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HYDROCHLORIDES
CHAPTER II

PART (A)

PREPARATION AND PROPERTIES OF HYDROXYAMIDINES AND AMIDINES

SUMMARY

The synthesis and characteristics of five \(N\)-hydroxy-\(N,N'\)-diarylbenzimidines and five \(N,N'\)-diarylbenzamidines have been described. They are prepared by the reaction of \(N\)-arylbenzimidoyl chlorides with \(N\)-arylhydroxylamines and amines in absolute ether medium. The hydroxylamine and amidine hydrochlorides have been characterized in terms of their storage qualities, melting points, elemental analysis, infrared and ultraviolet spectra.

REACTION OF \(N\)-ARYLBENZIMIDOYL CHLORIDE
WITH \(N\)-ARYLHYDROXYLAMINES AND AMINES

The treatment of \(N\)-arylbenzimidoyl chloride, I, with \(N\)-arylhydroxylamine, II, and amine, III, in an absolute ether medium at low temperature produces the expected hydroxylamine, IV, and amidine, V, respectively.
\[
\begin{align*}
R - N = C - AR' + AR''NH_2 \xrightarrow{\text{Et}_2\text{O}} & \quad AR - N = C - AR' \\
\downarrow \text{(I)} & \quad \downarrow \text{(II)} \\
\text{OH} - N - AR'' & \quad \text{OH} - N - AR'' \\
\end{align*}
\]

Hydroxylamine itself gives the amidoxime, VI, which tautomerizes to, VII. However, N-substituted hydroxylamine gives the expected substitution product, which cannot tautomerize to amidoxime.

\[
\begin{align*}
R - N = C - AR' \\
\downarrow \text{(III)} & \quad \downarrow \text{(IV)} \\
\text{Ar}''NH_2 & \quad \text{H} - N - AR'' \\
\end{align*}
\]

The hydroxyamidines synthesised in the present investigation were prepared using N-phenylhydroxylamine, N-\(\text{m}\)-tolylhydroxylamine, N-\(\text{p}\)-tolylhydroxylamine, N-\(\text{m}\)-
chlorophenylhydroxylamine and N-p-chlorophenylhydroxylamine whereas amides were prepared using aniline, m-toluidine, p-toluidine and m-chloroaniline, p-chloroaniline.

**PREPARATION OF N-ARYLIMIDYL CHLORIDES**

A number of methods have been suggested in literature for the synthesis and isolation of imidoyl chlorides. The preparation of these compounds can be accomplished by the procedure involving the reaction of N-substituted carboxylic acid amides with phosphorus pentachloride. This reaction was employed by Wallach and co-workers for the synthesis of imidoyl chlorides. This reaction can also be carried out in an anhydrous solvent such as benzene, toluene, xylene or nitrobenzene.

\[ R - \text{CO} - \text{NR}^1 + \text{PCl}_5 \rightarrow R - \text{C} = \text{NR}^1 + \text{Cl} \]

\[(\text{VIII})\]

\[ \text{heat} \downarrow \rightarrow -\text{HCl} \]

\[ R - \text{C} = \text{NR}^1 + \text{Cl} \]

\[(\text{IX})\]

The hydrochloride, \text{VIII}, on simple heating undergoes dehydrochlorination forming the corresponding imidoyl chloride, \text{IX}. The solvent and phosphorus oxychloride
are removed by distillation and the remaining imidoyl chloride is distilled under reduced pressure. Phosphorus pentachloride can be replaced by thionylchloride, which yields good quantity of imidoyl chlorides, especially with those derived from aromatic carboxylic acid amides. The imidoyl chlorides, produced from aliphatic carboxylic acid amides having hydrogen adjacent to the \( \mathcal{C} = \mathcal{N} \) bond are quite labile and undergo self condensation apparently due to isomerisation of the imidoyl chloride to the corresponding vinylamine, \( x \), which is attacked by the imidoyl chloride to generate the amidine derivative, \( \text{XI}, \text{XII}, \text{XIII} \).

\[
\begin{align*}
\text{CH}_3 - \mathcal{C} = \mathcal{N} \text{R} & \quad \text{CH}_2 - \mathcal{C} = \mathcal{N} \text{HNR} & \quad \text{HCl} \\
\text{Cl} & \quad \text{Cl} & \quad \text{Cl} \quad \text{Cl} \\
\text{XI} & \quad \text{CH}_3 - \mathcal{C} = \mathcal{N}(\text{H}) - \mathcal{C} = \text{Cl}_2 & \\
\text{NR} & \quad \text{Cl} & \\
\end{align*}
\]

If an ortho-substituted benzene ring is attached to the nitrogen, the self condensation is minimized due to steric hindrance and the yields of the imidoyl chlorides increases in this order:\n
\[
\text{CH}_3 < \text{Cl} < \text{Br}
\]

Similarly lowering of the basicity of the nitrogen prevents condensation. Thus, \( \text{H-sulphonimidoyl chlorides of aliphatic carboxylic acids} \) are obtained in excellent yields.\n
**PHYSICO-CHEMICAL PROPERTIES**

The imidoyl chlorides possessing functional grouping $-\text{N} = \text{C} (\text{Cl}) -$ are structurally related to aldozomethines in the same way as the acylhalides are related to the aldehydes.

\[
\begin{align*}
\text{Acyl chloride} & \quad \text{Aldimine} \\
R - C = O & \quad R - C = NH \\
\mid & \quad \mid \\
\text{Cl} & \quad \text{H}
\end{align*}
\]

They are usually pale yellow oily liquids or low melting point solids, soluble in inert solvents such as benzene, light petroleum and chloroform. It is often difficult to establish melting points, because recrystallisation results in exposure to moisture which causes partial conversion to the corresponding carboxylic acid amides. Many of the imidoyl chlorides have unpleasant irritating odours. The imidoyl chlorides are highly reactive substances and therefore must be prepared as and when required.
SYNTHESIS OF IMIDOYL CHLORIDE FROM ANILIDE

In the present investigation the imidoyl chloride has been prepared following essentially the method of Wallach and co-workers. They suggested the use of phosphorus pentachloride as chlorinating agent for the conversion of anilide to corresponding imidoyl chloride. However, the use of phosphorus pentachloride is a little disadvantageous in the sense that inspite of distillation, the imidoyl chloride is liable to be contaminated with phosphoryl chloride. Thionyl chloride which gets converted into gaseous products in the reaction is a more convenient reagent. The small amount of unreacted thionyl chloride could be easily removed by distillation under reduced pressure. The remaining pale yellow to light brown product of imidoyl chloride was used as such, as it was found to be sufficient pure for direct use.

The o-chlorobenzoylaniline was subjected to thionyl chloride treatment for preparing the N-phenyl-o-chlorobenzimidoyl chloride. Anilide was prepared by the action of o-chlorobenzyl chloride on aniline in 10 per cent aqueous sodium hydroxide medium following Schotten-Baumann reaction. The yield of the N-phenyl-o-chlorobenzimidoyl chloride was about 75 per cent. The detail experimental condition for preparation of N-phenyl-o-chlorobenzimidoyl chloride is described below.
EXPERIMENTAL

N-PHENYL-o-CHLORO TRINITROYL CHLORIDE: 15.0 g (0.076 mole) pure o-chlorobenzoylaniline was taken in a 50-ml pear shaped flask fitted with a water condenser guarded by a calcium chloride tube. Thionyl chloride, 9 ml (0.12 mole) was added over a period of 5 min in small portions. This includes a 20 per cent excess of thionyl chloride. The mixture was heated at 100-120°C on an oil bath for an hour or till the formation of a clear liquid. The excess of unreacted thionyl chloride was removed by distillation under reduced pressure. The yield of the product was 12.0 g.

PREPARATION OF N-ARYLHYDROXYLAMINES

N-phenylhydroxylamine\(^\text{16}\) was prepared by reducing nitrobenzene with zinc dust in aqueous medium, buffered with ammonium chloride. While N-o-tolyl, N-m-tolyl, N-p-tolyl, \(\text{N-}p\)-chlorophenyl\(^\text{17}\), \(\text{N-o}\)-chlorophenyl, \(\text{N-m}\)-chlorophenyl hydroxylamine were synthesised by reduction of respective nitro derivatives with zinc dust in aqueous alcoholic medium buffered with ammonium chloride. The typical procedure for two hydroxylamines is described below:

EXPERIMENTAL

N-o-TOLYLHYDROXYLAMINE: 30 g of o-nitrotoluene was mixed with 30 ml of ethanol, 20 ml water and 2.5 g of ammonium
chloride in a 250 ml conical flask. 30 g of zinc dust was added at the rate of about 1 g/min, maintaining the temperature of the reaction medium at 60-65°C throughout. After completion of the reduction hydrated zinc oxide and unreacted zinc dust were filtered off and the residue was washed with ether and the ethereal solution of N-o-tolyl-hydroxylamine was separated with the help of separatory funnel and kept in ice. This extract was used for synthesis of hydroxyamidine assuming 50 per cent yield of the hydroxylamine.

N-p-CHLOROPHENYLHYDROXYLAMINE: 25 g of p-chloronitrobenzene and 2.5 g of ammonium chloride were dissolved in 30 ml (60%) hot ethanol in a 250 ml flask. To this zinc dust 30 g was added during the course of 20-25 min while stirring vigorously. It was filtered and the filtrate was diluted to 150 ml with cold water and placed in an ice salt bath for an hour. The N-p-chlorophenyl hydroxylamine crystallised as yellow crystals and was collected on a tuchner filter. It was recrystallised from a mixture of benzene and petroleum ether (1:2), yield, 15.0 g.

PREPARATION OF HYDROXYAMIDINES

HYDROXYAMIDINE HYDROCHLORIDE: The hydroxyamidine hydrochloride, is prepared by the condensation of equimolar ratio of N-arylbenzimidoyl chloride and N-arylhydroxylamine in absolute ether medium at low temperature.
They are high melting, white crystalline substances, insoluble in water, sparingly soluble in carbon tetrachloride, benzene and ether, moderately soluble in chloroform, ethyl acetate and acetone and freely soluble in alcohol. In hot water they tend to hydrolyze slowly to the corresponding hydroxylaminic free bases.

**Preparation of Amidines**

**Amidine Hydrochloride**: The amidine hydrochloride \(^{20}\), Y, is prepared by the condensation of equimolar ratio of \(N\)-aryl-senzimidoyl chloride and \(N\)-arylamine in absolute ether medium at low temperature.

\[
\text{Ar} - \text{N} = \text{C} - \text{Ar}^1 \quad + \quad \text{Ar}^2\text{NH}_2 \quad \text{Ether} \quad \text{Ar} - \text{N} = \text{C} - \text{Ar}^1 \quad \text{HO} \quad \text{N} = \text{Ar}^2
\]

They are white crystalline substances, insoluble in water, sparingly soluble in benzene and ether, moderately soluble in chloroform and freely soluble in ethanol.
PREPARATION OF HYDROXYAMIDINE AND AMIDINE FREE BASE: On treatment with dilute ammonia, hydroxyamidine and amidine hydrochlorides liberates free bases.

\[
\begin{align*}
\text{Ar} - \text{N} = \text{C} - \text{Ar}^1 & \quad \text{Ar} - \text{N} = \text{C} - \text{Ar}^1 \\
\text{OH} - \text{N} = \text{Ar}^\text{II} & \quad \text{H} - \text{N} = \text{Ar}^\text{III}
\end{align*}
\] (XIII)  \quad (XIV)

EXPERIMENTAL

GENERAL PROCEDURE:

HYDROXYAMIDINE AND AMIDINE HYDROCHLORIDE: A solution of N-arylhydroxylamine or N-arylamine in absolute ether was taken in a 500 ml conical flask. To this was added equi- molar proportion of ethereal solution of N-arylbenzimidoyl chloride in small portions over a period of 5-10 min with constant stirring. A light brown oil separated in the initial stages of the reaction. Shaking and scratching were continued till the oil solidified into white shining crystals resembling sodium chloroide. The time required for the complete crystallisation of the light brown oil varied between 10-90 min. The precipitated hydroxyamidine or amidine hydrochloride was filtered off, washed with 3x25 ml portions of absolute ether and air dried. The yield varied between 60-75 per cent.

ISOLATION OF HYDROXYAMIDINE AND AMIDINE FREE BASES: The crude hydrochloride thus obtained, was treated with 5 N
ammonia solution in a conical flask but the pale yellow liquid could not be crystallized.

**Preparation of N-Hydroxy-N,N'-Di-phenyl-o-chlorobenzamidine Hydrochloride:** N-phenylhydroxylamine, 3.2 g was taken in 50 ml absolute ether in a 500-ml conical flask. To this, 7.4 ml of o-phenyl-o-chlorobenzimidoyl chloride in 100 ml ether was added in small quantities during the course of 15 min with constant stirring. A light brown oil slowly separated out. Stirring and scratching were continued till the oil solidified and separated in the form of white shining crystals. The complete recrystallization of the light brown oil took about 80 min. This was filtered off and washed with 3 x 25 ml portions of ether and air dried. The resulting crude hydrochloride weighed 5.72 g. This hydrochloride was recrystallized from absolute alcohol to get pure white shining crystals.

Yield: 60%, m.p., 186°, Mol. wt. 359.238.

Analysis: Calculated for C\textsubscript{19}H\textsubscript{16}N\textsubscript{2}OCl\textsubscript{2}

C, 63.52; H, 4.48; N, 7.79%

Found: C, 63.47; H, 4.56; N, 7.04%

**N-Hydroxy-N-\textsubscript{o}-tolyl-N' -phenyl-o-chlorobenzamidine hydrochloride:**

Yield: 70%, m.p., 195°, Mol. wt. 373.264.

Analysis: Calculated for C\textsubscript{29}H\textsubscript{13}N\textsubscript{2}OCl\textsubscript{2}

C, 64.35; H, 4.85; N, 7.50%

Found: C, 64.80; H, 4.70; N, 7.19%.
hydrochloride:

Yield, 65% m.p., 208°, mol. wt. 373.66.
Analysis: Calculated for C_{20}H_{19}ClNO_{12}

C, 64.35; H, 4.86; N, 7.50%
Found: C, 63.00; H, 4.94; N, 7.40%

1-hydroxy-N-p-tolyl-N'-phenyl-o-chlorobenzimididine hydrochloride:

Yield, 63%, m.p., 189°, mol. wt. 395.69.
Analysis: Calculated for C_{19}H_{15}N_{2}O_{3}Cl

C, 57.96; H, 3.84; N, 7.11%
Found: C, 56.35; H, 4.16; N, 7.68%

1-hydroxy-N-p-chlorophenyl-N'-phenyl-o-chlorobenzimididine hydrochloride:

Yield, 72%, m.p., 192°, mol. wt. 393.69.
Analysis: Calculated for C_{19}H_{15}N_{2}O_{3}Cl

C, 57.96; H, 3.84; N, 7.11%
Found: C, 58.12; H, 4.17; N, 7.28%

Preparation of N-p-tolyl-o-chlorobenzimididine hydrochloride:

Aniline, 3.0 g was taken in 50 ml absolute ether in a 500-ml conical flask. To this 8.0 g of N-p-phenyl-o-chlorobenzimidoyl chloride in 100 ml ether was added in small quantities during the course of 20 min with constant stirring. A light brown oil slowly separated
out. Stirring and scratching were continued till the oil solidified and separated in the form of white crystals. The complete crystallization of the light brown oil took about 1 min. This was filtered off and washed with 3×25 ml portions of ether and air dried. The resulting crude hydrochloride weighed 7.35 g. It was re-crystallized with absolute alcohol to get white shining crystals.

Yield, 72%, m.p., 260°, Mol. wt. 343.238

Analysis: Calculated for $C_{19}H_{15}N_2Cl_2$

\[ C, 66.48; H, 4.69; N, 9.12\% \]

Found: C, 66.44; H, 4.84; N, 7.93\%

N-α-tolyl-N'-phenyl-o-chlorobenzamidine hydrochloride:

Yield, 52%, m.p., 245°, Mol. wt. 357.264

Analysis: Calculated for $C_{20}H_{18}N_2Cl_2$

\[ C, 77.23; H, 5.07; N, 7.83\% \]

Found: C, 67.53; H, 5.24; N, 7.18\%

N-α-tolyl-N'-phenyl-o-chlorobenzamidine hydrochloride:

Yield, 74%, m.p., 239°, Mol. wt. 357.264

Analysis: Calculated for $C_{20}H_{18}N_2Cl_2$

\[ C, 77.23; H, 5.07; N, 7.83\% \]

Found: C, 67.68; H, 4.89; N, 8.12\%
**N,N-dichlorophenyl-N'-phenyl-o-chlorobenzamidine hydrochloride:**

Yield, C.P. m.p., 224°, Mol. wt. 377.63

*Analysis:* calculated for C_{19}H_{15}N_2Cl_3

C, 59.41; H, 4.00; N, 7.41

Found: C, 60.63; H, 4.02; N, 8.44

**N,N-dichlorophenyl-N'-phenyl-o-chlorobenzamidine hydrochloride:**

Yield, 70%; C.P. m.p. 219°, Mol. wt. 377.69

*Analysis:* calculated for C_{19}H_{15}N_2Cl_3

C, 59.41; H, 4.00; N, 7.41

Found: C, 60.70; H, 4.12; N, 7.89

N-Hydroxy-N-o-toly-N'-phenyl-o-chlorobenzamidine hydrochloride, N-hydroxy-N-o-chlorophenyl-N'-phenyl-o-chlorobenzamidine hydrochloride, N-o-toly-N'-phenyl-o-chlorobenzamidine hydrochloride, N-o-chlorophenyl-N'-phenyl-o-chlorobenzamidine hydrochloride were also tried, but the pale yellow oil obtained did not crystallise probably due to steric hindrance because of ortho substitution in two phenyl rings.
CHAPTER II

Part (B)

ULTRA-VIOLET SPECTRA OF HYDROXYAMIDINES AND AMIDINES HYDROCHLORIDES

Ultraviolet spectra of hydroxyemidine and amidine hydrochloride salts in ethanolic solution have been studied. The spectra comprise of three intense absorption bands around 207 nm (local excitation of the phenyl chromophore), 260 nm and 310 nm (electron transfer band). The assignment of the electronic transitions associated with these bands has been done on the basis of available data of Schiff bases. The effect of substitution in the aromatic system of the compounds on the position and intensity of these bands, has also been discussed briefly.

The ultraviolet spectra were studied primarily with the object of characterising the newly synthesised hydroxyemidine and amidine hydrochlorides. The absorption of ultraviolet light is chiefly caused by electronic excitation. This absorption can be, with reasonable assurance, attributed to a particular group of arrangement of atoms within the molecule, although it provides limited information about the structure of the molecule.

ULTRAVIOLET ABSORPTION SPECTRA: The three indispensable contributions to electronic absorption are the single bond
(σ electrons), the multiple bond (π-electrons), and the unshared electron pair (μ-electrons). Benzene absorbs strongly at 184 nm (ε, 50,000) and at 203.5 nm (ε, 74,000), and has a series of bands in the region between 230 and 270 nm of relatively low intensity. All the bands are associated with the π - π transitions. Different nomenclatures have been used for describing these transitions. In present investigation, the convention of Longuet-Higgins and Kurrel has been adopted. According to this nomenclature the transitions in benzene chromophore are described as local excitation (L.E.) bands.

When a second chromophore is conjugated with benzene nucleus, the system then acquire potentiality for electron transfer absorption and then intense bands appear in the spectrum. The electron transfer depends on the nature of the substituents. If a group attached to phenyl ring contains a lone pair of electrons (e.g. –NH₂, –OH) the shifting of electron takes place, away from the group to the phenyl nucleus; on the other hand with multiple bond substituents (e.g. –CH=CH₂, C=O, –NO₂) the direction of electron transference is reversed.

EXPERIMENTAL

APPARATUS: A Carl-Zeiss spectrophotometer equipped with 1-cm quartz cuvettes was employed for recording the ultraviolet absorption spectra. The molar absorptivities of the absorption bands at the wavelength of maximum absorption were calculated.
by taking the average of at least three solutions of
different concentrations.

ETHANOL: Ethanol of spectroscopic grade (95% w/v) was
prepared by distilling rectified spirit twice over
potassium hydroxide and silver nitrate.

HYDROXYAMIDINE AND AMIDINE HYDROCHLORIDES: The compounds
were prepared as described in Chapter II (A). For spectro-
scopic measurements, these compounds were further purified
by recrystallization from suitable solvents.

The ultraviolet absorption curves of the compounds
are shown in Fig. 2.2 and 2.3. The relevant spectral data
are presented in Table 2.1.

RESULTS AND DISCUSSION

The ultraviolet spectra of hydroxyamidine and
amidine hydrochloride show three strong bands in 95 per
cent ethanol. These absorption bands are probably due to
$\pi - \pi^*$ transitions. The absorption band at 207 nm is
considered to arise from the local excitation of phenyl
chromophore, while the bands in the range 260 nm and 310 nm
may be due to electron transfer absorptions.

LOCAL EXCITATION BAND (205-210 nm): A constant and highly
intense band around 207 nm is located in the ultraviolet
spectra of these substances. The position of this band
is either unaffected or very slightly affected by molecular
environment. The assignment of this band as a local excit-
<table>
<thead>
<tr>
<th>Compound</th>
<th>λ max, nm</th>
<th>ε max, M^(-1) cm^(-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>345</td>
<td>2.95</td>
</tr>
<tr>
<td>2.</td>
<td>265</td>
<td>1.82</td>
</tr>
<tr>
<td>3.</td>
<td>263</td>
<td>1.32</td>
</tr>
<tr>
<td>4.</td>
<td>250</td>
<td>1.93</td>
</tr>
<tr>
<td>5.</td>
<td>260</td>
<td>1.55</td>
</tr>
<tr>
<td>6.</td>
<td>250</td>
<td>1.78</td>
</tr>
<tr>
<td>7.</td>
<td>1.23</td>
<td></td>
</tr>
<tr>
<td>8.</td>
<td>1.02</td>
<td></td>
</tr>
</tbody>
</table>

Excitation: Electron transfer.
FIG. 21 A. N-HYDROXY-N,N-DIPHENYL-0-CHLOROBENZAMIDINE HYDROCHLORIDE.
FIG. 2.2  A. N,N'-DIPHENYL-0-CHLOROBENZAMIDINE HYDROCHLORIDE.  
B. N-m-CHLOROPHENYL-N'-PHENYL-0-CHLOROBENZAMIDINE HYDROCHLORIDE.  
C. N-m-CHLOROPHENYL-N'-PHENYL-0-CHLOROBENZAMIDINE HYDROCHLORIDE.  
D. N-p-CHLOROPHENYL-N'-PHENYL-0-CHLOROBENZAMIDINE HYDROCHLORIDE.
ation band of phenylchromophore (a perturbed benzene transition, $1_g - 1_u$) has been made on the basis of various Schiff bases \(^{36-41}\), benzamidines \(^{42}\), $\ldots,N'$-diphenylbenzamidine \(^{43}\) and $N$-hydroxy-$N,N'$-diarylbenzamidine \(^{44}\).

**Electron Transfer Band I** (260 nm) This band occurs in the region 260-265 nm in the spectra of hydroxylamide and amide hydrochlorides. Most probably the $\pi$ electrons of the $C = N$ group and $\pi$ orbital of the aryl ring attached to azomethine nitrogen are involved in this transition. This assignment has been made on the basis of the data on Schiff bases \(^{57}\), where electron transfer band has been assigned around 260 nm.

**Electron Transfer Band II** (310 nm) The band in region 310-313 nm, assigned an electron transfer band II, can be attributed to electron transfer along the whole chain of conjugated bands. This assignments is in analogy with that made by Minkin et al. \(^{51}\) who have discussed a range of 305-358 nm for absorption of different Schiff bases. The band II in case of amide hydrochloride is absent.
CHAPTER II

PART (C)

INFRARED SPECTRA OF HYDROXYAMIDINE
AND AMILINE HYDROCHLORIDES

In contrast to the relatively few absorption peaks observed in the ultraviolet region for most organic compounds, the infrared spectrum provides a rich array of absorption bands. Many of the absorption bands cannot be assigned accurately; those that can, however, provide a wealth of structural information about a molecule. In this portion a detail study of infrared absorption spectra of newly synthesised hydroxyamidine and amidine hydrochlorides have been studied in the region 3700 - 600 cm\(^{-1}\).

The position of the absorption bands arising from C-N, + , =N-H, N-O and N-H groups have been assigned. The spectra showed that the band positions are not influenced by further substitution in the phenyl ring of hydroxylamine.

EXPERIMENTAL

The spectra were recorded in potassium bromide on Perkin-Elmer model 221 equipped with sodium chloride optics in the region 3700 - 600 cm\(^{-1}\). The characteristics frequencies for the absorption bands along with their probable assignments have been summarised in Table 2.2. The infrared spectra of hydroxyamidine and amidine hydrochlorides are shown in fig. 2.3 - 2.8.
V: $\text{STRETCHING ABSORPTION IN HYDROXYAMIDINE HYDROCHLORIDE}$

The functional grouping (I) of hydroxyamidines allow the formation of a strong intramolecular OH ... N bond in

\[
\begin{aligned}
\text{H} & \quad \text{N} \\
\text{O} & \quad \text{N}
\end{aligned}
\]

which the hydroxyl group is the proton donor and nitrogen as the proton acceptor atom. The OH stretching absorption in hydroxyamidines appears at 3080 cm$^{-1}$, apparently this shift is due to H-bonding as reported by Mishra et al.$^{44,45}$ but in case of hydroxyamidine hydrochloride they fail to locate this band. In present investigation the similar effect has been observed. In hydroxyamidine hydrochloride the absorption due to -OH group should be observed around 3600 cm$^{-1}$ because the intramolecular hydrogen bonding involving the azomethine nitrogen is not possible due to protonation. However, failure to locate this band in the hydrochlorides could not be explained. Similar observations have been reported in the case of salicylideneamidine hydrochloride$^{46}$.

C$^+ \text{-NH STRETCHING IN HYDROXYAMIDINE AND AMIDINE HYDROCHLORIDES}$: In all the hydroxyamidine and amidine hydrochlorides a band at 1610-1630 cm$^{-1}$ is observed which is probably due to the formation of a C$^+ - \text{NH}$ group by the protonation of azomethine nitrogen. This displacement of frequency to higher values in hydroxyamidine and amidine
| Compound | Band(s) | Intensity | Resolution | Raman |wavenumber | 6000· | 3000· | 1600· | 1500· | 1400· | 1300· | 1200· | 1100· | 1000· | 900· | 800· | 700· | 600· | 500· | 400· | 300· | 200· | 100· |
|----------|--------|-----------|------------|--------|-----------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| CH₄       |        |           |            |        |           |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| H₂O       |        |           |            |        |           |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| CH₃OH     |        |           |            |        |           |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| CH₃CN     |        |           |            |        |           |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| CH₃COOH   |        |           |            |        |           |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| CH₃CN      |        |           |            |        |           |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| CH₃COOH   |        |           |            |        |           |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| CH₃CN     |        |           |            |        |           |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| CH₃COOH   |        |           |            |        |           |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |

**Note:** Intensity is categorized as follows: w = weak, m = medium, s = strong, v = very strong.
hydrochlorides with respect to C-N absorption in free bases (1595-1500 cm\(^{-1}\))\(^{44,45}\) is due to salt formation\(^{48-50}\). This observation and assignment is in analogy with that in Schiff bases (II) and their hydrochlorides\(^{46}\) (III)

\[
\begin{align*}
\text{C}_6\text{H}_5 - \text{N} = \text{C} \equiv \text{C}_6\text{H}_5 & \quad [\text{C}_6\text{H}_5 - \text{N} = \text{C} - \text{C}_6\text{H}_5] \text{Cl}^- \\
\uparrow & \quad \uparrow \\
1627 \text{ cm}^{-1} & \quad 1654 \text{ cm}^{-1}
\end{align*}
\]

In addition to this amonium band another strong broad amonium band \(\equiv \text{NH}_2\), characteristic of all the hydrochlorides is clearly detected at 2420 - 2630 cm\(^{-1}\).

\(\equiv\text{N}-\text{stretcing frequency in hydroxyimidines}\): The aromatic \(\equiv\text{C}\equiv\text{N}\) stretching vibrations generally give rise to bands in the 1360 - 1240 cm\(^{-1}\) region\(^{51}\). The best values for a hypothetical \(\equiv\text{C}-\text{N}\) stretching frequency of N-deuterated amidines are reported by Prevořsk\(^{52}\).

\[
\begin{align*}
\text{C}_6\text{H}_3 - \text{C} = \text{N} - \text{C}_6\text{H}_5 & \quad \text{C}_6\text{H}_5 - \text{N} - \text{D} \\
\uparrow & \quad \uparrow \\
1406 \text{ cm}^{-1}
\end{align*}
\]

In hydroxyimidines also, this band is observed around 1410-1425 cm\(^{-1}\) region\(^{44,45}\). It has been shown for amidines and hydroxyimidines that the partially ionic character manifests in a shortening of the carbon-nitrogen single bond length. This results in higher \(\equiv\text{C}-\text{N}\) frequencies. The \(\equiv\text{C}-\text{N}\) stretching band observed around 1410-1425 cm\(^{-1}\) in all hydroxyimidines disappeared as expected.
Fig. 25. A. N-hydroxy-N-p-chlorobenzil-N-phenyl-C-NO2. B. N-(2-nitrophenyl)benzamide.
AG S.A. N-P-ANILINOPHENYL-N'-P-ENYL-O-CHLOROBENZAMIDINE HYDROCHLORIDE
<table>
<thead>
<tr>
<th>Name of Compound</th>
<th>Local Electron Transfer</th>
<th>Local Electron Transfer</th>
<th>Local Electron Transfer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 1-Hydroxy-N-m-phenyl-N'-phenyl-o-chlorobenzamidine hydrochloride 205</td>
<td>4.98</td>
<td>6.96</td>
<td>7.97</td>
</tr>
<tr>
<td>2. N-M-chlorophenyl-N'-phenyl-o-chlorobenzamidine hydrochloride 208</td>
<td>4.02</td>
<td>3.95</td>
<td>3.90</td>
</tr>
<tr>
<td>3. N-phenyl-N'-phenyl-o-chlorobenzamidine hydrochloride 206</td>
<td>5.58</td>
<td>5.55</td>
<td>5.50</td>
</tr>
<tr>
<td>4. N-phenyl-N'-phenyl-o-chlorobenzamidine hydrochloride 208</td>
<td>4.98</td>
<td>4.95</td>
<td>4.90</td>
</tr>
<tr>
<td>5. N-phenyl-N'-phenyl-o-chlorobenzamidine hydrochloride 206</td>
<td>6.96</td>
<td>6.95</td>
<td>6.90</td>
</tr>
<tr>
<td>6. N-phenyl-N'-phenyl-o-chlorobenzamidine hydrochloride 208</td>
<td>7.97</td>
<td>7.95</td>
<td>7.90</td>
</tr>
<tr>
<td>7. N-phenyl-N'-phenyl-o-chlorobenzamidine hydrochloride 206</td>
<td>8.98</td>
<td>8.95</td>
<td>8.90</td>
</tr>
<tr>
<td>9. N-phenyl-N'-phenyl-o-chlorobenzamidine hydrochloride 206</td>
<td>10.98</td>
<td>10.95</td>
<td>10.90</td>
</tr>
<tr>
<td>10. N-phenyl-N'-phenyl-o-chlorobenzamidine hydrochloride 208</td>
<td>11.98</td>
<td>11.95</td>
<td>11.90</td>
</tr>
</tbody>
</table>
FIG. 21.3: N-N-HYDROXY-N':-CHLOROPHENYL-N-PHENYL-O-CHLOROBENZAMIDINE HYDROCHLORIDE.

FIG. 21.4: N-N-HYDROXY-N':-CHLOROPHENYL-N-PHENYL-O-CHLOROBENZAMIDINE HYDROCHLORIDE.

FIG. 21.5: N-N-HYDROXY-N':-CHLOROPHENYL-N-PHENYL-O-CHLOROBENZAMIDINE HYDROCHLORIDE.

FIG. 21.6: N-N-HYDROXY-N':-CHLOROPHENYL-N-PHENYL-O-CHLOROBENZAMIDINE HYDROCHLORIDE.

FIG. 21.7: N-N-HYDROXY-N':-CHLOROPHENYL-N-PHENYL-O-CHLOROBENZAMIDINE HYDROCHLORIDE.
FIG. 22
A. N,N'-DIPHENYL-0-CHLOROBENZAMIDINE HYDROCHLORIDE.
B. N-m-TOLYL-N'-PHENYL-0-CHLOROBENZAMIDINE HYDROCHLORIDE.
C. N-m-CHLOROPHENYL-N'-PHENYL-0-CHLOROBENZAMIDINE HYDROCHLORIDE.
D. N-p-CHLOROPHENYL-N'-PHENYL-0-CHLOROBENZAMIDINE HYDROCHLORIDE.
<table>
<thead>
<tr>
<th>Name of compound</th>
<th>Hydrochloride</th>
<th>Hydrogen chloride</th>
<th>Acetone</th>
<th>Ethanol</th>
<th>Chloroform</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. N-Hydroxy-N-m-chlorophenyl-N'-phenyl-o-chlorobenzamidine</td>
<td>205 4.96</td>
<td>205 5.02</td>
<td>205 5.02</td>
<td>205 5.02</td>
<td>205 5.02</td>
</tr>
<tr>
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<td>205 5.02</td>
<td>205 5.02</td>
<td>205 5.02</td>
<td>205 5.02</td>
<td>205 5.02</td>
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<tr>
<td>3. N-Hydroxy-N-m-tolyl-N'-phenyl-o-chlorobenzamidine</td>
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<td>205 5.02</td>
<td>205 5.02</td>
<td>205 5.02</td>
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<tr>
<td>4. N-Hydroxy-N-m-tolyl-N'-phenyl-o-chlorobenzamidine</td>
<td>205 5.02</td>
<td>205 5.02</td>
<td>205 5.02</td>
<td>205 5.02</td>
<td>205 5.02</td>
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<tr>
<td>5. N-Hydroxy-N-m-tolyl-N'-phenyl-o-chlorobenzamidine</td>
<td>205 5.02</td>
<td>205 5.02</td>
<td>205 5.02</td>
<td>205 5.02</td>
<td>205 5.02</td>
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<tr>
<td>6. N-Hydroxy-N-m-tolyl-N'-phenyl-o-chlorobenzamidine</td>
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<td>205 5.02</td>
<td>205 5.02</td>
<td>205 5.02</td>
<td>205 5.02</td>
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<tr>
<td>7. N-Hydroxy-N-m-tolyl-N'-phenyl-o-chlorobenzamidine</td>
<td>205 5.02</td>
<td>205 5.02</td>
<td>205 5.02</td>
<td>205 5.02</td>
<td>205 5.02</td>
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<tr>
<td>8. N-Hydroxy-N-m-tolyl-N'-phenyl-o-chlorobenzamidine</td>
<td>205 5.02</td>
<td>205 5.02</td>
<td>205 5.02</td>
<td>205 5.02</td>
<td>205 5.02</td>
</tr>
<tr>
<td>9. N-Hydroxy-N-m-tolyl-N'-phenyl-o-chlorobenzamidine</td>
<td>205 5.02</td>
<td>205 5.02</td>
<td>205 5.02</td>
<td>205 5.02</td>
<td>205 5.02</td>
</tr>
<tr>
<td>10. N-Hydroxy-N-m-tolyl-N'-phenyl-o-chlorobenzamidine</td>
<td>205 5.02</td>
<td>205 5.02</td>
<td>205 5.02</td>
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<td>205 5.02</td>
</tr>
</tbody>
</table>
FIG. 2: A. N-HYDROXY-N-DIPHENYL-0-CHLOROBENZAMIDINE HYDROCHLORIDE.

B. N-HYDROXY-N-M-PHENYL-N-CHLOROPHENYL-0-CHLOROBENZAMIDINE HYDROCHLORIDE.

C. N-HYDROXY-N-P-TOLYL-N-0-CHLOROBENZAMIDINE HYDROCHLORIDE.

D. N-HYDROXY-N-M-PHENYL-N-PHENYL-0-CHLOROBENZAMIDINE HYDROCHLORIDE.

E. N-HYDROXY-N-P-CHLOROPHENYL-N-PHENYL-0-CHLOROBENZAMIDINE HYDROCHLORIDE.
FIG. 2.2 A. N,N'-DIPHENYL-0-CHLOROBENZAMIDINE HYDROCHLORIDE.
B. N-m-CHLOROPHENYL-N'-PHENYL-0-CHLOROBENZAMIDINE HYDROCHLORIDE.
C. N-m-CHLOROPHENYL-N'-PHENYL-0-CHLOROBENZAMIDINE HYDROCHLORIDE.
D. N-p-CHLOROPHENYL-N'-PHENYL-0-CHLOROBENZAMIDINE HYDROCHLORIDE.
<table>
<thead>
<tr>
<th>Compound</th>
<th>7496v</th>
<th>7478v</th>
<th>7490v</th>
<th>7460v</th>
<th>3350v</th>
<th>3670v</th>
<th>4290v</th>
<th>4050v</th>
<th>3000v</th>
<th>1650v</th>
<th>1550v</th>
<th>1350v</th>
<th>1250v</th>
<th>955v</th>
<th>655v</th>
<th>565v</th>
<th>465v</th>
<th>345v</th>
<th>245v</th>
<th>145v</th>
<th>2670v</th>
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<tr>
<th>Compound</th>
<th>7496v</th>
<th>7478v</th>
<th>7490v</th>
<th>7460v</th>
<th>3350v</th>
<th>3670v</th>
<th>4290v</th>
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### Table 2.1

<table>
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<th>3000v</th>
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<th>1550v</th>
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</tbody>
</table>

**Note:** The table describes various compound bands and their corresponding frequencies in wave numbers (cm⁻¹). The intensity of each band is noted as weak, medium, strong, very strong, or not resolved.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Band (cm⁻¹)</th>
<th>Intensity</th>
<th>H - N</th>
<th>13612 cm⁻¹</th>
<th>1520 cm⁻¹</th>
<th>Resolved</th>
<th>m</th>
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<td>14869</td>
<td>-</td>
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<td>3359</td>
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</table>

**Table 2.1**: Radical group frequencies in peroxides of aryl and vinyl hydrocarbons.
<table>
<thead>
<tr>
<th>Compound</th>
<th>3230 cm⁻¹</th>
<th>3130 cm⁻¹</th>
<th>3000 cm⁻¹</th>
<th>2970 cm⁻¹</th>
<th>2920 cm⁻¹</th>
<th>2870 cm⁻¹</th>
<th>2820 cm⁻¹</th>
<th>2770 cm⁻¹</th>
<th>2720 cm⁻¹</th>
<th>2670 cm⁻¹</th>
<th>2620 cm⁻¹</th>
<th>Intensity</th>
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<tbody>
<tr>
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<td>10</td>
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<td>3.0</td>
<td>2.0</td>
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<td>0.5</td>
<td>0.3</td>
<td>0.2</td>
<td>0.1</td>
<td>0.05</td>
<td>weak</td>
</tr>
<tr>
<td>H</td>
<td>20</td>
<td>10</td>
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<td>0.1</td>
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<td>3.0</td>
<td>2.0</td>
<td>1.0</td>
<td>0.5</td>
<td>0.3</td>
<td>0.2</td>
<td>0.1</td>
<td>0.05</td>
<td>weak</td>
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</tbody>
</table>

*Table 2.1: IR Absorption and Raman Frequencies of 4-R-1-Phenyl-3,5-dimethyl-2-pyridyl compounds*
from the spectra of hydroxyamidine hydrochlorides. This is presumably due to loss of mesomerism which gives insignificant double bond character to the carbon-nitrogen single bond. We are, however, unable to locate the bond of carbon-nitrogen single bond in the hydrochlorides. It is quite possible that the \((C-N)\) mode is overlapped by other stronger bands in the region.

**\(\text{C-H stretching and } N-H \text{ stretching vibration in amidine hydrochlorides}\):** In case of amidine hydrochlorides vibrations associated predominantly with \(N-H\) bonding and a \(C=N\) stretching mode occur near 1490 and 1355 \(\text{cm}^{-1}\) \(^\text{52}\).

**\(\text{N-\(\equiv\) stretching vibration in hydroxyamidine hydrochlorides}\):** The \(N-\equiv\) stretching vibration of hydroxyamidines arises in the region 920-935 \(\text{cm}^{-1}\). The bands are less intense due to salt formation in hydrochlorides. The position of this band is supported on the basis of available data on \(N\)-arylhydroxylamines \(^\text{53,54}\) (919 \(\text{cm}^{-1}\)) and oximes \(^\text{55,56}\) (910-930 \(\text{cm}^{-1}\)) similar assignment is made in \(N\)-arylhydroxamic acids \(^\text{57}\).

**\(\text{C-H (aromatic) stretching vibration}\):** A sharp band at 3000-3040 \(\text{cm}^{-1}\) characteristic of aromatic \(C=H\) stretching was observed in all the spectra examined. The frequency of this band does not correlate too well with the molecular environment.
REFERENCES

2. Limroth, F., German Pat., 1, 166, 771 (1964).
7. Wallach, O., ibid., 184, 1 (1877).
18. Ley, H., Ber., 34, 2620 (1901).