to obtain solutions uniformly and hence no attempt

is made to calculate molar extinction coefficients. The wave-length maxima (λ max) for these complexes in methanol are presented in table XXX.

TABLE XXX

Ultra-violet absorption spectra of nickel complexes of vic-oxime imines

Reagent :



No.	R =	X =	Formula of the complex	in methanol λ max (mμ)	λ max (mμ)
1.	C_6H_5	C_6H_5	$Ni_2C_{48}H_{49}O_{10}N_9$	244-46	312
2.	$C_6H_5CH_2$	C_6H_5	$NiC_{34}H_{32}O_4N_6$	246	304-8
3.	p-$CH_3C_6H_4$	C_6H_5	$NiC_{34}H_{32}O_4N_6$	246	308
4.	p-$C_2H_5OC_6H_4$	C_6H_5	$NiC_{36}H_{36}O_6N_6$	248	312
5.	C_6H_5	o-$CH_3C_6H_4$	$Ni_2C_{51}H_{61}O_{13}N_9$	243-44	314-16
6.	$C_6H_5CH_2$	o-$CH_3C_6H_4$	$NiC_{36}H_{36}O_4N_6$	242-44	312
7.	p-$CH_3C_6H_4$	o-$CH_3C_6H_4$	$NiC_{36}H_{36}O_4N_6$	244-46	316
8.	p-$C_2H_5OC_6H_4$	o-$CH_3C_6H_4$	$NiC_{38}H_{40}O_6N_6$	238-40	308-12
9.	$C_6H_5CH_2$	o-ClC_6H_4	$NiC_{34}H_{30}O_4N_6Cl_2$	248-50	314-18

The absorption spectra of these complexes in methanol are presented in figs. 11 and 12.

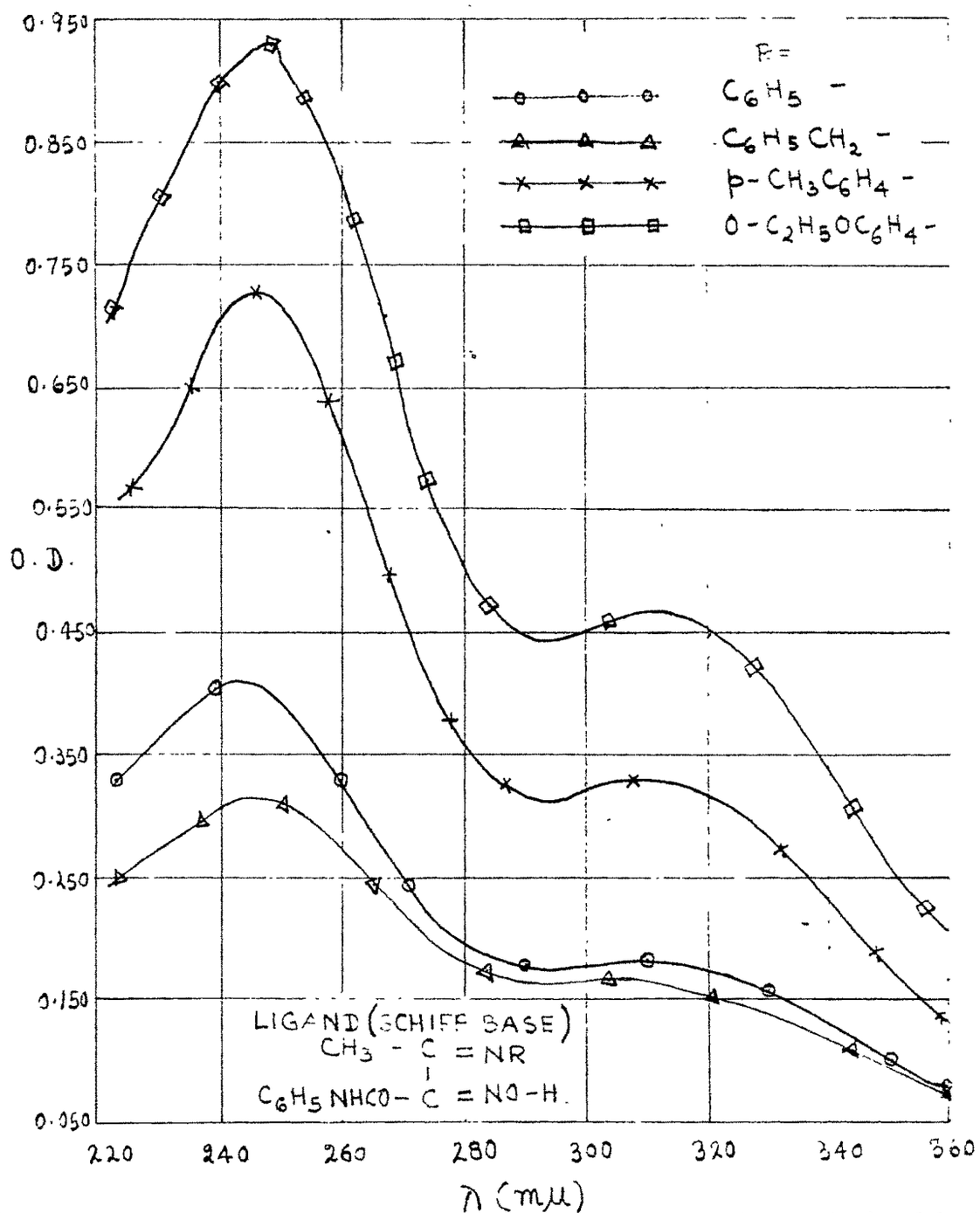


FIG. II : ULTRA-VIOLET ABSORPTION SPECTRA OF THE NICKEL (II) COMPLEXES OF THE SCHIFF BASES FROM 2,3- DIOXO- BUTYRANILIDE 2-OXIME (IN METHANOL)

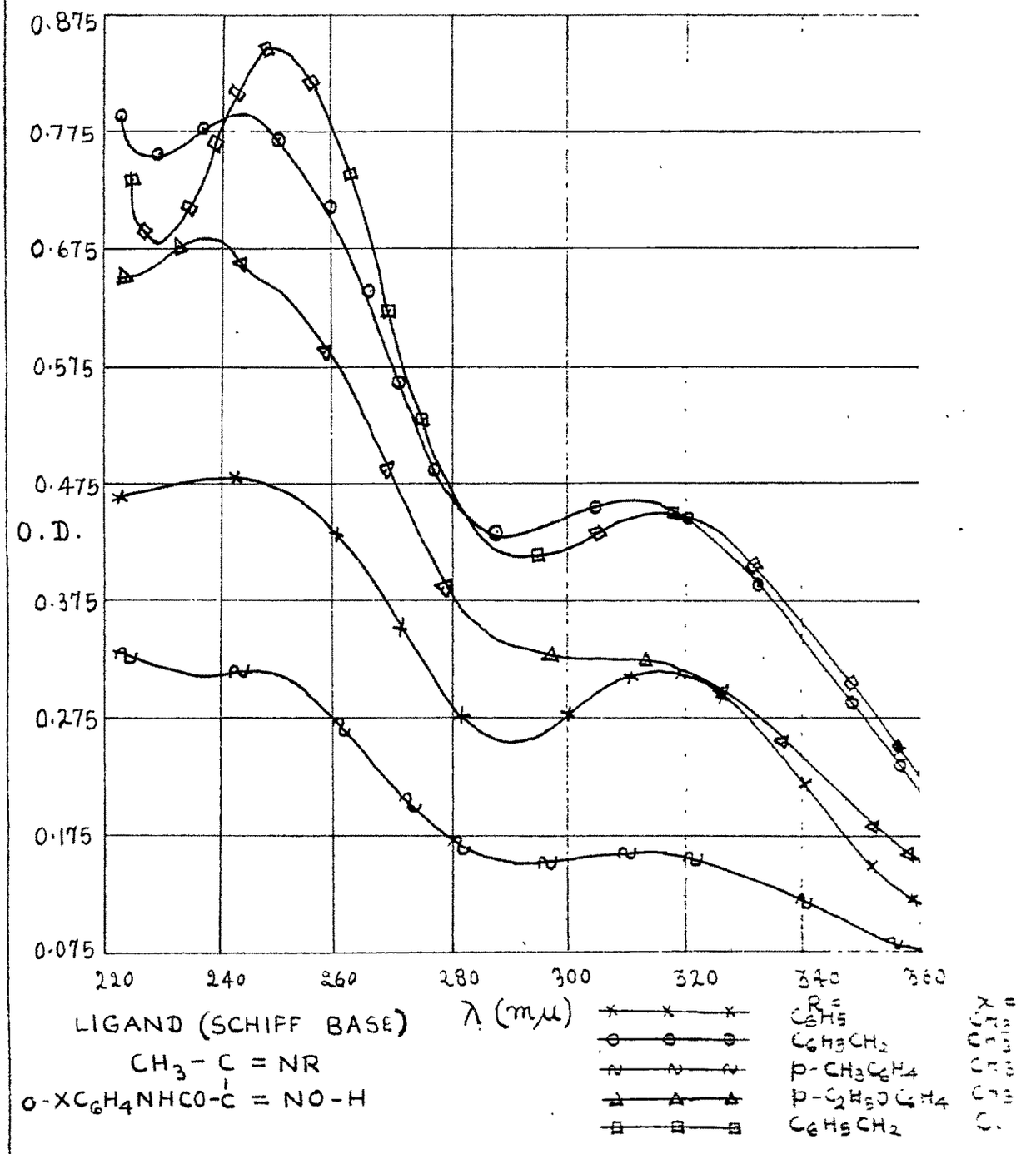


FIG. 12: ULTRA-VIOLET ABSORPTION SPECTRA OF THE NICKEL (II) COMPLEXES OF THE SCHIFF BASES FROM N-ARYL 2,3-DIOXO-BUTYRAMIDE 2-OXIME (IN METHANOL)

The results indicate that the spectra of these complexes are widely different from those of the corresponding ligands. Hence it is suggested that the bonding in these complexes is essentially co-valent. It is noted that two bands are observed in the spectra of the complexes of all the ligands under investigation, but not in the spectra of all the ligands. Further the separation of the two bands in the spectra of complexes is greater than that in the spectra of ligands in alkali solutions.

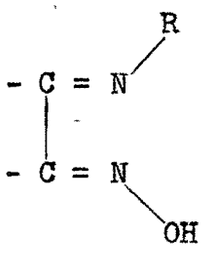
The infra-red spectra of nickel complexes of the Schiff bases from 2,3-dioxobutyranilide 2-oxime and aniline (and benzylamine) were investigated (vide tables XV, XVI). The st.frequency for oxime OH group is absent in these spectra.

All these data lead us to believe that the complexes NiR_2 where R may be the anion of the ligand molecule may have structural resemblances with that of nickel dimethylglyoximate and may have coplanar distribution of ligand nitrogen atoms attached to nickel. Such resemblances have been observed earlier.

Pfeiffer (141) prepared nickel complex of the Schiff base from 2,3-butanedione monoxime and methylamine and suggested similarity of its structure to that of nickel dimethyl glyoximate.

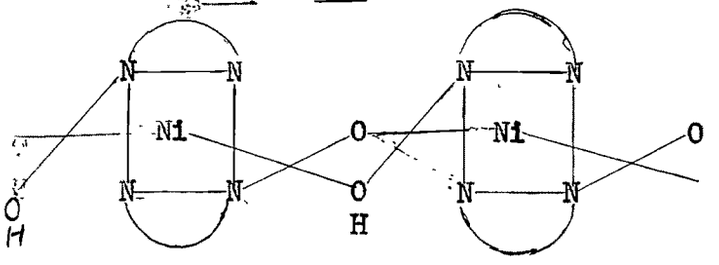
Talati (187) prepared nickel complex of the dioxime of 2,3-dioxobutyranilide and Desai (188) obtained

nickel complex of the phenyl hydrazone of 2,3-dioxo-butyranilide 2-oxime. Both complexes were diamagnetic and their structures were believed to be similar to that of nickel dimethyl glyoximate. Hence it was assumed that nickel complexes of vic-oxime-imines would also be diamagnetic. Magnetic susceptibility measurements of some of them were carried out (vide table XVII). The results showed that the complexes are paramagnetic. To our knowledge, this is the first example of a series of paramagnetic nickel complexes with glyoxime type ligands

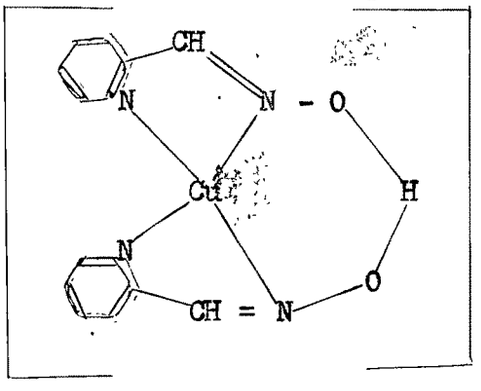


A related ligand of interest is pyridine 2-aldoxime (abbreviated as RH). Its nickel complexes have been investigated recently by Krause and Busch (211). All the nickel complexes prepared are paramagnetic. The complexes $\boxed{Ni\ (RH)_2}\ Cl_2$ and $\boxed{Ni\ (RH)_3}\ I_2$ are suggested to have octahedral configuration. When $\boxed{Ni\ (RH)_2Cl_2}$ is dissolved in water there is no apparent reaction and the solution retains its green colour. On the other hand the nickel complex of dimethylglyoxime $Ni(dmg\ H)_2\ X_2$ is unstable and readily reverts to the more stable $Ni(dmg)_2$. The unstable nickel complexes of vic-oxime-imines under investigation namely

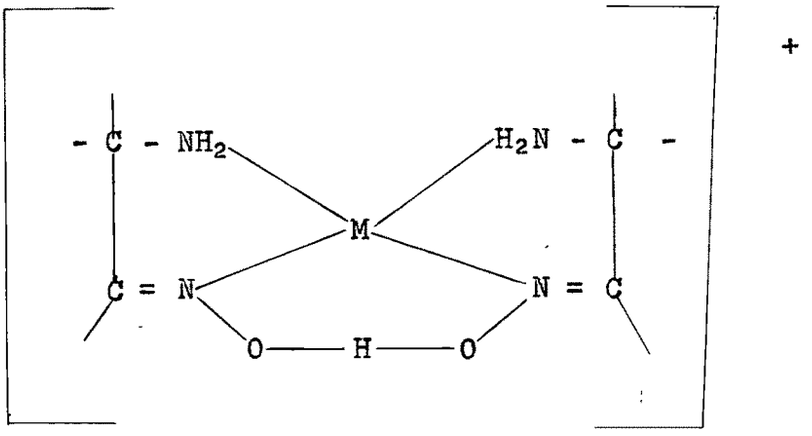
$Ni(oxime\text{-}imine)_2X_2$ could not be prepared . It indicates different nature of pyridine-2-aldoxime and vic-oxime-imines under investigation. Other complexes of interest are $Ni(R)(RH)X\ H_2O$, $NiR_2(pyridine)_2$ and NiR_2. All these complexes are paramagnetic and assumed to have octahedral configuration. They observed Curie-Weiss dependence of magnetic moment of these complexes and suggested trans-bridge structure for $[NiR(RH)]^+$



It may be noted here that Liu and Liu (212) have recently suggested cis configuration for $[Cu\ R(RH)]^+$



Similarly, Murmann (213) observed that copper (II) and nickel (II) complexes of 2-methyl-2-amino 3-butanone oxime have cis configuration



M = Cu or Ni

wherein the amino-oxime rings with the metal lie in the same plane.

The magnetic moments of the nickel (II) complexes XXIX, XXX and XXXII are found to be 2.88, 3.45 and 3.13 B.M. respectively, indicating the presence of two unpaired electrons in these complexes. The following possibilities arise as regards the structure of the complexes namely that they may be

(i) ionic complexes

(ii) octahedral complexes

(iii) tetrahedral complexes

(iv) higher energy square planar complexes

Non-ionic nature of the complexes is already suggested from the electrical conductivity measurements of these complexes.

An octrahedral complex may be formed through intermolecular bonding between metal atoms or between metal and oxygen atoms. Paramagnetic nature of the complex

indicates the absence of the metal-metal bonding in the complex. Steric considerations disfavour intermolecular metal-oxygen bonding in the complex. Further, absorption band at 400 mμ is not observed in the absorption spectra of the complexes as expected for octahedral complexes (214). Hence it is suggested that these complexes may not have octahedral configuration.

Selwood (215) writes : All complexes in which nickel is bonded to four nitrogen atoms, irrespective of whether these nitrogen atoms belong to pyrrole ring, oxime or triazene group have proved to be diamagnetic. But if for some reason the chelate groups are prevented from assuming a co-planar configuration, it is to be expected that the resulting distortion will be reflected in the magnetic moment of the metal ion.

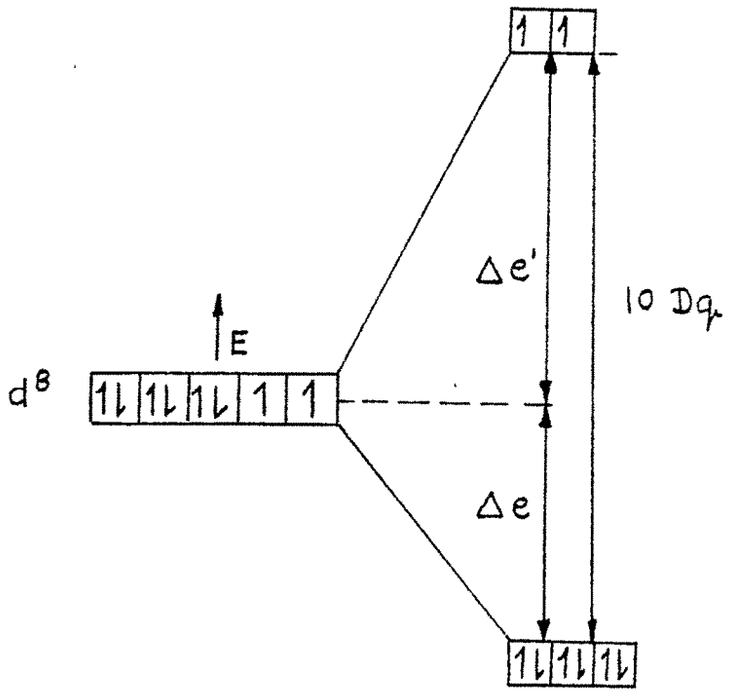
Venanzi (216) also suggested that tetrahedral paramagnetic complexes of bivalent nickel will be formed only when the ligands do not have enough perturbing power to cause spin pairing and when tetrahedral arrangement of atoms is forced by the steric requirements of the ligands.

Two general types of tetrahedral nickel (II) compounds are now known (217). The first class consists of truely tetrahedral ones $\boxed{NiX_4}$ or $\boxed{Ni(XX)_2}$. These include tetrahalo anions (218 to 221), various substances wherein nickel (II) ions are trapped in tetrahedral holes in host lattices (222 to 224) and such complexes as bis-salicylaldehyde nickel (II) (225), bis-acetylacetone

nickel (II) (226), etc. The second class embraces those which may be called pseudo-tetrahedral. They have four ligands at about the apices of a tetrahedron surrounding nickel (II) ion, and two or more different kinds of ligands are present. Of the various cases possible only L_2NiX_2 and $LNiX_3$ have been realised. Some of these are $(R_3P)_2 NiX_2$ (227 to 231), $(R_3PO)_2 NiX_2$ and $(R_3AsO)_2NiX_2$ (232,233); $(Quinoline)_2 NiX_2$ (234), bis N(α-branched-alkyl) salicylaldiminato nickel (II) (235,236), $(R_3P)NiX_3$ (217, 237), $(R_4N)NiX_3$ (238, 239); etc.

The occurrence of paramagnetic tetrahedral complexes is still relatively rare. It appears that most paramagnetic complexes of bivalent nickel have a strong tendency to possess octahedral structure rather than a tetrahedral one. It cannot be explained in terms of valence-bond theory. Explanation is, however, supplied by the ligand field theory. Fig 13 shows the crystal field splittings of the degenerate d-orbitals of nickel (II) under different ligand fields. Crystal field stabilization energy is used, in particular, to support the view that tetrahedral nickel (II) complexes (CFSE = 8 Dq) are less stable than octahedral nickel (II) complexes (CFSE = 12 Dq).

It is considered that ligands under investigation do not have enough perturbing power to cause spin-pairing of d-electrons in nickel (II) and that aromatic rings attached to imine nitrogen atoms sterically hinder the formation of coplanar chelate rings. Thus the tetrahedral arrangement of atoms may be forced by the steric



$6\Delta e = 4\Delta e'$

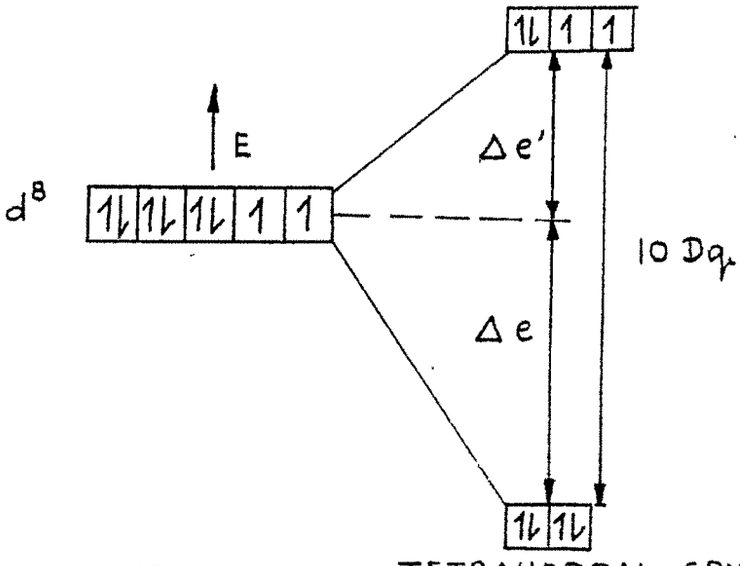
$\Delta e + \Delta e' = 10\ Dq$

$\Delta e = 4\ Dq$

$\Delta e' = 6\ Dq$

NO FIELD

OCTAHEDRAL CRYSTAL-FIELD STABILIZATION ENERGY 12 Dq



$4\ De = 6\Delta e'$

$\Delta e + \Delta e' = 10\ Dq$

$\Delta e = 6\ Dq$

$\Delta e' = 4\ Dq$

NO FIELD

TETRAHEDRAL CRYSTAL - FIELD STABILIZATION ENERGY 8 Dq

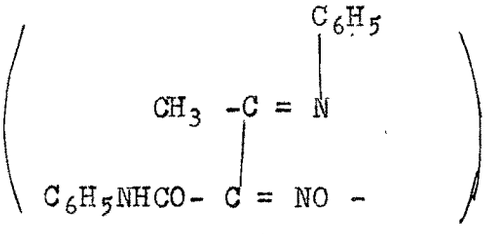
FIG. 13 d-ORBITAL SPLITTING DUE TO THE CRYSTAL-FIELD IN d^8 SYSTEM

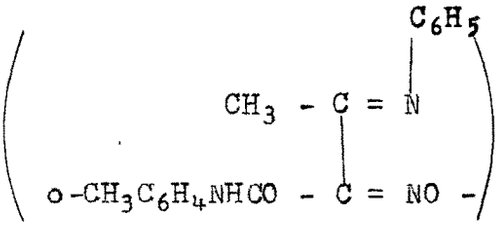
requirements of the ligands and give rise to the magnetic moment of the complex.

Further work, particularly x-ray diffraction data, would be necessary to confirm this structure and is being carried out in our laboratories.

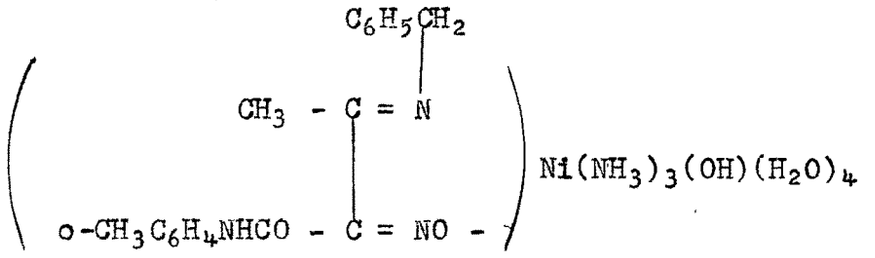
4.(b) Complexes of nickel (formed in presence of ammonia)

Since the nickel (II) complexes prepared earlier were found to be paramagnetic, attempts were made to prepare diamagnetic nickel complexes. Another series of products were obtained by treating nickel chloride with the Schiff bases from N-aryl 2,3-dioxo-butyramide 2-oxime in presence of excess of ammonia. These are formulated, on the basis of analysis, as follows :

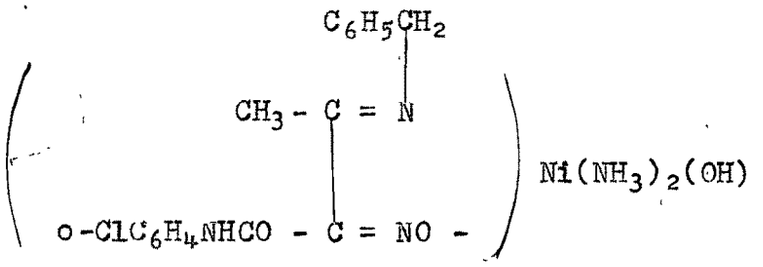
(XXXVI)  $Ni\,(NH_3)_2(OH)(H_2O)$

(XXXVII)  $Ni\,(NH_3)_3(OH)(H_2O)_5$

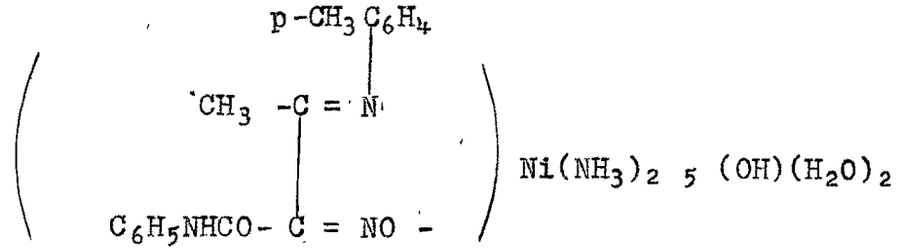
(XXXVIII)



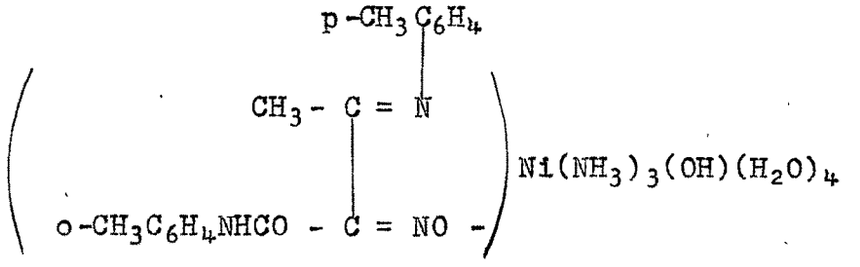
(XXXIX)

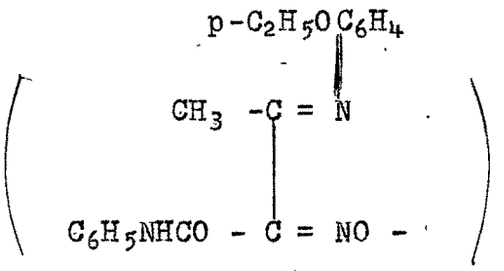


(XXXX)

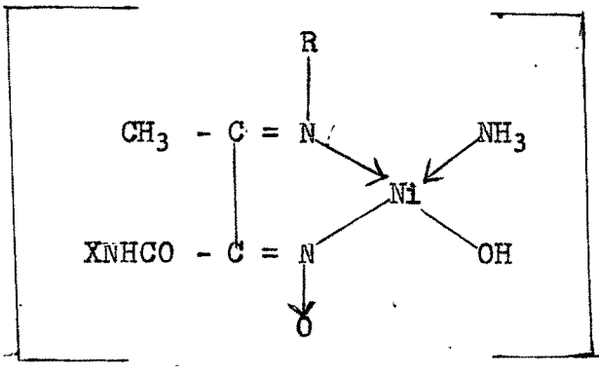


(XXXXI)



(XXXXII)  $Ni(NH_3)_3(OH)(H_2O)$

The products are orange yellow and insoluble in most of the solvents. Their colour is an indication of their diamagnetic nature (240). Magnetic suscaptibility measurements of some of these products were carried out (vide Table XVII). The results confirm their diamagnetic nature. Hence it is suggested that they should have square planar configuration.

 $(NH_3)_Y \quad (H_2O)_Z$

Alternative suggestions are possible regarding the arrangement of ligands in the molecule ; (the insolubility of the complex may indicate some degree of association of the molecules). Further work seems necessary to confirm their structure.

5. Complexes of copper with vic-oxime-imines

The products obtained by treating copper salt with the Schiff bases from N-aryl 2,3-dioxo butyramide 2-oxime and 2,3-butane dione monoxime are formulated, on the basis of analysis, as follows:

(XXXXIII) $\left(\begin{array}{c} C_6H_5 \\ | \\ CH_3 - C = N \\ | \\ C_6H_5NHCO - C = NO - \end{array} \right) Cu\ (OH)\ (H_2O)_3$

(XXXXIV) $\left(\begin{array}{c} C_6H_5 \\ | \\ CH_3 - C = N \\ | \\ o\text{-}CH_3C_6H_4NHCO - C = NO - \end{array} \right)_3 Cu_2\ (OH)\ H_2O$

(XXXXV) $\left(\begin{array}{c} C_6H_5 - CH_2 \\ | \\ CH_3 - C = N \\ | \\ C_6H_5NHCO - C = NO - \end{array} \right)_3 Cu_2\ (OH)\ (H_2O)_3$

(XXXXVI) $\left(\begin{array}{c} C_6H_5 - CH_2 \\ | \\ CH_3 - C = N \\ | \\ o\text{-}CH_3C_6H_4NHCO - C = NO - \end{array} \right) Cu\ (OH)\ (H_2O)_3$

(XXXXVII) $\left(\begin{array}{c} pCH_3 - C_6H_4 \\ | \\ CH_3 - C = N \\ | \\ C_6H_5NHCO - C = NO - \end{array} \right) Cu\ (OH)\ (H_2O)_2$

(XXXXVIII) $\left(\begin{array}{c} pCH_3-C_6H_4 \\ | \\ CH_3-C=N \\ | \\ o\text{-}CH_3C_6H_4NHCO-C=NO- \end{array}\right) Cu(OH)(H_2O)_2$

(XXXXIX) $\left(\begin{array}{c} pCH_3-C_6H_4 \\ | \\ CH_3-C=N \\ | \\ o\text{-}ClC_6H_4NHCO-C=NO- \end{array}\right)_4 Cu_3(OH)_2(H_2O)_2$

(L) $\left(\begin{array}{c} pC_2H_5O-C_6H_4 \\ | \\ CH_3-C=N \\ | \\ C_6H_5NHCO-C=NO- \end{array}\right)_4 Cu_3(OH)_2(H_2O)_4$

(LI) $\left(\begin{array}{c} p\ C_2H_5O-C_6H_4 \\ | \\ CH_3-C=N \\ | \\ o\text{-}CH_3C_6H_4NHCO-C=NO- \end{array}\right)_4 Cu_3(OH)_2(H_2O)_5$

(LII) $\left(\begin{array}{c} p\ C_2H_5O-C_6H_4 \\ | \\ CH_3-C=N \\ | \\ CH_3-C=NO- \end{array}\right) Cu(OH)(H_2O)_3$

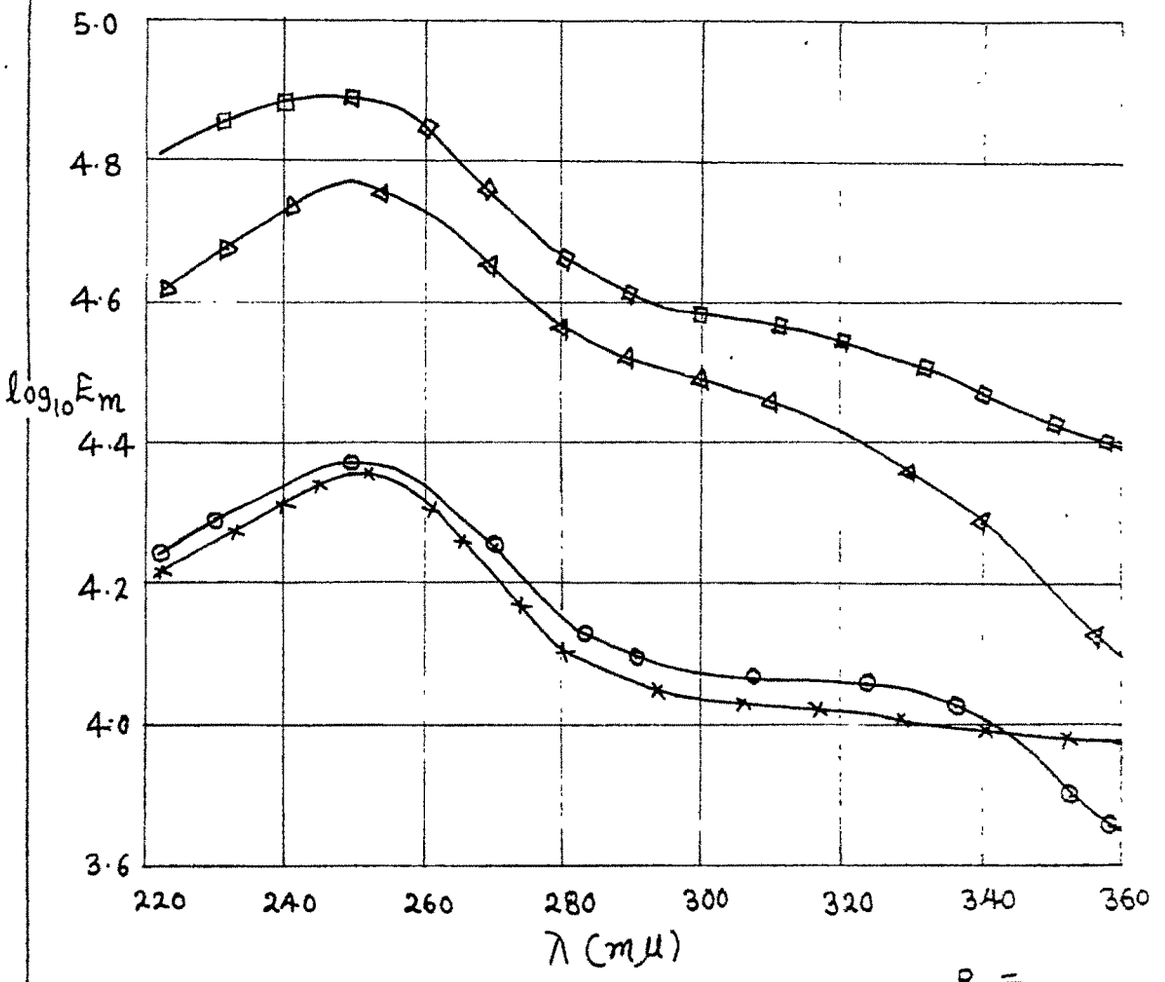
They are soluble in alcohol, acetone, benzene, ether, carbon tetrachloride, etc. It is suggested that they are complex compounds or chelates rather than salts. Electrical conductivity of copper complexes of Schiff bases from

2,3-dioxobutyramide 2-oxime and aniline (and benzylamine) in methanol was investigated. It was observed that they are non-ionic in solution.

The ultraviolet absorption spectra of the copper complexes were investigated in methanol (vide table XII). They are presented in figs. 14 and 15 and wave length maxima (λ max) and the corresponding molar extinction coefficients for the complexes are presented in table XXXI. The ultra-violet absorption spectra of these complexes are essentially different in most cases from those of their ligands in alkali solutions and hence "essentially covalent" bonding is suggested between metal and ligand in these compounds.

Infra-red spectra of the copper complexes of Schiff bases from 2,3-dioxobutyranilide 2-oxime and aniline (and benzylamine) were investigated (vide tables XV and XVI). St.frequency for oxime OH group is found absent in the spectra of these complexes.

Magnetic susceptibility measurements of some of these complexes were carried out (vide table XVII). The results indicate that all these complexes are paramagnetic. The magnetic moments of the complexes XXXXIV, XXXXV and XXXXVI per copper atom in the complex have been calculated as 1.88, 1.92 and 1.95 B.M. respectively.



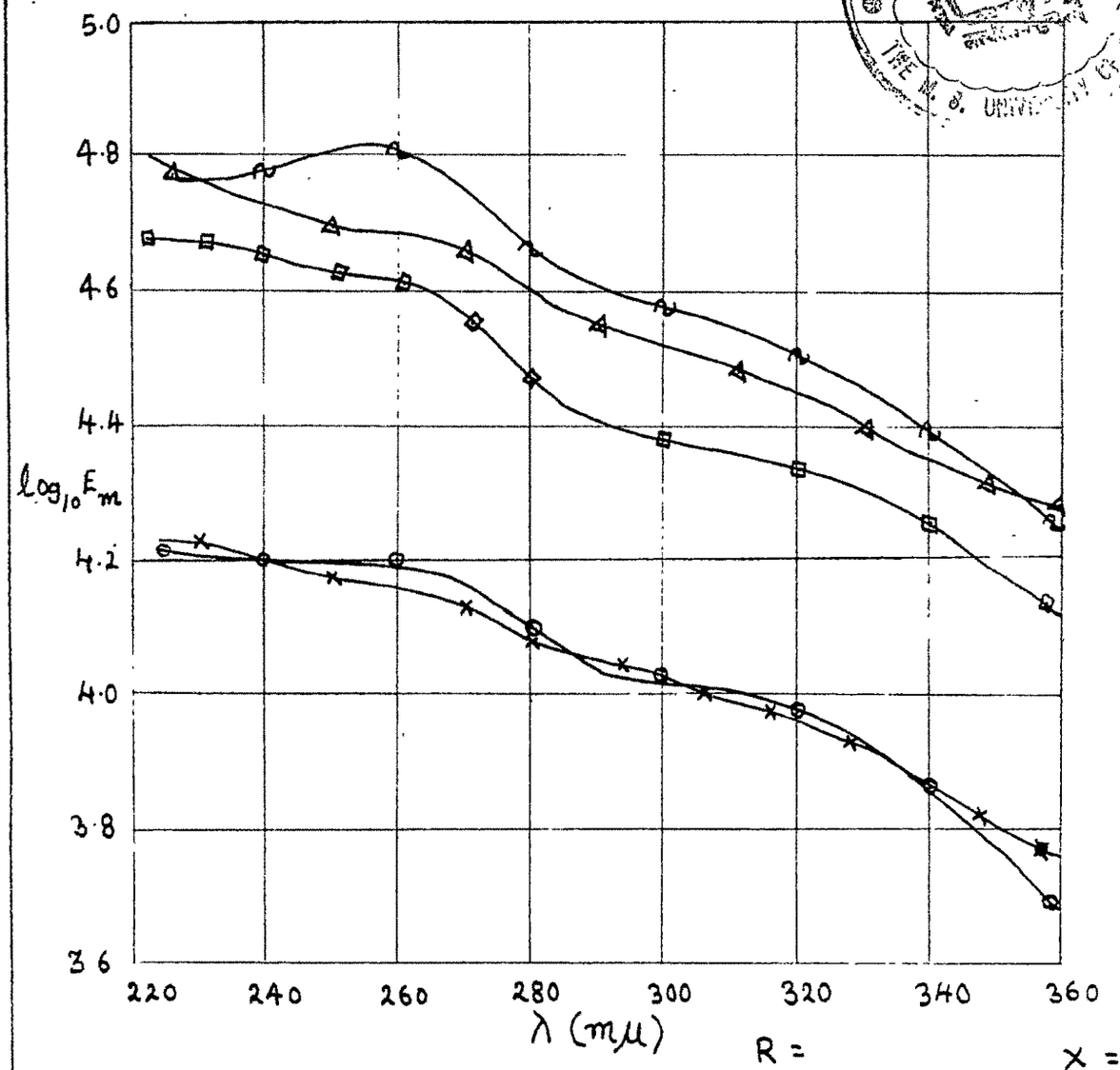
LIGAND (SCHIFF BASE)

$CH_3 - C(=NR) - C(=NO-H) - NHCOC_6H_5$

R =

- ×—×—× C_6H_5-
- △—△—△ $C_6H_5CH_2-$
- ○—○—○ $p-CH_3-C_6H_4-$
- □—□—□ $p-C_2H_5O\,C_6H_4-$

FIG:14 : ULTRA-VIOLET ABSORPTION SPECTRA OF THE COPPER (II) COMPLEXES OF SCHIFF BASES FROM 2,3- DIOXO- BUTYRANILIDE 2- OXIME (IN METHANOL)



LIGAND (SCHIFF BASE)

$CH_3-C(=N-R)-C(=NO-H)-CONHC_6H_4X$-o

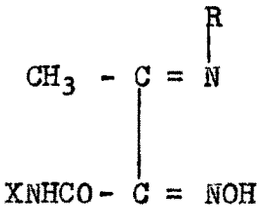
R =	X =
C_6H_5	CH_3
$C_6H_5CH_2$	CH_3
p-$CH_3C_6H_4$	CH_3
p-$C_2H_5OC_6H_4$	CH_3
p-$CH_3C_6H_4$	Cl

FIG. 15: ULTRA-VIOLET ABSORPTION SPECTRA OF THE COPPER(II)COMPLEXES OF SCHIFF BASES FROM N-ARYL 2,3-DIOXO-BUTYRAMIDE 2-OXIME (IN METHANOL)

TABLE XXXI

Ultra-violet absorption spectra of the complexes of copper (II) with vic-oxime imines in methanol

Reagent :



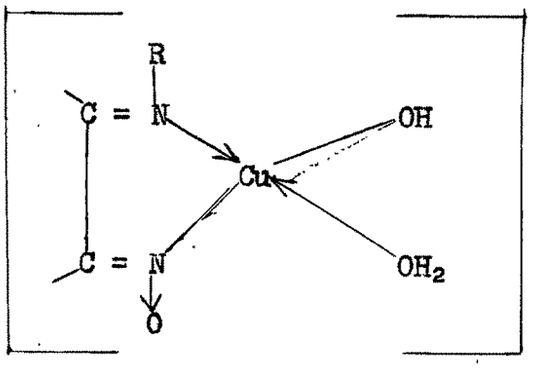
No.	Reagent		Formula of the complex	in methanol			
	R =	X =		λmax (mμ)	E_m	λmax (mμ)	E_m
1	2	3	4	5	6	7	8
1.	C_6H_5	C_6H_5	$CuC_{16}H_{21}O_6N_3$	252	23820	316-18	12160
2.	$C_6H_5CH_2$	C_6H_5	$Cu_2C_{51}H_{55}O_{10}N_9$	248-51	59110		
3.	p-$CH_3C_6H_4$	C_6H_5	$CuC_{17}H_{22}O_5N_3$	250-53	22930		
4.	p-$C_2H_5OC_6H_4$	C_6H_5	$Cu_3C_{72}H_{82}O_{18}N_{12}$	247-49	79000		

TABLE XXXI (Contd.)

1	2	3	4	5	6	7	8
5.	C_6H_5	o-$CH_3C_6H_4$	$Cu_2C_{51}H_{51}O_8N_9$				
6.	$C_6H_5CH_2$	o-$CH_3C_6H_4$	$CuC_{18}H_{25}O_6N_3$	254-58	16030		
7.	p-$CH_3C_6H_4$	o-$CH_3C_6H_4$	$CuC_{18}H_{23}O_5N_3$				
8.	p-$C_2H_5OC_6H_4$	o-$CH_3C_6H_4$	$Cu_3C_{76}H_{92}O_{19}N_{12}$				
9.	p-$CH_3C_6H_4$	o-ClC_6H_4	$Cu_3C_{68}H_{66}O_{16}N_{12}Cl_4$	255-57	65860		

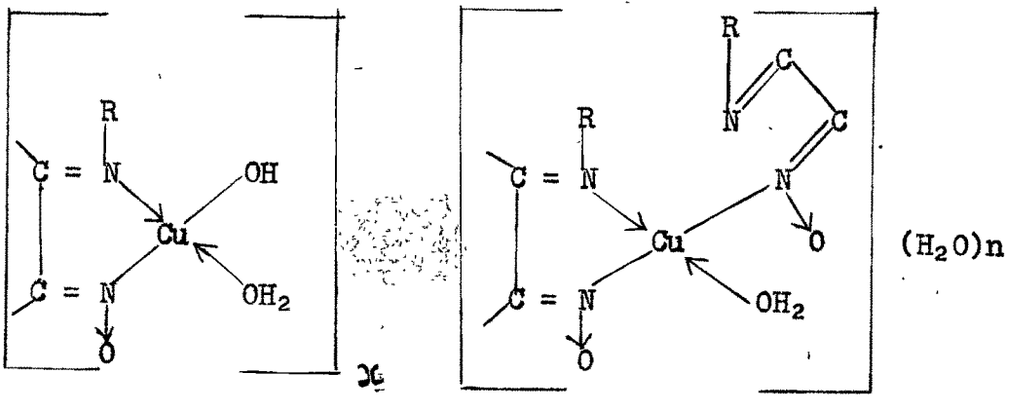
All the results lead us to believe that these complexes may be represented by either of the following structural formulae : ($x = 1$ or 2)

(i)



$(H_2O)_x$

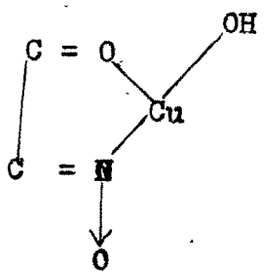
(ii)



$(H_2O)n$

$x = 1$ or 2.

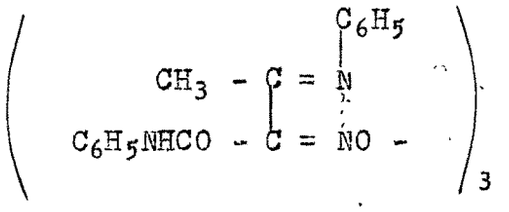
Taylor and Ewbank (82) observed that ethyl 2,3-dioxobutyrate 2-oxime forms a copper complex which may be represented as :

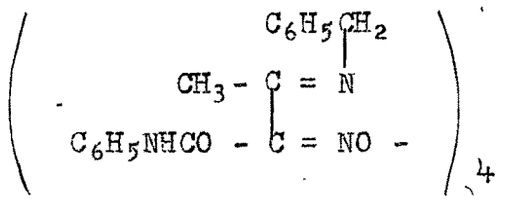


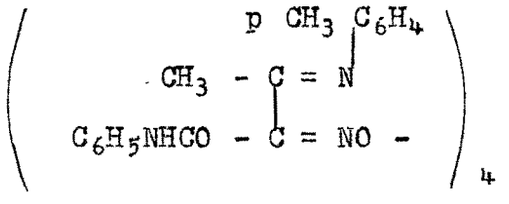
Talati (187) and Desai (188) observed that copper complexes of N-aryl 2,3-dioxobutyramide 2-oxime could not be characterised. However, Talati (187) observed that the oximes of N-aryl 2,3-dioxobutyramide 2-oxime form well-defined copper complexes, while Desai (188) observed that only methyl phenyl hydrazone of 2,3-dioxobutyranilide 2-oxime forms well defined copper complex and that phenyl hydrazones of N-aryl 2,3-dioxobutyramide 2-oxime underwent cyclisation through the intermediate formation of unstable copper complexes. Thus the Schiff bases derived from N-aryl 2:3-dioxobutyramide 2-oxime appear to form less stable copper complexes than the corresponding oximes or methyl phenyl hydrazones, but more stable complexes than the corresponding phenyl hydrazones or the unsubstituted N-aryl 2,3-dioxobutyramide 2-oxime. Because of the low stability of CuR_2 chelates and the steric hindrance due to the phenyl ring attached to imine nitrogen to the formation of square planar CuR_2 chelates, "hydrolysed" complexes are isolated.

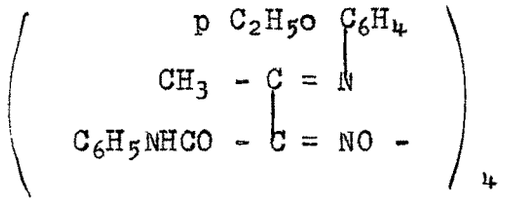
6. Complexes of palladium with vic-oxime-imines :

It was believed that complexes of palladium will be similar to those of nickel. Hence the complexes of palladium were prepared. The products were obtained by treating palladium chloride with the Schiff bases from N-aryl 2,3-dioxobutyranilide 2-oxime and are formulated, on the bases of analysis, as follows :

(LIII)  $Pd_2(OH)(H_2O)_4$

(LIV)  $Pd_3(OH)_2(H_2O)_2$

(LV)  $Pd_3(OH)_2(H_2O)$

(LVI)  $Pd_3(OH)_2$

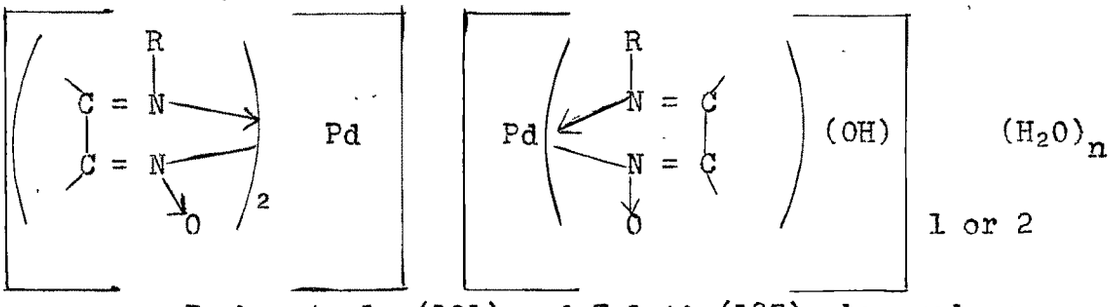
They are slightly soluble in alcohol, acetone, benzene, etc. Electrical conductivity of palladium complexes of Schiff bases from 2,3-dioxobutyranilide 2-oxime and aniline (and benzylamine) in methanol was investigated (vide table XVIII). It was observed that they are non-ionic in solution.

The absorption spectra of the palladium complexes were investigated. It was not possible to obtain solutions uniformly and hence no attempt is made to calculate molar extinction coefficients. The wave-length

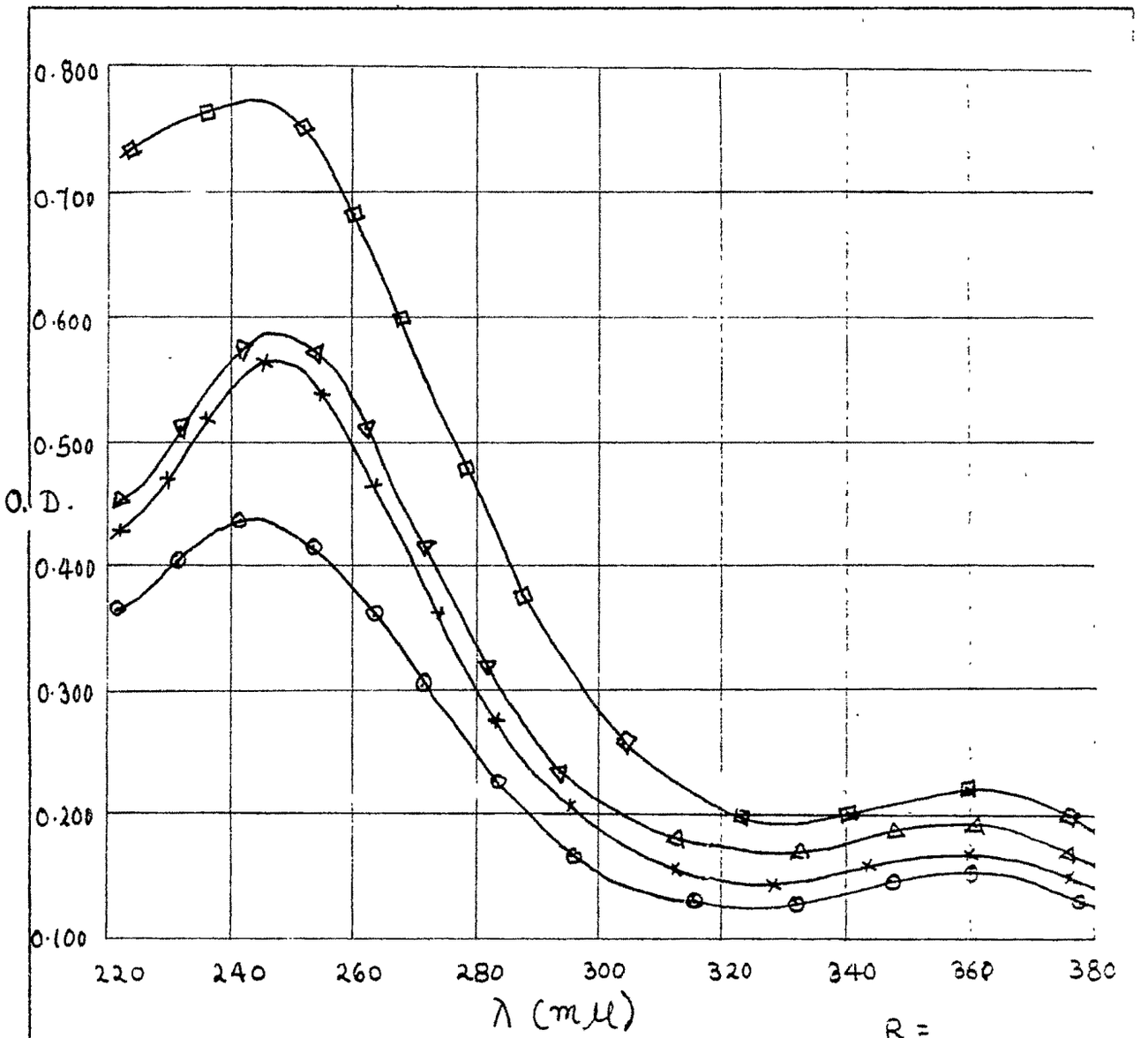
maxima (λ max) for these complexes in methanol are presented in (table XXXII). The absorption spectra of these complexes are shown in fig. 16. The spectra are suggestive of "essentially covalent " linking between metal and ligand in the complexes.

Infra-red spectra of the palladium complexes of the Schiff bases from 2,3-dioxobutyranilide 2-oxime and aniline (and benzylamine) were investigated (vide tables XV and XVI). St.frequency for the oxime OH group is found absent in these complexes.

Magnetic susceptibility measurements of some of these complexes were carried out (vide table XVII). The results indicate that all these complexes are diamagnetic. Hence these complexes may be represented by the following structural formula.



Banks et al. (131) and Talati (187) observed that vic-dioximes form complexes of the type PdR_2 and that these chelates possess a square planar configuration. Desai (188) observed that phenyl hydrazone and phenyl methyl hydrazone of 2,3-dioxobutyranilide 2-oxime form complexes of low stability with palladium, so that "hydrolysed " products were obtained. We now find that palladium chelates of vic-oxime-imines-PdR_2-could not be



LIGAND (SCHIFF BASE)

$CH_3 - C = NR$

$C_6H_5NHCO - C = NO - H$

FIG 16: ULTRA-VIOLET ABSORPTION SPECTRA OF THE PALLADIUM (II) COMPLEXES OF SCHIFF BASES FROM 2,3-DIOXO-BUTYRANILIDE 2-OXIME (IN METHANOL)

TABLE XXXII

Ultra-violet absorption spectra of palladium complexes of vic-oxime-imines

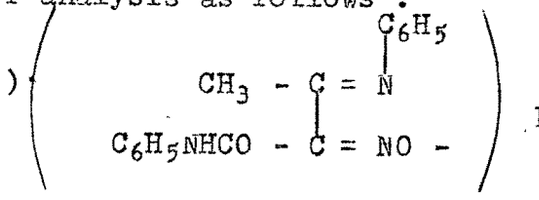
Reagent : $CH_3 - C = N - R$ / $XNHCO - C = NOH$

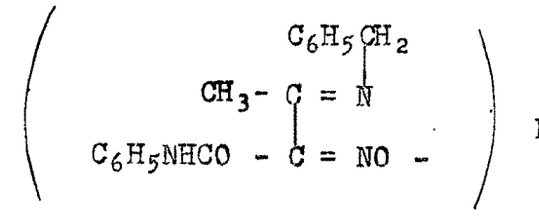
S.No.	Reagent R =	Reagent X =	Formula of the complex	in methanol λmax (mμ)	in methanol λmax (mμ)
1.	C_6H_5	C_6H_5	$Pd_2C_{48}H_{51}O_{11}N_9$	244	360
2.	$C_6H_5CH_2$	C_6H_5	$Pd_3C_{68}H_{70}O_{12}N_{12}$	248	356-60
3.	$p\text{-}CH_3C_6H_4$	C_6H_5	$Pd_3C_{68}H_{68}O_{11}N_{12}$	246-48	356-60
4.	$p\text{-}C_2H_5OC_6H_4$	C_6H_5	$Pd_3C_{72}H_{74}O_{14}N_{12}$	242-44	360

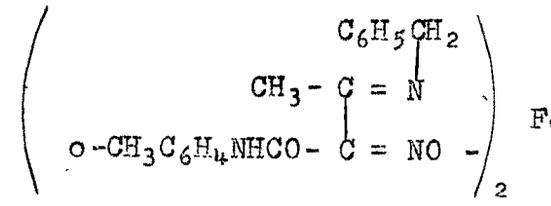
isolated. They may have low stability, so that "hydrolysed" products are obtained.

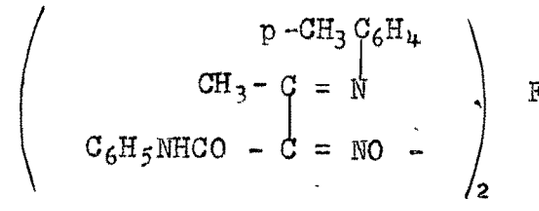
7. Complexes of iron (II) with vic-oxime-imines :

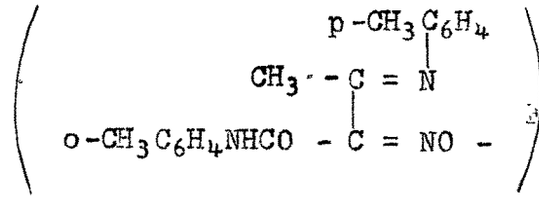
The products obtained by treating iron (II) ammonium sulphate with Schiff bases from N-aryl 2,3-dioxobutyramide 2-oxime are formulated on the basis of analysis as follows :

(LVII)  $Fe_2(SO_4)(OH)$

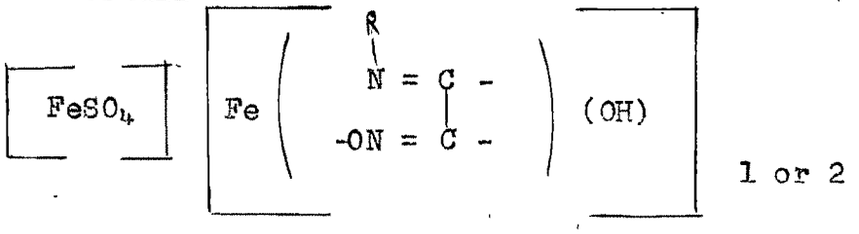
(LVIII)  $Fe_2(SO_4)(OH)$

(LIX)  $Fe_3(SO_4)(OH)_2$

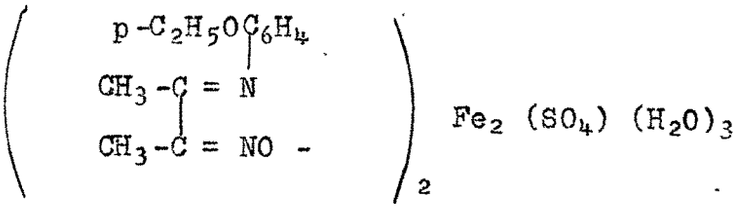
(LX)  $Fe(H_2O)_2$

(LXI)  $Fe_2(H_2O)_2$

They are violet-blue in colour and soluble in acetone, benzene, carbon tetrachloride, etc. Magnetic susceptibility measurements of some of these complexes were carried out (vide- table XVII). The results indicate that all the complexes are paramagnetic. The magnetic moments of the complexes LVII, LVIII, LIX and LX per iron atom in the complex have been calculated as 2.82, 2.64, 2.94 and 3.24 B.M. respectively. Hence presence of two "unpaired" electrons per iron atom in the complex is suggested. Crystal field splittings for the iron (II) atom (d^6 system) in various crystal fields are shown in fig 17. Tetrahedral stereochemistry for the complexes $FeR_2 (H_2O)_2$ is indicated. Structures of other complexes appear to be more complicated than indicated by the formula :



The iron (II) complex of the Schiff base from 2,3-butane dione monoxime and p-phenetidine is formulated on the basis of analysis as follows :

(LXII) 

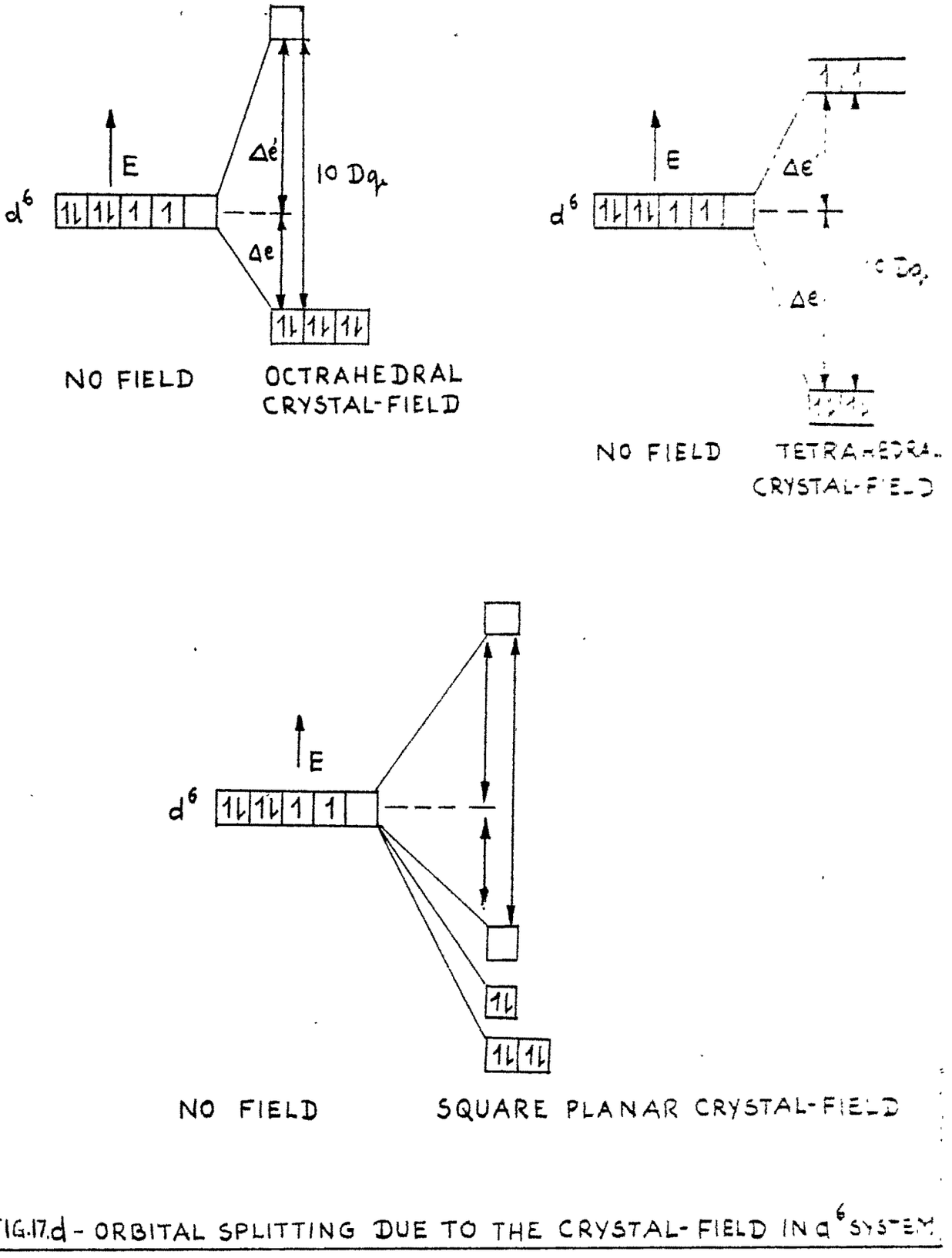


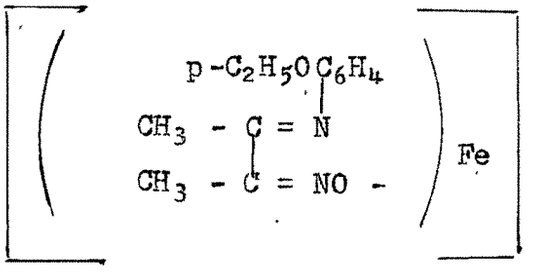
FIG.17.d - ORBITAL SPLITTING DUE TO THE CRYSTAL-FIELD IN a ^{6} SYSTEM.

Desai (188) prepared iron (II) complex of 2,3-dioxobutyranilide 2-oxime and suggested its structure as

$$Fe\ R_2\ (Fe\ R)_2\ SO_4\ (H_2O)_n$$

where R is the anion of the ligand molecule.

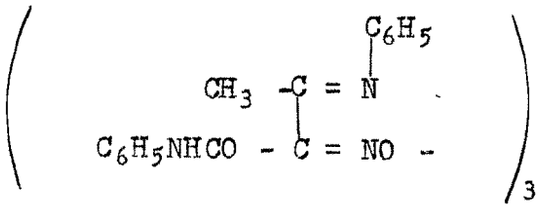
The present complex may be represented as



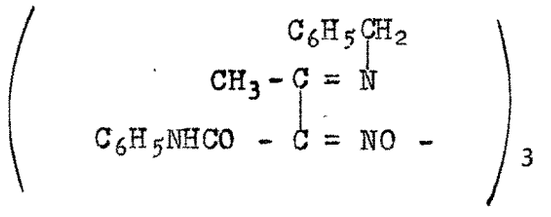
8. Complexes of cobalt (III) with vic-oxime-imines :

The products obtained by treating hexammine cobalt (III) chloride with Schiff bases from N-aryl 2,3-dioxobutyramide 2-oxime are formulated on the basis of analysis as follows :

(LXIII)



(LXIV)



(LXV) $\left(\begin{array}{c} C_6H_5CH_2 \\ | \\ CH_3 - C = N \\ | \\ C_6H_5NHCO - C = NO - \end{array} \right)_2 Co(OH)(NH_3)(H_2O)_3$

(LXVI) $\left(\begin{array}{c} p\text{-}C_2H_5OC_6H_4 \\ | \\ CH_3 - C = N \\ | \\ C_6H_5NHCO - C = NO - \end{array} \right)_2 Co(OH)(NH_3)(H_2O)_2$

(LXVII) $\left(\begin{array}{c} C_6H_5CH_2 \\ | \\ CH_3 - C = N \\ | \\ o\text{-}ClC_6H_4NHCO - C = NO - \end{array} \right)_2 Co(OH)(NH_3)(H_2O)_5$

They are soluble in alcohol, benzene, carbon tetrachloride, etc. Electrical conductivity of cobalt (III) complexes of Schiff bases from 2,3-dioxobutyranilide 2-oxime and aniline (and benzylamine) in methanol was investigated (vide table XVIII). The results indicate non-ionic nature of complexes in solution.

The ultra-violet absorption spectra of cobalt (III) complexes were investigated in methanol (vide table XIII). They are presented in fig. 18 and wave-length maxima (λ max) and the corresponding molar extinction coefficients for the complexes are presented in table XXXIII. The spectra are suggestive of "essentially covalent" bonding between metal and ligand in the complexes.

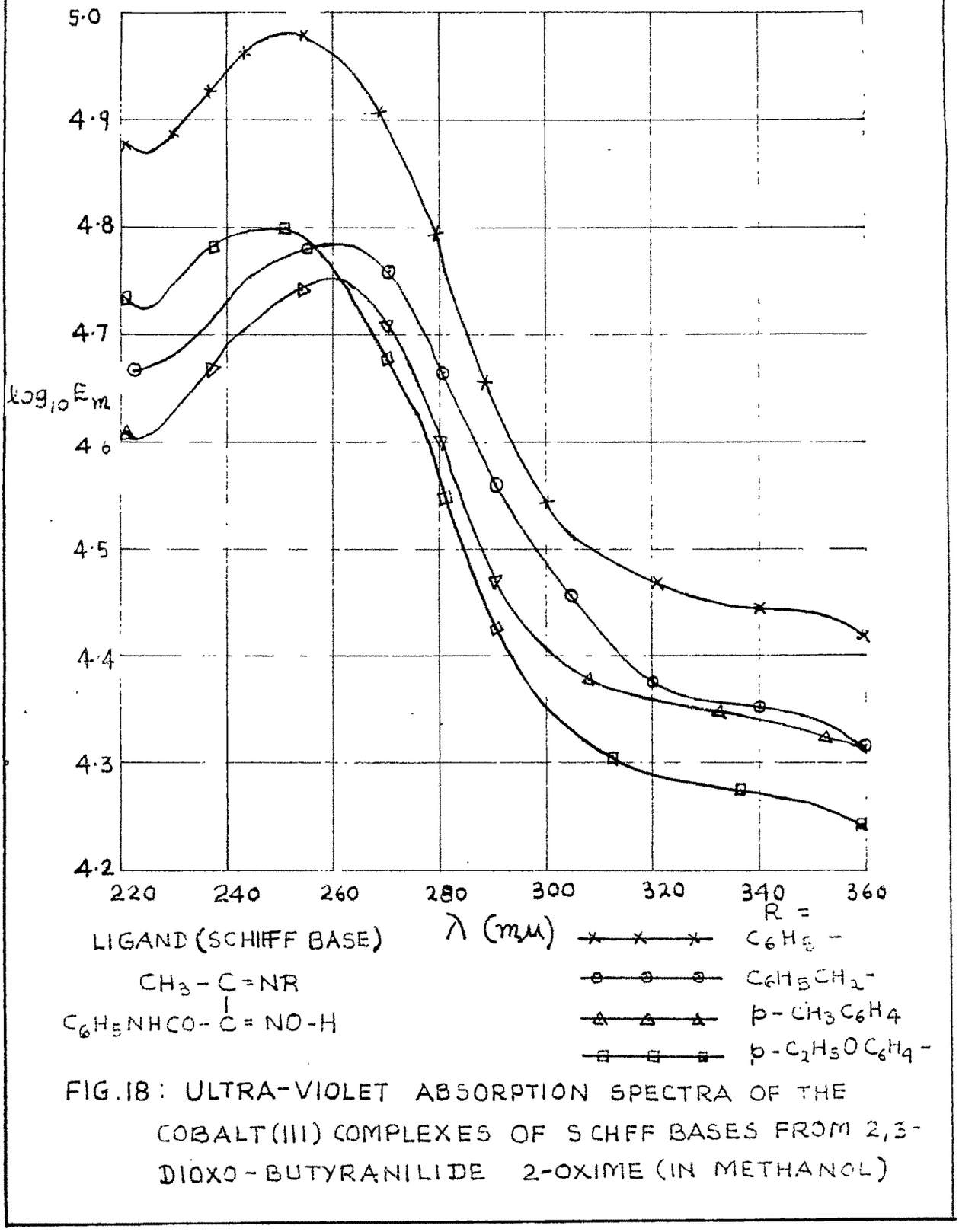
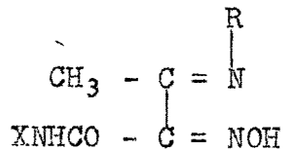


FIG. 18: ULTRA-VIOLET ABSORPTION SPECTRA OF THE COBALT(III) COMPLEXES OF SCHFF BASES FROM 2,3-DIOXO-BUTYRANILIDE 2-OXIME (IN METHANOL)

TABLE XXXIII

Ultra-violet absorption spectra of the complexes of cobalt (III) with vic-oxime imines in methanol.

Reagent :



S.No.	Reagent R =	Reagent X =	Formula of the complex	in methanol λmax (mμ)	in methanol E_m
1.	C_6H_5	C_6H_5	$CoC_{48}H_{42}O_6N_9$	250-52	95221
2.	$C_6H_5CH_2$	C_6H_5	$CoC_{51}H_{48}O_6N_9$	260-62	60840
3.	$p\text{-}CH_3C_6H_4$	C_6H_5	$CoC_{34}H_{42}O_8N_7$	259-60	57790
4.	$p\text{-}C_2H_5OC_6H_4$	C_6H_5	$CoC_{36}H_{44}O_9N_7$	249-51	62840

Infra-red spectra of the cobalt (III) complexes of the Schiff bases from 2,3-dioxobutyranilide 2-oxime and aniline (and benzylamine) were investigated (vide tables XV and XVI). St.frequency for oxime OH group is found absent in these complexes.

Magnetic susceptibility measurements of some of these complexes were investigated (vide table XVII). The results indicate that these complexes are diamagnetic. Hence it is considered that these are low-spin, inner-orbital complexes having octahedral structure. These are comparable to the octahedral cobalt (III) complexes of α-benzil dioxime monomethyl ether prepared by Brady and Muers (195) and of phenyl hydrazones of 2,3-dioxobutyranilide 2-oxime prepared by Desai (188).

9. Complexes in solution :

The investigations dealing with the preparation of complexes indicated that the transition metal complexes of vic-oxime-imines of the type ML_2 could not be isolated in many cases. Hence it was considered essential to study the types of complexes formed in solution. Job's continuous variation method was adopted and the formation of some of the complexes of nickel and copper in solution was studied.

9.(a) Complexes of nickel with vic-oxime-imines in solution :

It has been observed during the isolation of nickel complexes (in absence of excess of ammonia) that Schiff bases from N-aryl 2,3-dioxobutyramide 2-oxime and aniline formed complexes with nickel where metal-to-ligand

ratio was 2:3, whereas other vic-oxime-imines formed complexes with nickel where metal-to-ligand ratio was 1:2. Hence solution studies were made to find out if complexes with the same metal-to-ligand ratios of 1:2 and 2:3 as those for isolated complexes were formed in solution or were isolated after "reformation" from other complexes formed in solution. For this purpose complexes of three ligands were investigated under two conditions and usually at three wave-lengths which were selected by previous experiments with the solutions of the ligands and nickel chloride seperately. Corrected optical densities were calculated for mixtures and are presented in figs 19 to 24. The results indicate that (i) same metal-to-ligand ratio is observed for a set of solutions at different wave-lengths, (ii) in case of the Schiff base from 2,3-dioxobutyranilide 2-oxime and aniline, metal-to-ligand ratio of 1 : 1 is observed in methanol solution and ratio 2 : 3 in presence of sodium acetate (iii) in case of the Schiff base from 2,3-dioxo-o-butyrotoluidide 2-oxime and aniline, metal-to-ligand ratio of 1 : 1 is observed under both conditions and (iv) in case of the Schiff base from 2,3-dioxobutyranilide 2-oxime and benzylamine, metal-to-ligand ratio of 1 : 2 is observed under both conditions. The results lead us to believe that the formation of a single complex could be identified in a set of solutions at different wave-lengths. However, different complexes are suggested to be formed under different conditions for the Schiff base derived from

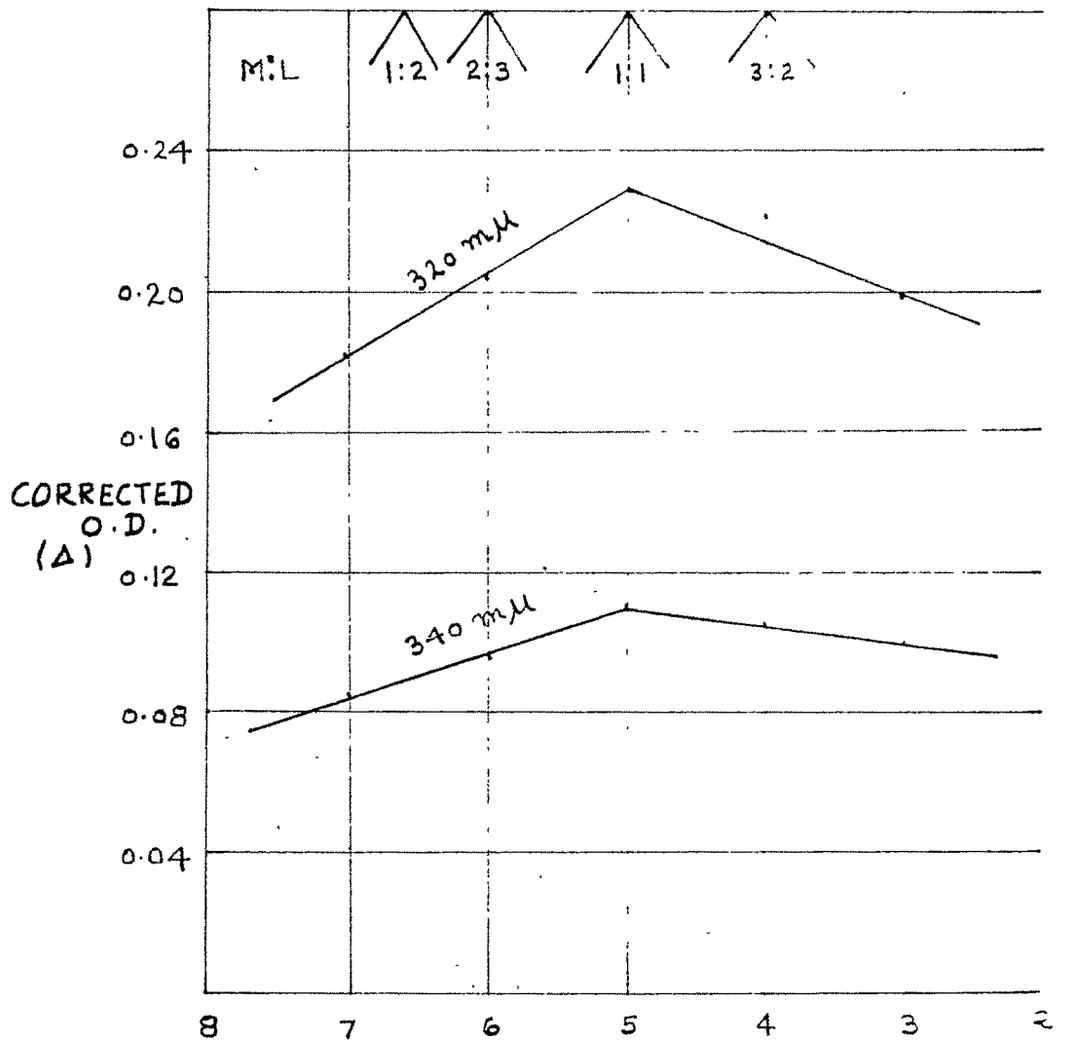


FIG: 19: JOB'S CONTINUOUS VARIATION METHOD. (MIXTURE OF NICKEL CHLORIDE AND SCHIFF BASE FROM 2,3 DIOXO-BUTYRANILIDE 2-OXIME AND ANILINE IN METHANOL)

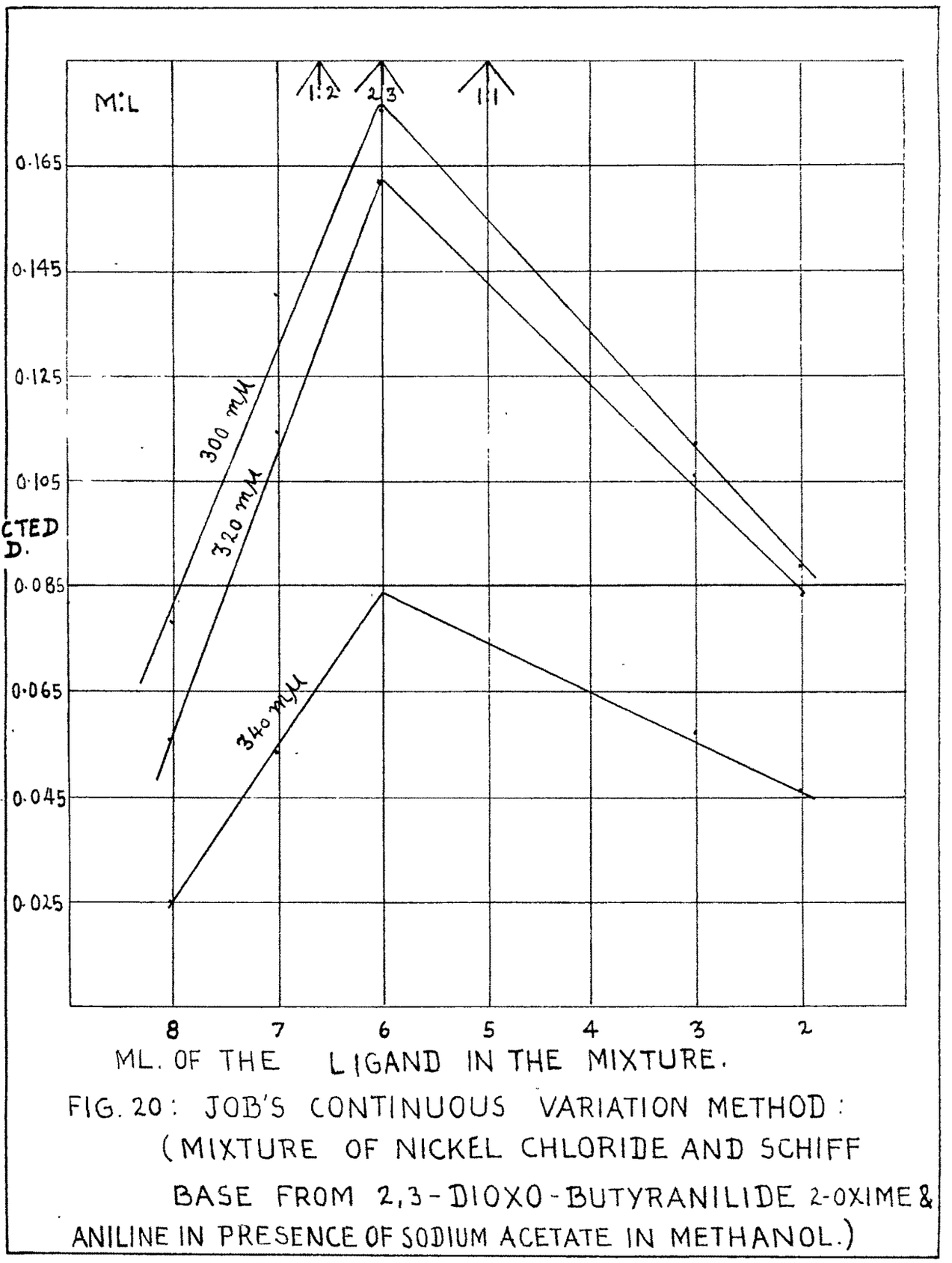


FIG. 20: JOB'S CONTINUOUS VARIATION METHOD: (MIXTURE OF NICKEL CHLORIDE AND SCHIFF BASE FROM 2,3-DIOXO-BUTYRANILIDE 2-OXIME & ANILINE IN PRESENCE OF SODIUM ACETATE IN METHANOL.)

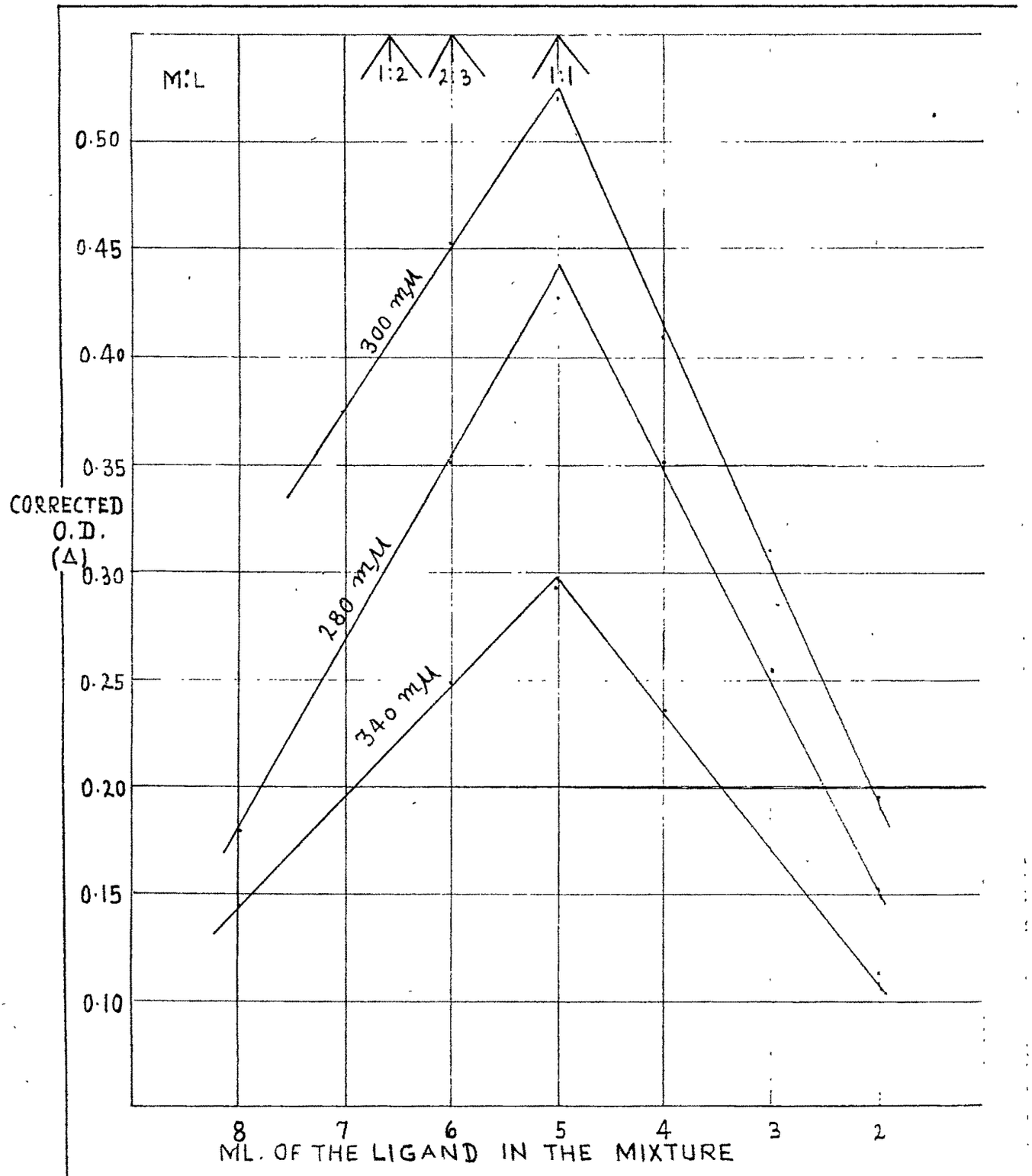


FIG.21: JOB'S CONTINUOUS VARIATION METHOD:
(MIXTURE OF NICKEL CHLORIDE AND SCHIFF BASE FROM 2,3-DIOXO-O-BUTYROTOLUIDIDE 2-OXIME AND ANILINE IN METHANOL)

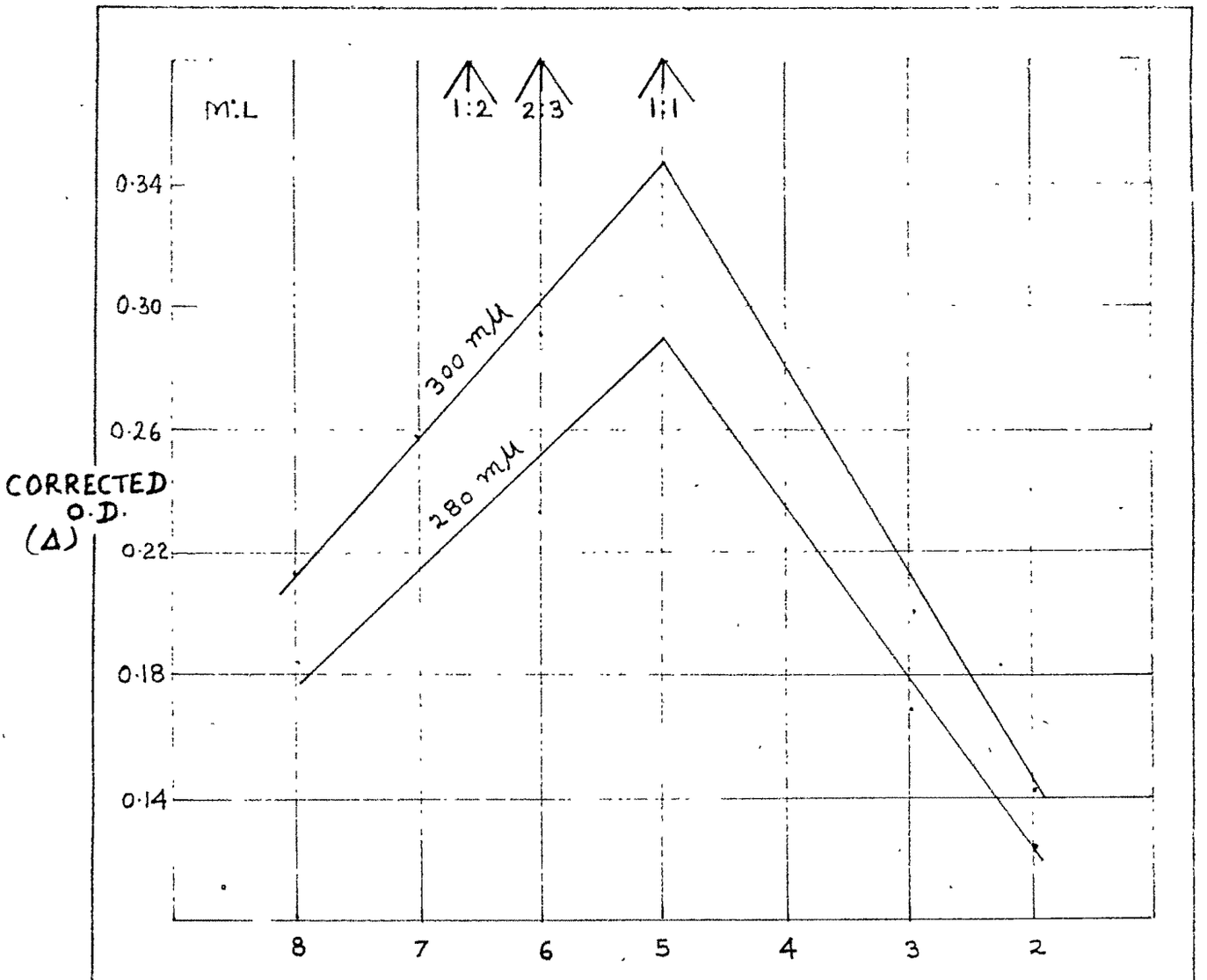


FIG. 22: JOB'S CONTINUOUS VARIATION METHOD: (MIXTURES OF NICKEL CHLORIDE AND SCHIFF BASE FROM 2,3-DIOXO-o-BUTYROTOLUIDIDE 2-OXIME AND ANILINE IN PRESENCE OF SODIUM ACETATE IN METHANOL.)

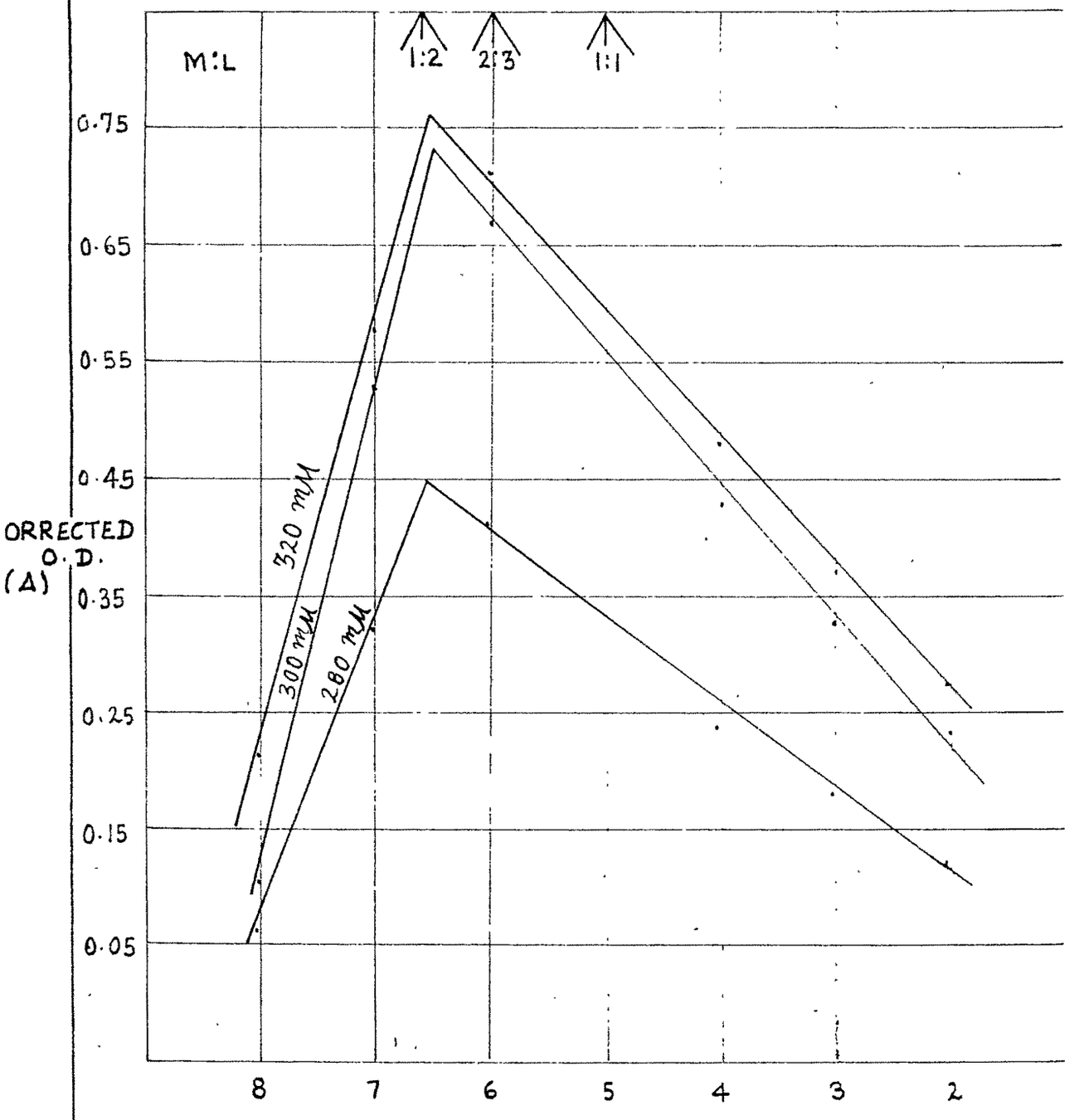


FIG.23: JOB'S CONTINUOUS VARIATION METHOD: (MIXTURE OF NICKEL CHLORIDE AND SCHIFF BASE FROM 2,3-DIOXO-BUTYRANILIDE 2-OXIME AND BENZYLAMINE IN METHANOL.)

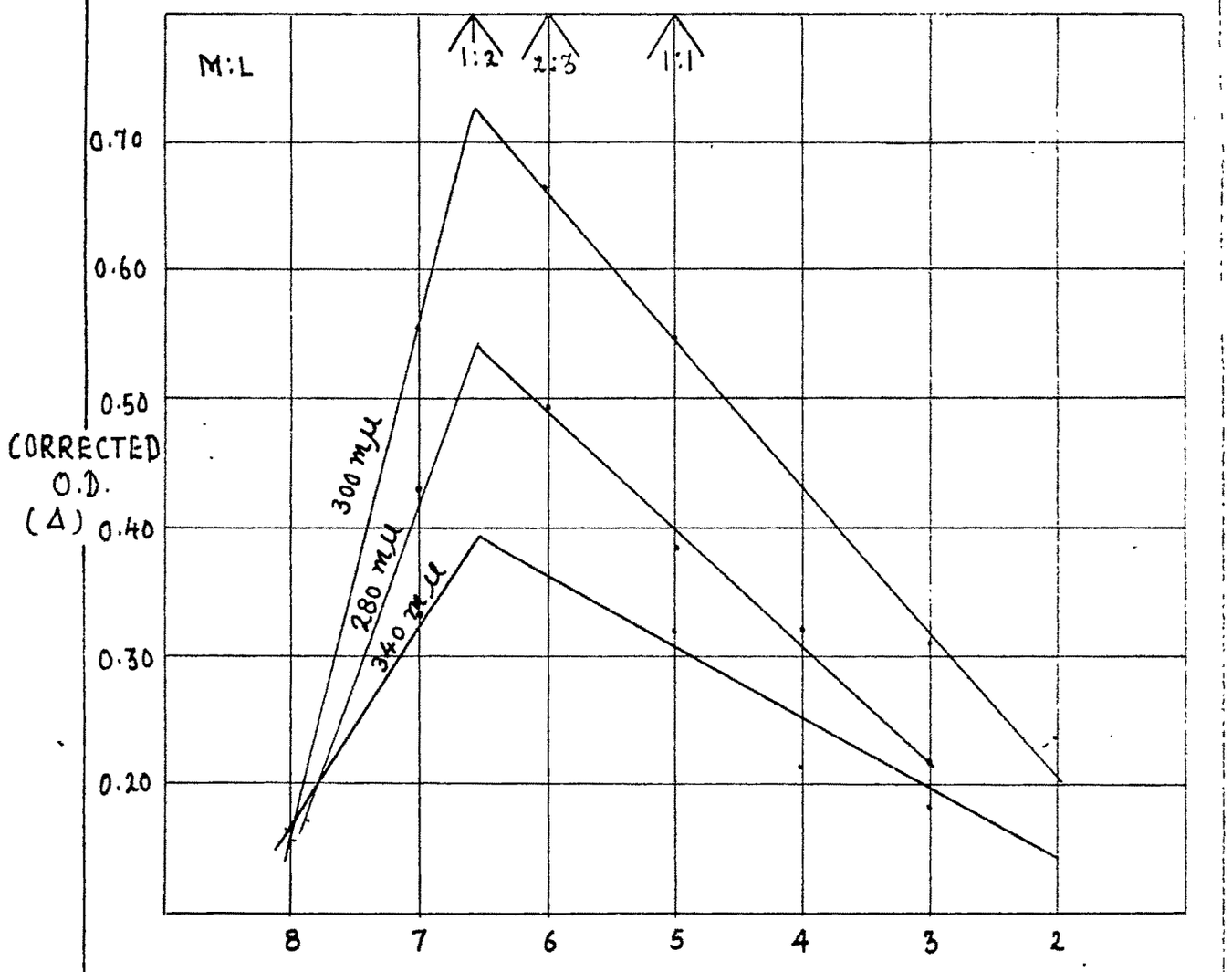


FIG: 24: JOB'S CONTINUOUS VARIATION METHOD.
(MIXTURE OF NICKEL CHLORIDE AND SCHIFF BASE FROM 2-3-DIOXO-BUTYRANILIDE 2-OXIME AND BENZYLAMINE IN PRESENCE OF SODIUM ACETATE IN METHANOL.)

2,3-dioxobutyranilide 2-oxime and aniline. It may be further suggested that "vic-oxime-anils" differ from other vic-oxime-imines in their tendency to form complexes of the type NiL_2 in solution. Thus the Schiff base derived from benzylamine forms the complex NiL_2 in solution, whereas "vic-oxime-anils" appear to form preferentially the complex $[NiL]^+$ rather than $[Ni_2L_3]^+$ in solution. The results also indicate that in the case of complexes formed by "vic-oxime-anils" the complexes present in most of the solutions have different metal-to-ligand ratio than the complexes isolated. Further investigations are necessary to understand the change in the nature of the complex as a result of the transition from solution state to the solid state.

9.(b) Complexes of copper with vic-oxime-imines in solutions :

It has been observed during the isolation of copper complexes that vic-oxime-imines formed complexes with copper where metal-to-ligand ratio was 1 : 1 ; 2 : 3 or 3 : 4. With a view to find out if complexes with similar ratios existed in the mixed solutions of the reactants, continuous variation studies were carried out usually under two conditions and at three selected wave-lengths. Corrected optical densities were calculated for mixtures and are presented in figs 25 to 32.
1 : 1 copper-ligand complexes were prepared where the Schiff base was derived from 2,3-dioxobutyranilide 2-oxime

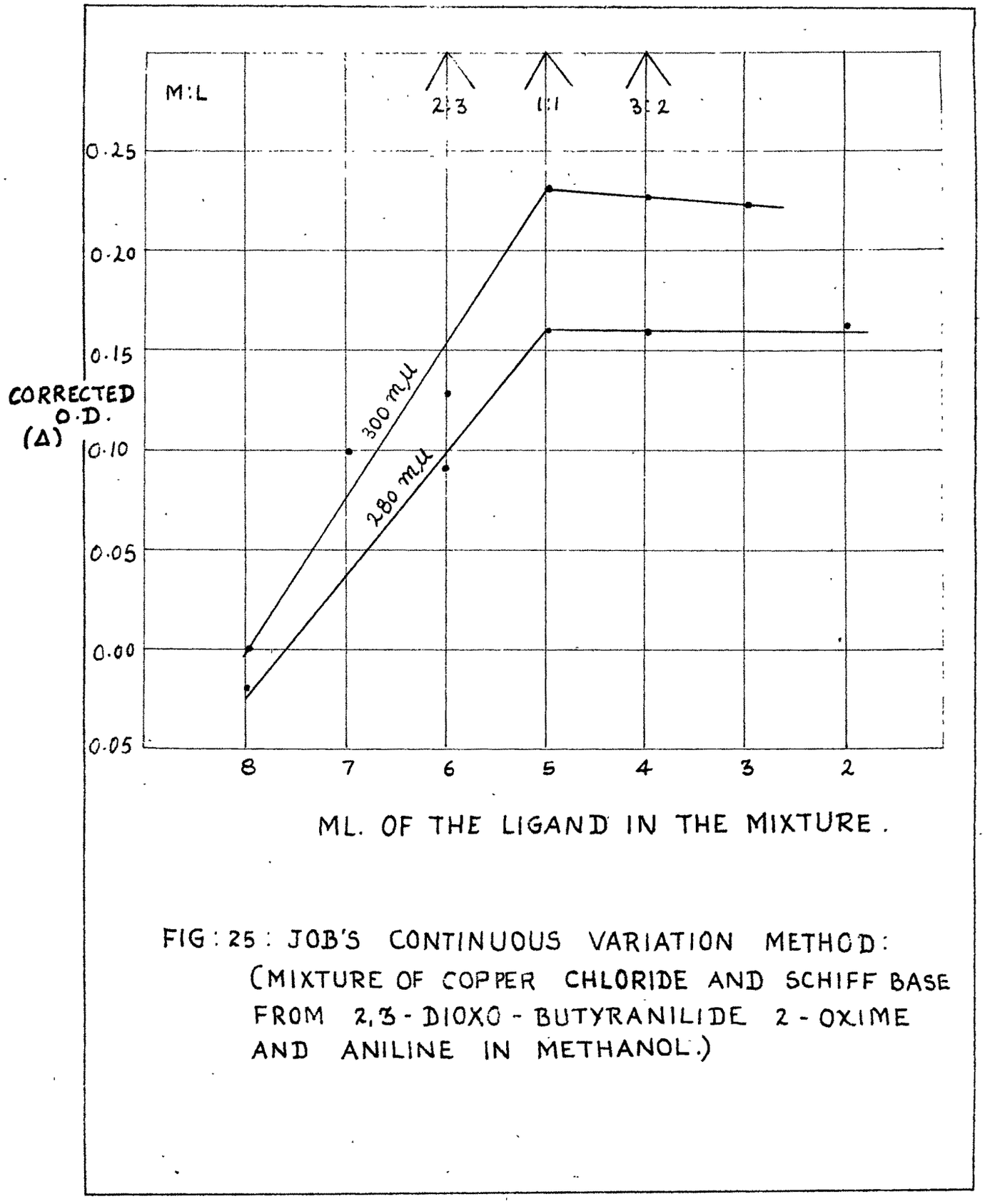


FIG: 25: JOB'S CONTINUOUS VARIATION METHOD: (MIXTURE OF COPPER CHLORIDE AND SCHIFF BASE FROM 2,3-DIOXO-BUTYRANILIDE 2-OXIME AND ANILINE IN METHANOL.)

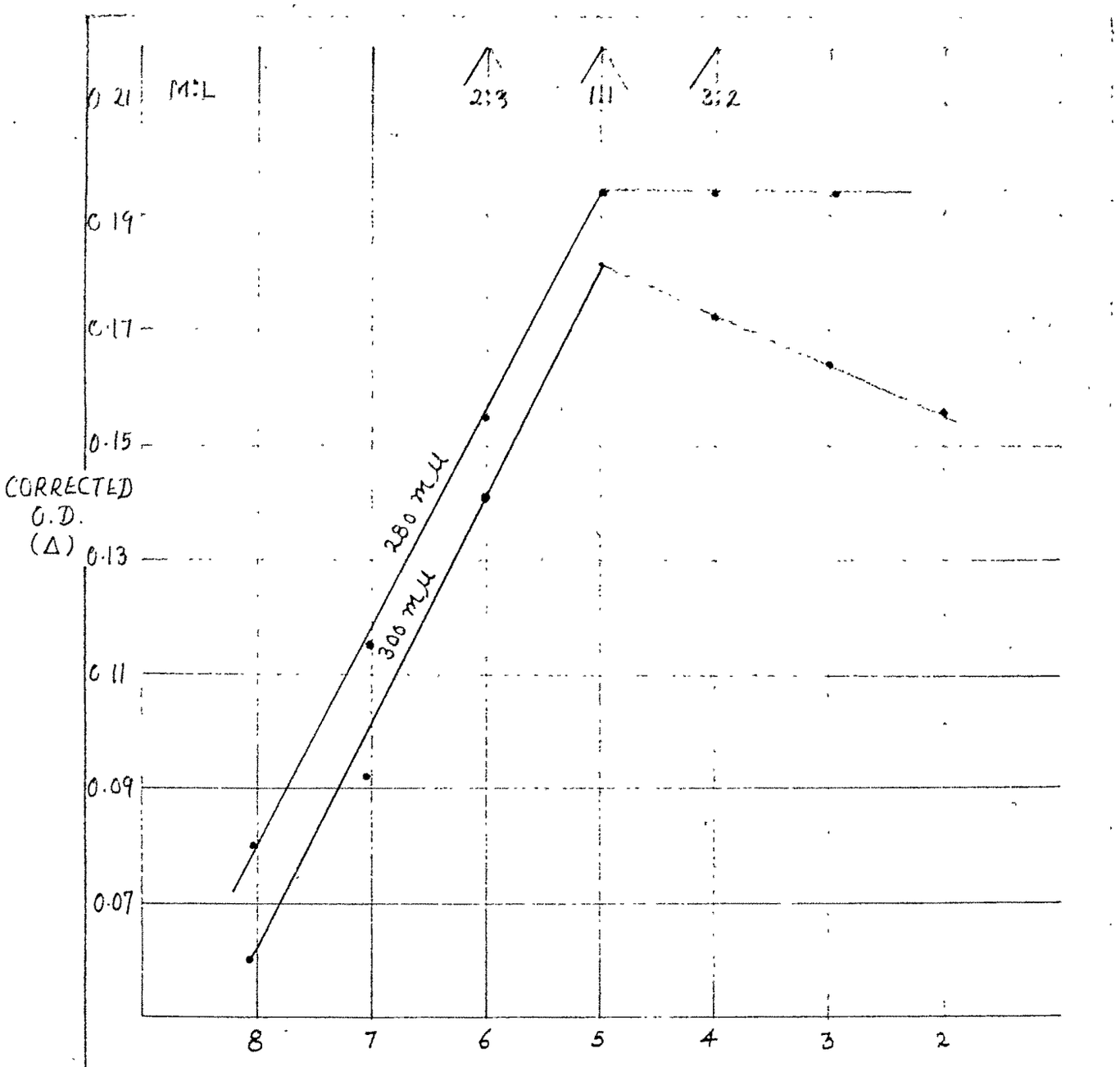


FIG: 26: JOB'S CONTINUOUS VARIATION METHOD. (MIXTURE OF COPPER CHLORIDE AND SCHIFF BASE FROM 2,3-DIOXO-BUTYRANILIDE 2-OXIME AND ANILINE IN PRESENCE OF SODIUM ACETATE IN METHANOL.)

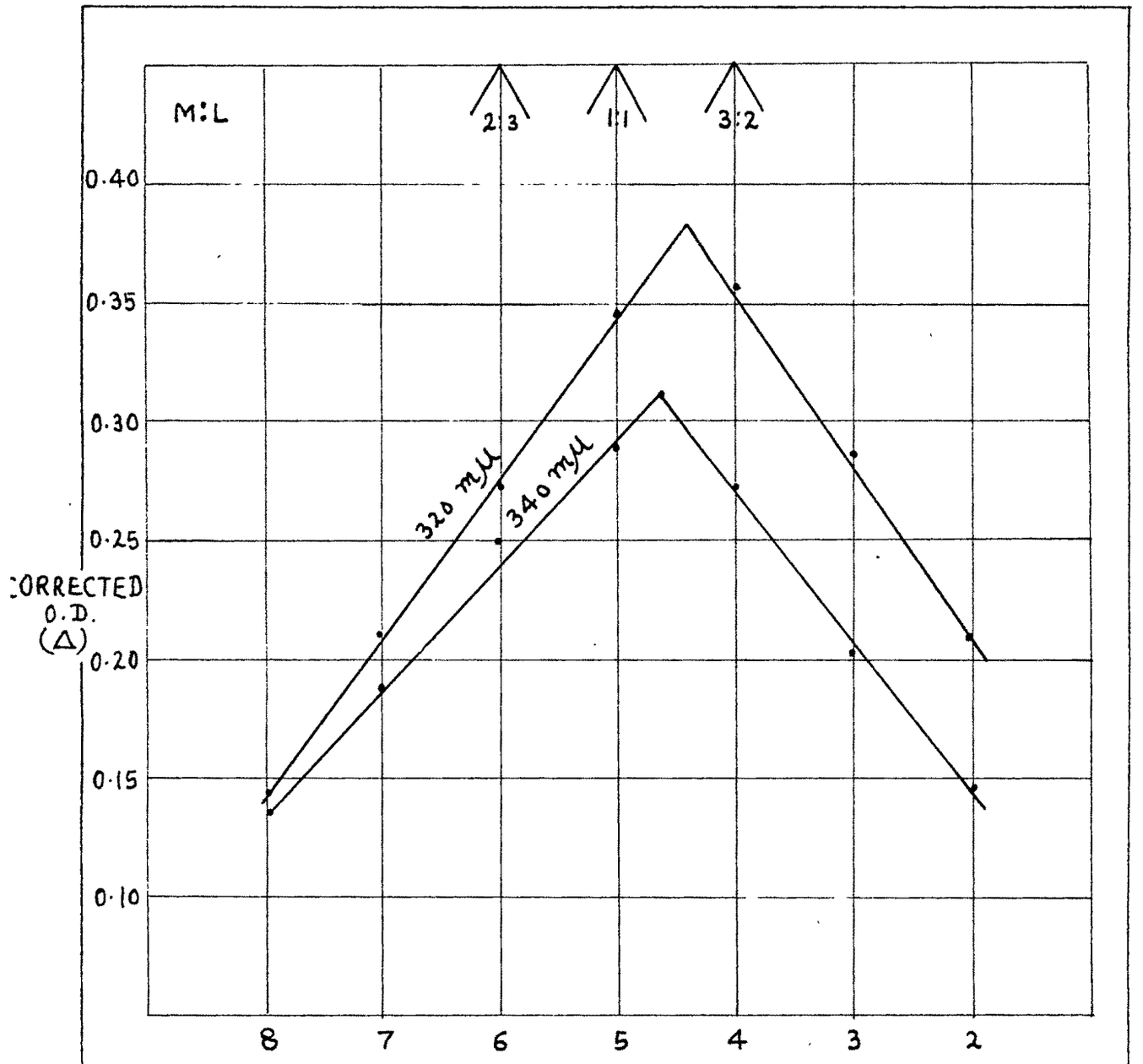


FIG. 28: JOB'S CONTINUOUS VARIATION METHOD.
(MIXTURE OF COPPER CHLORIDE AND SCHIFF BASE FROM 2,3-DIOXO-BUTYRANILIDE 2-OXIME AND BENZYLAMINE IN METHANOL.)

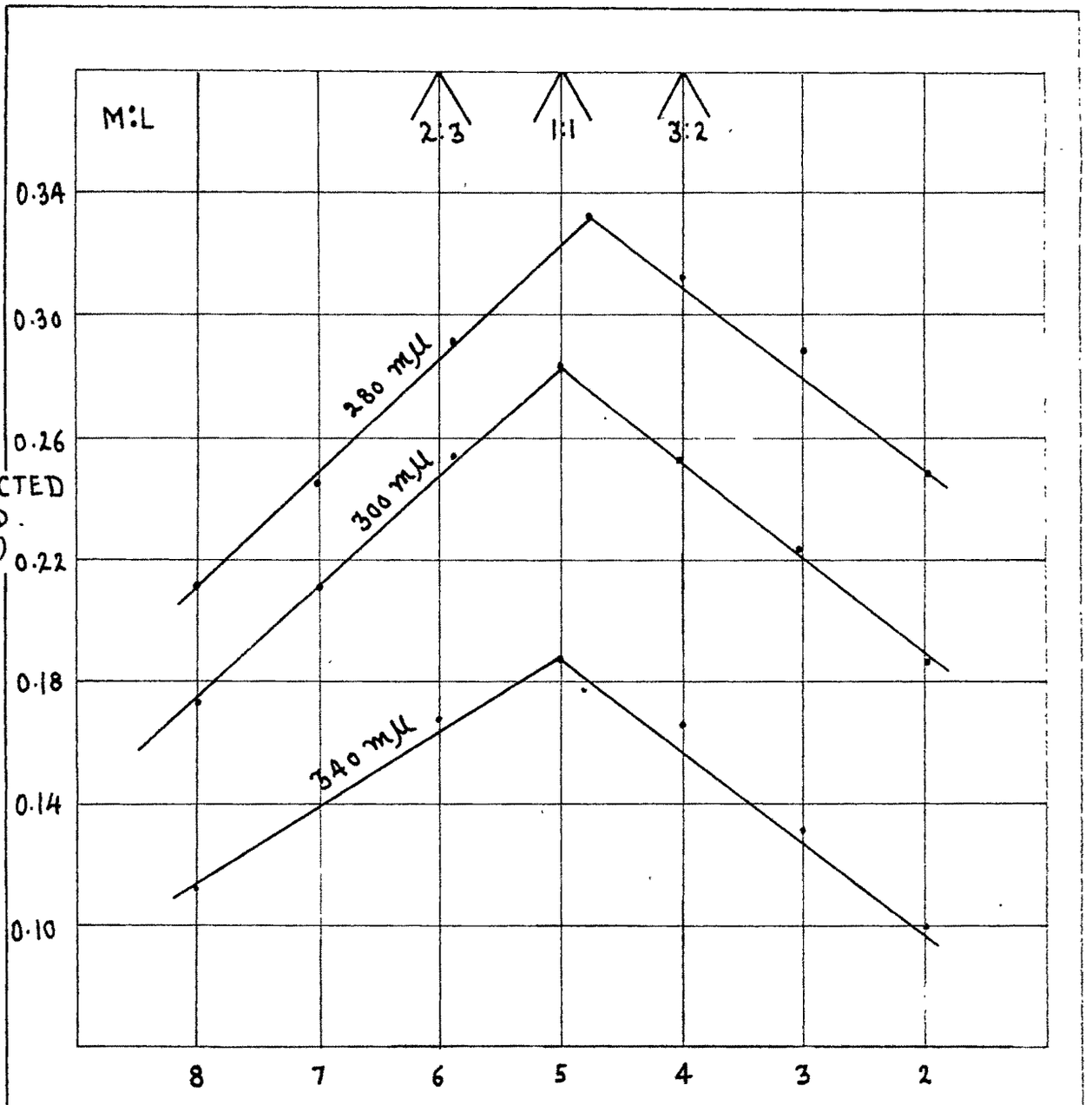


FIG. 29 : JOB'S CONTINUOUS VARIATION METHOD : (MIXTURE OF COPPER CHLORIDE AND SCHIFF BASE FROM 2,3-DIOXO-BUTYRANILIDE 2-OXIME AND BENZYLAMINE IN PRESENCE OF SODIUM ACETATE IN METHANOL.)

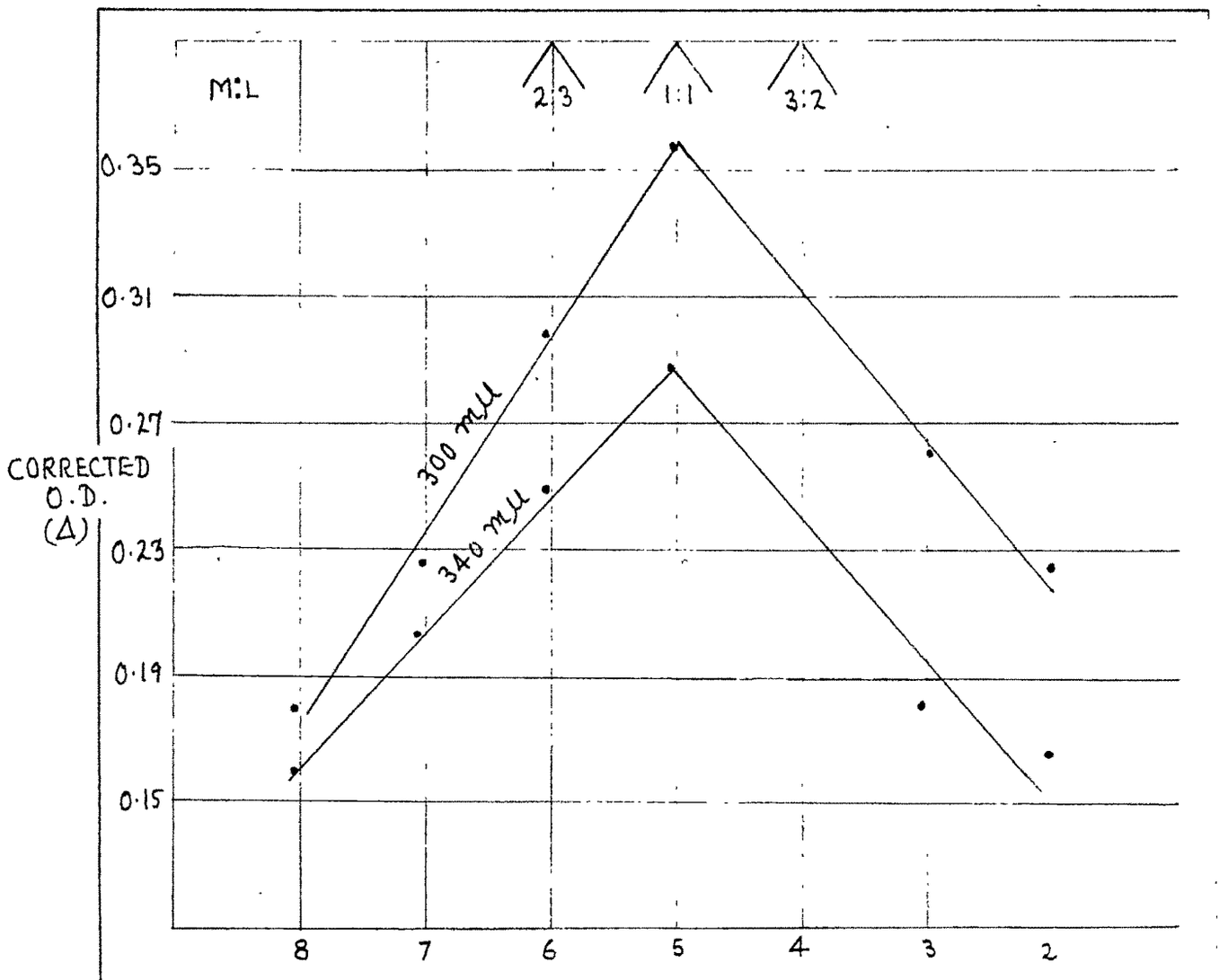


FIG. 30 : JOB'S CONTINUOUS VARIATION METHOD : (MIXTURE OF COPPER CHLORIDE AND SCHIFF BASE FROM 2,3- DIOXO - BUTYRANILIDE 2-OXIME AND p-TOLUIDINE IN METHANOL)

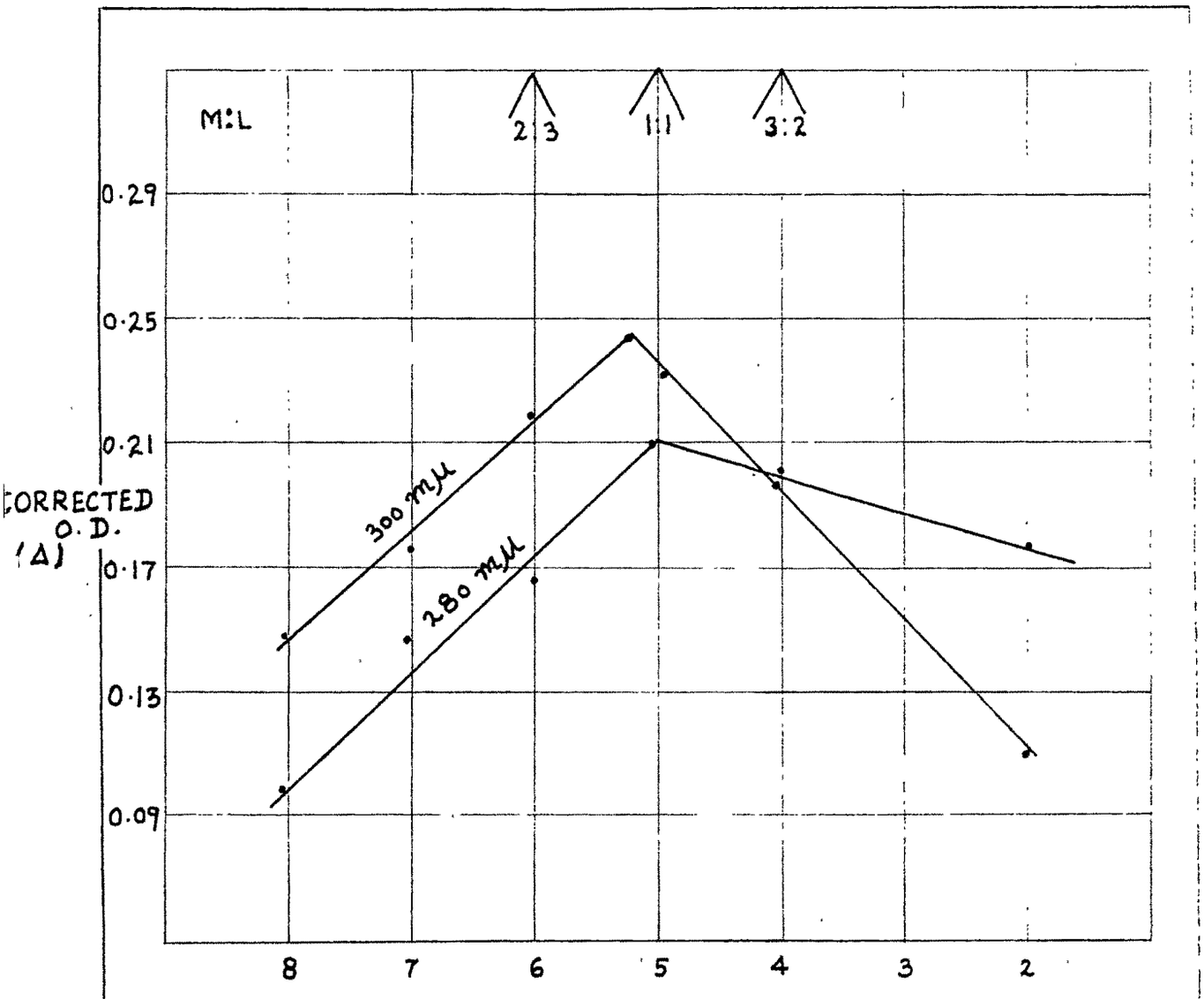


FIG. 31: JOB'S CONTINUOUS VARIATION METHOD. (MIXTURES OF COPPER CHLORIDE AND SCHIFF BASE FROM 2,3-DIOXO-BUTYRANILIDE 2-OXIME AND p-PHENETIDINE IN METHANOL.)

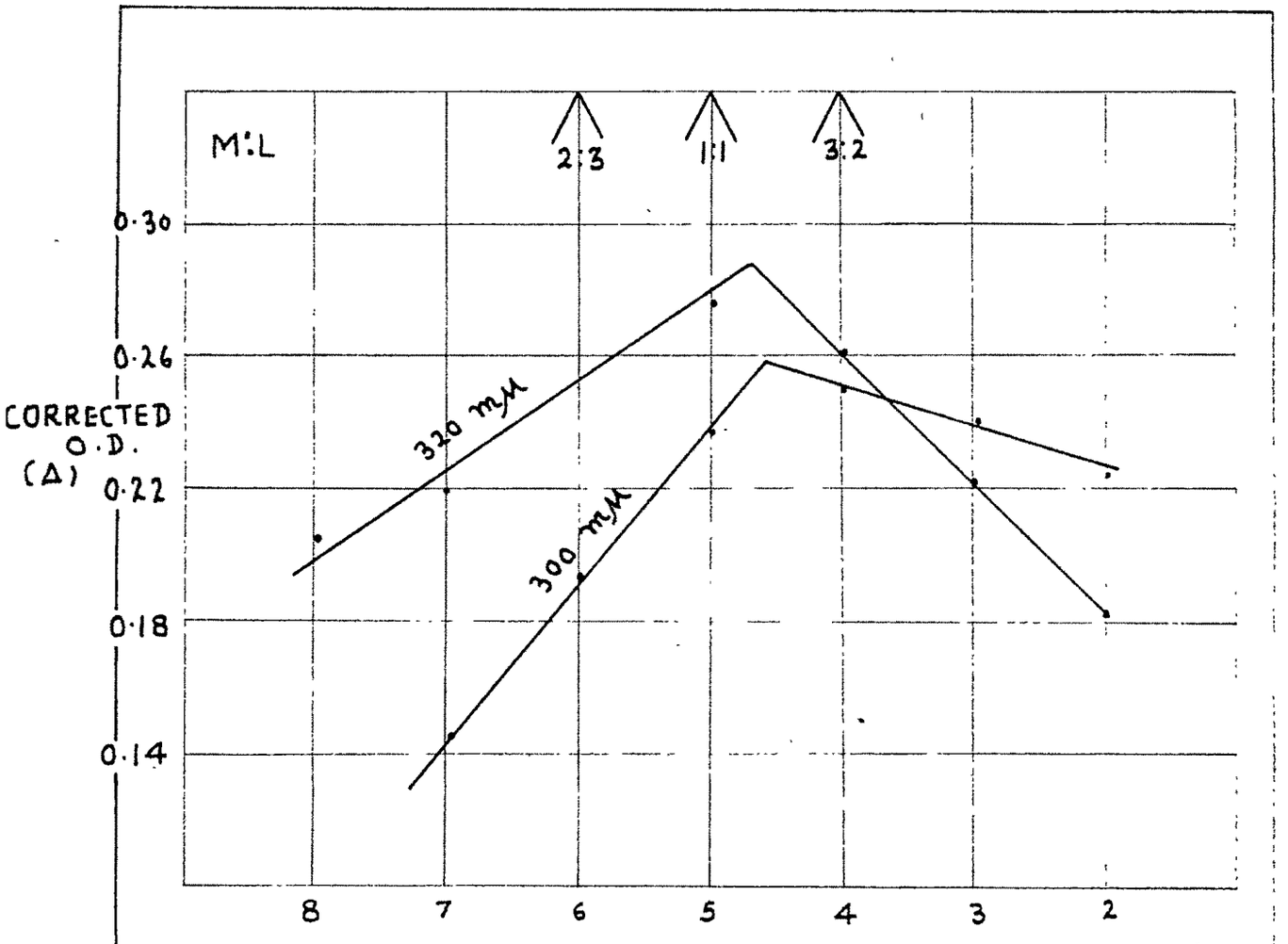


FIG. 32: JOB'S CONTINUOUS VARIATION METHOD: (MIXTURE OF COPPER CHLORIDE AND SCHIFF BASE FROM 2,3-DIOXO-BUTYRANILIDE 2-OXIME AND p-PHENETIDINE IN PRESENCE OF SODIUM ACETATE IN METHANOL.)

and aniline or p-toluidine and the same ratio of 1 : 1 is observed for their complexes in solution. 2 : 3 copper-ligand complexes were prepared in case of the Schiff bases from 2,3-dioxobutyranilide 2-oxime and benzylamine or 2,3-dioxo-o-butyrotoluidide 2-oxime and aniline. The solution studies in these cases appear to favour the formation of complexes with metal-to-ligand ratio of 1 : 1 but the formation of other complexes or rather a mixture of complexes in solution is not excluded.

Similar possibilities arise in case of the copper complex of the Schiff base from 2,3-dioxobutyranilide 2-oxime and p-phenetidine. 3 : 4 copper-ligand complex was isolated ; however, the formation of 1 : 1 complex is favoured in solution. Further, different complexes appear to be formed at different wave-lengths. The results appear to be complicated and need further investigations.