

## Ultra Violet Spectra of N-Hydroxy Amidines

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**Abstract:-** Hydroxyamide Hydrochloride was prepared by condensation of N (4- Fluoro) benzamidoyl chloride and N- phenyl hydroxylamine at 0<sup>o</sup>-5<sup>o</sup>C in ether medium. White crystals of N-HydroxyN- phenyl benzamide hydrochloride were separated. They were separated and recrystallized from absolute alcohol. The newly synthesized reagent was characterised on the basis of melting point, elemental analysis and ultra violet spectra. The molecular formula C<sub>19</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>Cl is confirmed from elemental analysis data.

The ultra violet absorption spectra of hydroxyamidine in ethanol show three distinct absorption band attributed to  $\pi$ - $\pi^*$  transitions. The band observed around 207nm has been assigned as local excitation band of phenyl chromophore and the other two bands around 250-260 nm and 300-322 nm have been assigned as electron transfer band. Electron transfer band are sensitive to substitution in the aromatic system of compound.

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### I. Introduction

Organic reagents have an established position in Inorganic analysis<sup>1-4</sup>. Their use greatly increases the specificity and selectivity of the analytical reactions introducing simple method. Ligands that can bind with more than one donar atom to the same metal ion or atom are called chelate ligands or chelators.

Since innumerable compounds have been proposed and studied resulting in many excellent analytical procedure, low solubility and high molecular mass of chelate favours its use in analysis. In general chelating reagent reacts not only with one or two metals but with a group of metals<sup>5</sup>.

The selectivity of the organic reagent and the mechanism of its reaction with metal ion depend on the presence of a functional group. The analytical value of a reagent can be improved by suitable substitution into the molecule of the reagent According to kulberg<sup>6</sup>, substitution of an electronegative group increases the acidity and decreases the basicity of acid and basic group. Such an electronegative atom can enhance acidity and thus make the reagent more selective as the complexes formed are less stable<sup>7-8</sup>. A number of monobasic and bidentate chelating reagents have been reported for extraction and photometric determination of transition metal ions<sup>9-10</sup>.

K Satyanarayan and R.K. Mishra<sup>11-15</sup> discussed for the first time the analytical chemistry of Hydroxyamidine Hydrochloride. The complexing properties of the reagents are modified by substitution in reagent molecule, hence a new N- hydroxyamidine hydrochloride has been prepared and characterised by elemental analysis, mp and UV spectra.

The introduction of hydroxyamidine hydrochloride as a new type of metal chelating agents opens a new field both of synthetic as well as of analytical interest. As compared to the established reagents such as oximes, hydroxytriazine<sup>16</sup>, the present compound have wider scope as analytical reagents. The hydroxyamidine functional group has three sites for substitution with various groups and a better understanding of the influence of substituent in the aromatic ring will help in a new N- Hydroxy- N- (phenyl) N- (4 fluoro) phenyl benzamide hydrochloride was synthesized and characterised on the basis of m.p., elemental analysis and ultraviolet spectra.

The newly synthesized hydroxyamidine hydrochloride have characterised on the basis of ultraviolet spectra in ethanolic solution. The introduction of substituents into aromatic ring produces several changes in the appearance of ultra violet spectrum, a new intense band appear in the spectrum<sup>17-19</sup>. Alkyl substituents displace the maxima to red but have no marked effect of intensity of absorption<sup>20-21</sup> with substituted aromatics. The band shifts to longer  $\pi$ - $\pi^*$  wavelength. The absorption maximum of the electron transfer bands move to longer wavelength. In case where the new substituents in electronic donating (Like-OH, NH<sub>2</sub>) or capable of conjugation (Like-CHO-COOH). While with electron withdrawing substituents (Like Cl-Br), no change in the maximum position is observed. The fusion of additional rings to benzene results bathochromic shift<sup>22</sup>.

### II. Experimental

The reagent N-hydroxy N-phenyl. N<sup>o</sup>(4-Fluoro) phenyl benzamide hydrochloride was repurified by one more crystallisation from suitable solvents. These were dried under vacuum for spectroscopic studies

“Spectro grade” ethanol was prepared by twice distilling 95% ethanol over potassium hydroxide and silver nitrate<sup>23</sup>.

#### **APPARATUS :-**

Ultraviolet spectra were recorded on “PERKIN - ELMER LAMBDA” 2UV/VIS SPECTRO-PHOTOMETER having 1 cm quartz cells and calibrated by standard methods.

### **III. Results And Discussion**

The absorption spectra of hydroxyamidine shows three intense bands in ultraviolet region the absorption band at 207-210 nm arises most likely from local excitation of phenyl chromophores while the bands in the range 252-264 nm and 290-322 nm may be due to electron transfer absorption.

#### **$\pi$ - $\pi^*$ EXCITATION :-**

The band in 180-210 nm region has been assigned to two overlapping, symmetry allowed<sup>24</sup>. The position of this band is either unaffected or slightly affected by substitution in the phenyl group attached to azomethine and the hydroxyl nitrogen. The assignment of this band as a local excitation band of phenyl chromophore (a perturbed benzene transition  $A_{1g}B_{1u}$ ) has been made on the basis of similar assignments in various aromatic schiff's bases<sup>25-26</sup> benzamidine<sup>27</sup> and N-hydroxy- N, N'diphenylbenzamidines.

#### **ELECTRON TRANSFER BAND I (250-260 nm) :-**

$\pi$ - $\pi^*$ The band at 250-260 nm represents a symmetry forbidden transition which has finite but low probability due to interaction with a nontotally symmetric vibration. A constant band occurs around 250-260 nm in these compounds which is probably due to transference of electron in which the electrons of the azomethine group (C=N) and  $\pi$ -Orbitals of the aryl ring attached to the azomethine nitrogen are involved. This assignment is in accordance with the data on schiff's bases in which this band has been observed around 260nm. This electron transfer band around 250-260 nm is profoundly affected by 2 and 2, 6 substitution in several other compounds and often missing from the spectra<sup>28</sup>. In the spectrum of N-hydroxy N-(4-methyl) phenyl N'-(4-fluoro) phenyl benzamidine hydrochloride this band appears at 250 nm.

#### **ELECTRON TRANSFER BAND II (310-322 nm) :-**

The position of this band is also influenced by substitution. Min kin et al<sup>26</sup> have described a range of 305-358 nm for this absorption in differently substituted schiff's bases<sup>29-30</sup>. In analogy with this the band in the spectra of hydroxyamidines in the region 310-322 nm, designated as electron transfer band II, denotes electron along the whole chain of conjugated band.

### **IV. Conclusion**

Ultra violet spectra of newly synthesised hydroxyamidines have been studied in ethanol. The assignment of electronic transitions, associated with the bands obtained has been made on the basis of available data on schiff's bases and amidines. The effect of substitution in the aromatic system of the compounds on the position and intensity of the bands has also been discussed

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