CHAPTER - II

ELECTRONIC, VIBRATIONAL SPECTRAL STUDIES
AND THERMODYNAMIC FUNCTIONS OF
3,5-DIBROMO PYRIDINE
The vibrational (Infrared and Laser Raman) spectra of solid 3,5-dibromo pyridine have been reported. The assignments of fundamental frequencies to various mode of vibration have been proposed. Moreover electronic spectra of these compounds in various polar and non-polar solvents are reported. Effect of solvents on electronic transitions of the compound is explained, along with the hypsochromic shift. Existence of mesomeric (resonance) form is also given. Thermodynamic function have been computed and discussed.
The aromatic compounds like benzene, benzaldehyde, pyridine, pyrimidine, uracil, cytosine and their derivatives are of great biological importance, as they play an important role in the structure and properties of nucleic acids\textsuperscript{1-14}. Recent spectroscopic studies of pyridine and their derivatives have been motivated by their biological importance. Spectral analysis of pyridine and its mono substituted derivatives have been studied in detail by several workers\textsuperscript{15-20}, and the analysis of disubstituted pyridines have been reported in literature\textsuperscript{21-24}. Mochizuki et al\textsuperscript{25} have reported the systematic study of the electronic absorption and Raman spectra of pyridine and its derivatives. The electronic spectra of 6-amino-2-methyl pyridine and 2-chloro-3-nitro pyridine had been already reported by Goel et al\textsuperscript{26} and Yadav et al\textsuperscript{27}. Kasha\textsuperscript{28} suggested that the electronic transitions in pyridine exhibit two band system in the near ultra violet region. The system corresponds to n-π* and π-π* transitions and the later is analogous to 2600Å (\textsuperscript{1}A\textsubscript{1g} \rightarrow \textsuperscript{1}A\textsubscript{2u}) system of benzene. The π-π* system represents the shorter wavelength system has shown the usual behavior towards the substitution and the polarity of the solvents. The n-π* transition represents larger wavelength has evidenced a usual behavior towards the solvent polarity, which is symmetry allowed and polarized perpendicular to the molecular plane has been assigned as due to n-π* transition by Kasha\textsuperscript{28}. Further, a systematic and complete vibrational analysis and electronic spectra of pyridine and some of its deuterated analogous has been made by some previous workers\textsuperscript{29-37}. On substitution, the π-π* and n-π* systems of pyridine normally produce bathochromic and hypsochromic shifts, respectively, the vibrational frequencies also get modified. In the case of 2-bromo pyridine
Stephenson\textsuperscript{38} and in 3-bromo pyridine Mishra\textsuperscript{39} pointed out that due to large inductive and resonance influence of halogen atom on the sp\textsuperscript{2} electron of the nitrogen atom of the ring n-\(\pi^*\) transition could not be observed. However Srivastava and Prasad\textsuperscript{40} have observed a band corresponding to n-\(\pi^*\) transition around 3300 Å in 2-chloro-3-pyridinol, 5-chloro-2-pyridinol and 6-chloro-2-pyridinol. In view of these observations, it was thought worthwhile to study the vibrational electronic spectra of 3-5-dibromo pyridine. In the molecules n-\(\pi^*\) transitions has been observed which shows a blue shift (hypsochromic shift). The electronic spectra of the compound in various solvents such as ethanol, methanol and water are also reported and discussed.

**EXPERIMENTAL**

Spec-pure chemicals 3,5-Dibromo Pyridine (M.P. 114\textdegree C) (hereafter referred as 3,5-DBP) was obtained from M/s Aldrich Chemic, West Germany and used as such. It’s purity was confirmed by elemental analysis and melting point determination. The infrared spectra were recorded in the region 400-4000 cm\textsuperscript{-1} using KBr pellets on Perkin-Elmer M-52 spectrophotometer. The laser Raman spectrum was recorded on “Spex Rama Lab” spectrophotometer using 52-mw argon-krypton laser beam of wavelength 488 nm in the range (50-4000 cm\textsuperscript{-1}). Near ultraviolet absorption spectra of the compound were recorded on “Backman M-35” spectrophotometer in the range 200-400 nm using ethanol, methanol and water solvents. All the solvents used in recording the spectra were of spectroscopic grade successfully on the same instrument. The concentration of the solutions in all the cases was kept constant (i.e. 8 x 10\textsuperscript{-3} gm/litre) The near ultraviolet spectra of the compound in
vapour phase were tried on under best experimental conditions reportable bands were not observed.

RESULTS AND DISCUSSION

The molecular structure of the compound is given in Fig. 2.1

FIG. 2.1 MOLECULAR STRUCTURE OF 3, 5-DIBROMO PYRIDINE

The infrared (IR) spectrum of 3,5-DBP in KBr pellet is shown in Fig. 2.2. The laser Raman spectrum of 3,5-DBP is shown in Fig. 2.3. The observed fundamental frequencies and their proposed assignment are given in Table 2.1. Near ultraviolet absorption spectra of 3,5-DBP in various polar solvents are shown in Fig. 2.4. Electronic transitions (n-π* I and n-π*II) observed in various polar and non-polar solvents for the compound are given in Table 2.2. The resonating structures of 3,5-DBP are given in Fig. 2.5. The statistically computed thermodynamic functions viz enthalpy, free energy, entropy and heat capacity with absolute temperature are given in Table 2.3 for 3,5-DBP. The variation of enthalpy function and heat capacity function with absolute temperature is
shown in Fig. 2.6, while that of free energy function and entropy function with absolute temperature is shown in Fig. 2.7.

VIBRATIONAL SPECTRA

Ring vibrations

C-H, N-H, C-C and C-N Vibrations

The nitrogen atom of pyridine is isoelectric with the C-H group. As there is little difference in mass or in the bond strengths to adjacent atoms. It is to be expected that the majority of the fundamental frequencies will be very close to those of benzene and the difference will only arise due to substituents attached to the ring.

Bellamy\textsuperscript{43} had suggested the range 3000-3100 cm\textsuperscript{-1} for C-H stretching modes. The molecule 3,5-DBP is disubstituted pyridine. Therefore, three hydrogen atoms are left around the ring at position 2,4 and 6 and as such, only three (C-H) valance oscillation is expected. This C-H stretching mode lies in the region 3000-3100 cm\textsuperscript{-1}.\textsuperscript{41-43} In the cases in the vibrational region (Fig 2.2 and 2.3) the above bands were observed between 3017-3099 cm\textsuperscript{-1}, just like that of benzene. In view of this IR absorption band at 3017, 3099 cm\textsuperscript{-1} (in KBr) and Raman band at 3073 cm\textsuperscript{-1} has been assigned to (C-H) stretching mode in 3,5-DBP. Srivastava et al\textsuperscript{44} have assigned C-H in-plane bending and out-of-plane bending modes at 1067,1080,1220 cm\textsuperscript{-1} and 1067,1140,1240 cm\textsuperscript{-1} and 747,927,967 cm\textsuperscript{-1} and 733,927,967 cm\textsuperscript{-1} respectively in 3-ethyl-4-methyl pyridine and 5-ethyl-4-methyl pyridine. Yadav et al\textsuperscript{45} reported these modes at 1106,1127 cm\textsuperscript{-1} and 814 cm\textsuperscript{-1} have been assigned to C-H in plane and out-of-plane bending in 5-chloro-2,3-dihydroxy pyridine, while Isaq et al\textsuperscript{50} have assigned in-plane and out-of-plane bending modes at 1291,
1155,1092,1040 cm\(^{-1}\) (in KBr) with Raman bands at 1298,1155,1062,1045 cm\(^{-1}\) and 910 cm\(^{-1}\), 782 cm\(^{-1}\) with the Raman band at 779 cm\(^{-1}\) in 2-cyanopyridine while in 3-cyanopyridine this mode have been assigned at 1244,1185,1080 cm\(^{-1}\) (in KBr) with the corresponding Raman bands at 1290,1189,1062 cm\(^{-1}\) another Raman bands at 1035 cm\(^{-1}\) and 927 cm\(^{-1}\) and 810 cm\(^{-1}\) (in KBr) with the counter part of Raman bands at 780 cm\(^{-1}\) in 3-cyanopyridine. The IR bands observed at 1100,1113, 1150 cm\(^{-1}\) (in KBr) with the counter part of Raman band at 1106,1136, 1150 cm\(^{-1}\) has been assigned to (C-H) in-plane bending mode while another IR band at 762,884, 968 cm\(^{-1}\) (in KBr) with the counter part of Raman band at 750, 862, 967 cm\(^{-1}\) has been assigned to (C-H) out-of-plane bending mode in 3,5-DBP. These assignments find support from the literature value\(^{43,46-50}\).

From the data available in N-heterocyclic molecule\(^{51-53}\). The laser Raman band observed at 3116 cm\(^{-1}\) in the molecule 3,5-dibromo pyridine may be assigned to N-H stretching mode, this is possible only when there is a proton migration from the ring. It can be Raman band that in the said molecule, proton migration takes place to the nitrogen of the ring, giving rise to the N-H stretching mode. The Raman band at 1662 cm\(^{-1}\) has been assigned to N-H in-plane bending mode which find support from the literature value\(^{54}\), while the Raman band observed at 816 cm\(^{-1}\) has been assigned to N-H out-of-plane bending vibration mode. The band observed at 3224 cm\(^{-1}\) and 3450 cm\(^{-1}\) has been assigned to N-H symmetric and asymmetric vibrations respectively in 3,5-DBP.

In benzene and substituted benzenes four bands are usually observed in the region 1400-1650 cm\(^{-1}\). In heterocyclic compound C-C aromatic ring vibrations occur in the region 1350-1600 cm\(^{-1}\) by Rao et
al. Bellamy has suggested the range 1400-1600 cm\(^{-1}\) for C-C stretching vibrations in substituted pyridine. Yadav et al. reported C-C ring stretching modes at 1485, 1493, 1560, 1602 cm\(^{-1}\) (in KBr) with the corresponding Raman band at 1600 cm\(^{-1}\) in 2-chloro-6-fluoro benzene. While Chaman and Verma et al. have been assigned C-C ring stretching modes at 1338, 1428, 1212, 1536, 1559 cm\(^{-1}\) is 2,3,5-tri-idobenzoic acid.

Pyridine show these vibrations in the region 1484-1601 cm\(^{-1}\). Consequently four bands in 3,5-DBP has been assigned at 1484 cm\(^{-1}\) (in KBr), and 1510, 1546, 1601 cm\(^{-1}\) (in KBr) with the counter part of Raman bands at 1525, 1560, 1596 cm\(^{-1}\) for ring C-C stretching modes. These assignment find support from the literature values.

Some workers assigned (C-N) stretching mode at 1310, 1340, 1363 cm\(^{-1}\) with Raman band at 1368 cm\(^{-1}\) in substituted pyridine while Goel et al. and Yadav et al. have assigned this mode at 1395 cm\(^{-1}\) and 1370 cm\(^{-1}\) with the counter part of Raman band at 1376 cm\(^{-1}\) in case of 2-chloro pyridine and 2-amino-3-nitro pyridine. In the present study the band observed at 1367 cm\(^{-1}\) (in KBr) with the counter part of Raman band at 1380 cm\(^{-1}\) in 3,5-DBP have been assigned to C-N ring stretching mode. The vibrational energies corresponding to \(a_{1g}\) (995 cm\(^{-1}\)) and \(b_{1u}\) (1010 cm\(^{-1}\)) vibrations of benzene are close to each other which under reduced symmetry Cs belong to the same symmetry and thus there will be an appreciable mixing between the two, as a result of which the remains around 1010 cm\(^{-1}\) while the other reduces up to 700 cm\(^{-1}\). It had been found that the ring stretching vibration reduces by a large amount depending upon the mass, nature and number of substituents, where as the bending vibration remains close to 1010 cm\(^{-1}\), similarly, the vibration is totally symmetric which should appear as a polarized and intense band.
Thus the very intense IR band observed at 1006 cm$^{-1}$ (in KBr) with the counter part of the Raman band at 994 cm$^{-1}$ in 3,5-DBP were assigned to the C-C ring breathing mode. The band at 1100 cm$^{-1}$ (in KBr) with the counter part of Raman band at 1006 cm$^{-1}$ in 3,5-DBP were assigned to the C-C-C trigonal bending mode. These assignments also find support from the literature values$^{36,65}$.

Ahmed et al$^{66}$ assigned C-C in-plane and out-of-plane bending modes at 418,635,785 cm$^{-1}$ (in KBr) with the Raman band at 420,638, cm$^{-1}$ and 643 cm$^{-1}$, 425 cm$^{-1}$, 625 cm$^{-1}$ and 490,668,665,670 cm$^{-1}$ have been assigned to C-C ring in-plane and out-of-plane bending modes in o,m,p-iodonitro benzene, while Sundarganesan et al$^{67}$ have assigned these mode at 634,892 cm$^{-1}$ (in KBr) with the counter part of the Raman band at 646,898 cm$^{-1}$, another IR band at 999 cm$^{-1}$ (in KBr) and 444,670,747 cm$^{-1}$ (in KBr) with the counter part of the Raman band at 432,670,706 cm$^{-1}$ in 2-amino-5-bromo pyridine and IR band observed at 825 cm$^{-1}$ (in KBr) have been assigned to C-N in-plane bending mode by Sundraganesan et al$^{67}$. The IR bands observed at 695 cm$^{-1}$ (in KBr) with the counter part of Raman band at 690 cm$^{-1}$ and another Raman band at 769 cm$^{-1}$ have been assigned to C-C in-plane bending modes. While the strong Raman band observed at 816 cm$^{-1}$ have been assigned to C-N in-plane bending mode in 3,5-DBP. For C-C out-of-plane bending, three bands were observed for the molecules under study. The frequencies were located at 417, 433 cm$^{-1}$ (in KBr) with the counter part of Raman band at 406,443 cm$^{-1}$ and another Raman band at 479 cm$^{-1}$ in 3,5-DBP. These assignments supports the literature values very well$^{49,68-73}$.
C-X Vibration

Since the little work has been done on Bromo substituted pyridines, the C-Br stretching frequency usually appears in the region 500-700 cm\(^{-1}\). Green et al\(^{74}\) assigned C-Br stretching mode at 610 and 500 cm\(^{-1}\) in 2,4-dibromofluoro benzene, while Sundaraganesan et al\(^{67}\) have assigned C-Br stretching mode at 515 cm\(^{-1}\) (in KBr) with the Raman band at 511 cm\(^{-1}\) in 2-amino-5-bromo pyridine. In the present study the Raman band at 545 cm\(^{-1}\) and 650 cm\(^{-1}\) (in KBr) with the counter part of Raman band at 657 cm\(^{-1}\) has been assigned to C-Br stretching mode in 3,5-DBP. These assignments are supported by the work of Szymansky\(^{75}\) and Suzuki\(^{76}\) and Singh and Prasad\(^{77}\). Varsanyi\(^{78}\) assigned the C-Br in-plane bending mode at 275 and 170 cm\(^{-1}\) and C-Br out-of-plane deformation at 210 cm\(^{-1}\) in 2, 6-dibromo-4-cyano-phenol. While Belgaum et al\(^{79}\) assigned the C-Br in-plane and out-of-plane bending modes at 244, 217 cm\(^{-1}\),282, 219 cm\(^{-1}\) and 197, 130 cm\(^{-1}\), 161, 131cm\(^{-1}\) in 1,3-dibromo-5-fluorobenzene and 2, 4-dibromo-1-fluoro benzene. In view of the above, the Raman bands at 307 and 327 cm\(^{-1}\) has been taken to represent the C-Br in-plane bending vibrations, while those at 182 and 215 cm\(^{-1}\) represent the C-Br out-of-plane bending deformation. These assignments also find support from the literature values\(^{76, 77, 80}\).

ELECTRONIC SPECTRA

The all electronic interpretations are based assuming C\(_s\) point group for the molecule. Thus there will be only two types of electronic levels, those which are symmetric to molecular plane and those are antisymmetric to it. Under reduced symmetry C\(_s\) forbidden transition of benzene \(^1\)A\(_{1g}\) → \(^1\)B\(_{2u}\) (2600A\(^b\)) and \(^1\)A\(_{1g}\)→ \(^1\)B\(_{1u}\) (2100A\(^b\)) correspond to the
allowed type $A^1 \rightarrow A^1$ transition with the transition moment lying in the plane of the molecules should appear with sufficient intensity. As suggested by Ram et al.\(^8\) in Pyridine, the introduction of –N= group in place of -CH in benzene, exhibit a blue shift in n-\(\pi^*\) transition and the red shift in \(\pi-\pi^*\) transition. In the present study the near ultraviolet spectra of the molecule 3,5-DBP were recorded in the different solvents viz ethanol, methanol and water. The band system which corresponds to \(1A \rightarrow 1U\) transition n-\(\pi^*\)I and n-\(\pi^*\)II has been observed between 283-291 and 281-286 nm in 3,5-DBP. The band system which corresponds to \(1A_{1g} \rightarrow 1B_{2u}\) and \(1A_{1g} \rightarrow 1B_{1u}\) transitions\(^8\) \(\pi-\pi^*\) and n-\(\sigma^*\) has not been observed in 3,5-DBP.

**EFFECT OF SOLVENTS**

An increase in the solvent polarity does not effect either the position or the intensity of the Benzene, but produces a hyperchromic effect (an increase in absorption intensity) for pyridine and its homologos\(^8\). This effect is assigned to the hydrogen bonding through the lone pair of electrons of the nitrogen atom.\(^8\) The lone pair electrons of N-atom of the ring are readily available for intermolecular H-bonding to result in the increase in absorption intensity in less polar solvent than in more polar solvent.

The azaaromatic compounds have a nonbonded pair of electrons in nitrogen sp\(^2\) orbital, which lies in the plane of the ring and is essentially perpendicular to the \(\pi\) and \(\pi^*\) molecular orbitals. Since the nonbonding orbital lies at higher energy than the highest filled \(\pi\) molecular orbital, the n-\(\pi^*\) transition is expected to occur at higher wavelength. This suggests that the 330 nm band system is due to the transition of a nonbonding
electron from lone pair orbital (n) of a nitrogen atom to a (π) orbital of
the ring (Fig.2.4.)

Dyer\textsuperscript{84} has also reported a blue shift for n-π* transitions and red
shift for π-π* transitions with the increasing polarity of solvents. The
n-π* transition shows a blue shift on increasing polarity of the solvent\textsuperscript{83}. According to Ram et al\textsuperscript{81} and Yadav et al\textsuperscript{85}, the blue shift with increasing
polarity of solvent is the useful means of the recognizing n-π* transitions.
The π-π* transition has red shifted in a more polar solvent. Becker et al\textsuperscript{86}
has suggested that π-π* transition undergo red shifted (bathochromic
shift) as the polarity of the solvent increases.

Srivastava and Prasad\textsuperscript{40} and Yadav et al\textsuperscript{87} have also observed a
band corresponding to n-π* transition around in 2-chloro-3-pyridinol and
2,3,6- DMNA. The bands which are blue shifted on a change from non-
polar to polar solvents are attributed to n-π* transitions and the red
shifted bands are considered to be π-π* transitions\textsuperscript{86,88}. Methanol is
comparatively more polar than ethanol, as methyl group is less
electropositive than ethyl group. There is a pronounced hypsochromic
shift at 330 nm.

Becker\textsuperscript{86} had suggested that the fluorine which has ionisation
energy of 17.4 ev. While chlorine which has an ionization energy of 13.0
ev to the longer wavelength side. Therefore, the introduction of more
electronegative atom in the aromatic nucleus results in hypsochronic
shift. It is a well known fact that fluorine is highly electronegative
followed by chlorine and bromine (ionization energy 11.8 ev). From
Table-2.2 it is evident that as we move from ethanol, methanol, water in
3,5-DBP. There is remarkable blue shift in n-π* transition but in
$^1A_{1g} \rightarrow ^1B_{2u}$ system the trend is not consistent. These assignments also find support from the literature values $^{89-91}$

In this work the blue shift (hypsochromic shift) has been observed n-$\pi^*$ I and n-$\pi^*$ II transition as the polarity of the solvents increased i.e. ethanol, methanol and water Table (2.2)$^{92,93}$ in 3,5-DBP. The amount of blue shift has been used as a measure of the strength of the H-bonding$^{91}$. In 3,5-DBP (Fig.2.3 and Table 2.2) there is no marked bathochromic shift (red shift) with increasing polarity of the solvents.

Further more, the greater the polarity of the solvent, the greater is the attraction between solute and solvent molecules. Thus the system would be more Table$^{94}$ also with increasing dielectric constant of the solvent the ionising potentiality of the solute molecule is increased. The higher the polarity of the solvent, the greater will be the degree of solvation$^{95}$.

In general a conspicuous red shift has been observed in n-$\pi^*$ transition of the compound 3,5-DBP under present investigation, with the increasing refractive index from ethanol→water and methanol→water which is an accordance with trend reported by Mataga and Kubota$^{96}$.

**THERMODYNAMIC FUNCTIONS**

Thermodynamic functions enthalpy function $\left(\frac{H^0 - E^0}{T}\right)$, heat capacity function $\left(\frac{C^0_{p}}{T}\right)$, free energy function $\left(\frac{F^0 - E^0}{T}\right)$ and entropy function $\left(\frac{S^0}{T}\right)$ appears to be one of the most important application of the study of IR and Laser Raman spectra of the complex molecules. From the vibrational data obtained from the spectra, Urey$^{97}$, Tolman and Badger$^{98}$
first suggested that it is quite possible to calculate with accuracy the
values of various thermodynamic quantities. This is of great practical
importance particularly since the direct experimental measurement of
these quantities is quite difficult and some time impossible. The values of
thermodynamic functions calculated from the spectroscopic data are
more accurate than the values obtained by the thermal measurement. The
various thermodynamic functions were computed at different
temperatures between (200-1500 K) using 3n-6 fundamental frequencies
and assuming rigid rotor, harmonic oscillator approximation. The
calculations were performed for one mole of an ideal gas at one
atmospheric pressure. These functions have been calculated by using
standard expressions refined from time to time by taking Y-axis
perpendicular to the molecular plane, Z-axis pass through the para
position. For determining the rotational contribution of the said molecule,
the following parameter of the said molecule, the following parameter of
the said molecule were used.

<table>
<thead>
<tr>
<th>Bond Lengths (Å)</th>
<th>Bond Angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₁C₂=1.32</td>
<td>C₆N₁C₂=128°</td>
</tr>
<tr>
<td>C₂C₃=1.42</td>
<td>N₁C₂C₃=119°</td>
</tr>
<tr>
<td>C₃C₄=1.38</td>
<td>C₂C₃C₄=114°</td>
</tr>
<tr>
<td>C₄C₅=1.38</td>
<td>C₃C₄C₅=126°</td>
</tr>
<tr>
<td>C₅C₆=1.42</td>
<td>C₄C₅C₆=114°</td>
</tr>
<tr>
<td>C₆N₁=1.32</td>
<td>C₅C₆N₁=119°</td>
</tr>
<tr>
<td>C₂Br₁=1.85</td>
<td>C₂C₃Br₁=123°</td>
</tr>
<tr>
<td>C₄Br₂=1.85</td>
<td>Br₁C₃C₄=123°</td>
</tr>
<tr>
<td></td>
<td>C₄C₅Br₂=123°</td>
</tr>
<tr>
<td></td>
<td>Br₂C₅C₆=123°</td>
</tr>
</tbody>
</table>
The values of moment of inertia were $I_{xx} = 4.544513$, $I_{yy} = 6.034829$, $I_{zz} = 3.526448$, $I_{xy} = 1.598029$, $I_{xz} = -2.974168$, $I_{yz} = -1.894770 \times 10^{-19}$ gm-cm$^2$. The principal moment of inertia was found to be $4.921458 \times 10^{-23}$ gm-cm$^2$.

The calculated values of enthalpy and heat capacity function, free energy and entropy function have been shown in Table 2.3 for the said molecule under present investigations.

The graphical representation of enthalpy function $\left( H^0 - E^0_0 \right)/T$ and heat capacity function $\left( C^0_\rho \right)$ with absolute temperature have been shown in Fig 2.6, and the free energy function $\left( F^0 - E^0_0 \right)/T$ and entropy function $\left( S^0 \right)$ with absolute function have been shown in Fig 2.7 respectively. The thermodynamic functions calculated here are in good agreement with the trend reported in the literature$^{105-107}$.
### TABLE 2.1

**ASSIGNMENTS OF VIBRATIONAL FREQUENCIES (cm\(^{-1}\)) OF 3,5-DBP**

<table>
<thead>
<tr>
<th>IR cm(^{-1}) (in KBr)</th>
<th>Intensity</th>
<th>Raman bands</th>
<th>Intensity</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>-</td>
<td>66</td>
<td>VS</td>
<td>Lattice vibration</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>92</td>
<td>VS</td>
<td>Lattice vibration</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>136</td>
<td>M</td>
<td>Lattice vibration</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>182</td>
<td>M</td>
<td>(\gamma) (C-Br)</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>215</td>
<td>M</td>
<td>(\gamma) (C-Br)</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>307</td>
<td>W</td>
<td>(\beta) (C-Br)</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>327</td>
<td>MS</td>
<td>(\beta) (C-Br)</td>
</tr>
<tr>
<td>417</td>
<td>M</td>
<td>406</td>
<td>M</td>
<td>(\gamma) Ring</td>
</tr>
<tr>
<td>433</td>
<td>W</td>
<td>443</td>
<td>M</td>
<td>(\gamma) Ring</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>479</td>
<td>VS</td>
<td>(\gamma) Ring</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>545</td>
<td>VW</td>
<td>(\nu) (C-Br)</td>
</tr>
<tr>
<td>650</td>
<td>S</td>
<td>657</td>
<td>VS</td>
<td>(\nu) (C-Br)</td>
</tr>
<tr>
<td>695</td>
<td>VS</td>
<td>690</td>
<td>M</td>
<td>(\beta) Ring</td>
</tr>
<tr>
<td>762</td>
<td>S</td>
<td>750</td>
<td>S</td>
<td>(\gamma) (C-H), (\beta) (C-C-C)</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>769</td>
<td>S</td>
<td>(\beta) Ring</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>816</td>
<td>S</td>
<td>(\beta) (C-N) Ring, (\gamma)(N-H)</td>
</tr>
<tr>
<td>884</td>
<td>VS</td>
<td>862</td>
<td>VW</td>
<td>(\gamma) (C-H)</td>
</tr>
<tr>
<td>968</td>
<td>MS</td>
<td>967</td>
<td>VS</td>
<td>(\gamma) (C-H)</td>
</tr>
<tr>
<td>1006</td>
<td>S</td>
<td>994</td>
<td>W</td>
<td>(C-C) Ring breathing</td>
</tr>
</tbody>
</table>
Cont. ………. Table 2.1

<p>| | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1100</td>
<td>S</td>
<td>1106</td>
<td>S</td>
<td></td>
<td>β (C-H ), (C-C-C) Trigonal bending</td>
</tr>
<tr>
<td>1113</td>
<td>MS</td>
<td>1136</td>
<td>VS</td>
<td></td>
<td>β (C-H )</td>
</tr>
<tr>
<td>1150</td>
<td>M</td>
<td>1150</td>
<td>S</td>
<td></td>
<td>β (C-H )</td>
</tr>
<tr>
<td>1367</td>
<td>W</td>
<td>1380</td>
<td>VVS</td>
<td></td>
<td>ν (C-N )</td>
</tr>
<tr>
<td>1484</td>
<td>MS</td>
<td>-</td>
<td>-</td>
<td></td>
<td>ν Ring</td>
</tr>
<tr>
<td>1510</td>
<td>S</td>
<td>1525</td>
<td>W</td>
<td></td>
<td>ν Ring</td>
</tr>
<tr>
<td>1546</td>
<td>M</td>
<td>1560</td>
<td>W</td>
<td></td>
<td>ν Ring</td>
</tr>
<tr>
<td>1601</td>
<td>W</td>
<td>1596</td>
<td>M</td>
<td></td>
<td>ν Ring</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>1662</td>
<td>M</td>
<td></td>
<td>β (N-H )</td>
</tr>
<tr>
<td>1801</td>
<td>VW</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2956</td>
<td>M</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3017</td>
<td>MS</td>
<td>-</td>
<td>-</td>
<td></td>
<td>ν (C-H )</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>3073</td>
<td>W</td>
<td></td>
<td>ν (C-H )</td>
</tr>
<tr>
<td>3099</td>
<td>MS</td>
<td>-</td>
<td>-</td>
<td></td>
<td>ν (C-H )</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>3116</td>
<td>MS</td>
<td></td>
<td>ν (N-H )</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>3224</td>
<td>W</td>
<td></td>
<td>ν (N-H ), Sym.</td>
</tr>
<tr>
<td>3450</td>
<td>VW</td>
<td>-</td>
<td>-</td>
<td></td>
<td>ν (N-H ), Asym.</td>
</tr>
</tbody>
</table>

Where ν = Stretching, W = Weak, β = In-plane bending
VS = Very strong, γ = Out-of-plane bending, VVS = Very very strong
Sym = Symmetric, VW = Very weak, Asym = Asymmetric
M = Medium, MS = Medium strong, S = Strong
### TABLE 2.2
EFFECT OF SOLVENTS ON ELECTRONIC TRANSITIONS OF 3,5-DBP
(All values in nm)

<table>
<thead>
<tr>
<th>SOLVENT</th>
<th>DC*</th>
<th>RI**</th>
<th>n-π*I</th>
<th>n-π*II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>25.0</td>
<td>1.3773</td>
<td>291</td>
<td>286</td>
</tr>
<tr>
<td>Methanol</td>
<td>32.0</td>
<td>1.3362</td>
<td>292</td>
<td>288</td>
</tr>
<tr>
<td>Water</td>
<td>80.5</td>
<td>1.3380</td>
<td>283</td>
<td>281</td>
</tr>
</tbody>
</table>

*Dielectric Constant

** Refractive Index
### TABLE 2.3

**THERMODYNAMIC FUNCTIONS OF 3,5-DIBROMO PYRIDINE**

*(Cal./mole -K)*

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$(H^o - E^o_0)/T$</th>
<th>$(C^o_p)$</th>
<th>$(F^o - E^o_0)/T$</th>
<th>$(S^o)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>200°</td>
<td>13.760</td>
<td>19.474</td>
<td>100.790</td>
<td>114.09</td>
</tr>
<tr>
<td>300°</td>
<td>16.572</td>
<td>24.742</td>
<td>100.1402</td>
<td>120.29</td>
</tr>
<tr>
<td>400°</td>
<td>19.144</td>
<td>28.757</td>
<td>100.151</td>
<td>126.83</td>
</tr>
<tr>
<td>500°</td>
<td>21.369</td>
<td>31.612</td>
<td>123.66</td>
<td>132.22</td>
</tr>
<tr>
<td>600°</td>
<td>23.255</td>
<td>33.567</td>
<td>127.73</td>
<td>138.06</td>
</tr>
<tr>
<td>700°</td>
<td>24.855</td>
<td>35.180</td>
<td>131.44</td>
<td>143.43</td>
</tr>
<tr>
<td>800°</td>
<td>26.222</td>
<td>36.365</td>
<td>134.85</td>
<td>148.57</td>
</tr>
<tr>
<td>900°</td>
<td>27.404</td>
<td>37.316</td>
<td>138.01</td>
<td>153.29</td>
</tr>
<tr>
<td>1000°</td>
<td>28.435</td>
<td>38.100</td>
<td>140.95</td>
<td>157.66</td>
</tr>
<tr>
<td>1100°</td>
<td>29.345</td>
<td>38.756</td>
<td>143.70</td>
<td>161.75</td>
</tr>
<tr>
<td>1200°</td>
<td>30.153</td>
<td>39.311</td>
<td>146.29</td>
<td>165.51</td>
</tr>
<tr>
<td>1300°</td>
<td>30.876</td>
<td>39.785</td>
<td>148.74</td>
<td>169.14</td>
</tr>
<tr>
<td>1400°</td>
<td>31.527</td>
<td>40.191</td>
<td>151.65</td>
<td>173.32</td>
</tr>
<tr>
<td>1500°</td>
<td>32.117</td>
<td>40.541</td>
<td>153.24</td>
<td>177.61</td>
</tr>
</tbody>
</table>

Where $H^o$ = enthalpy, $S^o$ = entropy, $F^o$ = free energy, $E^o_0$ = zero point energy
REFERENCES

64. B.S. Yadav, M.K. Yadav, Vipin Kumar and Pradeep Kumar, Communication in Instrumentation, 6 (4) (1999) 191.

87. B.S. Yadav, Nitin Kumar and Seema, Ultra Science, 17 (3) (2005) 469.


