

Research Paper :

Spectral analysis and effect of temperature on thermodynamic parameters and biological activities of some substituted quinoline

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ABSTRACT

The present paper concerns with an introduction of the molecular spectroscopy in brief, selection rule for infrared, Raman spectra and electronic transition. Electronic and vibrational spectra of benzene and quinoline substituents have been discussed. The present paper also concerns the effect of substituents, their position on the vibrational and electronic spectra and the effect of polar and nonpolar solvents have also been discussed. The present investigation also concerns the effect of pH on the vibrational and electronic spectra have also been discussed. The subject also concerns Thermodynamic parameters and biological studies have also been discussed.

KEY WORDS : Infrared spectra, Raman spectra, Electronic and vibrational spectra of quinolines substituents

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When a molecule absorbs its energy increases in proportion to the energy of the photon as expressed by the relation:

$$\Delta E = h\nu' = \frac{hc}{\lambda}$$

where, h is Planck's constant, ν' and λ are the frequency and the wavelength of radiation and c the velocity of light. The increase may be in the form of electronic, vibrational and rotational energy of the molecule. Changes in the electronic energy involves relatively large quanta, while in the vibrational energy involve smaller quanta and the change in the rotational energy involves even smaller than those of vibrational energy. If a molecule absorbs radiation in the microwave or far infrared region, only its rotational energy will change. If the energy of the radiation is much greater, as in the case of ultra-violet light, there will be a change in the electronic, vibrational and rotational energies of the molecule. Thus the infrared absorption spectra of the molecules result from transition between vibrational and rotational energy levels. In conclusion, molecular spectroscopy is the study of the absorption or emission of electro-magnetic radiation by the molecules. The spectral regions, infrared, visible and ultra-violet are classified from 0.8 microns to 1000 microns, from 400

nm to 800nm, from 1 nm to 400 nm, respectively. The modes which involve a change of dipole moment during vibration will yield infrared bands, while change in the polarizability may give to Raman bands and the modes which neither involve a change in dipole moment nor in polarizability may appear in the electronic spectra. Although the mechanism of absorption of energy is different in the ultra-violet, visible and infrared region, the fundamental process is the absorption of a certain amount of energy which provide complete information about the vibrational frequencies of the molecule in the ground and excited electronic states^{1,2}.

If a molecule is placed in an electromagnetic field, a transfer of energy from the field to the molecule will occur only when the difference of the energy E between two quantized states as given below:

$$\Delta E = h\nu = E_2 - E_1$$

where, h is the Planck's constant, and ν is the frequency of radiation. These transitions (E_1 to E_2 , absorption or E_2 to E_1 , emission) involve different amount of energy.

The nature of the molecular changes that are responsible for the emission or absorption of the radiation can be easily understood with advanced experimental techniques to a high degree of accuracy. The experimental

data, that such studies provide, are the frequencies of wavelengths of the radiation, the amount of radiation emitted or absorbed and exact measurements of the size, shape flexibility and electronic arrangement of the molecule. If these data are properly analyzed, valuable information can be obtained about the structure and characteristics of a molecule which is of considerable importance and interest in the field of chemistry as well as in physics.

Recently the increasing interest in the study of polyatomic molecules is mainly due to their fundamental importance. Further the N-heterocyclic molecules e.g. quinolines and their derivatives are the basic constituents of alkaloids. These compounds are of great biological and pharmaceutical importance due to their vital role in the structure and properties of alkaloids and wide applications in biological chemistry. In N-heterocyclic molecules the substituents in the form of functional groups like $-OH$, No_2 or $-NH_2$ may show tautomerism and hydrogen bonding. The spectra of the solutions of these molecules change to a large extent with different polar and nonpolar solvents. Secondly, the various substituents modify the vibrational frequencies, although the aromatic character is retained in all substituted benzenes. Thus such studies have stimulated a great interest in research in the field of electronic and vibrational spectroscopy.

In the view of above, the present work comprises studies on :

- Infrared, laser Raman and ultraviolet spectra of 7-chloro-4-hydroxy quinoline
- The effect of different substituents and their position.
- The effect of polar and non polar solvent n electronic transition.
- The effect of pH on electronic transition.
- The calculations of thermo dynamic parameters.
- Fungicidal activity of these compounds have also

been studied and correlated with spectroscopic data.

EXPERIMENTAL METHODOLOGY

Spec-pure grade sample of 7-chloro-4-hydroxy quinolines (abbreviated as 7,4-CHQ) was obtained from M/s Sigma Aldrich Chemicals, U.S.A.. The purity of the sample was confirmed by elemental analysis and melting point determination (276-279°C). The laser Raman Spectra of 7, 4-CHQ molecule was recorded on a ipex spectrophotometer, using laser source with exciting radiation at 488 nm in the region 4000-50 cm^{-1} . Its infrared spectra were recorded on Perkin Elmer M-500 FTIR spectrophotometer in the region 4000-400 cm^{-1} using Nujolmull techniques. While the $\pi-\pi^*$ and $n-\pi^*$ transition

bands for 7,4-CHQ molecule has been measured on UV-VIS double beam Perkin Elmer spectrophotometer M-Lambda-20 in the region 400-200nm in liquid state, using various polar solvents (*i.e.* ethanol, methanol and water). The solvents used for preparation of the solution of the above said compound were of spectroscopic grade. The pH of the solutions was measured with a systolic-digital pH meter. The system was standardized at pH 4.0 \pm 0.01, 7.0 \pm 0.01 and 9.0 \pm 0.01 at room temperature with the help of buffer solutions, the concentration of the solution in all cases was kept constant at 8 x 10⁻³ gm/leter. The ratios of pure solvent and acid or alkali were maintained at 9:1 by volume.

EXPERIMENTAL FINDINGS AND ANALYSIS

The molecular structure of 7, 4-CHQ molecule is shown in Fig. 1. The infrared spectra were shown in Fig. 2 using Nujol mull techniques, respectively. While Fig. 3 shows the laser Raman spectrum of 7, 4-CHQ molecule. Furthermore, the observed vibrational frequencies of 7,4-CHQ molecule along with their relative intensities and probable assignments are presented in Table 1. The correlation of chloro and hydroxy gp frequencies with those of similar molecules are given in Table 2 and 3. Tautomerism and intermolecular hydrogen bonding in the said compound are shown in Fig. 4 and 5.

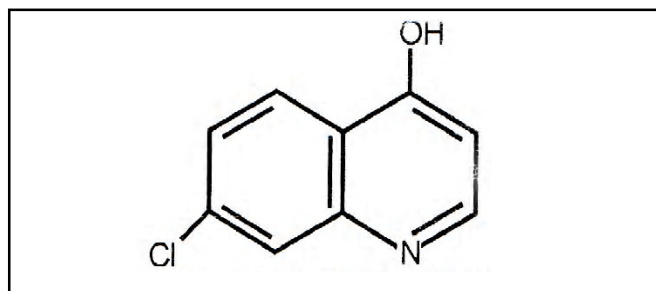


Fig. 1 : Molecular structure of 7-chloro-4-hydroxy quinoline

However, the ultraviolet absorption spectra of the said molecule are shown in Fig. 6 using various solvents (*i.e.* ethanol, methanol, water). The effect of substitution (*i.e.* inductive and mesomeric effects) responsible for shift $\pi-\pi^*$ and $n-\pi^*$ transitions of ultraviolet absorption spectra are shown in Fig. 7 while the effect of solvent on the same is shown in Fig. 8. The effect of pH variation in ultraviolet absorption of 7,4-CHQ molecule are shown in Fig. 9, molecule the neutral, cationic, anionic and canonical forms of the said molecule are shown in Fig. 10. The electronic transitions and corresponding bands of the said molecule (using various solvents) are given in Table 6. While the effect of pH on the position of the

Table 1 : Assignment of vibrational frequencies of 7, 4-CHQ (All value are in cm⁻¹)

Raman		IR		Assignment
Frequency	Intensity	Frequency	Intensity	
70	w	-	-	Lattice vibration
96	w	-	-	Lattice vibration
190	w	-	-	Y (C-Cl)
298	w	-	-	Y (-OH)
331	w	-	-	Y (C-OH)
358	w	-	-	(C-Cl)
418	vw	-	-	Y (C-C)
438	vw	432	w	Y (C-C)
472	vw	-	-	Y (C-C)
498	w	499	vs	Y (C-C)
539	w	544	s	(C=O)
599	w	-	-	β ring
-	-	616	w	β ring, β (C-OH)
639	vw	632	w	β ring
646	w	-	-	β ring
-	-	664	w	ν(O-H.....N)
726	s	-	-	Y (C-C)
740	w	744	s	Y (C-C)
773	w	776	s	Y (C-C)
807	w	802	vs	Y (C-C)
847	w	848	s	sym.(C-H) wagging ring breathing mode
860	w	864	vs	Y (C-H)
914	vw	-	-	Y (C-H)
927	vw	933	w	asym, Y(C-H) wagging, ring breathing mode
947	vw	-	-	Y (C-H)
-	-	967	s	Y (C-H)
988	w	998	s	(C-C-C) trigonal banding ring breathing mode and ν (C-X)
1041	w	-	-	ν(C-Cl), ring breathing mode
1115	w	1116	s	β (C-H)

Contd..... Table 1

Table 1 contd....

1215	w	1209	vs	β (C-H)
1229	vw	-	-	β (C-H)
1256	vw	1266	w	β (C-OH)
1309	s	-	-	ν(C-OH)
-	-	1329	s	β (-OH)
1346	w	-	-	νring
-	-	1383	vs	νring
1403	w	-	-	νring
1430	w	1433	s	νring
1477	w	1466	vs	νring
1503	s	1510	vs	νring
1564	s	1566	vs	νring
1597	w	-	-	νring
-	-	1617	vs	νring
1637	w	1633	vbs	ν(C-N)
-	-	1650	vs	ν(C-N)
1671	s	1666	vs	ν(C=O)
1765-	w and	1767-	w and	overtones of aryl ring vibrations
1999	vw	1966	vw	
3031	w	3033	s	ν(C-H)
3058	vw	3058	s	ν(C-H)
3091	w	-	-	ν(C-H)
-	-	3231	w	ν(N-H)
-	-	3448	w	ν(C-H.....N)
-	-	3649	s	ν(O-H)

where,

ν	:	stretching
y	:	Out-of-plane bending
w	:	weak
vw	:	very weak
β	:	In-plane bending
sym	:	Symmetric
s	:	Strong
VS	:	Very strong

ultraviolet absorption band given in Table 7.

The statistically computed thermodynamic functions viz. enthalpy function $(H^0 - E_0^0)/T$, heat capacity (C_p^0) , free energy function $\{(F^0 - E_0^0)/T\}$ and entropy (S^0) function with absolute temperature are given in Table 8 for 7,4-CHQ molecule. The variation of enthalpy and Heat capacity function with absolute temperature are shown in Fig. 11, while that of free energy and entropy functions are shown in Fig. 12.

Vibrational spectra:

The interpretation are based on the assumption of the C_s point group symmetry or the molecule 7,4-CHQ and the observed fundamentals have been assigned to different normal modes of vibration, In addition to the above, the analysis of the vibrational bands and the

Table 2 : Correlation of vibration frequencies of C–OH and hydroxy group (All values are in cm⁻¹)

Group vibrations	8-HQ	5,7,8-DMHP	2,4,6-DMHP	2,4,3,-HMNP			7,4,-CHQ	
				Raman	IR		Raman	I.R.
					KBr	Nujolmull		
ν (O–H)			3420	3563		3559		3649
β (O–H)		1330	1280	1320	1309	1309	1329	
γ (O–H)								298
ν (C–OH)			1240	1262	1244	1254	1256	1266
β (C–OH)	612			610	622	618		616
γ (C–OH)				321				331
ν (C=O)	1660	1652	1640		1664	1667	1671	166
β (C=O)							539	544

where

8-HQ	:	8-hydroxy quinoline
5,7,8-DBQ	:	5,7-di bromo-8-hydroxy quinoline
2, 4, 6, DMHP	:	2, 4-di methyl-6 hydroxy pyridine
2, 4, 3-HMNP	:	2-hydroxy-4-methyl-3-nitro pyridine
7, 4-CHQ	:	Title compound
ν	:	Stretching
β	:	In-plane-of bending
γ	:	Out-of-plane bending

assignments of the fundamental frequencies have been made in analogy with the substituted pyridine and benzene derivatives by various workers^{6-9, 11-13}.

The vibrational assignment are discussed in details as –

Ring vibration:

C-H vibration:

The 7,4-CHQ molecule have total five hydrogen atoms left around the aromatic rings, therefore five C–H valance oscillations are expected. The aromatic C–H stretching vibrations usually give rise to multiple absorption bands in the region 3100-3000 cm⁻¹⁴⁰⁻⁴². In this region, the bands are not affected appreciable by the nature of the substituents. Out of five vibrational bands, Only two

infrared bands observed at 3058 and 3033 cm⁻¹ in 7,4-CHQ with the counterpart Raman values at 3091, 3058 and 3031 cm⁻¹ and have been assigned to C–H stretching mode, These assignments are also in agreement with the literature value^{15,28,43-47}

Colthup *et al.*⁴² displays frequencies corresponding to C–H planer bending mode aromatic ring in the region 1600–1000 cm⁻¹. These in-plane bending C–H vibrational interact sometimes strongly, with vibrations involving C–C stretching modes. Tripathi⁴³ assigned these modes at 1165, 1070 cm⁻¹ in 2,6- di chloropyridine and at 1290, 1165 and 1090 cm⁻¹ in 3,5 di chloropyridine. In view of this, the present studies of the infrared frequencies of this of mode were assigned at 1266, 1209, 1150 and 116 cm⁻¹. With the counterpart Raman values reserved at 1256, 1229,

Table 3: Correlation of frequencies of chloro group (All values are in cm⁻¹)

Group vibration	1,3- DCB	4,7- DCQ	2,6-CMP			7,4-CHQ	
			Raman	IR		Raman	I.R.
				KBr	Nujolmull		
ν (C–CL)	–	1050	–	–	–	1041	–
	1052	1070	1072	1072	1071	–	–
	1152	–	–	–	–	–	–
β (C– CL)	–	–	–	–	–	358	–
τ (C– CL)	–	189	–	–	190	190	–

where,

1,3-DCB	:	1-di chloro benzene
4,7-DCQ	:	4,7-di chloro quinoline
2,6-CMP	:	2-chloro-6-methoxy pyridine
7,4-CHQ	:	Title compound
ν	:	Stretching
β	:	In-plane-of bending
τ	:	Out-of-plane bending

Table 4 : Electronic absorption bands of benzene molecule²⁹

184 nm	204 nm	256 nm	Reference
E ₁ -band	E ₂ -band	B-band	106
–	K-band	b-band	107

Table.5 : Electronic absorption band of Naphthalene molecule²⁹

221 nm	286 nm	312 nm	References
E ₁ -band	E ₂ -band	B-band	106
–	K-band	b-band	107

1215 and 1115 cm⁻¹. Green⁴⁴ reported the corresponding frequency in m-di chloro benzene at 1161 cm⁻¹.

Colthup *et al.*⁴² also displays frequencies corresponding to C–H nonplanar bending mode of aromatic ring in the region 1000-700 cm⁻¹. While Bellamy⁴⁵ displays the region 1000-650 cm⁻¹ for the same vibrational mode.

during C–H nonplanar bending vibrations of substituted aromatics, the substituent tend to stay nearly motionless and these vibrations tend to stay substituent insensitive. So it is most useful to designate aromatic hydrogen into sets of adjacent hydrogens⁴⁹. Although all these vibrations are group frequencies in the sense that they found with in a relatively small frequency range, they are not all useful group frequencies because many are weak or absent in the spectrum. The most useful of the modes are: (a) where all the hydrogens move in-phase and thus, give rise to a large dipole moment change and a strong infrared band. (b) Another useful mode is the mode in meta- and 1, 2, 4, -trisubstituted benzenes, which involves the isolated hydrogen wag (out-of-plane bending), usually see in the infrared near 170 cm⁻¹. The (c) mode is monosubstituted benzenes usually absorb weakly near 900 cm⁻¹ in the infrared. Moreover in-phase, out-of-plane

Table 6 : Effect of solvent polarity on electronic absorption transition/bands of 7,4-CHQ (All values are in nm)

Solvent	$\pi-\pi^*$ transition/ B-band	$\pi-\pi^*$ transition /R- Band	$\pi-\pi^*$ transition /B- Band	$\pi-\pi^*$ Transition /E ₂ -band or K-band
Water	326	316.12	235.7	215.12
Methanol	328.99	317.99	244.98	214.72
Ethanol	332.98	321.72	245.48	215.12

Table 7: Effect of pH on electronic transitions of 7,4-CHQ (All values in nm)

Solvent	Reference index	pH	7,4-CHQ		
			$\pi-\pi^*$	$\pi-\pi^*$	$\pi-\pi^*$
H ₂ O + NaOH	–	12.79	325.56	306	231
H ₂ O	1.338	5.8	326	316	235.7
H ₂ O+HCl	–	1.04	320	310	230

Table 8 : Thermodynamic parameters of 7,4-CHQ (All value in cal./degree/mole)

Temperature	Enthalpy function	Heat capacity	Free energy function	Energy
(K)	(H ⁰ – E ⁰ / T)	(C ⁰ P / T)	–(F ⁰ – E ⁰ / T)	(S ⁰)
200	15.558	21.964	112.147	127.706
300	18.985	29.987	118.682	137.667
400	22.82	38.603	124.375	147.194
500	26.772	46.362	129.669	156.441
600	30.594	52.821	134.709	165.302
700	34.156	58.051	139.542	173.698
800	37.416	62.266	144.185	181.601
900	40.373	65.677	148.648	189.021
1000	43.047	68.462	152.937	195.985
1100	45.465	70.756	157.061	202.526
1200	47.665	72.661	161.025	208.679
1300	49.641	74.257	164.839	214.480
1400	51.449	75.605	168.511	219.960
1500	53.009	76.750	172.048	225.147

bending vibrations give rise to strong infrared band as follows⁴⁹⁻⁵¹. Two adjacent hydrogen in 1,2,4-trisubstitution at 920–820 cm^{-1} (in quinoline the nitrogen which has no hydrogen is counted as a substituted carbon atom and the correlation used for benzene rings can then be applied^{42, 52-55}). In view of this in the present study, the infrared band observed at 848 cm^{-1} along with the Raman value at 847 cm^{-1} has been assigned to symmetrical-nonplaner C–H bending vibration for two adjacent hydrogen of quinoline ring. Vibrations the Raman band observed at 927 cm^{-1} along with the infrared band observed at 933 cm^{-1} has assigned to asymmetrical, nonplaner C–H bending vibrations^{41, 42}.

C-C and C-N vibrations:

The 7, 4-CHQ molecule has N-heterocyclic quinoline ring (Fig. 1). So ten C–C and two C–N valance oscillations are expected. However, an appreciable mixing of C–C and C–N stretching modes of vibrations take place due to the near equality of these vibrations. Under such circumstances, the normal vibrations of the system cannot be identified with the vibration for a particular bond alone and thus, the bands in the region are assigned to the nucleus as a whole. According to Kalsi²⁸, frequencies of C–C and C–N stretching modes for quinoline ring are found in the region 1600–1430 cm^{-1} . However Colthup *et al.*⁴² displays frequencies for C–C stretching modes of an aromatic ring in the region 1600–1400 cm^{-1} . The vibrations near 1600 cm^{-1} mainly “quadrant stretching” of the aromatic for C–C bonds but there is a little interaction with C–H in plane bending variations⁴². However the vibrations near 1500 cm^{-1} involve “semicircle stretching” of the C–C bonds, which mixes strongly with the C–H in plane-banding modes and absorbs in the infrared spectra at 1486 and 1037 cm^{-1} .⁴² Moreover, the alternating ring stretching vibrations of benzene occur at 311 cm^{-1} to be considerably lower than expected (about 1700 cm^{-1})⁴², because the electronic structure can change and approach the Kekule benzene structure form where the electrons have partially slipped away from the stretched bonds to contracted bonds. In view of the above, in the Raman spectra of 7,4-CHQ molecule bands observed at 1597, 1564, 1477, 1430 and 1346 cm^{-1} with the counterpart infrared bands observed at 1617, 1566, 1510, 1466, 1433 and 1333 cm^{-1} and assigned to various whole ring stretching modes. Moreover, the two Raman bands observed at 1384 and 1364 cm^{-1} have been assigned to alternating ring stretching vibrations^{7, 40, 42, 56-60}. Inspire of these ring vibrations the Raman bands observed at 1637 cm^{-1} along with the infrared bands observed at 1633 and 1617 cm^{-1} have been assigned to C–N stretching modes. These assignment are further

supported by the literature value^{21, 27, 28, 42, 47, 61, 62}. Colthup *et al.*⁴² displays the planer bending vibrations of aromatic ring in the region 850–600 cm^{-1} . Some modes of in-plane bending vibrations interact with the stretching of the bond connecting the substituent to the ring⁶¹. In the present study, the Raman bands observed at 646, 639 and 599 cm^{-1} with the counterpart infrared at 632 and 616 cm^{-1} have been assigned to this mode. Out of these three bands, the only infrared observed at 632 cm^{-1} with the Raman value 639 cm^{-1} has been assigned to couple substituent stretching and in-plane bending mode^{48, 49, 59, 60, 61, 63}.

Colthup *et al.*⁴² also displays the band at 700 cm^{-1} involves out-of-plane bending by sextants. In mono substitution a band appear at 710–665 cm^{-1} , while in 1,2,3-trisubstitution the band appear at 720–685 cm^{-1} . The out of planar carbon bending vibrations are derived from the nondegenerate e_g^2 (703 cm^{-1}) and degenerate e_u (404 cm^{-1}) modes of benzene. In the present work, the C–C out of plane bending vibrations have been observed at 807, 773, 740, 726, 498, 776, 744, 491 and 432 404 cm^{-1} have been found support by the Raman values, which is in agreement with the literature^{41, 42, 47-49, 51-54}.

Ring breathing and trigonal bending vibrations:

The radial skeletal vibrations of benzene derivatives can, be divided into two groups: - the breathing or C–C–C bending vibrations and the C–X stretching vibrations. The separate discussion of these vibrations is however, impossible due to the strong coupling of these modes⁵². Except the ring breathing vibrations of benzenes all the frequencies are remaining practically unaffected by substitution. Due to this interaction, one of the modified modes reduces to about 800 cm^{-1} , while the other keeps itself around 1000 cm^{-1} in substituted benzene^{22, 68}. In the present work, the infrared band observed at 848 and 933 cm^{-1} with the counterpart Raman bands at 847 cm^{-1} and 927 cm^{-1} has been assigned to the coupled substituent stretching (C–X) and ring breathing of ring translational vibrations. Furthermore, an infrared band observed at 998 cm^{-1} along with the Raman value at 988 cm^{-1} has been assigned to the coupled substituent bending and C–C–C trigonal vibration. These assignments are further verified by the literature^{22, 58, 60, 69-78}.

C–X vibration:

According to Colthup *et al.*⁴², in aryl halides no band obviously comparable to the aliphatic C–X stretching bands due to interaction with ring vibrations. Those ring vibrations which are ring ‘X’ sensitive and involves C–Cl⁷⁹ stretching are found at 1096 cm^{-1} for para, 1078–174 cm^{-1} for meta and 1057–1034 cm^{-1} for ortho

substituted chloro benzenes⁸⁰, Scherer and Evans⁸¹ assigned the C–Cl stretching mode at 1070 cm⁻¹, 1152 cm⁻¹ in m-dichloro benzene. Bishnoi⁸² assigned this mode at 150, 1070 cm⁻¹ in case of 2,6-ducgkiriabukube. Thus the strong Raman band at 1041 cm⁻¹ has been assigned to the C–Cl stretching mode in the case of 7,4-CHQ. These assignments also find support from the literature value^{64,79,83–90}.

Varsanyi *et al.*⁵⁴, displays the frequency of C–X out-of-plane bending vibrations lower than 500 cm⁻¹ for aromatic ring. In the present investigation, the Raman band observed at 358 cm⁻¹ has been assigned to C–Cl in-plane bending mode. This assignment is in agreement with the literature^{48, 91–93}.

Varsanyi *et al.*⁵⁴, further displays that the out-of-plane bending C–X vibrations for trisubstitution lie in between 270–140 cm⁻¹ in various chloro substituted benzenes. In view of this the strong Raman band observed at 190 cm⁻¹ has been assigned to C–Cl out-of-plane bending mode, (as in quinoline the nitrogen which has no hydrogen is counted as substituted carbon atom and the correlation used for benzene rings can be applied^{44, 54, 55}). This further found support by the literature value^{7, 28, 62, 69}.

According to Colthup *et al.*⁴², the bands found in the region 1300–1150 cm⁻¹ arise from those C–OH bands somewhat stiffened by resonance – such as esters, phenols, phenyl ethers and vinyl ethers⁹⁴. Phenols in solid state absorb at 1390–1330 and 1260–1180 cm⁻¹, which represent OH deformation and C–OH stretch, which interact somewhat⁹⁵. Sanyal *et al.*⁹⁶ have assigned C–OH stretching 1305 and 1332 cm⁻¹ in dihydroxy quinoline. Goel *et al.*⁹⁷ have assigned this mode at 1254 and 1230 cm⁻¹ to similar mode in 2, 4 di methyl, 6-hydroxy quinoline, respectively. The C–OH stretching mode is not independent vibrational mode because it couples with the vibrations of adjacent group⁹. In this present study, the Raman band observed at 1309 cm⁻¹ has been assigned to C–OH stretching mode. This assignment is in agreement with the literature value^{9–13, 39, 59}. Further more, Singh *et al.*⁹⁷ have assigned the C–OH in-plane-bending mode at 550 cm⁻¹ in 2,4-dichloro-6 hydroxy pyrimidine. While Sanyal *et al.*⁹⁶ have assigned this mode at 546 and 635 cm⁻¹ in 4, 6 di hydroxyl-2-methyl quinoline. In the present study the infrared band observed at 616 cm⁻¹ has been assigned to C – OH in-plane bending. These assignment are in agreement with the literature value^{27, 70, 71}.

Varsanyi *et al.*⁵⁴ also displays the regions of various vibrational modes *i.e.* 17a (10b) in the region 307-4000, 10a(11) in the region 240-374, 17b(10a) in the region 116-

170 and 5 in the region 89-15 cm⁻¹ for C–X out-of-plane bending of di substitution. According to Colthup* *et al.*⁴² in quinoline (the nitrobenzene which has no hydrogen) is counted as a substituted carbon and the correlation used for benzene ring can then be applied. So that 7,4-CHQ molecule has been treated as di substituted molecule and the Raman band observed at 331 cm⁻¹ has been assigned to C–OH out-of-plane bending modes, respectively. These assignments are in agreement with the literature value^{7, 27, 70 – 72}.

Overtones of aryl ring vibrations:

According to Kalsi²⁸, usually intense overtones of aryl ring vibrations occur in the region 2000-1650 cm⁻¹. These bands are somewhat weaker than fundamentals and are most clearly seen in the spectra of moderately thick samples⁴³. In the present study, in the infrared bands observed in the region (1767-1966) cm⁻¹ along with the Raman bands observed at (1765-1999) cm⁻¹ have been assigned to aryl ring vibrations. These assignments are further in agreement with the standard literature^{29, 41}.

Group vibrations:

OH (hydroxy) group vibrations:

According to Silverstein *et al.*²⁹ the unbounded or free hydroxyl group of alcohols and phenols absorbs strongly in the region 3650-3584 cm⁻¹. Sharp 'free' hydroxyl bands are observed only in the vapour phase or in very dilute solution in nonpolar solvents. Clothé *et al.*⁴² displays free OH stretch absorbs near 3640 cm⁻¹ in CCl₄ solution. Yadav *et al.*²⁷ have assigned this mode at 3560⁻¹ in the infrared spectra of 4,6-dihydroxy-5. Nitropyrimidine. In the present investigation Raman band observed at 3584 cm⁻¹ has been assigned to O–H stretching mode³⁷.

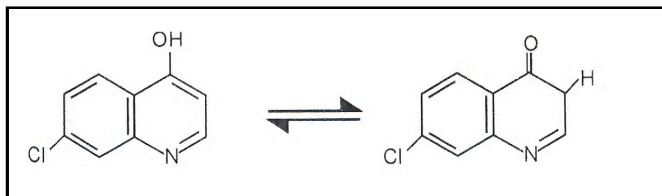
Silverstein *et al.*²⁹ further display that mulls, pellets or melts of phenols absorb at 1390-1330 cm⁻¹ and 1260-1180 cm⁻¹. These bands apparently result from interaction between O–H bending and C–O stretching mode. In view of this the Raman band observed at 1329 cm⁻¹ has been assigned to O-H in-plane bending mode.

Evans⁷⁴ studied the behavior of the out-of-plane OH vibration of phenol derivatives as a function of the strength of hydrogen bond. He established, that the frequency value is 650 cm⁻¹ in the middle of the chain, while it is 300 cm⁻¹ in the free state Green *et al.*⁷⁵ also identified that OH out-of-plane bending vibration of the free OH group at 300 cm⁻¹ in the far-infrared spectrum of phenol, while for the same vibration of m-cresol they obtained 330 cm⁻¹. On the basis of the spectra of many phenolic derivatives. Jacobsen *et al.*⁷⁸ assigned the out-of-plane

frequency of the free –OH group to the range 312-280 cm^{-1} in the liquid state. In the present investigation, the Raman band observed at 298 cm^{-1} has been assigned to OH out-of-plane bending mode^{75, 78}.

Vibrations due to tautomerism:

Spectral studies establish that N-heterocyclic substituted by –OH, –SH and –NH₂ groups exhibit tautomerism. In sharp contrast to other heterocyclic system, several of these bases found in natural alkaloids and nucleic acid were found to exist predominantly in the



keto or amino forms. Keto-enol, thione-thiol and amino-imino tautomerism have long been and are still evoked as the major and even unique, source of spontaneous mutagenesis. Apart from its presumed relevance to spontaneous and induced mutagenesis, such tautomerism is of major significance in the structure of alkaloids nucleic acid is of current additional importance in relation to the antimetabolic activity of alkaloids, nucleic acid and of some N-Heteronucleic aromatic ring analogues⁸⁴.

Although both infrared and ultraviolet spectroscopy may be employed for studies on tautomeric equilibrium yet as shown by Nowak *et al.*⁸⁹, the former is by far the more accurate and unequivocal in interpretation. In this present investigation of 7, 4-CHQ molecule, the molecule is supposed to show tautomeric behavior.

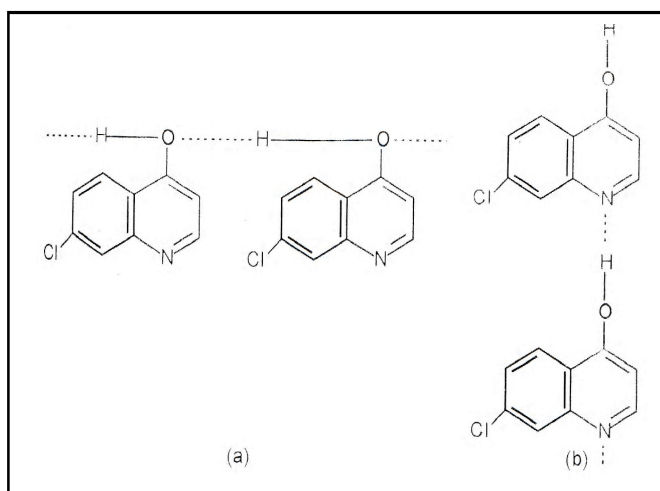


Fig. 2 : Intermolecular hydrogen bonding shown by 7 chloro-4-hydroxy quinoline

Vibration due to hydrogen bonding:

It is interesting to note additional N – H and O – H stretching and bending frequencies in the present study, showing the presence of either hydrogen bonding or tautomerism. Hydrogen bonding can occur in any system containing proton donor group and a proton acceptor⁹. In organic molecules, the common proton donor groups are carboxyl, hydroxyl, amine or amide groups and common proton atoms are oxygen, nitrogen and halogens.

The 7, 4-CHQ has one proton donor group (*i.e.* hydroxyl group) and one proton acceptor atom (*i.e.* N – atom of the quinoline ring). According to Hoyer⁸⁹, the stretching frequency of the O – H group of benzyl alcohol is 3640. When the group is free and it decreases to 3350 cm^{-1} when associated. Similar frequency drops are observed for the O – H stretching of Phenol and carboxylic acid⁴¹. In the present investigation the weak infrared band at 3464 cm^{-1} has been assigned to bonded O – H stretching. The stretching frequency of the acceptor group is also reduced, but to a lesser degree than proton donor group⁹.

According to Silvertin⁹, the bending vibration of hydrogen bonded group usually shifts to a shorter wavelength (longer frequency) this shift is less pronounced than that of stretching frequency. Evans⁷⁴ studied the behaviour of the out-of-plane –OH vibration of phenol derivatives as a function of the strength of hydrogen bond. He established the frequency value is 650 cm^{-1} in the middle of the chain, while it is 300 cm^{-1} in the free state. In the present investigation, the Raman band at 331 cm^{-1} has been assigned to out-of-plane bending mode of free –OH group.

Electronic spectra:

The electronic assignment is discussed in details as:

Bands due to $\pi - \pi^*$ transition:

The spectra of heteroaromatic compounds are on the whole similar to their corresponding hydrocarbons. The spectrum of quinoline is comparable with that of naphthalene. Naphthalene itself displays three electronic absorption bands at 221nm (ϵ , the molar absorptivity or extinction coefficient = 133,000), at 286nm ($\epsilon = 9,300$ and 312nm ($\epsilon = 289$), due to $\pi - \pi^*$ transition. The intense bands at 220nm result from an allowed transition, whereas the weaker bands at 210 and 280 nm result from forbidden transition in the highly symmetrical naphthalene molecule^{28,29}. Different notations have been used to designate the absorption bands of naphthalene, these are summarized in table. We shall discuss these using Brude's E and B notations²⁹. B-band is generally found in between

230-270nm.

The only difference between naphthalene and quinoline is that the B-band of quinoline more intense with some what diminished fine structure, where as in naphthalene the B-band at 312 nm displays fine structure *i.e.* the band contains multiple peaks. Thus transition is allowed for quinoline but forbidden for more asymmetrical quinoline^{29,30,105}. In the present study, the band observed at 332, 98, 328, 98 and 326 nm in ethanol, methanol and water solvents are originated from $\pi - \pi^*$ transition and designated as B-band.

While the very weak shoulder band observed at 321, 72, 317.99 and 316.12 nm in ethanol, methanol and water are originated from $\pi - \pi^*$ transition and designated as B-band. The very intense bands observed at 215.12, 215.14 and 215.15 nm in ethanol, methanol and water, respectively are also originated from $\pi - \pi^*$ transition and designated as E_2 bands (K-bands).

Band due to $n-\pi^*$ transition:

The weak R-bands expected for an $n-\pi^*$ transition for quinoline molecule has been observed in vapour phase spectra. This is generally swamped by the more intense B-band when the spectrum is determined in solution²⁹, because of intermolecular hydrogen bonding found between the N-atom of the quinoline ring and the solvent molecule. In the present study, the r-bands originated from $n-\pi^*$ transition are observed due to the attachment of group containing lone pair electron *i.e.* OH group and occurred at 245,98, 244.98 and 235.70 nm in ethanol, methanol and water, respectively.

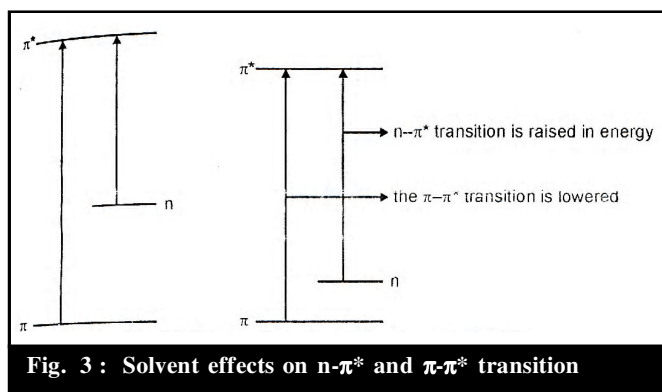
Effect of substitution on electronic transition:

An auxochrome (*i.e.* a saturated group with nonbonded electrons, e.g. -OR, -OH, -NH₂ and -Cl etc) attached to a chromophore (a covalently unsaturated group responsible for electronic absorption, e.g. aromatic ring, -C=C-, -C=C-), alters both the wavelength and intensity of the absorption^{28,29,25}. Auxochrome substitution on the aromatic ring shifts B-band towards the longer wavelength, frequently with intensification of the B-band and loss of its fine structure because of $n-\pi^*$ conjugation¹⁹. Generally, the B-band occurred in between (270–230 nm) and displays a fine structure *i.e.* the band contains multiple peaks^{9,10}. In the present investigation, B-bands observed at 332.98, 328.98 and 326 nm in ethanol, methanol and water, respectively, without a fine structure.

Auxochrome on the aromatic ring forms the e_2 -band in the near ultraviolet region¹⁹, although in many cases it does not appear at wavelength much greater than 210 nm. In auxochrome substitution, the hetero atom with the

lone pair of electron share these electrons with the n -electron system of the ring facilitation the $\pi-\pi^*$ transition and thus causing a red shift of the e_2 -band. In auxochrome substitution, the e -band are formed and the B-band further shifts to longer wavelength with frequently increase in intensity. In the present study, a sharp intense band observed at 215.12, 215.14 and 215.15 nm in ethanol, methanol and water, respectively are designated as E_2 -band. The occurrence of E_2 -bands above 210 nm is due to the shift $\pi - \pi^*$ transition towards the longer wavelength, which is originated due to the combined mesomeric and inductive effects, extends by ausochromic substitution on the aromatic ring (Fig. 7). This is further find support by the literature value^{106, 107}.

The ausochromic groups present on aromatic ring responsible for $n-\pi^*$ transition due to the presence electrons available on the ausochromic group. In 7, 4-CHQ the additive effect of two ausochromic groups is responsible for $n-\pi^*$ conjugation. The -Cl group has three lone pair of electrons to that of -OH group in which O-atom has only two pair of electrons. Furthermore, the -Cl group is highly electronegative and have much more negative inductive effect in comparison to that of -OH group: also the size of Cl group is much lower than that of -OH group, as a result of which valence shell electrons of -Cl group contribute large nuclear charge in comparison to that of -OH group. Hence in 7,4-CHQ molecule, the lone pair electrons present on O - atom of the -OH group are largely responsible for the $n-\pi$ transition. In conjugated system, the energy separation between the groups at the excited state is reduced and the system absorbs at longer wavelength with an increased intensity¹⁰. Moreover, due to lowering of the energy gap, the $n-\pi^*$ transition (due to the presence of heteroatom) *i.e.* the r-band also under goes a red shift^{95,96} with a little change in intensity¹⁰. The shift in absorption results from a combination of inductive and resonance effects (Fig. 7). In 7,4-CHQ molecule, an unusual feature found that $n-\pi^*$ system shows a red shift with respect to the $n-\pi^*$ system of quinoline which is probably due to the presence of hydrogen bonding since the nonbonding electrons of the free base atom and non involved in inter or intermolecular hydrogen bonding. This is further confirmed by the Infrared and Raman spectra of 4,2-HMQ molecular which shows the presence of 7, 4-CHQ molecule which shows the presence of additional N-H and O-H stretching bands. This unusual behaviour is also influence by tautomerism which is observed in present investigation (as discussed in vibrational spectra of the said molecule). In 7, 4-CHQ molecule, R-bands observed at 245.48 and 235.70 nm in ethanol, methanol and water, respectively.



Effect of solvents on electronic transitions:

An increase in the solvent polarity does not affect either the position or intensity of the B-band of benzene, but produces a hyperchromic effect (an increase in absorption intensity) for quinoline and its homologue^{29,30}. This effect is assigned to the hydrogen bonding through the lone pair of electrons of the nitrogen atom^{29,30}. In 7,4-CHQ molecule, hyper chromic effect is not observed with an increase in solvent polarity because of the presence of α -halogen atom (-Cl) which has high negative inductive effect (-I) and influence the sp^2 electrons of the N-atom of the ring. As a result, it makes the lone pair electrons of N-atom of the ring available for H-bonding. The negative inductive effect of chloro group becomes much greater as the solvent polarity increases by the dipole-dipole interaction between the solute and solvent particle. As the solvent polarity decreased, the negative inductive effect of -Cl group also decreased, as a result, the lone pair electrons of N-atom of the ring are readily available for intermolecular hydrogen bonding and results an increase in absorption intensity of the B-band in less polar solvent than in more polar solvent¹⁰⁸.

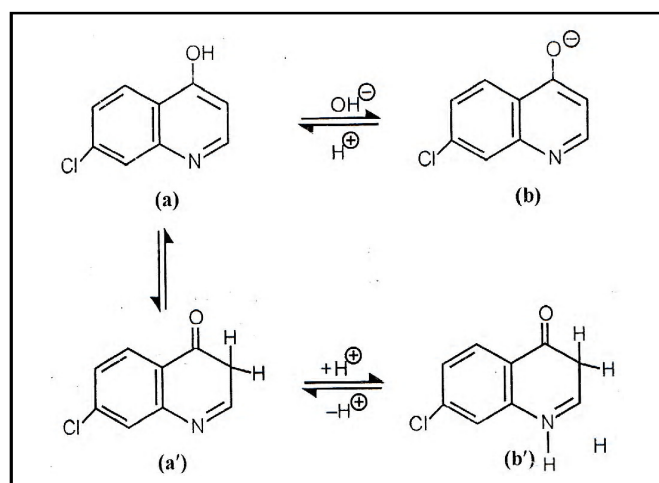
The R-band shows a blue shift on increasing the polarity of the solvent²⁹. When the nonbonding electrons of oxygen atom of the hydroxyl group (as discuss above that the lone pair electrons of O-atom of the hydroxyl group are largely responsible for $n-\pi^*$ transition) coordinate with a hydroxyl solvent^{29, 109}, the net energy of pair electrons is lowered. Thus the distance to π^* (antibonding π orbital)-level will be higher and as a result in polar solvent the $n-\pi^*$ transition (R-band) will be higher energy *i.e.* of lower wavelength (blue shift), (Fig. 8). In this work the blue shift has been observed by $n-\pi^*$ transition (R-band) as the polarity of the solvent increased *i.e.* ethanol > methanol > water^{21, 110}. The amount of blue shift has been used as a measure of the strength of the hydrogen bonding.

The K-band (so called E_2 -band) *i.e.* the $\pi-\pi^*$ transition, on the other hand has shifted to the longer

wavelength *i.e.* red shifted (lower energy) in a more polar solvent^{29,30}. The polar excited state of the $\pi-\pi^*$ transition is stabilized by hydrogen bonding in more polar solvent. This lowers the distance between δ and δ^* levels with a subsequent lowering in the energy or raising the wavelength of the transition^{29, 110} (Fig. 8), we have observed the red shift by the $\pi-\pi^*$ transition (E_2 -band) as the polarity of the solvent has increased from ethanol to water²¹, (Table 5).

Effect of pH variation on electronic transitions:

Hug *et al.*¹⁰⁰ have reported a distinct blue shift $\pi-\pi^*$ and $n-\pi^*$ transitions of uracil with increase of pH. Vir Singh *et al.*¹⁰¹ also observed a marked Fig. 10.



Hypsochromic shift with the increase of pH in $\pi-\pi^*$ and $\pi-\pi^*$ transitions of 5 carboxy -2- thio uracil in all the solvents. Albert *et al.*¹⁰² and Borodavkin *et al.*¹⁰³ have also reported the hypsochromic shift with the increase of pH in the absorption spectra of 2- mercapto pyrimidine an cytosine, respectively. In the $\pi-\pi^*$ transition bands as the pH of the solvent increases. the natural cationic and anionic forms of 7,4-CHQ molecule is shown in Fig. 10.

Thermodynamic parameters:

On the basis of the molecular data obtained from the spectra, as was first suggested by Urey¹⁰⁹, Tolman¹¹⁰ and Badger¹¹¹, it is possible to predict with great precision the values of thermodynamic properties, such as, the heat capacity, free energy, enthalpy and entropy of the particular gases. The possibilities of great practical importance, particularly since the direct experimental measurement of these quantities is usually difficult and tedious and sometimes impossible also^{112, 114}. The values calculated from the spectroscopic data are more accurate than those determined by direct thermal measurement.

Thermodynamic functions *viz.*, enthalpy function

Bond angles ($^{\circ}$)			
$\angle N_1C_2C_3$	123	$\angle C_6C_7C_8$	121
$\angle C_2C_3C_4$	114	$\angle C_7C_8C_{10}$	120
$\angle C_3C_4C_9$	124	$\angle C_3C_4O_1$	120
$\angle C_4C_9C_{10}$	116	$\angle O_1C_4C_9$	116
$\angle C_9C_{10}N_1$	124	$\angle C_6C_7Cl_1$	120
$\angle C_{10}N_1C_2$	122	$\angle Cl_1C_7C_8$	119
$\angle C_4C_9C_5$	120	$\angle C_8C_{10}N_1$	120
$\angle C_9C_5C_6$	120	$\angle C_5C_9C_4$	120
$\angle C_5C_6C_7$	121	$\angle C_5C_9C_{10}$	124

Bond length (\AA)			
N_1C_2	1.35	C_8C_{10}	1.46
C_2C_3	1.44	C_9C_{10}	1.40
C_3C_4	1.41	$C_{10}N_1$	1.32
C_5C_9	1.41	Cl_1C_7	1.71
C_5C_6	1.43	C_4O_1	1.40
C_6C_7	1.40	C_4C_9	1.31
C_7C_8	1.43		

$\{(H^0 - E^0)/T\}$, heat capacity function (C_B), free energy function $\{(F^0 - E^0)/T\}$ and entropy function (S^0) of 7, 4-CHQ have been computed using the standard expressions^{85, 108-111} taking Z-axis perpendicular to the molecule plane and y-axis to pass through the para position. For determining rotational contribution the following structural parameters were used¹²⁷⁻¹³⁰.

I_{xx}	5.38×10^{-41}	I_{xy}	8.47×10^{-42}
I_{yy}	6.57×10^{-41}	I_{xz}	3.51×10^{-41}
I_{zz}	4.33×10^{-41}	I_{yz}	2.22×10^{-41}

The thermodynamic functions have been calculated at different temperature between 200-1500 K using fundamental frequencies in 7,4-CHQ. Assuming Cl and OH as a single mass atom and also assuming the rigid rotor harmonic oscillator approximation, the calculations were performed for 1 mol ideal gas at 1 atmospheric pressure. The symmetric number for overall rotation is 1. The principal moments of inertia were found to be (gm cm^2) in 7, 4-CHQ.

The variation of thermodynamic function viz. enthalpy $\{(H_0 - E_0)/T\}$ and heat capacity function (C_p^0) with absolute temperature have been shown in Table 8. This table shown that at very high temperature the influence of anharmonicity will make itself felt and will no longer give an accurate representation. The variation of free energy $\{FH_0 - E_0\}/T$ and entropy function (S^0) is shown

in Table 8. Which shows that in case of free energy function at temperature as high as 1000K, the effect is quite small. While in case of entropy, at very high temperature the vibrational contribution is very small, compared to other contributions thus, a statistical calculation of the entropy is much less dependent upon vibrational data than the other thermodynamic function. The trend of variation of thermodynamic parameters is similar to those reported for similar molecules in literature^{11,21,22,37,93,107, 115-120}.

Experimental:

The antifungal of 7-chloro-4-hydroxy quinoline, (7, 4-CHQ) have been evaluated at different concentrations against *Aspergillus's flavus*, *Aspergillus's Niger*,

Compound	Quantity (g)
Sodium nitrate	2.00
Potassium dihydrogen phosphate	1.00
Magnesium sulphate	0.50
Potassium chloride	0.50
Ferrous sulphate	0.01
Sucrose	30.0
Agar-Agar	15

Aspergillus fumigates and *Rizopus* (abbreviated as Af, An, As and Rz, respectively) by growth Method¹²⁰ which consist of following steps:

Preparation of Czapek's Dox Agar Medium:

Czapek's Dox Agar Medium¹²¹ was prepared by dissolving the following compounds in the quantity mentioned against each in one liter double distilled water in a beaker

The beaker was autoclaved at 10-15 lbs pressure for about half an hour. The hot medium was filtered. The test solutions of 7,4-CHQ < %< and <*_CHQ, 4,2-HMQ, 6,8-MNQ and 5,6-ANQ were prepared by dissolving the appropriate amount in double distilled water.

Measurement of fungal growth:

Czapek's Agar medium was divided into ten equal parts of 100 ml each and poured into 500 ml conical flasks. Now the solution of different concentrations of the compound was added into nine flasks, while one flask serves the control set containing zero concentration of the test compound.

All the ten flasks were tightly closed with sterilised cotton and autoclaved at 15 lbs pressure for about 15 minutes. Their contents were then poured into 50 x 17 mm sterilised petridishes (Borosil) keeping three

replicates of each treatment. Thus, three petridishes were required for the contents of one flask. so, in all, 30 petridishes were needed at a time for one fungus for one compound. when the contents of the dishes solidify, they were inoculated with the respective fungus for about 168 hours at $27 \pm 1^\circ\text{C}$.

The growth of test fungi have been measured in terms of colony diameter from each petridish. The diameters of 20 colonies have been measured. The values from the three replicates give the average colony diameter at the given concentration. The percentage inhibition has been then calculated as follows :

$$\% \text{ inhibition} = [(C - T)/C] \times 100$$

where, C and T are the average diameter (in ml) of fungus colony in check set and treated set, respectively.

Most fungi are completely resistant to that action of antimicrobial drugs. Only a few substances have been discovered which exert an inhibitory effect on the fungi pathogenic for man and most of these are relatively toxic. Consequently, spurred by the need of new antifungal agents and the fact that many effective antimicrobial drugs possess heterocyclic systems in their structure. is observed .

Antifungal activity:

Antifungal data of the compounds 7, 4-CHQ, has been observed against *Aspergillus flavus*, *Aspergillus Niger*, *Aspergillus fumigates* and *Rizopus* (abbreviated as Af, An, As and Rz, respectively) at varying concentration. (0.005% to 0.50%).

The observations show, that in case of 7, 4-CHQ, the antifungal growth were effected with the addition of the compounds. The percentage inhibition is directly proportional to the concentration of the compound up to an optimum value (MIC) *i.e.* the compound has minimum toxic effect at low concentration while maximum at high concentration. But, in case of 6,8-MNQ and 5,6-ANQ molecules. The observation also that definite amount of the concentrations are different fungi.

It is found from the experimental results of the test compound 7,4-CHQ, that their exists a correlation between $\lambda_{\text{max}} (n-\pi^*)$ and antifungal activity *i.e.* the activity varies directly with the said parameter.

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