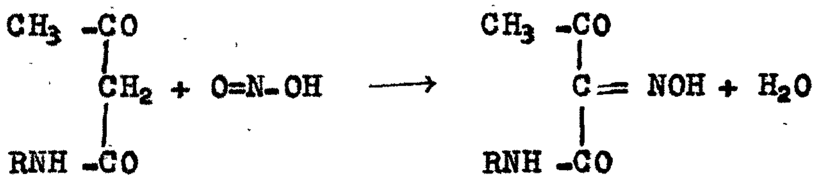
DISCUSSION

1. Structure and stereoisomerism of the monoximes.

1 (a). Structure of the monoximes.

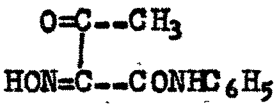
The aryl amides of acetoacetic acid (namely, anilide, o-toluidide, o-chloranilide, o-anisidide, p-chloranilide, p-phenetidide and 2:4-xylidide) were treated with nitrous acid to obtain the respective α-oximino compounds. In the earlier stages of the work, the method suggested by Knorr (173) was followed, but later, the method was modified as given in the experimental part. The uncertainty of the reactivity of the suspended amide was practically overcome by taking the amide in solution in the beginning and getting it in the finely divided form at the reaction stage.



$$\begin{matrix} CH_3\text{-}CO \\ | \\ CH_2 \\ | \\ RNH\text{-}CO \end{matrix} + O{=}N\text{-}OH \longrightarrow \begin{matrix} CH_3\text{-}CO \\ | \\ C{=}NOH \\ | \\ RNH\text{-}CO \end{matrix} + H_2O$$

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

(A)



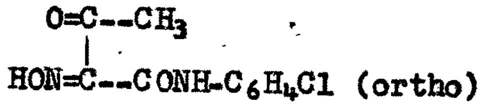
$$\begin{matrix} O{=}C\text{--}CH_3 \\ | \\ HON{=}C\text{--}CONHC_6H_5 \end{matrix}$$

(B)

$$\begin{matrix} O{=}C\text{--}CH_3 \\ | \\ HON{=}C\text{--}CONH\text{-}C_6H_4CH_3 \end{matrix}$$

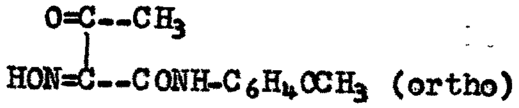
(ortho)

(C)



$$\begin{array}{l} \mathrm{O{=}C{-}{-}CH_3} \\ \quad | \\ \mathrm{HON{=}C{-}{-}CONH{-}C_6H_4Cl}\ \text{(ortho)} \end{array}$$

(D)



$$\begin{array}{l} \mathrm{O{=}C{-}{-}CH_3} \\ \quad | \\ \mathrm{HON{=}C{-}{-}CONH{-}C_6H_4OCH_3}\ \text{(ortho)} \end{array}$$

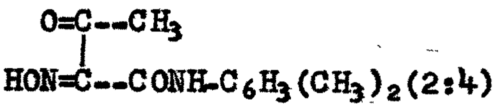
(E)

$$\begin{array}{l} \mathrm{O{=}C{-}{-}CH_3} \\ \quad | \\ \mathrm{HON{=}C{-}{-}CONH{-}C_6H_4Cl}\ \text{(para)} \end{array}$$

(F)

$$\begin{array}{l} \mathrm{O{=}C{-}{-}CH_3} \\ \quad | \\ \mathrm{HON{=}C{-}{-}CONH{-}C_6H_4OC_2H_5}\ \text{(para)} \end{array}$$

(G)



$$\begin{array}{l} \mathrm{O{=}C{-}{-}CH_3} \\ \quad | \\ \mathrm{HON{=}C{-}{-}CONH{-}C_6H_3(CH_3)_2(2{:}4)} \end{array}$$

The evidence that might be adduced in favour of these structures is as follows:

(a) Quantitative micro-analysis (percentage nitrogen) of the new products (C, D, E, F, and G) is in accord with the suggested formulae (vide table-1).

(b) Victor Meyer (73) prepared α-oximino derivative of ethyl acetoacetate by the action of nitrous acid on ethyl acetoacetate and suggested the structure

$$\mathrm{CH_3CO{-}\ C({=}NOH)\ -\ COOC_2H_5}$$

(c) Knorr (173) prepared α-oximino derivative of acetoacetanilide by the action of nitrous acid on acetoacetanilide and attributed the following structure to the product.

$$\mathrm{CH_3CO{-}\ C({=}NOH)\ -\ CONHC_6H_5}$$

(d) Naik, Trivedi and Mankad (174) prepared α-oximino derivatives of the substituted amides of acetoacetic acid by the action of nitrosyl chloride on the respective amides and proposed the following structure.

$$CH_3CO-\ C(=NOH)\ -\ CONHR$$

where R is a phenyl, o-tolyl, p-tolyl, α-naphthyl or β-naphthyl group. They found that α-oximino acetoacetanilide prepared by them was similar in properties to the compound described by Knorr (173).

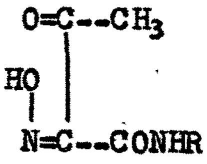
(e) The chelating properties of the group $\begin{matrix}-C=O\\ |\\ -C=NOH\end{matrix}$ are specific. Whiteley (141) observed that the compounds containing $\begin{matrix}-C=O\\ |\\ -C=NOH\end{matrix}$ group form yellow alkali metal compounds and blue or violet ferrous complexes. It is found that the present products exhibit these characteristic reactions. Hence, they should contain the grouping $\begin{matrix}-C=O\\ |\\ -C=NOH\end{matrix}$ and can be represented as

$$CH_3CO-\ C(=NOH)\ -\ CONHR$$

where R is C_6H_5- , $o-CH_3C_6H_4-$, $o-ClC_6H_4-$, $o-CH_3OC_6H_4-$, $p-ClC_6H_4-$, $p-C_2H_5OC_6H_4-$, or $2{:}4(CH_3)_2C_6H_3-$.

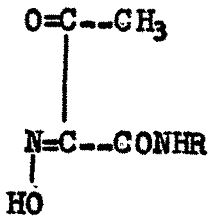
1 (b). Stereoisomerism of the monoximes.

As discussed under the structure of oximes in the introduction, the unsymmetrical monoximes would exhibit stereoisomerism. Thus, the stereo-isomers that might be obtained in the present case may be represented as



$$\begin{array}{l} O{=}C{-}CH_3 \\ HO \quad | \\ \ \,|\ \quad | \\ N{=}C{-}CONHR \end{array}$$

(i)



$$\begin{array}{l} O{=}C{-}CH_3 \\ \quad\ | \\ N{=}C{-}CONHR \\ | \\ HO \end{array}$$

(ii)

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

(1) Whiteley (141) obtained only one compound by the action of nitrosyl chloride on ethyl acetoacetate.

(2) Knorr (173) obtained only one derivative of acetoacetanilide by the action of nitrous acid on acetoacetanilide.

(3) Naik, Trivedi and Mankad (174) obtained only one isomer of α-oximino acetoacet(aryl)amides by the action of nitrosyl chloride on the respective acetoacet(aryl)amides.

(4) Zanetti (202) observed that acetyl acetone, by the action of nitrous acid, yields only one derivative.

(5) According to Hantzsch (203), only one form of isomer is obtained because of the relative instability of the other.

It is known that most of the pairs of isomers have been obtained from aromatic aldehydes and ketones whereas in the aliphatic series only one form is usually isolated. The monoximes under investigation being of the aliphatic series may be considered to have only one stable isomer.

To determine the cis or trans form of the monoxime, Hantzsch' rule may be applied. Hantzsch (203) has arranged the groups in a series on the basis of their attraction for the OH of the oxime group. The series is

$$CH_3 > C_nH_{2n+1} > o\text{-}C_6H_4X > C_6H_5CO > C_6H_5 > CO_2H > CH_2CO_2H \quad .$$

Thus, in the oxime prepared from C_6H_5COR, syn-R form is stable if R comes before C_6H_5 and anti-R form is stable if R follows C_6H_5 in the series. The groups involved in the compounds under investigation are $COCH_3$ and CONHR (where R is an aryl group), which are not found in Hantzsch' series. Hence an attempt is made here to extend Hantzsch' rule on the basis of the attraction of OH of the oxime group as evidenced by the dipole nature of the groups.

The oxime group itself has definite electrical polarity and the groups surrounding it will also have some (or no) polarity with the result that the molecule will exhibit a resultant dipole nature. If it is considered that the electrical polarity of the groups influences the stereochemical arrangement of the groups in a molecule, Hantzsch' rule can be extended on the basis of the electrical polarity of the groups. It can be argued that the most stable arrangement of groups in a molecule will be such that the dipole moment of the molecule will tend to zero. Further, in any arrangement of groups in a molecule, the attraction or repulsion between various polar groups will be of utmost importance. The groups of the same polarity will repel, while the groups of the opposite polarity will attaract. Hence in a stable isomer a negative group will have a tendency to lie towards the more positive of the groups surrounding it. Applying these considerations to the oximes, it can be suggested that the OH of the oxime group will be more attracted by positive than by negative groups and will lie towards the more positive of the two groups. Accordingly some of the important groups may be arranged in order of their decreasing electrical polarity (204) as

$$NH_2 > CH_3 > C_6H_5 > CO > CO_2H \sim CN \quad .$$

This can be interpreted in this way. In the oxime prepared from C_6H_5COR, syn-R form will be stable if R comes before C_6H_5 and anti-R form will be stable if R comes after C_6H_5 in the series.

The same idea can be extended a little further to involve mixed groups. C_nH_{2n+1} will have polarity comparable with that of CH_3, while $COCH_3$ will have polarity less than CH_3, $CONH_2$ will have polarity less than NH_2 and $COCH_3$ will have polarity less than $CONH_2$. Hence, in an oxime RC(=NOH)R' where R is $COCH_3$ and R' is $CONH_2$ (or $CONHC_6H_5$, etc.) the probability is that the anti-R form will be a more stable one as R would follow R'. Thus, from the extended Hantzsch' rule as discussed above, it is deduced that the monoximes under investigation have an anti-acetyl structure (ii).

The stable isomer of these oximes can also be deduced from the considerations of hydrogen-bonded chelate ring. The presence of hydrogen bonded chelate ring in these compounds is concluded from the following evidence:

(1) The compounds form metal chelates with ferrous salts.

(2) The spectroscopic evidence favours the existence of H-bond.

(3) The magnetic susceptibilities of the compounds also indicate the existence of a ring in the molecule.

(These are discussed later under "absorption spectra of the oximes", "stereochemistry of metal chelates and magnetism" and "oximes and inorganic analysis").

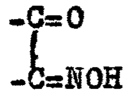
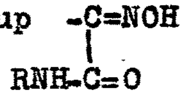
The possibilities of the chelate rings of various sizes can be discussed on the basis of the Bayer's strain theory. Hence it will not be out of place to consider briefly the essential features of the strain theory. This theory is based on the assumption that the angle between two of the valency bonds of an atom has a natural value which is determined by an atomic model and any departure of the angle from this value gives rise to a corresponding strain or instability of the molecule. Many of the common elements like carbon behave as regular tetrahedra with their nuclei at the centres and their valency forces directed towards the apices. These elements include those belonging to the first short period in the periodic classification of elements as well as silicon, phosphorus, sulphur, etc.

The angle formed by the lines joining the centre and the two apices of a regular tetrahedron is $2\tan^{-1}\sqrt{2} = 109°28'$. Hence the angle formed between two single bounds would be 109°28'. When two atoms are joined by two covalent bounds, the tetrahedral figures are regarded as having an edge in common. In such a case (one single bond and one double bond) the angle is $180 - \tan^{-1}\sqrt{2} = 125°16'$. Assuming that the atoms of the cyclic structures lie in the same plane, 3,4,5,6,7, and 8-membered rings would be represented by corresponding polygonal figures. The angles of regular polygons having 3,4,5,6,7, and 8 sides have values of 60°, 90°, 108°, 120°, 128° and 135° respectively. The average strain per atom in rings having different number of double bonds is summarised in the following table:

Average strain per atom in rings

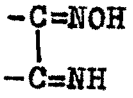
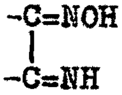
No. of double bonds :	0	1	2	3
No. of atoms in ring				
5	1°28'	7°47'	14°6'	-
6	-10°32'	-5°16'	0°0'	5°16'
7	-19°6'	-14°35'	-10°5'	-5°34'

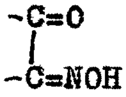
It is important to note here that the basic assumption of the strain theory is that the atoms conform structurally to a tetrahedral symmetry,but considerable evidence has been offerred to show that this is not strictly true.Pauling (205),for example,reports that the natural bond angle for oxygen may often be nearly 90° than 109°28'. Hence the presence of oxygen atoms in a ring will affect the strain and hence also the stability of the ring.It is also known that substituent groups and other adjacent structures may alter conditions of strain; hence attention must be directed to the entire molecule rather than merely to the groups capable of chelation.The possible ring structures present in these compounds,therefore,should be considered keeping these views in mind.

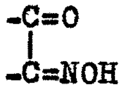
The stable ring structures that might be obtained in the present case would be either 5-or 6-membered ones. That the group  $\begin{array}{l}-C=O\\ |\\ -C=NOH\end{array}$ and not the group  $\begin{array}{r}-C=NOH\\ |\\ RNH-C=O\end{array}$ is involved in the ring formation is deduced from the following evidence:

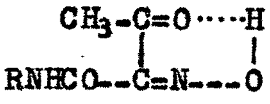
(1) Ethyl α-oximino acetoacetate gives reactions with metal ions which are similar to those of α-oximino acetoacetanilide (178;206).This indicates that NH of -CONHR group is not involved in the chelate ring formation.

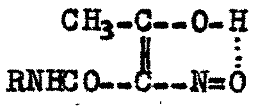
(2) Pfeiffer (207) has shown that anti-oxime-imines having

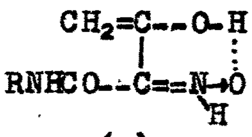
the structural group  $\begin{array}{l}-\mathrm{C{=}NOH}\\ \ \,|\\ -\mathrm{C{=}NH}\end{array}$ form red complexes with nickel in the same manner as with anti-dioximes. It is observed that the compounds under investigation do not exhibit this characteristic property. Desai (206) also found that the metal chelates of nickel with α-oximino acetoacet(aryl)amide, where aryl amide was anilide, o-toluidide, p-toluidide, α-naphthylamide or β-naphthylamide were green. Hence it can be suggested that the ring structure involving the group  $\begin{array}{l}-\mathrm{C{=}NOH}\\ \ \,|\\ -\mathrm{C{=}NH}\end{array}$ is not present in these compounds.

(3) Whiteley (141) and Feigl (208) have observed that the compounds containing the group  $\begin{array}{l}-\mathrm{C{=}O}\\ \ \,|\\ -\mathrm{C{=}NOH}\end{array}$ give a characteristic reaction with ferrous salts-known as the iron-blue reaction. The compounds under investigation give this characteristic iron-blue reaction(vide-table-18). This indicates that the oxime group is involved in the ring structure and that the other group would be an enolisable ketonic group. Further, the iron-blue reaction has been given by compounds which do not contain the amido group. Hence the amido group should not be considered essential for the ring formation.

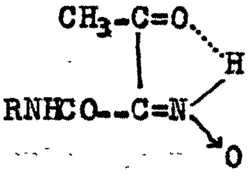
The various possible ring structures involving the group  $\begin{array}{l}-\mathrm{C{=}O}\\ \ \,|\\ -\mathrm{C{=}NOH}\end{array}$ can now be considered. If syn-acetyl configuration is considered to be a stable one, the following (iii, iv and v) 6-membered ring structures may be considered possible.

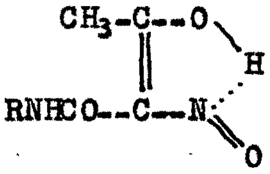

(iii)

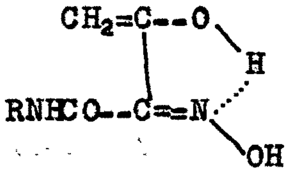

(iv)


(v)

Similarly, if the anti-acetyl structure is considered to be a stable one, the following (vi, vii and viii) 5-membered ring structures may be considered possible.

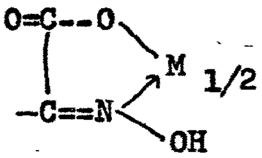

(vi)


(vii)

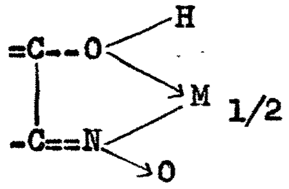

(viii)

Since the syn-acetyl isomer forms 6-membered rings and anti-acetyl isomer forms 5-membered rings, determination of the presence of 5-or 6-membered ring in these compounds may be used to elucidate the isomeric configuration. That the 5-membered ring is present in these compounds is deduced from the following evidence:

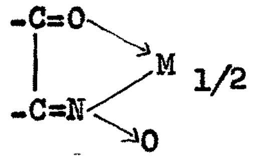
(a) α-Oximino acids form metal chelates (with bivalent metals) having the configuration



(b) α-Hydroxy oximes form metal chelates with bivalent metals, which have the configuration



(c) Monoximes of α-diketones form metal chelate compounds (with bivalent metals) of the following configuration



From the above, it may be suggested that the anti-acetyl isomer would be a more stable one.

Further, it may be noted that in the ring structures of syn-acetyl isomer, H is linked to O atoms, while in the ring structures of anti-acetyl isomer, H is linked to N and O atoms. It will be observed in the above cases (a), (b) and (c) that N and O are linked to M in metal chelates. Hence it may be concluded that the anti-acetyl isomer is a more stable one.

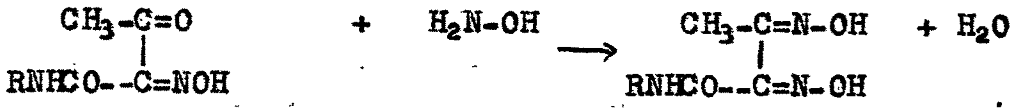
Additional evidence is the observation of Taylor(209) that α-oximino derivative of ethyl acetoacetate has an anti-acetyl structure.

It is concluded, from the above discussion, that α-oximino acetoacet(aryl)amides have an anti-acetyl configuration.

2. Structure and isomerism of the dioximes.

2 (a). Structure of the dioximes.

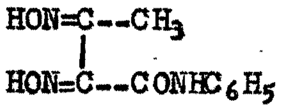
The monoximes, prepared earlier, were converted into dioximes by treating them with hydroxylamine hydrochloride. The reaction is represented as



$$\begin{array}{l}\mathrm{CH_3{-}C{=}O}\\ \qquad\ \ |\\ \mathrm{RNHCO{-}{-}C{=}NOH}\end{array} + \mathrm{H_2N{-}OH} \longrightarrow \begin{array}{l}\mathrm{CH_3{-}C{=}N{-}OH}\\ \qquad\ \ |\\ \mathrm{RNHCO{-}{-}C{=}N{-}OH}\end{array} + \mathrm{H_2O}$$

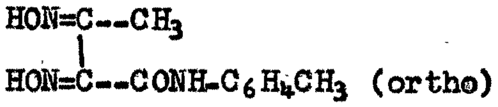
As a result, the products of the following structures are considered to be formed:

(H)



$$\begin{array}{l}\mathrm{HON{=}C{-}{-}CH_3}\\ \qquad\ \ |\\ \mathrm{HON{=}C{-}{-}CONHC_6H_5}\end{array}$$

(I)



$$\begin{array}{l}\mathrm{HON{=}C{-}{-}CH_3}\\ \qquad\ \ |\\ \mathrm{HON{=}C{-}{-}CONH{-}C_6H_4CH_3}\ \text{(ortho)}\end{array}$$

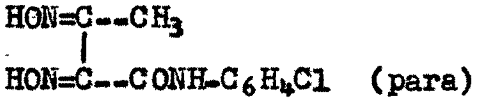
(J)

$$\begin{array}{l}\mathrm{HON{=}C{-}{-}CH_3}\\ \qquad\ \ |\\ \mathrm{HON{=}C{-}{-}CONH{-}C_6H_4Cl}\ \text{(ortho)}\end{array}$$

(K)

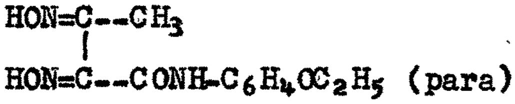
$$\begin{array}{l}\mathrm{HON{=}C{-}{-}CH_3}\\ \qquad\ \ |\\ \mathrm{HON{=}C{-}{-}CONH{-}C_6H_4OCH_3}\ \text{(ortho)}\end{array}$$

(L)



$$\begin{array}{l}\mathrm{HON{=}C{-}{-}CH_3}\\ \qquad\ \ |\\ \mathrm{HON{=}C{-}{-}CONH{-}C_6H_4Cl}\ \text{(para)}\end{array}$$

(M)



$$\begin{array}{l}\mathrm{HON{=}C{-}{-}CH_3}\\ \qquad\ \ |\\ \mathrm{HON{=}C{-}{-}CONH{-}C_6H_4OC_2H_5}\ \text{(para)}\end{array}$$

(N)

$$\begin{array}{l}\mathrm{HON{=}C{-}{-}CH_3}\\ \qquad\ \ |\\ \mathrm{HON{=}C{-}{-}CONH{-}C_6H_3(CH_3)_2(2{:}4)}\end{array}$$

The evidence that might be adduced in favour of these structures is as follows:

(1) Knorr and Reuter (181) have prepared the oxime of α-oximino acetoacetanilide and have attributed the following structure to the product:

$$CH_3C(=NOH)C(=NOH)CONHC_6H_5 .$$

(2) Quantitative micro-analysis (percentage nitrogen) of the new products (vide table-2) is in accord with the suggested formulae.

(3) The chelating properties of the α-dioxime group

$$--C(=NOH)-C(=NOH)--$$

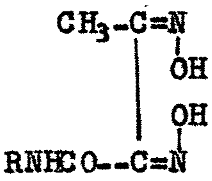
are specific. They have a specific reaction with nickel. (Negative test does not indicate the absence of the dioxime group). It is found that the present products exhibit this specific chelating reaction. Hence they should contain the α-dioxime group and be represented as

$$CH_3C(=NOH)C(=NOH)CONHR$$

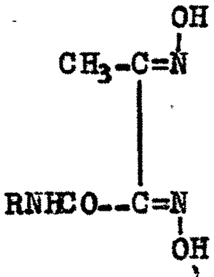
where R is C_6H_5- , $o-CH_3C_6H_4-$, $o-ClC_6H_4-$, $o-CH_3OC_6H_4-$, $p-ClC_6H_4-$, $p-C_2H_5OC_6H_4-$ or $2:4(CH_3)_2C_6H_3-$.

2 (b). Stereoisomerism of the dioximes.

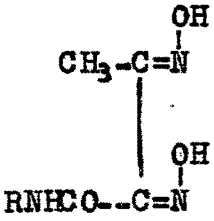
These dioximes would be capable of existing in four stereoisomeric forms:



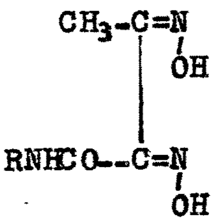
(ix)



(x)



(xi-a)



(xi-b)

Although it would be possible to separate these isomers, only one product is obtained in each case. The stereoisomeric nature of the products can be deduced in the following way:

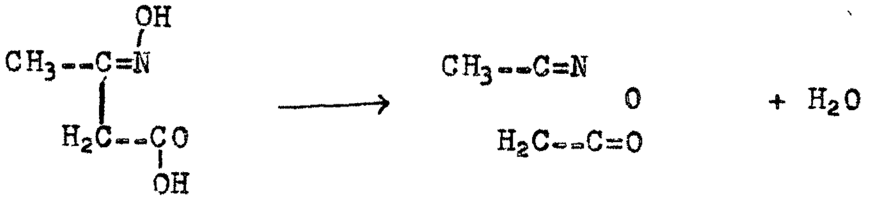
(1) As stated in the introduction under "metal chelates of dioximes" the chelating properties of the isomeric forms are different and hence can be utilised in the determination of the isomeric configuration. Syn-dioxime(ix) would be incapable of forming metallic complexes. Amphi-dioxime (xi-a or xi-b) would form yellow or greenish yellow compounds with nickel in which the dioxime molecule would act as a dibasic acid. Anti-dioxime(x) would form well defined metal chelates with nickel in which the dioxime molecule would act as a monobasic acid. The dioximes under investigation form yellow, orange or red metal chelates with nickel in which the dioxime molecule is found (from analysis) to work as a monobasic acid (vide table-3). Hence it is suggested that the present products have an anti-dioxime structure.

(2) Further evidence which might be presented is based on the following considerations: If the stereoisomeric configuration of α-oximino acetoacet(aryl)amide and β-oximino acetoacet(aryl)amide can be determined, the isomeric configuration of the dioxime molecule can be arrived at on the assumption that the changes in steric configuration are not taking place when α-oximino acetoacet(aryl)amide

is converted into α-β-dioximino acetoacet(aryl)amide. It is shown earlier that α-oximino acetoacet(aryl)amide has an anti-acetyl structure, indicating that the syn-dioxime structure is untenable. Syn-methyl configuration is attributed to β-oxime of acetoacetic acid and its derivatives on the basis of the following evidence:

(a) Application of extended Hantzsch's rule: In the compound RC(=NOH)R', R stands for CH_3 and R' stands for CH_2COOH or $CH_2CONHC_6H_5$. Now, R will have an effective positive polarity and R' will have a polarity less than that of CH_3. Hence R will precede R', suggesting a syn-methyl structure.

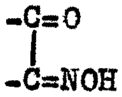
(b) The reactions of the β-oximes of acetoacetic acid and its derivatives indicate the syn-methyl structure of the molecule. Thus, the β-oxime of acetoacetic acid is known to get itself converted into isoxazolone (184-186)



Similarly, β-oxime of acetoacetanilide has been converted into isoxazolone (181). It was believed, earlier, that such elimination would indicate the cis-configuration; but it is now considered more probable that such reactions take place by trans-elimination. Hence the syn-methyl configuration may be attributed to the molecule.

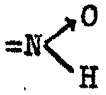
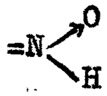
(c) Khromov (183) has also observed that β-oxime of acetoacetic acid has a syn-methyl configuration.

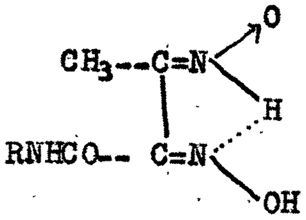
Hence if α-oxime has an anti-acetyl configuration and β-oxime a syn-methyl configuration, the α-β-dioxime should be represented as anti-dioxime.

(3) Ishidata (210) has observed that the dioximes obtained from  $\begin{array}{l}-C=O\\ \;|\\ -C=NOH\end{array}$ have an anti-dioxime configuration.

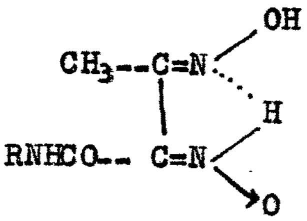
It can be concluded from this evidence that the dioximes under investigation have an anti-dioxime configuration.

2 (c). Structural isomerism of the dioximes.

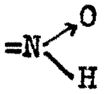
Another point of interest is the determination of the structural isomerism of these dioximes. It has been observed that the oxime group reacts in two isomeric forms =N-OH and  $=N\genfrac{}{}{0pt}{}{\nearrow O}{\searrow H}$. In the case of anti-dioximes which form the compounds of the type $M(DH)_2$ where M is a bivalent metal atom and DH_2 is a dioxime molecule, it is considered that one group will be present as =N-OH and the other as  $=N\genfrac{}{}{0pt}{}{\nearrow O}{\searrow H}$. In the "symmetrical" molecules such as dimethyl glyoxime it is immaterial which of the two groups is present as =N-OH; but in the "unsymmetrical" dioxime molecules under investigation, the difference in the structure will be marked as is shown by the ring structures (xii-a) and (xii-b).



(xii-a)



(xii-b)

To determine the configuration, one may consider the chelating properties of α- and β-monoximes. It has been found that β-monoximes have no chelating abilities. Instead, they are known to be converted into isoxazolones (181;184-186). Hence it may be suggested that the oxime group in β-oxime would be present as =N-OH. On the other hand α-monoximes have been found to form metal chelates with bivalent metals (178;206). In these H of NOH is considered to be replaced. Hence it may be said that the oxime group in α-monoxime would be present as  $=N\begin{smallmatrix}\nearrow O\\ \searrow H\end{smallmatrix}$.

It can be concluded from this evidence that the structural isomer under investigation should have the configuration represented by the structure (xii-b).

3. Absorption spectra of the oximes.

Absorption bands of compounds in the ultraviolet region are attributed to the presence of certain chromophoric and auxochromic groups present in the molecules of the compounds. Conjugation of the chromophoric groups leads to new bands at longer wave-lengths(211-213). It is also observed that (i)isomerism(both structural and geometrical)and (ii) substitution in the chromophore have definite influences on the position and the intensity of the absorption bands(214-215).

The presence of internal hydrogen-bond is suggested in a variety of organic compounds. Qualitatively this has been suggested from the formation of differently coloured metal chelates obtained from such compounds. In the case of phenols, Morton and Stubbs(216) and Burawoy and coworkers(217-218) have shown that an internal hydrogen-bond displaces B and K bands of phenols to longer wave-lengths. Burawoy et al.(218) have also shown that the absorption bands of chelated phenols are almost unchanged in different solvents.

In the case of glyoximes and mono-and di-oximes of α-diketones the presence of intramolecular hydrogen-bond is suggested from the chemical behaviour of these compounds and is shown from the studies of Raman spectra and infra red spectra of these compounds (87-90). Ultraviolet and visible absorption spectra of such compounds do not appear to have been much investigated with a view to determine the presence of such a bond. In the present investigations an attempt has been made to investigate the presence of internal hydrogen-bond in the molecules and to correlate some of the absorption bands with the chromophoric groups present in the molecules.

Absorption spectra of acetoacet(aryl)amides in the ultraviolet region have been investigated by Ramart-Lucas, Naik and Trivedi(219) in alcoholic solution by means of Zeiss spectrograph. They concluded from their results that a considerable quantity of the enol form was present in the alcoholic solutions. They also studied the effect of methyl substituent in the benzene nucleus on the nature of the absorption curves.

Naik, Trivedi and Mankad(220) studied the absorption spectra of acetoacet(aryl)amides in aqueous solution in the ultraviolet region by means of Hilger Quartz spectrograph. They observed absorption bands in the range 240-280 mu and ascribed them to the presence of ketonic group in the aqueous solution. They(220) also investigated the absorption spectra of α-chloro and α-oximino derivatives of acetoacet(aryl)amides in aqueous solution in the ultraviolet region. They observed that the effect of the transormation of $-CH_2-$ group into $-\underset{|}{C}HCl$ or into $=C=NOH$ is to increase the degree of absorption and to shift the curves towards the visible. They also pointed out that generally the heavier the substituent in the benzene nucleus the greater is the shifting of the absorption curves towards the visible.

In the present investigations the absorption spectra of monoximes and dioximes of acetoacet(aryl)amides in aqueous, alcoholic and chloroform solutions in the ultraviolet region and of some monoximes of acetoacet(aryl)amides in alcoholic and sodium hydroxide solutions in the visible region are studied.

3 (a). Absorption spectra of the monoximes in aqueous solution.

O.D. (optical density) of some monoximes in aqueous solutions were measured for different wave-lengths in the ultraviolet region and the corresponding $\log_{10} E_m$ values are given in the table-7; the corresponding absorption spectra are traced in fig. 2. The wave-length maxima(λ_{max}) and the corresponding molar extinction coefficient (E_m) for these monoximes are recorded in table-34.

TABLE-34

Monoxime (A- denotes α-oximino acetoacet-)	λ_{max} (mμ)	E_m
A-anilide	237-39	14570
	280-81	9043
A-o-toluidide	224-27	14940
	264-68*	3900-4000*
A-o-chloranilide	231-33	17800
	280-81	9759
A-o-anisidide	233-35	23620
	282-84	9840
A-2:4-xylidide	-	-
	268-76*	4800-4900*

* inflection or shoulder

The results indicate that in general these monoximes

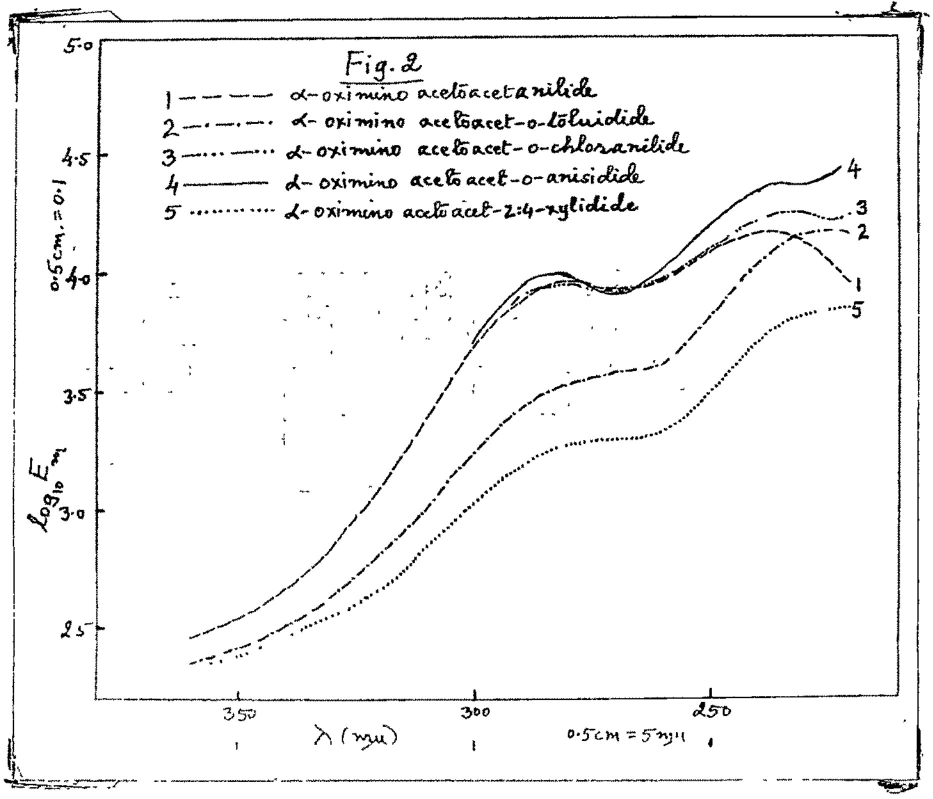


Fig.2 : Absorption spectra of the monoximes in aqueous solutions(in the ultraviolet region).

exhibit two bands in aqueous solution-first in the region 224-39 mμ and the second in the region 264-84 mμ. It may be pointed out that both bands appear to be affected by the presence of substituents in the benzene nucleus. It may be suggested that in the case of α-oximino acetoacet-2:4-xylidide the first band has moved to the end (less than 224 mμ) and hence has not been observed. The hypsochromic shift observed in the case of the first band is in the order

$$2{:}4\ (CH_3)_2 > o\text{-}CH_3 > o\text{-}Cl > o\text{-}CH_3O > H .$$

Burawoy et al. (218) have observed recently that in the case of nitrosobenzene derivatives, p-methoxy group causes a red shift of K band and a blue shift of B band; the reverse is true in the case of o-methoxy group. In the present investigation, o-substituents cause a blue shift of the band. This indicates that the absorption band in the region 224-39 mμ is a K band. In the case of the second band (264-84 mμ) o-methoxy group causes a red shift of the band. This indicates that the absorption band in the region 264-84 may be a B band.

3 (b). Absorption spectra of the monoximes in alcoholic solutions.

O.D. of some monoximes in alcoholic solutions were measured for different wave-lengths in the ultraviolet region and the corresponding $\log_{10} E_m$ values are given in table-8; the corresponding absorption spectra are traced in fig-3. The λ_{max} and the corresponding E_m for these monoximes (in alcoholic solutions) are recorded in table-35.

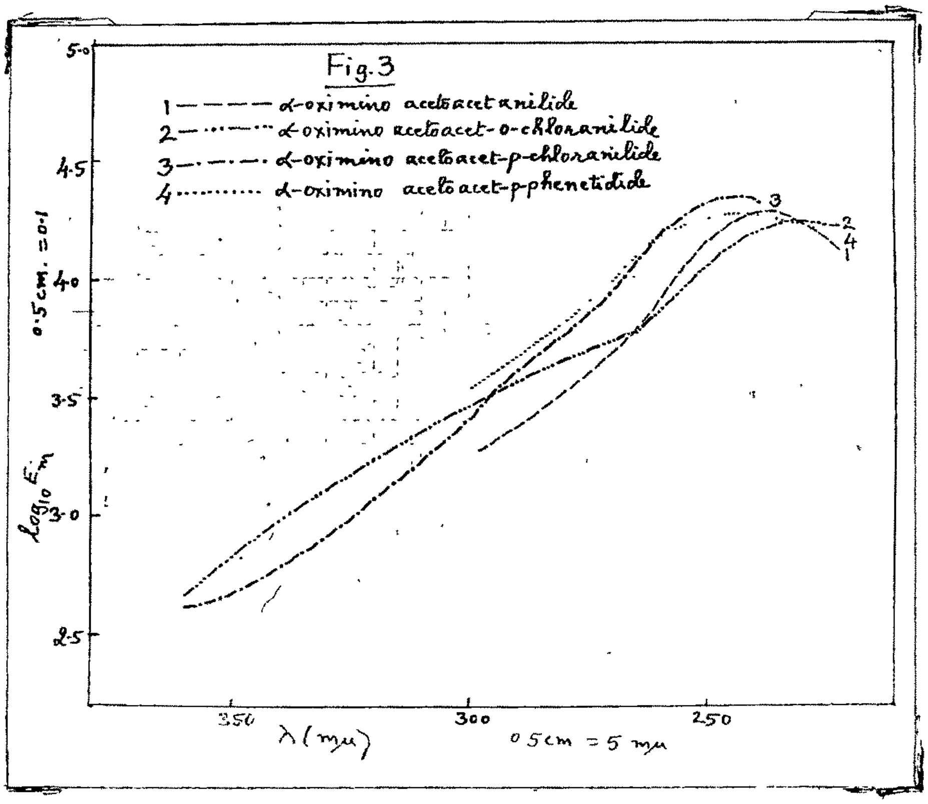


Fig.3 : Absorption spectra of the monoximes in alcoholic solutions(in the ultraviolet region).

TABLE-35

Monoxime (A- denotes α-oximinoacetoacet-)	λ_{max} (mμ)	E_m
A-anilide ≠	236-38	18940
A-o-chloranilide +	231-33	17280
	264 *	6233 *
A-p-chloranilide +	242-46	21220
A-p-phenetidide +	241-44	18310

≠ solution in rectified spirit

\+ solution in methanol

* inflection or shoulder

The results indicate that the monoximes(except α-oximino-acetoacet-o-chloranilide) in alcoholic solutions exhibit a single band in the region 231-46 mμ. This band is influenced by the substitutents in the benzene nucleus.

It is observed that o-substitutents cause a hypsochromic shift of the band and p-substituents a bathochromic one. As suggested in the case of aqueous solutions of monoximes, this shift of the band in alcoholic solutions indicates that the band is a K-band. It is further observed that in the case of chloro-substituted compounds, o-and p-chloro-substituents have nearly the same but opposite value of the shift.

In the table-36 are given the values of λ_{max} for some of the monoximes in aqueous and alcoholic solutions for the purpose of studying the solvent effect.

TABLE-36

Monoxime (A- denotes a-oxmininoacetoacet)	λ max (aqueous solution) (mμ)	λ max (alcoholic solution) (mμ)
A-anilide	238-9	236-8
A-o-chloranilide	231-3	231-3

These results indicate that there is not any appreciable shift when water is replaced by alcohol. This indicates that both -C=O and -C=NOH should not be free; hence these may be considered to form a chelate ring involving hydrogen-bond (218).

O.D. of some monoximes in methanol and sodium hydroxide solutions were measured for different wave-lengths in the visible regions and the corresponding E_m values are given in table-9; the corresponding absorption spectra are traced in fig 4. It is seen from the figure that there is no absorption band in the region 400-650 mμ. The curve can be divided, however, into two parts-one of nearly complete transmittance and the other of absorption. These two meet in the region 445-60 mμ in the case of alcoholic solutions and in the region 470-80 mμ in the case of sodium hydroxide solutions. It may be suggested that the pale yellow colour of the solutions is not due to the presence of any chromophoric groups present in the molecule and absorbing in the visible region.

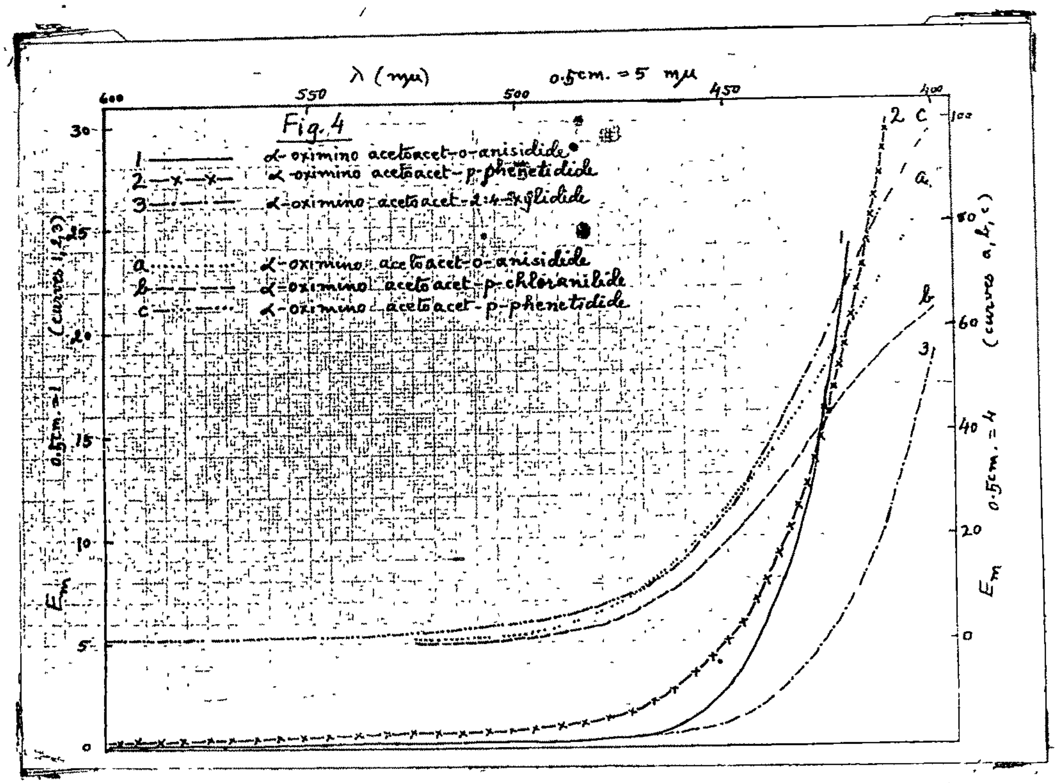


Fig.4 : Absorption spectra of the monoximes in alcoholic and sodium hydroxide solutions (in the visible region).

3 (c). Absorption spectra of the monoximes in chloroform solutions.

O.D. of some monoximes in chloroform solutions were measured for different wave-lengths in the ultraviolet region and the corresponding $\log_{10} E_m$ values are given in table-10; corresponding absorption spectra are traced in fig 5. The λ_{max} and the corresponding E_m for these monoximes (in chloroform solutions) are recorded in table-37.

TABLE-37

Monoxime (A- denotes α-oximinoacetoacet-)	λ_{max} (mμ)	E_m
A-o-toluidide	306-10	5031
A-o-chloranilide	306-08	6566
A-o-anisidide	290-94	3780
	328-34	5134
A-p-phenetidide	298-301	4359
	334-38	5289

It is observed from the results that (i) a single band in the region 306-10 mμ is observed if the substituent in the benzene nucleus is CH_3 or Cl; and (ii) two bands-one in the region 290-301 mμ and the other in the region 328-38 mμ are observed if the substituent in the benzene nucleus is an alkoxy group.

3 (d). Absorption spectra of the dioximes in aqueous solutions.

O.D. of the dioximes in aqueous solutions were

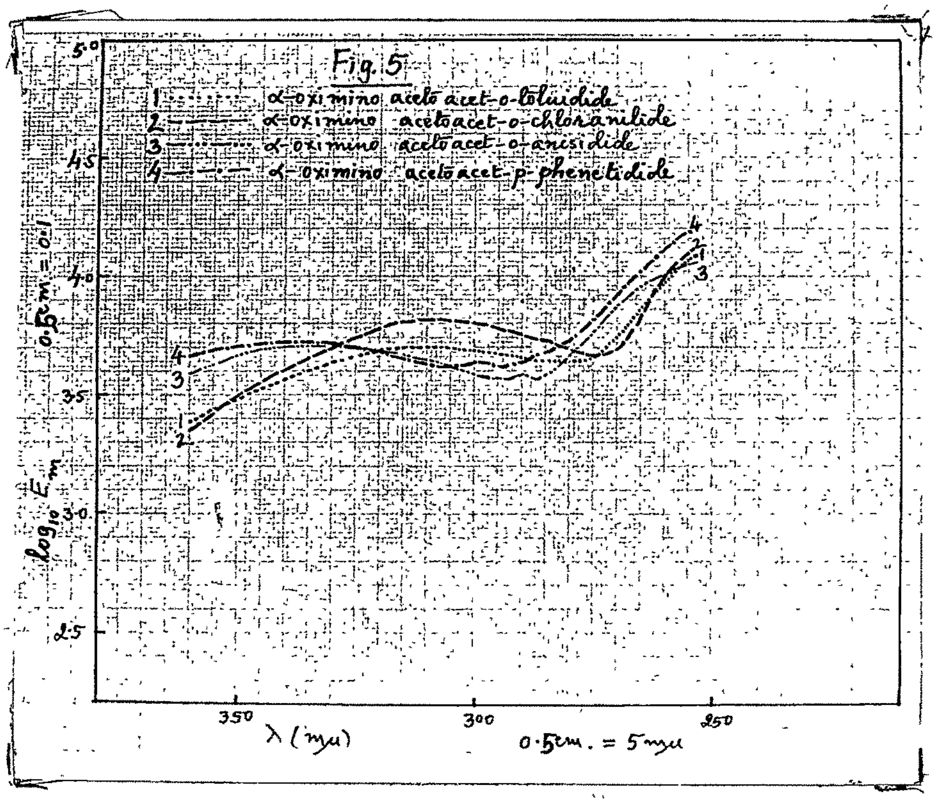


Fig. 5 : Absorption spectra of the monoximes in chloroform solutions (in the ultraviolet region).

measured for different wave-lengths in the ultraviolet region and the corresponding $\log_{10} E_m$ values are given in table-11; the corresponding absorption spectra are traced in fig-6. The λ max and the corresponding E_m values for the dioximes in aqueous solutions are recorded in table-38.

TABLE-38

Dioxime	λ max (mμ)	E_m
(D-denotes α-β-dioximinoacetoacet-)		
D-Anilide	233-34	19820
D-o-toluidide	230-31	18820
D-o-chloranilide	231-32	18660
D-o-anisidide	280-82	7192
D-p-chloranilide	238-39	18090
D-p-phenetidide	234-36	21330
D-2:4-xylidide	228-31	18630
	308-31*	9454*

* inflection or shoulder

The results indicate that in general these dioximes (except D-anisidide and D-2:4-xylidide) in aqueous solution exhibit a single band in the region 228-42 mμ. It is seen from the table that o-substituents in benzene nucleus cause a blue shift of the band and p-substituents, a red shift of the band.

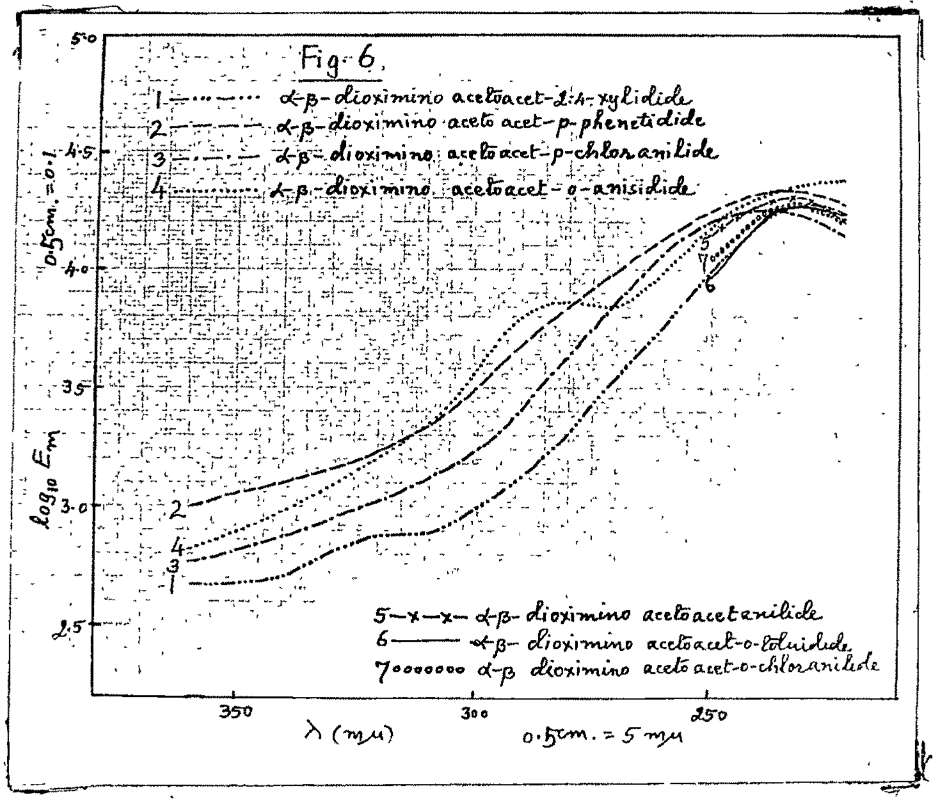


Fig.6 : Absorption spectra of the dioximes in aqueous solutions(in the ultraviolet region).

As suggested in the case of monoximes this is indicative of the K-nature of the band. The bathochromic shift observed in the case of p-substituents is in the order

$$p\text{-}Cl > p\text{-}C_2H_5O > H$$

and the hypsochromic shift observed in the case of o-substituents is in order

$$o\text{-}CH_3 > o\text{-}Cl > H$$

3 (e). Absorption spectra of the dioximes in alcoholic solutions.

O.D. of some dioximes in alcoholic solutions were measured for different wave-lengths in the ultraviolet region and the corresponding $\log_{10} E_m$ values are given in table-12; the corresponding absorption spectra are traced in fig-7. The λ max and the corresponding E_m values for the dioximes in alcoholic solutions are recorded in table-39.

TABLE-39

Dioxime	λ max (mμ)	E_m
(D-denotes α-β-dioximinoacetoacet)		
D-anilide	236-38	25930
D-o-anisidide	234-36	19340
	282-83	6029
D-p-phenetidide	235-40	12290
D-2:4-xylidide	230-32	20300

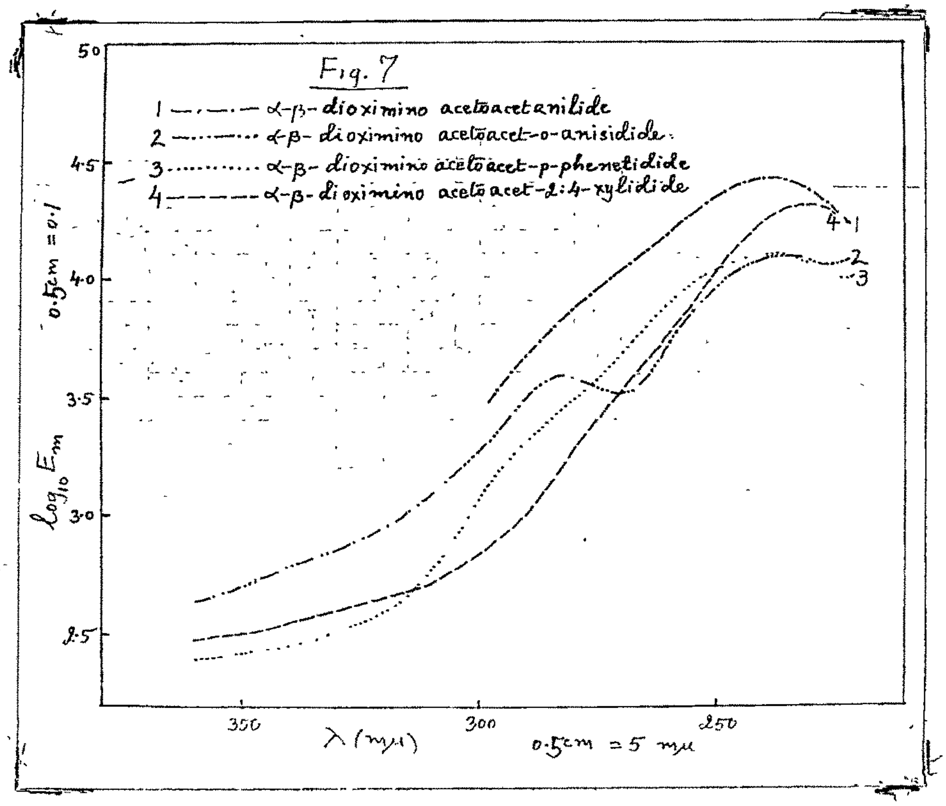


Fig.7 : Absorption spectra of the dioximes in alcoholic solutions(in the ultraviolet region).

The results indicate that the dioximes(except α-β-dioximinoacetoacet-o-anisidide) in alcoholic solution exhibit a single K-band in the region 230-40 mμ. The shift of the band by the substituents in benzene nucleus is as observed before.

The values of λ max of the dioximes in aqueous and alcoholic solutions are compared in table-40

TABLE-40

Dioxime (D-denotes α-β-dioximinoacetoacet)	λ max (mμ) (aqueous solutions)	λ max (mμ) (alcoholic solutions)
D-anilide	233-34	236-38
D-o-anisidide	280-82	282-83
D-p-phenetidide	234-36	235-40
D-2:4-xylidide	228-31	230-32

In general the normal solvent effect is not observed; instead a slight blueshift is observed when the dielectric constant of the solvent increases. This indicates that the oxime groups are involved in an intramolecular chelate ring.

3 (f). Absorption spectra of the dioximes in chloroform solutions.

O.D. of some dioximes in chloroform solutions were measured for different wave-lengths in the ultraviolet region and the corresponding $\log_{10} E_m$ values are given in table-13; corresponding absorption spectra are traced in fig 8. The λ max and the corresponding E_m for these dioximes (in chloroform solutions) are recorded in table-41.

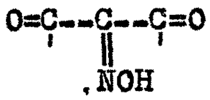
TABLE-41

Dioxime	λ max (mμ)	E_m
(D-denotes α-β-dioximinoacetoacet-)		
D-o-anisidide	310-14	6940
D-p-phentidide	310-14	5600
D-o-toluidide	-	-
D-o-chloranilide	-	-
D-2:4-xylidide	-	-

The results indicate that (i) a single band in the region 310-4 mμ is observed, if the substituent in the benzene nucleus is alkoxy group; and (ii) no band is observed if the substituent in the benzene nucleus is CH_3 or Cl.

3 (g), Absorption spectra of the oximes and conjugation.

The monoxime and the dioxime of acetoacetanilide absorb maximally in the region 233-39 mμ in the aqueous and alcoholic solutions. This band may be attributed to the conjugated system



$$O{=}\underset{|}{C}{-}{-}\underset{\underset{NOH}{\|}}{C}{-}{-}\underset{|}{C}{=}O$$

(in the case of monoxime)

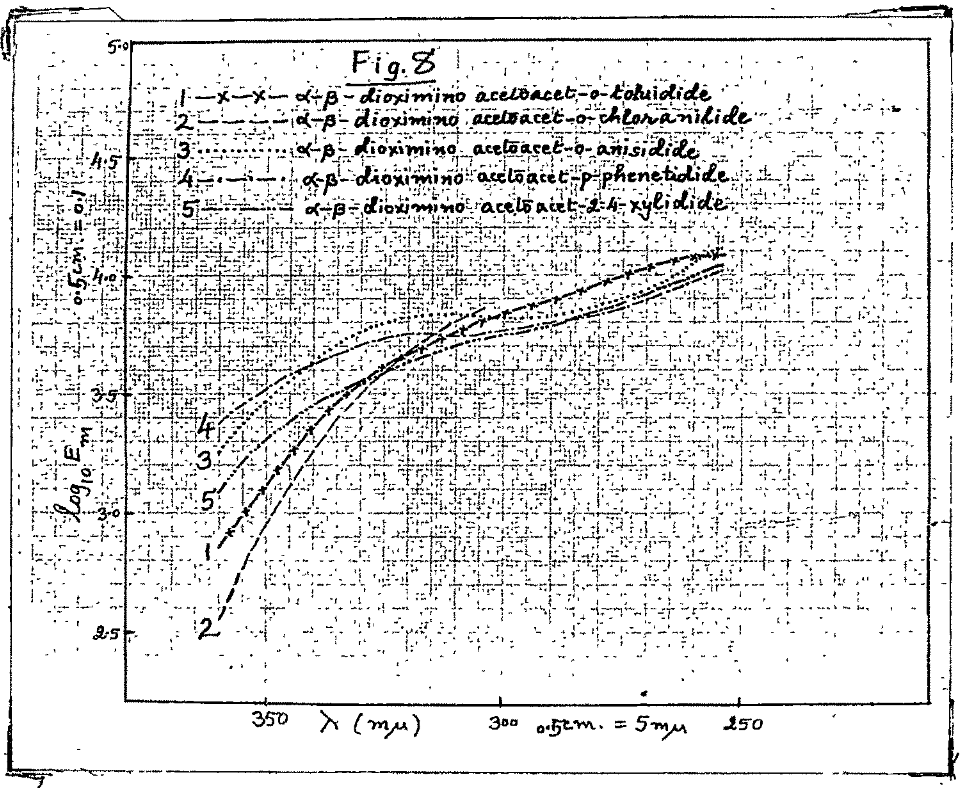
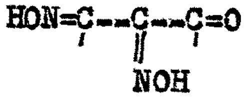


Fig. 8 : Absorption spectra of the dioximes in chloroform solutions (in the ultraviolet region).

or 

$HON{=}\underset{|}{C}{-}{-}\underset{\underset{NOH}{\|}}{C}{-}{-}\underset{|}{C}{=}O$

(in the case of dioxime). It has been observed by others (221-222) that the formation of oxime from the ketone does not cause considerable shift in the band. This is confirmed from the present investigations as shown in the table-42.

TABLE-42

Substance	α-monoxime of X-amide λ max (mμ)	α-β-dioxime of X-amide λ max (mμ)	
(X-denotes acetoacet-)			
X-anilide	236-38	236-38	*
X-o-chloranilide	231-33	231-32	+
X-o-toluidide	224-27	230-31	+

* alcoholic solution

\+ aqueous solution

Thus, the two conjugated systems can have the absorption band in the same region.

That the band in the region 233-39 mμ is due to the **conjugation** of three unsaturated groups in crossed manner, as suggested above, is concluded from the following evidence:

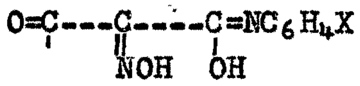
(1) Braude (223) has suggested that the conjugation of three unsaturated centres absorb maximally at 240-65 mμ and that

crossed conjugation often leads to a lower value of λmax. Hence the band in the region 233-39 mμ may be attributed to the crossed conjugation system as given above.

(2) Dimethyl glyoxime (224) has a conjugated system

$HON{=}\overset{|}{C}{-}{-}\overset{|}{C}{=}NOH$ and absorbs maximally at 226 mμ. If the system is further conjugated to a carbonyl group in a crossed manner a bathochromic shift of about 10-15 mμ may be observed. This would shift the band to 235-40 mμ as is observed in the present oximes.

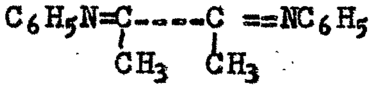
In the chloroform solutions the oximes have a band in the region 306-14 mμ or at 290-300 mμ and 328-38 mμ. This may be attributed to the conjugated system



$$O{=}\underset{|}{C}{-}{-}{-}\underset{NOH}{\underset{\|}{C}}{-}{-}{-}{-}\underset{OH}{\underset{|}{C}}{=}NC_6H_4X$$

The following evidence is added in favour of the above suggestion:

(1) Diacetyl dianil



$C_6H_5N{=}\underset{CH_3}{\underset{|}{C}}{-}{-}{-}{-}\underset{CH_3}{\underset{|}{C}}{=}{=}NC_6H_5$ (224) absorbs maximally at 300 mμ and 325 mμ, the values of E_m being 2000 for both bands. The oximes under investigation also have $\log_{10} E_m$ values (4000-7000) and hence should have a conjugation of four unsaturated centres as shown above.

(2) Cinnamal acetone $C_6H_5{-}{-}CH{=}CH{-}{-}CH{=}CH{-}{-}COCH_3$ (225) has an absorption band at 320 mμ, corresponding to the presence of a conjugated system of four unsaturated centres.

4. Chelation.

4 (a). Detection of chelation.

The monoximes and the dioximes under investigation form metal chelates with some of the transitional metals. The formation of the metal chelates is suggested from the following evidence:

(1) Synthesis: The dioximes form well defined metal chelates with copper, nickel, cobalt and palladium (vide tables-3 to 6). Their molecular composition is established by analysis and their chelate nature is suggested from valency and coordination number considerations.

(2) Colour reactions: With the dioximes nickel forms yellow, orange or red compounds, copper forms brown compounds, cobalt forms chocolate brown compounds, ferrous iron forms brown black compounds and palladium forms yellow or red compounds. Similarly, the monoximes form blue or bluish violet compounds with ferrous iron (vide table-18). All these colour reactions are characteristic of complex or chelate formation.

(3) Solubility of the complex compounds: These compounds have very low solubility in water and some of them e.g. those with ferrous iron, have solubility in organic solvents, indicating their complex or chelate nature.

(4) pH effect: Addition of the dioxime solution to the solution of the salts of copper, nickel, cobalt or pelladium or of the monoxime solution to the solution of ferrous iron salt

causes a drop in the pH. This indicates that weak acidic protons of the chelating agents are displaced by the metal ions.

(5) Magnetism: Magnetic measurements (vide <u>table-14</u>) suggest that the compounds formed by the dioximes with copper, nickel, cobalt and palladium are not salts involving ionic bonds but can be represented as chelates involving strong covalent bonds.

4 (b). Effect of chelating agent on chelation.

Many properties of the chelates are determined by the nature of the organic chelating agent which combines with the metal ion. Thus the size of the ring, the number of rings formed with the given metal ion, the nature of the groups involved in chelation, etc., are governed by the structure of the chelating agent. One of these namely, the size of the chelate ring is considered here with reference to the structure of the dioximes discussed before.

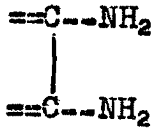
Size of the chelate ring:

It has been observed that 5-or 6-membered rings are almost always encountered with chelate compounds. That 5-membered rings are present in these compounds is shown from the following evidence:

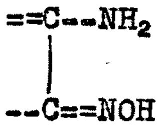
(1) The structure of the α-dioximes is shown to be anti-dioxime. The anti-dioximes can form only 5 membered rings

with metals. Hence metals forming chelates with these dioximes would form 5-membered rings.

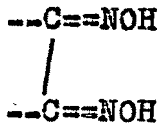
(2) The chelating agents involving the groups



$$\begin{array}{l}=C-NH_2\\ \quad|\\ =C-NH_2\end{array}$$



$$\begin{array}{l}=C-NH_2\\ \quad|\\ -C=NOH\end{array}$$



$$\begin{array}{l}-C=NOH\\ \quad|\\ -C=NOH\end{array}$$

(anti)

are known to form five membered rings with metals(40;48; 116;117;120;226). Hence the dioximes under investigation would form 5-membered rings with the metals.

4 (c). Influence of metal ion on chelation.

It may be said that although chelation takes place with substantially all positive metals, the transitional metals are considered to have the strongest tendency for combining with electron donors. The factors which govern the relative tendencies for various metals to combine with a given donor may be divided into two classes:

(a) ionic forces related to charge and radius of the metal ion; and

(b) relative tendencies of metal ions to form covalent bonds with electron donors.

The relative effects of these two properties would be the same whether the donor is a chelating agent or merely a complexing agent. However, in the case of chelates other factors, particularly of a stereochemical nature also operate and further complicate the interpretation of the experimental work. In spite of this, many properties of chelates have been related in a qualitative manner to the properties of the metal ions.

Mellor and Maley (32) have correlated the stability constants of some chelates with the nature of the metal ions linked. They suggested the order of the bivalent metal ions as

$Pd > Cu > Ni > Pb > Co > Zn > Cd > Fe > Mn > Mg$.

Stability seemed to decrease with increasing basicity of the metal. Irving and Williams (34) have plotted stability constants against at.no.of metal ions. The curves obtained for different chelating agents are similar. They give the order as

$Mg < Fe < Co < Ni < Cu > Zn$.

They have used (a) pH for 50 % precipitation (b) pH for 50 % extract ion and (c) pH for incipient precipitation as indicative of the stabilities.

In the present investigations (a) pH of incipient precipitation and (b) pH of complete precipitation of copper, nickel and palladium by the dioximes have been determined. The results are recorded in <u>tables-16 and 17</u>. The results are in accordance with the observations of others (32;34;227). The relative stabilities are in the order

$Pd > Cu > Ni$.

5. Structures of metal chelates.

Metal chelates of nickel, copper, cobalt and palladium with the dioximes under investigation were prepared and their colour, m.p., analysis (micro), etc., are tabulated in tables 3 to 6.

5 (a). Nickel chelates.

The products obtained by treating nickel chloride with the dioximes under investigation are formulated as follows on the basis of analysis:

(1) $NiC_{20}H_{20}N_6O_6$

(2) $Ni\ C_{22}H_{24}N_6O_6$

(3) $Ni\ C_{20}H_{18}N_6O_6Cl_2$

(4) $Ni\ C_{22}H_{24}N_6O_8$

(5) $Ni\ C_{20}H_{18}N_6O_6Cl_2$

(6) $Ni\ C_{24}H_{28}N_6O_6$

(7) $Ni\ C_{24}H_{28}N_6O_6$

The reaction can be represented as

$$Ni^{++} + 2HC_4H_5N_3O_3R \longrightarrow Ni\ (C_4H_5N_3O_3R)_2 + 2H^+$$

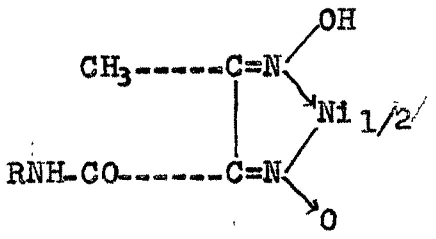
where R is an aryl group.

These products are insoluble in water and in organic solvents and do not melt upto 280°C. These properties suggest that the products may be salts. These properties, however, should not be taken as conclusive evidence in deciding the nature of the substances, as the following properties clearly suggest that the products are complex compounds or chelates:

(1) The products have red, orange or yellow colour. Such colours are known in the cases of complex or chelate compounds only and not in the cases of purely ionic compounds.

(2) Magnetic studies of the compounds investigated have shown that the compounds are diamagnetic and not paramagnetic (vide table-14). This suggests that the products are not salts involving ionic bonds but should be chelates involving strong covalent bounds.

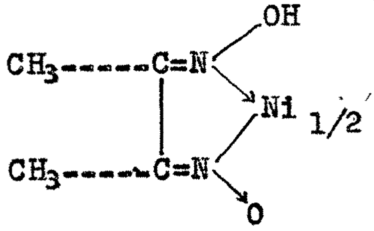
Hence the products may be represented as



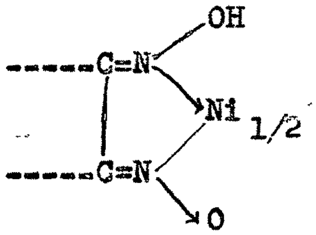
where R is an aryl group .

Further evidence in support of this structure is as follows:-

(1) Pfeiffer (116,117) has attributed the following structure to the nickel chelate of dimethyl glyoxime:



(2) Voter and Banks (115) have suggested the following structure for the nickel chelates of the dione dioximes of cycloparaffins:



(3) The dioximes under investigation are shown to have an anti-dioxime structure involving H-bond; nickel chelate will be formed by the replacement of H atom involved in H-bond.

5 (b). Copper chelates.

The products obtained by treating copper chloride with the dioximes under investigation are formulated as follows on the basis of analysis:

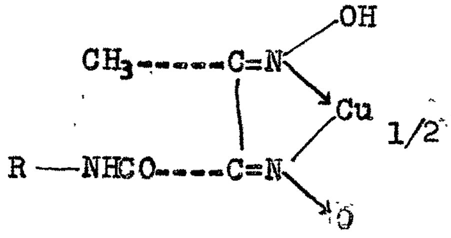
(1) Cu $C_{20}H_{20}N_6O_6$
(2) Cu $C_{22}H_{24}N_6O_6$
(3) Cu $C_{20}H_{18}N_6O_6Cl_2$
(4) Cu $C_{22}H_{24}N_6O_6$
(5) Cu $C_{20}H_{18}N_6O_6Cl_2$
(6) Cu $C_{24}H_{28}N_6O_8$
(7) Cu $C_{24}H_{28}N_6O_6$

The reaction can be represented as

$$Cu^{++} + 2HC_4H_5N_3O_3R \longrightarrow Cu\,(C_4H_5N_3O_3R)_2 + 2H^{+}$$

where R is an aryl group

These are insoluble in water and in organic solvents and melt below 280°C. Further they are brown in colour and the magnetic evidence indicates the presence of strong covalent bonds in them (discussed later under stereochemistry of metal chelates and magnetism). Hence the compounds may be considered to be chelates and not salts. Since the dioximes are considered to have an anti-dioxime structure, the chelates may be represented as



where R is an aryl group.

5 (c). <u>Cobalt chelates</u>.

The products obtained from the acidified solution of the dioxime and cobalt chloride by adding ammonium acetate are formulated as follows:

(1) Co $C_{20}H_{24}N_6O_8$

(2) Co $C_{22}H_{28}N_6O_8$

(3) Co $C_{20}H_{22}N_6H_8Cl_2$

(4) Co $C_{24}H_{32}N_6O_{10}$

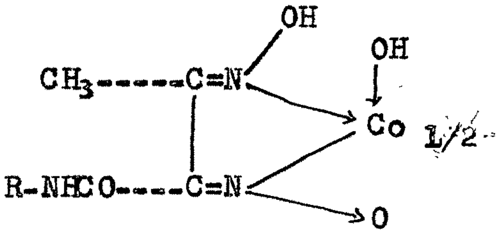
(5) Co $C_{24}H_{32}N_6O_8$

The reaction can be represented as

$$Co^{++} + 2HC_4H_5N_3O_3R + 2H_2O \longrightarrow Co\,(C_4H_5N_3O_3R)_2\,(H_2O)_2 + 2H^+$$

where R is an aryl group.

These are insoluble in water and in organic solvents and do not melt upto 280°C. Further, the magnetic evidence indicates the presence of strong covalent bonds. Hence the compounds may be considered to be chelates and not ionic salts. Since the dioximes are considered to have an anti-dioxime structure, the chelates may be represented as



where R is an aryl group.

5 (d). Palladium chelates.

The products obtained by treating palladium chloride with the dioximes are formulated as follows on the basis of analysis:

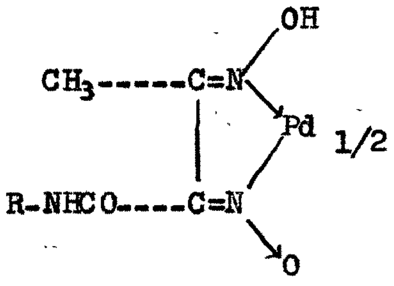
(1) Pd $C_{20}H_{20}N_6O_6$
(2) Pd $C_{22}H_{24}N_6O_6$
(3) Pd $C_{20}H_{18}N_6O_6Cl_2$
(4) Pd $C_{24}H_{28}N_6O_8$
(5) Pd $C_{24}H_{28}N_6O_6$

The reaction can be represented as

$$Pd^{++} + 2HC_4H_5N_3O_3R \longrightarrow Pd(C_4H_5N_3O_3R)_2 + 2H^{+}$$

where R is an aryl group.

These are insoluble in water and in organic solvents and do not melt upto 280°C. Further, the magnetic evidence is considered to suggest the presence of covalent bonds in them, as in the case of nickel chelates. Hence the compounds may be considered to be chelate compounds and be represented as follows on the basis of the anti-dioxime configuration of the dioxime:



where R is an aryl group.

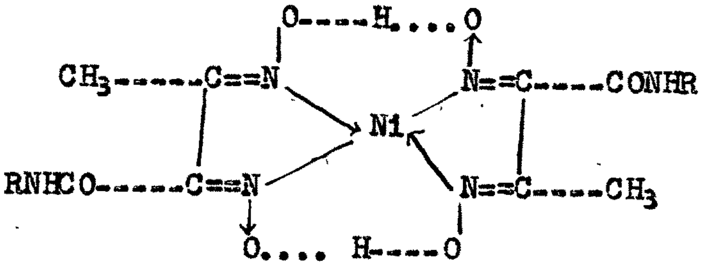
6. Stereochemistry of the metal chelates and Magnetism.

Magnetic measurements of some of the chelates prepared are carried out on the Gouy's magnetic balance, and the values of the magnetic susceptibilities obtained, together with the magnetic moments of these compounds are presented in <u>table-14</u>.

6 (a). <u>Nickel chelates</u>.

Bivalent nickel has two unpaired electrons with a normal moment of about 3 B.M. In a tetrahedral complex involving ionic bonds or only 4s and 4p orbitals in weak covalent bonds, the moment remains unchanged. But square planar nickel complexes, involving $3d4s4p^2$ covalent bonds, are diamagnetic. Therefore the classification of nickel complexes as tetrahedral or planar is readily made on the basis of magnetic measurements. The three nickel chelates studied are all diamagnetic. This indicates that $3d4s4p^2$ covalent bonds are involved in these chelates and that they have a square planar configuration. It may be mentioned here that all the red or yellow nickel chelates of anti-dioximes studied by others (119-122) have been shown to be diamagnetic, and to possess square planar configuration.

Since the products are suggested to have a planar structure, they may be considered to exist in cis and trans. isomeric forms. Several attempts to isolate them have failed. It is believed, however, that the stable isomer obtained is a trans one (vide, Brady and Muers, 128) and that the cis isomer might be formed at the stage of incipient precipitation. Further, OH of the oxime group is not considered to be free; hence, in accordance with the structures suggested by Brady and Muers (128) and by Voter et al.(129), these can be represented as follows:



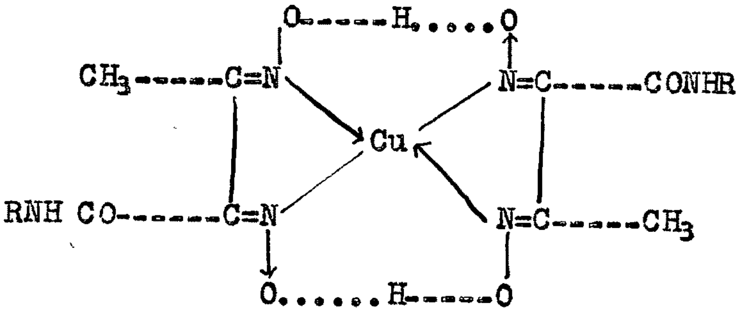
6 (b). Palladium chelates.

Palladium is an analogue of nickel in the periodic table but is considered to have no unpaired electron in 4d shell. Hence palladium may be considered to form diamagnetic complexes (228). A number of palladium complexes have been investigated by Janes (229) and are found to be diamagnetic. The palladium chelates studied here are diamagnetic. They may be considered to involve $4d5s5p^2$ covalent bonds and to have a planar configuration as in the case of nickel chelates. Banks et al.(230) have observed that palladium chelates of some vic-dioximes possess a square planar configuration.

6 (c). Copper chelates.

Bivalent copper has one unpaired electron with a magnetic moment of about 2 B.M. Both the planar and the tetrahedral structures would have the same moment and hence the magnetic criterion is not of much service in determining the structure of cupric complexes. Very few tetrahedral complexes of copper are known (231). Since most of the cupric complexes are square planar, Pauling (231) assumed that the bonds are $3d4s4p^2$, one d electron being promoted to 4p orbital; Huggins(232), on the other hand, suggested that the bonding orbitals are $4s4p^24d$, without electron promotion. Ray and Sen (233) have re-examined these considerations, investigating a number of compounds, and have suggested that magnetic moments fall into two groups- one of 1.8 to 1.9 B.M. and the other of 1.9 to 2.2. The first group is believed to involve $3d4s4p^2$ bonds, while the second group is considered to be either $4s4p^3$ tetrahedral or $4s4p^24d$ planar. The magnetic moments of the copper chelates under investigation are found to be 1.8 to 1.9 B.M. These results suggest that copper chelates under investigation involve $3d4s4p^2$ bonds and are square planar. Brown colour of these chelates is also an indication of dsp^2 bonds, as suggested by Ray and Sen (233).

Since the compounds are considered to have a square planar structure, there can exist cis-trans isomers of these compounds. No planar complexes of copper have, however, been separated into their isomers and it is considered that only trans form exists. Hence the present products are represented as follows, as in the case of nickel chelates.

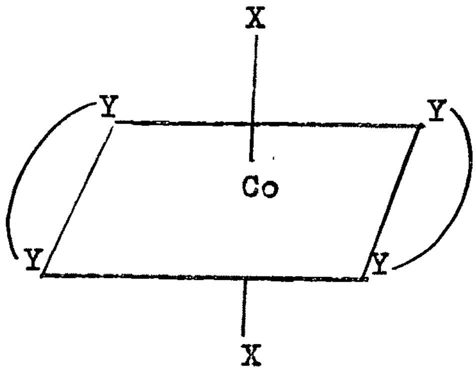


6 (d). Cobalt chelates.

Bivalent cobalt has three unpaired electrons with a magnetic moment of about 4 B.M. Co(II) forms both tetrahedral ($4s4p^3$) and octahedral ($4s4p^34d^2$) complexes in which no electron pairing occurs. It also forms square planar ($3d4s4p^2$) and octahedral ($3d^24s4p^3$) complexes which contain only one unpaired electron. Hence magnetic moments may be used to distinguish between planar or tetrahedral 4-covalent complexes and to decide between the type of bonds in octahedral complexes. The magnetic moments of the cobalt chelates under investigation are found to be 1.8 to 1.9 B.M. These results suggest that the octahedral cobalt chelates under investigation involve $3d^24s4p^3$ covalent bonds.

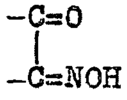
Thus the results of magnetic measurements indicate that the 4-covalent metal chelates of Cu(II), Ni(II) and

Pd(II) possess a square planar configuration, involving dsp^2 strong covalent bonds, while 6-covalent cobalt chelates may be considered to be formed from this square planar configuration and hence it can be represented as

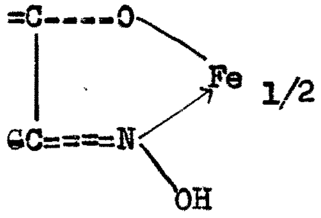


7. Oximes and inorganic analysis.

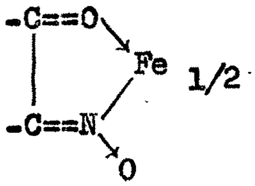
7 (a). Detection of cations by the oximes.

The monoximes have been investigated as reagents for the detection of cations and the results are recorded in table-18. It has been observed that ferrous iron reacts specifically with monoximes in neutral or alkaline solutions. The reaction appears to be characteristic of monoximes of α-diketones. The group  $\begin{array}{l} -C=O \\ \;| \\ -C=NOH \end{array}$ gives the 'iron-blue reaction ' which was first observed by Whiteley (141). Feigl and coworkers(208) have suggested that the iron-blue reaction is obtained only with those compounds in which there is an enolisable carbonyl group in proximity to the oxime group.

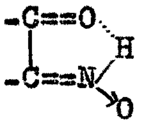
Thus they formulated the complex as



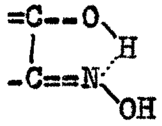
However,it is found that the possibility of enolisation cannot be the prerequisite for all cases in which the iron-blue reaction is observed (208). As a result the complex in such cases may be represented as



The monoximes under investigation give the characteristic iron-blue reaction and hence contain the specific group

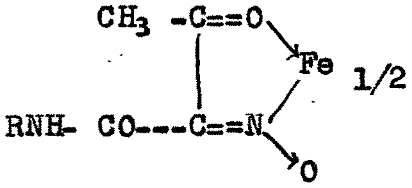


or

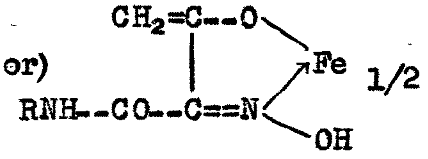


;

hence the iron complex may be represented as



or)



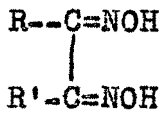
This indicates that the monoximes under investigation should have a syn-amide configuration.

The dioximes under investigation give characteristic reactions with copper, nickel, cobalt, ferrous iron, bismuth, uranium and palladium. The results are recorded in <u>table-18</u>. The α-dioximes, in general, are known to precipitate nickel and palladium, form soluble complexes with copper and cobalt and give characteristic reaction with ferrous iron and bismuth. It has been observed in the present investigations that these dioximes differ from others in the following respects:

(1) they form insoluble complexes with copper and cobalt; and

(2) they give characteristic colouration with uranium.

The reaction of α-dioximes with ferrous iron is considered to be characteristic of the groups R and R' in the dioximes

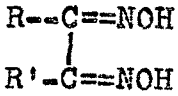


$$\begin{array}{l} R{-}{-}C{=}NOH \\ \qquad | \\ R'{-}C{=}NOH \end{array}$$

When R and R' are aliphatic groups, the dioxime gives water-soluble red complex with iron which is unstable; on the other hand, when the groups are aromatic, the dioxime forms water-insoluble bluish-violet complexes with iron which are stable. In the present case, one of the groups is aliphatic and the other one is an arylamide group. This explains the present observation- the formation of brown colouration or brown black precipitates which are unstable. It can be suggested that the groups R and R' affect the nature of ferrous chelates but not of nickel and palladium chelates. The present investigations further suggest that the presence of the group -CONHR affects the nature of copper and cobalt chelates.

7 (b). Gravimetric analysis of palladium by the dioximes.

While preparing the palladium chelates of the dioximes, it appeared that the precipitation of palladium by these dioximes was complete and hence the quantitative investigations were undertaken. It was also thought that the dioximes under investigation possess structure similar to that of numerous α-dioximes and hence they should react in a similar manner. The dioximes studied as reagents for the estimation of palladium are (1) dimethyl glyoxime investigated by Tschugaeff (108), Wunder and Thuringer (118) and others, (2) benzoyl methyl glyoxime investigated by Grisollet and Servigne (162), Hanus, Jilek and Lukas (163) and Holzer (164), (3) oxalenediamidoxime investigated by Das Gupta (165), (4) α-furil dioxime investigated by Menis and Rains (234) and (5) dione dioximes of cyclic paraffins investigated by Pshevitsyn and Ivonina (235). If these dioximes are formulated as



$$\begin{array}{l} R\text{--}C{=}{=}NOH \\ \quad\;\, | \\ R'\text{-}C{=}{=}NOH \end{array}$$

,

the groups R and R' in the above dioximes are (1)R=R'=methyl, (2) R=methyl and R'=benzoyl, (3) $R=R'=NH_2$, (4) R=R'=α-furil and (5) R and R' forming a part of the alicyclic ring. The dioximes under investigation contain the groups R=methyl and $R'=XC_4H_4NHCO-$, and hence resemble the dioxime(2).

Three dioximes of acetoacet(aryl)amides(namely anilide, o-toluidide and o-chloranilide) were taken for the analytical investigations. The compositions of the precipitated palladium chelates are suggested in table-19. The results indicate that there is good agreement between the expected and the experimental values of palladium. Hence the composition of the precipitates may be represented as

(1) $Pd\ C_{20}H_{20}N_6O_6$

(2) $Pd\ C_{22}H_{24}N_6O_6$

(3) $Pd\ C_{20}H_{18}N_6O_6Cl_2$

The estimation of palladium was carried out by precipitating palladium from acidic solutions by excess reagent and weighing the washed and dried precipitates. The results, recorded in table-20, indicate close agreement between palladium taken and palladium found and suggest the uniformity of the precipitates formed.

To determine the pH range over which palladium would be quantitatively precipitated by these dioximes, estimations were carried out at different pH values and are recorded in table-21. The results indicate that the pH range within which the palladium could be completely precipitated are

reagent	pH range
α-β-dioximino acetoacetanilide	0.1 - 8.9
α-β-dioximino acetoacet-o-toluidide	0.1 - 10.0
α-β-dioximino acetoacet-o-chloranilide	0.1 - 10.1

It appears from these values that palladium can be estimated both from fairly acidic and alkaline solutions; thus palladium can be quantitatively precipitated over a wide pH range.

The interfering effect of various anions on the estimation of palladium by these dioximes was investigated and the results are recorded in table-22. It has been observed that the anions like nitrate, iodide and cyanide interfere with the estimation of palladium when carried out from acidic solutions; iodide ion, however, does not interfere when the estimation is carried out from neutral or alkaline solutions.

The effect of cations on the estimation of palladium was also investigated; the results are recorded in table-23. It is found that in presence of cations such as cadmium, tin(ous), iron(ic), chromium, zinc, mangenese, cobalt, calcium, barium, magnesium, antimony, mercury(ic), etc., palladium was quantitatively precipitated. Satisfactory results, however, are not obtained in presence of copper or nickel; the results indicate that in the case of anilide reagent, copper and nickel cause little interference; but it is marked in the case of o-toluidide reagent and more so in the case of o-chloranilide reagent. This can be explained in terms of the pH of incipient precipitation of copper and nickel; lower the pH values of precipitation of these metals, greater would be the interference caused by them in the estimation of palladium.

7 (c). Gravimetric analysis of copper by the dioximes.

The literature survey of the reactions of α-dioximes indicated that the dioximes under investigation would not precipitate copper quantitatively. But, while preparing the copper chelates of the dioximes, it appeared that copper was completely precipitated by the dioximes from neutral solutions. Hence three dioximes of acetoacet(aryl)amides(namely anilide, o-toluidide and o-chloranilide) were taken for analytical (gravimetric) investigations.

The composition of the copper chelates that were precipitated by these dioximes are suggested in table-24. The results indicate that there is good agreement between the expected and the experimental values of copper. Hence the compositions of the precipitates may be represented as

(1) $Cu\ C_{20}H_{20}N_6O_6$

(2) $Cu\ C_{22}H_{24}N_6O_6$

(3) $Cu\ C_{20}H_{18}N_6O_6Cl_2$

The estimation of copper was carried out by precipitating copper from slightly acidic solutions by excess reagent and weighing the dried precipitates. The results obtained are shown in table-25. These indicate good agreement between copper taken and copper found.

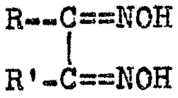
To determine the pH range over which copper would be quantitatively precipitated by these dioximes, estimations were carried out at different pH values and the results are recorded in table-26. The results indicate that the pH ranges within which copper can be completely precipitated are

reagent	pH range
α-β-dioximino acetoacet-anilide	4.4-8.3
α-β-dioximino acetoacet-o-toluidide	3.0-8.5
α-β-dioximino acetoacet-o-chloranilide	2.1-8.9

The effect of anions on the precipitation of copper by these reagents is investigated and the results are recorded in table-27. It is seen from the results that bromide, nitrate and sulphate ions do not interfere with the estimation of copper. The interfering effect of various cations on the estimation of copper was also investigated and the results are recorded in table-28. It has been observed that the cations such as barium, calcium, magnesium, cadmium and zinc, do not interfere with the estimation of copper by these dioximes.

7 (d). Gravimetric analysis of nickel by the dioximes.

The dioximes under investigation have a structure similar to that of α-dioximes and hence it was thought that they should precipitate nickel quantitatively under similar conditions. The α-dioximes studied earlier for the estimation of nickel are (1)dimethyl glyoxime investigated by Brunck (148) and others, (2)α-benzil dioxime investigated by Atack (158) and Strebinger(159), (3)α-furil dioxime investigated by Soule (160), (4)oxalene diamidoxime investigated by Chatterjee (112), (5)phenyl glyoxime investigated by Mironoff (236) and (6)dione dioximes of cycloparaffins investigated by Wallach (114) and Voter and Banks (115). If these dioximes are represented as



$$\begin{array}{l} R{-}{-}C{=}{=}NOH \\ \quad\;\; | \\ R'{-}C{=}{=}NOH \end{array} ,$$

the groups R and R' in these dioximes are(1)R=R'=methyl,(2) R=R'=phenyl, (3)R=R'=α-furil,(4)R=R'=NH_2, (5)R=phenyl and R'=hydrogen and (6)R and R' forming a part of alicyclic ring. In the dioximes under investigation, R=methyl and R'= $CONHC_6H_4X$, and hence these dioximes are unsymmetrical ($R \neq R'$). Further, while preparing the metal chelates of nickel by these dioximes, it appeared that the precipitation of nickel was complete from neutral solution. Hence three dioximes of acetoacet(aryl)amides (namely anilide, o-toluidide and o-chloranilide), were taken for analytical(gravimetric) investigations.

The composition of the precipitated metal chelates are suggested in table-29. The results indicate that there is good agreement between the expected and the experimental values of nickel. Hence the composition of the precipitates may be represented as

(1) $Ni\ C_{20}H_{20}N_6O_6$
(2) $Ni\ C_{22}H_{24}N_6O_6$
(3) $Ni\ C_{20}H_{18}N_6O_6Cl_2$

The estimation of nickel was carried out by precipitating nickel from nearly neutral solutions by the excess reagent and weighing the dried precipitates. The results obtained (table-30) indicate close agreement between nickel taken and nickel found. This indicates that the reagents can be used for the estimation of nickel.

To determine the pH ranges over which nickel would be quantitatively precipitated by these reagents, estimations were carried out at different pH values and the results are recorded in table-31. The results indicate that the pH ranges within which nickel could be completely precipitated are

reagent	pH range for nickel
α-β-dioximino acetoacetanilide	6.2 to 8.6
α-β-dioximino acetoacet-o-toluidide	5.2 to 9.1
α-β-dioximino acetoacet-o-chloranilide	4.4 to 9.5

It has been observed that the estimation of nickel by α-benzoin oxime is interfered by the nitrate ion (237).

Hence the effect of anions on the precipitation of nickel by these reagents is investigated. The results(table-32) indicate that in presence of anions like bromide, iodide, nitrate, acetate and sulphate, the results are fairly satisfactory.

The interfering effect of cations is also investigated(table-33). In presence of tervalent cations like Cr and Fe(ic) the estimations were carried out after complexing these ions with citric or tartaric acid. The results indicate that in presence of cations such as calcium, strontium, barium, magnesium, cadmium, mercury(ic), iron(ic), chromium, cobalt and mangenese, nickel was quantitatively precipitated. In case palladium was present, it was first precipitated off from fairly acidic solutions and then nickel was estimated from nearly neutral solutions. It is observed that in the case of anilide the results are satisfactory over a considerable range of concentration of nickel but in case of o-toluidide and o-chloranilide the results are satisfactory for low concentration of nickel. Estimation of Ni or Cu in presence of the other was not carried out by these reagents as the pH of incipient precipitation of copper and nickel by these reagents are very close together.

7 (e). Solubility of the dioximes.

Dimethyl glyoxime has been known as a specific reagent for nickel but because of its very slight solubility in water, alcoholic or acetone solutions are used for precipitations. This may result in the possible solubilising effect of the solvent on nickel precipitate and may endanger contamination of precipitates with excess reagent. Several attempts have been made to solubilise glyoxime and thereby minimise some of its disadvantages(238-241). Attempts are also made to find out water-soluble glyoximes(242-245).

In the present investigations, the solubility of the dioximes in water was investigated and is tabulated in table-15. It has been observed that anilide and o-substituted anilides have considerable solubility in water, comparable with that of dione dioximes of cycloparaffins(245). Hence the use of these dioximes would minimise the error due to the contamination of nickel precipitates with excess reagent. The solubility of these dioximes, however, is not sufficient to permit the use of their aqueous solutions in analysis. The dioximes of p-substituted anilides have very low solubility in water and hence would not be considered advantageous over dimethyl glyoxime.