

A brief analysis of Thermodynamic Parameters of 4,8 Dihydroxy quinoline 2-Carboxylic acid

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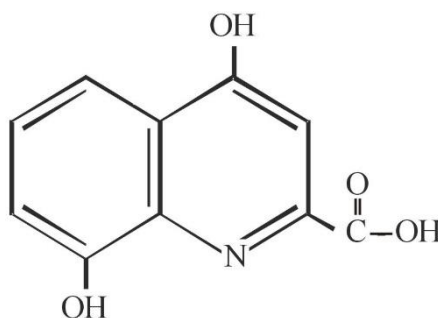
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ABSTRACT

In this paper, embodies the investigation on infrared absorption spectra ($4000-400\text{ cm}^{-1}$) and Raman effect ($4000-50\text{ cm}^{-1}$) of 4,8 Dihydroxy quinoline-2-carboxylic acid molecule. Spec-pure grade sample of 4,8 Dihydroxy quinoline-2-carboxylic acid (abbreviated as 2,4,8 DHQCA) 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 ($98-100^\circ\text{C}$). The laser Raman spectra of 2,4,8 DHQCA molecule was recorded on a spex spectrophotometer, using laser source with exciting radiation at 488 nm in the region $4000-50\text{ cm}^{-1}$. Its infrared spectra were recorded on Perkin Elmer M-500 FTIR spectrophotometer in the region $4000-400\text{ cm}^{-1}$ using Nujolmull techniques. While the $\pi-\pi^*$ and $n-\pi^*$ transition bands for 2,4,8 DHQCA molecule has been measured on UV-VIS double beam Perkin Elmer spectrophotometer M-Lambda-20 in the region 400-200 nm in liquid state, using various polar solvents (i.e. ethanol, methanol and water).



Molecular structure of 2,4,8 DHQCA

The molecule 2,4,8 DHQCA and the observed fundamentals have been assigned to different normal modes of vibration. The 2,4,8 DHQCA molecule is a trisubstituted quinoline therefore have total four hydrogen atoms left around the aromatic rings, therefore four C-H valence oscillations are expected. The aromatic C-H stretching vibrations usually give rise to multiple absorption bands. The thermodynamic functions have been calculated at different temperature between 200-1500K using 27 fundamentals frequencies in 2,4,8 DQCA.

INTRODUCTION

The N-heterocyclic aromatic compounds, e.g. quinoline etc, isoquinoline etc. and their derivatives are of great biological, spectroscopic and pharmaceutical importance. Recent spectroscopic studies of quinoline molecule have been motivated because of vibrational spectra of free base molecule is very useful for understanding of biological process and in the analysis of relatively complex system. Many attempts have been made to study the behaviour of N-heterocyclics. Thus many substituted quinoline were found to attach considerable biological relevance. In a number of synthetic material with important psychological properties such as antimalarial plasmoquin in the cyanine dyes. Quinoline and its derivatives is used as an analytical

reagent. Oxime and papeverine in opium and used as a muscle relaxant.

EXPERIMENTAL PROCEDURE

Spec-pure grade sample of 4,8 Dihydroxy quinoline-2-carboxylic acid (abbreviated as 2,4,8 DHQCA) 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 (98-100°C). The laser Raman spectra of 2,4,8 DHQCA molecule was recorded on a spex 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 2,4,8 DHQCA molecule has been measured on UV-VIS double beam Perkin Elmer spectrophotometer M-Lambda-20 in the region 400-200 nm in liquid state, using various polar solvents (i.e. ethanol, methanol and water). The solvents used for preparation of the solution of the said compound were of spectroscopic grade.

RESULTS AND DISCUSSION

The molecular structure of 2,4,8 DHQCA molecule is shown in Fig. 1.1, Furthermore, the observed vibrational frequencies of 2,4,8 DHQCA molecule along with their relative intensities and probable assignments are presented in Table 1.1.

The correlation of hydroxyl group frequencies with those of similar molecules are given in Table 1.1.

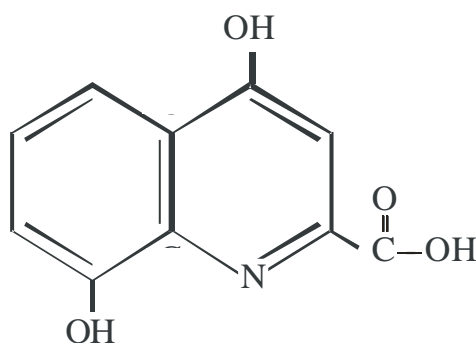


Fig. 1.1 Molecular structure of 2,4,8 DHQCA

Moreover, the ultraviolet absorption spectra of the said molecule using various solvents (i.e. ethanol, methanol, water). The effect of substitution (i.e. inductive and mesmeric effects) responsible for shift $\pi-\pi^*$ and $n-\pi^*$ transitions of ultraviolet absorption spectra. The electronic transitions and corresponding bands of the said molecule (using various solvents) are given in Table 1.5.

The statistically computed thermodynamic functions viz. enthalpy function $\{(H^\circ - E_o^\circ / T)\}$, heat capacity (C_p°), free energy function $\{(F^\circ - E_o^\circ / T)\}$ and entropy (S°) function with absolute temperature are given in Table 1.6 for 2,4,8 DHQCA molecule.

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 presumes relevance to spontaneous and induced mutagenesis, such tautomerism is of major significance in the structure of alkaloids nucleic acid and is of current additional importance in relation to the antimetabolic activity of alkaloids, nucleic acid and of some N-Heterocyclic aromatic ring analogous.

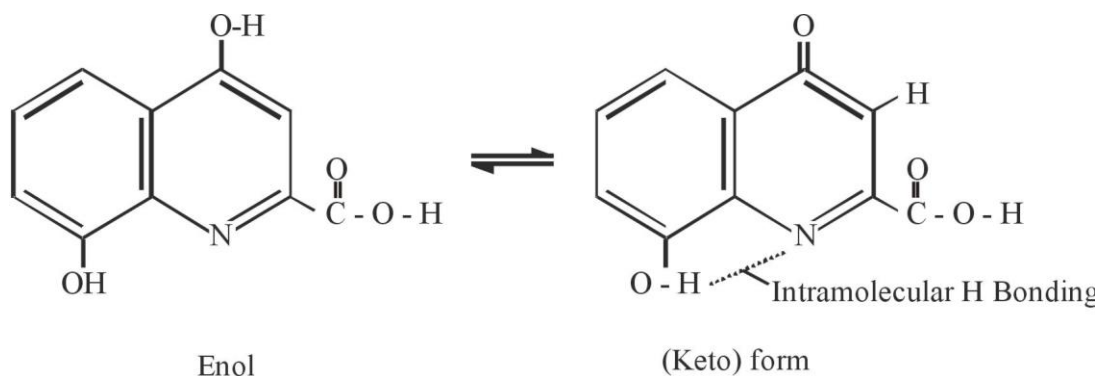


Fig. 1.2 Intramolecular H-bonding as well as keto Enol Tautomerism.

Although both infrared and ultraviolet spectroscopy may be employed for studies on tautomeric equilibrium yet as shown by Nowak et al. [2014], the former is by far the more accurate and unequivocal in interpretation. In this present investigation of 2,4,8 DHQCA, the molecule is supposed to show tautomeric behaviour.

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 and tautomerism. Hydrogen bonding can occur in any system containing proton donor group and a proton acceptor group. The organic molecules, the common proton donor groups are carboxyl, hydroxyl, amine or amide groups and common proton acceptor atoms are oxygen, nitrogen and halogens.

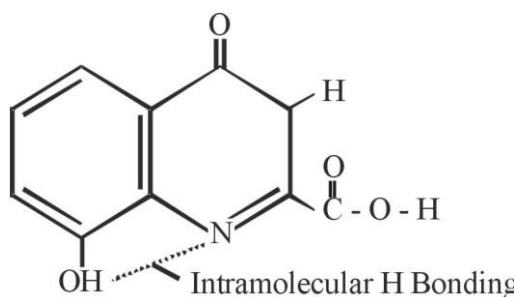


Fig. 1.3 Intramolecular hydrogen bonding of 4,8 Dihydroxy quinoline 2 carboxylic acid.

The 2,4,8 DHQCA has one proton donor group (i.e. hydroxyl group) and one proton acceptor atom (i.e. N-atom of the quinoline ring). According to Hoyer [2005], the stretching frequency of the O-H group of benzyl alcohol is 3640 cm^{-1} . 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 acid. 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 group.

According to Silverstein [2005], the bending vibration of hydrogen bonded groups usually shifts to a shorter wavelength (longer frequency) this shift is less pronounced than that of stretching frequency. Evans [2006] 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 333 cm^{-1} has been assigned to out-of-plane bending mode of free -OH group.

ELECTRONIC SPECTRA

The electronic assignment are discussed in details as :

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

The spectra of hetroaromatic 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 221 nm (ϵ , the molar absorptivity or extinction coefficient = 133,000), at 286 nm ($\epsilon = 9,300$) and at 312 nm ($\epsilon = 289$), due to $\pi - \pi^*$ transition. The intense bands at 220 nm results from an allowed transition, where as the weaker bands at 210 and 280 nm results from forbidden transition in the highly symmetrical naphthalene molecule. 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 notations. B-band is generally found in between 230-270 nm.

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. In the present study, the band observed at 230, 230 and 240 nm in ethanol, methanol and water solvents are originated from $\pi - \pi_I^*$ transition and designated as B-band.

While the very weak shoulder band observed at 236nm in ethanol, is originated from $\pi - \pi_{II}^*$ transition and designated as B-band. The very intense bands observed at 220 nm in water is also originated from $\pi - \pi^*$ transition and designated as E₂ bands (K-bands).

THERMODYNAMIC PARAMETERS

On the basis of the molecular data obtained from the spectra, as was first suggested by Urey [2006], Tolman [2015] and Badger [2014], 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 gasses. The possibility is of great practical importance, particularly since the direct experimental measurement of these quantities is usually difficult and tedious and sometimes impossible also. The values calculated from the spectroscopic data are more accurate than those determined by direct thermal measurement. The variation of thermodynamic function viz. enthalpy $\{(H_o - E_o^o)/T\}$ and heat capacity function (C_p^o) with absolute temperature have been very high temperature the influence of anharmonicity will make itself felt and will no longer give an accurate representation. The variation of free energy $\{(F_o - E_o^o)/T\}$ and entropy function (S^o) is shows that in of free energy function at temperature as high as 1000 K, the effect is quite small. While in case of entropy, at very high temperature of 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 functions. The trend of variation of thermodynamic parameters is similar to those reported for similar molecules in literature.

Table-1.1 : Assignment of vibrational frequencies of 2,4,8 DQCA (All values are in cm⁻¹)

Raman		IR		Assignment
Frequency	Intensity	Frequency	Intensity	
90	w	—	—	Lattice vibration
123	w	—	—	OH Torsion
156	w	—	—	OH Torsion
208	m	—	—	$\gamma(-OH)$
221	w	—	—	$\gamma(C-OH), \gamma(O-H)$
300	w	—	—	$\gamma(C-N)$

320	w	–	–	$\beta(\text{C-COOH})$
333	m	–	–	$\gamma(\text{C-OH})$
369	vw	–	–	$\beta(\text{C-OH})$
395	w	–	–	$\gamma(\text{C=O})$
–	–	466	–	$\gamma(\text{O-H})$
418	vw	–	–	$\gamma(\text{C-C-C})$
451	vw	–	–	$\gamma(\text{C=O})$
474	vw	–	–	$\beta(\text{C=O})$
–	–	481	s	$\gamma(\text{C=O})$
526	m	–	–	$\gamma(\text{C-H})$
540	m	–	–	$\beta(\text{C=O})$
–	–	565	s	$\beta(\text{C=O})$
572	m	–	–	$\gamma(\text{C-H})$
–	–	647	w	$\beta(\text{C=O}), \beta(\text{C-OH})$
608	w	–	–	$\gamma(\text{C-OH})$
641	w	–	–	$\gamma(\text{C-C-C})$
–	–	697	s	$\beta(\text{C-OH})$
733	m	730	s	$\beta(\text{O-H}), \beta(\text{C-C-C})$
–	–	779	vs	$\beta(\text{C-H}), (\text{C-N-C})$ bending vibrations
890	m	862	s	(C-C-C) trigonal bending and ring breathing mode
831	m	829	s	$\gamma(\text{C-H})$
930	m	–	–	$\gamma(\text{C-H})$
956	m	–	–	asym. $\gamma(\text{C-H})$ wagging, ring breathing mode
976	m	–	–	$\gamma(\text{C-H})$
996	m	928	s	$\nu(\text{C-C-O})$ Sym. $\nu(\text{C-C-O})$ Sym

–	–	1027	s	ν (C–H)
1081	m	1093	s	β (C–H)
–	–	1126	s	β (C–H)
–	–	1159	s	β (C–H)
1117(m)	vw	1192	m	β (C–H)
1219	s	1258	m	ν (C–OH), (C–COOH) ν
1264	m	–	–	β (C–OH) & (C–O)
1304	m	–	–	ν ring
–	–	1306	m	ν (C–OH)
–	–	1320	m	β (C–N)
–	–	1390	vs	ν (C–OH)
–	–	1423	m	ν (C–C)
1428	m	1472	m	ν ring
1520	m	1522	m	ν (C–N)
1599	m	1581	m	ν ring
1625	m	–	–	ν ring, ν (C=O)
–	–	1637	m	ν (C–N)
1651	m	o	–	ν (C=O)
1765-1999	w & vw	1767-1966	w & vw	overtones of aryl ring
2360	w	–	–	ν (O–H)
2380	w	–	–	ν (C–OH) overtones and
–	–	2614	m	ν (C–OH) sym
–	–	2663	m	ν (C–OH) asym
–	–	2713	m	ν (C–OH) asym
3049	m	3119	m	ν (C–H)

3095	m	3010	s	ν (C–H)
3116	s	–	–	ν (C–H)
3221	m	–	–	ν (C–H)
3276	m	–	–	ν (C–H)
3365	m	–	–	ν (O–H)
3385	w	3604	m	ν (O–H)
–	–	3653	w	ν asym (N–H)

ν : Stretching, β : In-plane bending
 γ : Out-of-plane bending, sym : Symmetric,
 w : Weak, s : Strong
 vw : Very weak, vs : Very strong
 m : medium

Table–1.2 : Correlation of vibrational frequencies of C-OH and hydroxyl group (All values are in cm^{-1})

Group vibrations	8-HQ	5,7,8-DCQ	2,4,6-DMHP	2,4,3-HMNP			7,4-CHQ		2,4,8- DQCA	
				Raman	IR		Raman	I.R.	Raman	I.R.
					KBr	Nujolmull				
ν (O–H)	–	–	3420	3563	–	3559	–	3649	3385	3604
β (O–H)	–	1330	1280	1320	1309	1309	1329	–	1264	–
γ (O–H)	–	–	–	–	–	–	–	298	–	208
ν (C–OH)	–	–	1240	1262	1244	1254	1256	1266	1219	1258
β (C–OH)	612	–	–	610	622	618	–	616	–	647
γ (C–OH)	–	–	–	321	–	–	–	331	333	–
ν (C=O)	1660	1652	1640	–	1664	1667	1671	1666	1651	–
β (C=O)	–	–	–	–	–	545	539	544	451	–

where

8-HQ : 8-hydroxy quinoline
 5,7,8-DCQ : 5,7-di chloro-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 : 7-chloro-4-hydroxy quinoline
2,4,8-DQCA : Title compound
 ν : Stretching
 β : In-plane-bending
 γ : Out-of-plane bending

Table-1.3 : Electronic absorption bands of Benzene molecule .

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

Table-1.4 : Electronic absorption bands of Napthalene molecule

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

Table-1.5 : Effect of solvent polarity on electronic absorption transitions/bands of 2,4,8-DQCA (All values are in nm)

Solvent	DC	RI	2,4,8-DQCA			
			$\pi - \pi_I^*$	$\pi - \pi_{II}^*$	$n - \pi^*$	$n - \sigma^*$
Water	80.5	1.3380	240	–	338	220
Methanol	31.0	1.3362	230	–	336	–
Ethanol	25.0	1.3773	230	236	–	–

DC – Dielectric Constant

RI – Refractive Constant

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