
ELECTRONIC SPECTRAL STUDIES AND THERMODYNAMIC FUNCTIONS OF 2-CHLORO-6-METHOXY PYRIDINE

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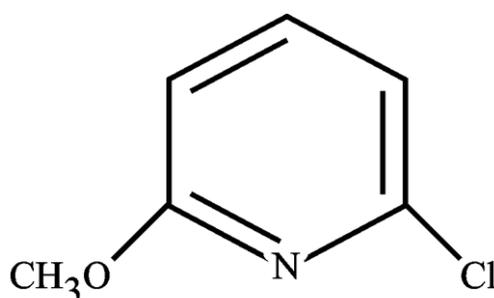
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ABSTRACT

The present paper deals with analysis and interpretation of the fundamental vibrational frequencies in 2-Chloro-6-methoxy pyridine assuming C_s point group symmetry for the molecule. The ultraviolet absorption spectra of the above molecule has been recorded in various polar solvents (ethanol, methanol and water) under the heading Solvent Effect. The statistical computation of thermodynamic function viz. enthalpy, heat capacity, entropy and free energy for 2-Chloro-6-methoxy pyridine is done.

INTRODUCTION

Nucleic acids and related compounds are object of spectroscopic studies like infrared, Raman and ultraviolet in biochemical and biophysics research. The N-heterocyclic compounds like pyridines, pyrimidines (cytosine, uracil, and thymine) and their derivatives are of biological importance since they play a major role in the structure and properties of the nucleic acids [1-7]. Spectroscopic study giving an account for vibrational spectra of these free base molecules gives an insight of complex biological process. Deoxyribonucleic acid (DNA) and Ribonucleic acid (RNA) consisting of pyridine molecule and their derivatives store the genetic information and play a vital role in protein synthesis. Also pyridine derivatives like amino pyridines and mercapto pyridines etc. are widely used in certain diseases [8,9]. Nicotine, cocaine, atropine, conine etc. used as drugs to cure several diseases and metabolic problems are alkaloids of pyridine group representing simplest natural heterocyclic compounds. Pyridine and its derivatives also find an application in analytical chemistry where they serve the purpose of solvent and are used as synthetic intermediate. Because of the widespread importance and easy availability a large number of attempts have been made to study N-heterocyclic compounds containing nitrogen atom in the ring. The vibrational and electronic spectral studies of pyridine have been carried out by various recent investigators [10-31]. The number, position as well as nature of the substituents is responsible for difference in absorption.

**Fig-1 Molecular Structure of 2-Chloro-6-methoxy pyridine****EXPERIMENTAL**

Spec-pure grade chemical 2-Chloro-6-methoxy pyridine was obtained from M/S Aldrich Chemie, West Germany and used as such. This chemical hereafter, is referred as 2,6-CMP. The purity of the said molecule was also confirmed by elemental analysis and melting point determination. The FTIR absorption spectra of 2,6 CMP was recorded on "Perkin Elmer" spectrophotometer model-52 in the region 4000-400 cm^{-1} and laser Raman spectra of the above molecule has been recorded on "Spex-Rama Lab" spectrophotometer using Argon-Neon Laser Beam of light of wavelength 488 nm and power of 200

mw. All the bands are expected to be accurate $\pm 7 \text{ cm}^{-1}$. The electronic spectra of these molecules were recorded in various solvents on Beckmann spectrophotometer model M-35. The solvent employed in the present work include spectroscopic grade ethanol, methanol and water. Their purity was confirmed by recording the spectra against empty cells as reference and checking the cut off wavelengths.

ELECTRONIC SPECTRA

One of the outstanding features of the selective absorption of the six-membered heterocyclic compounds is the fact that replacement of =CH– by =N–, or of –CH₂– by –NH– affects the position of the absorption band but little and generally causes but a slight increase in the intensity of absorption. Pyridine itself resembles benzene in its absorption properties. In non-polar solvents it has an E-band of high intensity (ϵ 7500) near 195 m μ and a region of "benzenoid absorption" (B-band) in the 250-260 m μ region (ϵ 2500). In polar solvents (neutral or alkaline) such as water, methanol, and ethanol the absorption properties are similar, but the fine structure of the B-band is reduced. Halogeno pyridines closely resemble pyridine in general absorption properties and the B-bands of chloro compounds exhibit interesting fine structures. It has been established by Kasha, that the electronic transition in pyridines exhibit two band system in the near ultraviolet region, one towards the longer wavelength side or at least one singlet singlet $n-\pi^*$ transition, and other towards the shorter wavelength side as $\pi-\pi^*$ system which is analogous to 2600 Å ($^1A_{1g} \rightarrow ^1B_{2u}$) system of benzene. The $A_{1g} \rightarrow B_{2u}$ transition is forbidden in benzene as a result of hexagonal symmetry of benzene molecule. Under reduced symmetry C_s of the molecules studied, these transitions becomes $1A' \rightarrow 1A'$ and under C_{2v} point group, this transition become $1A_1 \rightarrow 1B_2$ and $1A_1 \rightarrow 1A_1$ and these are allowed.

SOLVENT EFFECT

The shift of absorption bands occurring upon a change from vapour to solution or from one solvent system to another are the result of differences in solvation energies of the solute in the ground and excited states. The solvation energies include induced dipole-induced dipole interaction between non-polar solutes and solvents, induced dipole- dipole forces between polar solutes and non polar solvents or vice versa and dipole-dipole interaction between polar solutes and solvents.

Orientation strain is observed in cases where both solute and solvent are polar and where upon excitation the solute dipole moment is changed. If excitation changes the amount of hydrogen bonding between solute and solvents, then also orientation strain is expected. Packing strain is found in cases where the molecule in the excited state is larger than in the ground state. Since most organic molecules do not change size to any great extent upon excitation, packing strain is normally negligible in comparison to the other effects. The polar solvents and those which can form hydrogen bonds tend to interact electrostatically with several chromophores which changes the charge distribution in the molecule and results in increased delocalisation; the $\pi-\pi^*$ transitions are shifted towards longer wavelength and $n-\pi^*$ transition towards shorter wavelength with increasing polarity of the solvent.

THERMODYNAMIC FUNCTIONS

The energy of a molecule is the sum of translational, rotational, vibrational and electronic energy. For a first approximation these energy contributions can be treated separately. Once the vibrational frequencies of a molecule are known the contribution of the vibrational energy to the total energy possessed by a molecule can be calculated. Similarly the rotational energy contribution can be calculated if the moments of inertia of the molecule are known. Thus the observed frequencies and the moments of inertia are the important variables in computing the thermodynamic functions viz. enthalpy function $(H^\circ - E_0^\circ)/T$, Heat capacity (C_p°), free energy function $(F^\circ - E_0^\circ)/T$ and entropy (S°). However, direct experimental measurements of vibrational contribution of thermodynamic quantities of a molecule are difficult and sometimes impossible. But thermodynamic quantities of a molecule can be calculated more accurately than measured using fundamental wave numbers of the molecule.

The statistical mechanical calculations of thermodynamic properties for 2,6-CMP molecule requires atomic masses, molecular weights, molecular structural parameters, complete fundamental

vibrational frequencies (3N–6) and the symmetry number. For determining rotational contributions following structural parameters were used

Bond Lengths (Å)	Bond Angle (°)
N ₁ C ₂ = 1.31	N ₁ C ₂ C ₃ = 120
C ₂ C ₃ = 1.36	C ₂ C ₃ C ₄ = 120
C ₃ C ₄ = 1.34	C ₃ C ₄ C ₅ = 120
C ₄ C ₅ = 1.35	C ₄ C ₅ C ₆ = 120
C ₅ C ₆ = 1.35	C ₅ C ₆ N ₁ = 120
C ₆ N ₁ = 1.35	C ₆ N ₁ C ₂ = 120
C ₆ O ₈ = 1.35	N ₁ C ₂ Cl ₉ = 119
C ₇ O ₈ = 1.43	C ₃ C ₂ Cl ₉ = 118
C ₂ Cl ₉ = 1.78	C ₅ C ₆ O ₈ = 125
	N ₁ C ₆ O ₈ = 116
	C ₆ O ₈ C ₇ = 119

Since, the molecule is aromatic it is planar lying in XY plane with Y axis passing through para position and Z axis passing through molecular plane. The symmetry number for overall rotation is 2. The principal moments of inertia were found to be;

$$I_x = 3.23 \times 10^{-38} \text{ gm cm}^2$$

$$I_y = 9.85 \times 10^{-38} \text{ gm cm}^2$$

$$I_z = 1.31 \times 10^{-37} \text{ gm cm}^2$$

The calculation of the variation of the thermodynamic functions at different temperatures (200-1500° K) were carried out for one mole of an ideal gas at 1 atmospheric pressure using 21 fundamental frequencies for the said compound and assuming rigid rotor harmonic oscillator approximation. The variation of enthalpy function $(H^\circ - E_o^\circ)/T$ and heat capacity function (C_p°) with absolute temperature, while the variation of free energy function $(F^\circ - E_o^\circ)/T$ and entropy function (S°) with absolute temperature. Enthalpy functions $(H^\circ - E_o^\circ)/T$ represent the total energy stored in a system. When a system changes from solid to liquid to vapours the enthalpy of the system increases. Similar variation i.e. increase in enthalpy values for 2,6- CMP molecule are observed as the temperature varies from 200-1500°K.

Entropy (S°) is regarded as the measure of randomness in the system. As the temperatures increases, entropy of the system increases. Similarly, there is increase in free energy $(F^\circ - E_o^\circ)/T$ of the system for the title molecule as the temperature varies from 200-1500 °K. The thermodynamic functions rises more rapidly in the low temperature range and less rapidly in the high temperature range. The trend of variation of thermodynamic functions is similar to those reported in literature.

TABLE- 1
ASSIGNMENTS OF VIBRATIONAL FREQUENCIES OF 2-CHLORO -6- METHOXY PYRIDINE

(all values in cm^{-1})

FTIR	LASER RAMAN	ASSIGNMENTS
—	3146 vw	ν (C–H)
3104 vw	—	ν (C–H)
—	3082 ms	ν (C–H)
2997 vw	3013 vw	ν (C–H) Asym O–CH ₃ group
2956 vw	2951 ms	ν (C–H) Asym O–CH ₃ group
2905 vw	2905 vw	ν (C–H) Sym O–CH ₃ group
—	1641 w	ν ring
1602 s	—	ν ring
1566 s	1568 ms	ν ring
—	1538 w	ν ring
1476 s	—	ν (C–N)
1418 s	—	ν (C=N)
—	1390 w	β (C–H)
1305 s	1298 ms	β (C–H), ν (C–OCH ₃)
1266 w	1265 w	β (C–H) Asym O–CH ₃ group, ν ring
—	1238 w	β (C–H) Sym O–CH ₃ group
1149 ms	1148 ms	β (C–H)
—	1069 ms	CH ₃ Wagging
1026 ms	—	CH ₃ Rocking, ν (C _{alkyl} –O)
986 w	982 s	ν (C–Cl)
879 ms	—	γ (C–H), CH ₃ Rocking
—	862 w	γ (C–H)
—	847 w	Trigonal Bending
787 ms	—	Trigonal Bending
—	766 w	Ring Breathing
—	746 w	C–N–C Bending Vibration
731 vw	—	β (C–OCH ₃)
690 vw	—	γ (C–H)
—	678 ms	β ring
—	629 w	β ring
609 vw	605 ms	β ring
—	522 w	β (C–Cl)
—	467 ms	γ ring
416 vw	410 ms	γ ring
—	278 w	γ (C–OCH ₃)
—	185 ms	γ (C–Cl)

Where,

ν = stretching, β = in-plane bending, γ = out-of-plane bending,
 ν_{Asym} = asymmetric stretching, ν_{Sym} = symmetric stretching
 s = strong, ms = medium strong, w = weak, vw = very weak

TABLE-2
SOLVENT EFFECT ON ELECTRONIC TRANSITIONS OF
2- CHLORO-6-METHOXY PYRIDINE
 (all values in nm)

SOLVENT	D.C	R.I	$n - \pi^*$	$\pi - \pi^*$	$1n - \sigma^*$	$1\pi n - \sigma^*$
Ethanol	25	1.3773	276	227	–	–
Methanol	32	1.3362	280	233	207	203
Water	80.5	1.3380	274	221	–	–

D.C- Dielectric Constant

R.I- Refractive Index

TABLE- 3
THERMODYNAMIC FUNCTIONS OF 2-CHLORO-6-METHOXY PYRIDINE
 (in cal/mol °K)

Temperature (°K)	Enthalpy ($H^0 - E_0^0$)/T	Heat Capacity (C_p^0)	Free Energy ($F^0 - E_0^0$)/T	Entropy (S^0)
200	10.27	14.21	102.20	112.48
300	12.36	18.83	101.75	119.11
400	14.52	23.09	110.61	125.13
500	11.60	21.67	114.07	130.68
600	18.53	29.61	117.27	135.81
700	20.30	32.06	120.27	140.57
800	21.90	34.13	123.08	144.99
900	23.36	35.91	125.75	149.11
1000	24.69	37.45	128.28	152.98
1100	25.91	38.78	130.69	151.61
1200	27.04	39.93	133.00	160.04
1300	28.07	40.93	135.20	163.28
1400	29.02	41.80	137.32	161.34
1500	29.90	42.56	139.35	169.25

CONCLUSION

This paper deals with the electronic spectral investigation of 2-Chloro-6-methoxy pyridine. The vibrational spectra is analyzed and assigned on the basis of the magnitude and relative intensities of the observed bands. The electronic transition bands are also analyzed. The effect of substitution and solvent variation on the same has been reported. Thermodynamic functions of the said molecule have also been computed statistically at different temperatures by using vibrational frequencies and molecular geometry.

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