

ANALYSIS OF ULTRA VIOLET ABSORPTION SPECTRA OF 3-CARBOMETHOXY 1,2,3,4-TETRAHYDROISO QUINOLINE 1,4-DIONE

Dr. Neetu Raheja

Principal

Galaxy Preparatory School

Navdeep Colony Hisar, Haryana

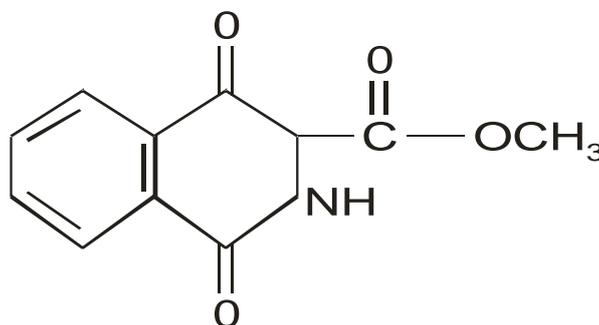
ABSTRACT

The ultra violet spectra of 1,2,3,4 tetra hydroiso quinoline 1,4-dione in different polar solvent have been recorded in the region 400-200nm. Solvent effect on electronic transitions is studied and explained.

Key Words: - Ultra Violet absorption spectra.

INTRODUCTION

The ultraviolet absorption spectra of uracil, quinolines and, cytosine nucleosides have been well predicted theoretically and experimentally [1,2]. Although very little spectroscopic studies are reported for them in literature. Experimentally [1,2] although very little spectroscopic studies are reported for them in literature. Experimentally some workers [2,3] have found evidence of the presence of electronic transitions other than $n-\pi^*$ and $\pi-\pi^*$ in the spectra of quinoline uracil, cytosine and their nucleosides. Steward and Jenson [4] were unable to detect the presence of any $n-\pi^*$ transition in the near-ultraviolet spectral region of quinoline derivations. Thus the detailed study of the electronic transition of substituted quinoline is of great importance in order to check the presence of $n-\pi^*$, $\pi-\pi^*$ and $n-\sigma^*$ transitions. On substitution, the $\pi-\pi^*$ and $n-\pi^*$ systems of quinoline normally produce bathochromic and hysochromic shifts, respectively, the vibrational frequencies also get modified. In view of above discussion the present paper reports the ultraviolet spectra of 3-Carbomethoxy 1,2,3,4 tetrahydroiso quinoline 1,4 dione in different polar solvents.



Molecular Structure

Fig.-1

EXPERIMENTAL

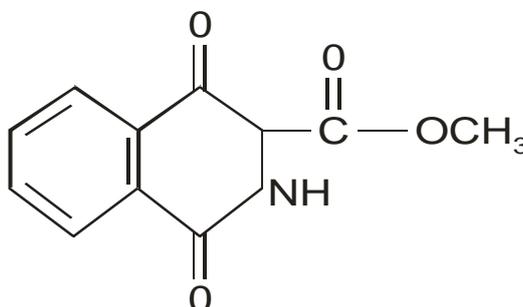
The Spec-Pure compound 3-Carbomethoxy 1,2,3,4 tetrahydroiso quinoline 1,4-dione (here after referred as 3C,1,2,3,4 THQ 1,4D) was obtained from M/s. Sigma Aldrich Chemicals, U.S.A and used as such. The purity of the compound was further confirmed by boiling (185°C) determination and elemental analysis.

We have measured the $\pi-\pi^*$ and $n-\pi^*$ transitions of 3C,1,2,3,4 THQ 1,4D in UV-VIS double beam spectrophotometer. Model Labda 20 (Mfg. by Perkin Elmer) in the region of 400-200nm in the liquid

state using various polar solvents i.e ethanol, methanol and water). The solvent used for preparing the solutions of the said compound were of spectroscopic grade.

RESULT AND DISCUSSION

The molecular structure of 3C, 1,2,3,4 THQ is shown in figure 1 and its near ultraviolet absorption spectra (region 400-200nm.) in various solvents (a) ethanol (b) methanol (c) water are presented in figure 2 and the electronic transitions and corresponding band of the said molecular in electronic absorption spectra are shown in Table 2 in various solvents.



Molecular Structure of 3C 1,2,3,4, THQ 1,4D

Fig.-2

BANDS DUE TO $\pi - \pi^*$ TRANSITION

The spectra of N-heterocyclic compounds are on the whole similar to their corresponding hydro carbans [5,6]. The spectrum of quinoline is comparable with that of benzene. Benzene it self displays three electronic absorption bands [5,6] at 184 nm (E , the molar absorptivity) or the extinction coefficient = 60,000), at 203.5 nm. ($E = 7900$) and at 256nm ($E = 200$) due to $\pi - \pi^*$ transitions. The intense band at 180nm results from an allowed transition [6], whereas the weaker bands at 200 and 260nm result from forbidden transition in the highly symmetrical benzene molecule. Different notation have been used to designate the absorption bands of benzene; these are summarized in Table 1. We shall discuss these using braude's E and B notation [6] B- band is generally found in between 230-270nm.

Table 1. Electronic absorption bands of benzene molecule [6].

184nm	204nm	256nm	References
E_1 -band	E_2 -band	B-band	[7]
-	K-band	B-band	[8]

Table 2-Solvent effect in electronic transitions of 3C, 1,2,3,4,THQ 1,4D (All values are in nm).

Solvent	DC	RI	3C 1,2,3,4, THQ 1,4D	
			$\pi - \pi^*$	n- π^*
Ethanol	25.0	1.3773	210	335
Methanol	32.0	1.3362	210	340
Water	80.5	1.3380	210	330

DC-Dielectric Constant

RI-Refractive Index

Between benzene, quinoline and pyridine, the B-band of pyridine is more intense with somewhat diminished fine structure whereas in benzene, the B-band at 256nm displays fine structure i.e the band contains multiple peaks. This transition is allowed for pyridine but forbidden for some more symmetrical benzene and quinoline [5,6]. The band observed at 201nm in ethanol, and the weak shoulder band at

202nm and at 210nm in methanol and water respectively are also originated from $\pi - \pi^*$ transition and designated as E₂-bands (K-bands).

BAND DUE TO N- π^* TRANSITIONS

The weak R-band expected for an n- π^* transition for quinoline molecule, the absorption band moves to shorter wavelength by increasing the polarity of the solvent. In n- π^* transition, the ground state is more polar as compared to the excited state. The hydrogen bonding with solvent molecules takes place to lesser extent with the carboxyl group in the excited state.

The R-bands found in this study, have originated from n- π^* transition due to the attachment of groups containing lone pair electrons i.e. -OCH₃ groups occurred at 335nm, 340nm and 330nm in ethanol, methanol and water respectively.

ELECTRONIC SPECTRA

In case of N-Heterocyclic compounds the band observed at 238nm corresponds to the A₁B₁ transition and it is derived from the A_{1g} → B_{1u} transition [1] on lowering the symmetry of D_{6h} or C_{2v}. According to Clark and Tinoco [3] bands at 210 and 200nm corresponding to A_{1g} → B_{1u} and A_{1g} → A_{1u} transitions respectively.

In quinoline bases the ultraviolet bands observed around 2400 Å⁰ which corresponds to A₁ → B₁ transitions are derived from A_{1g} → B_{2u} transitions of Benzene or lowering the symmetry of D_{6h} or C_{2v}. Singh et al [7] have assigned this band at 2200 Å⁰ in the ultraviolet spectra of 5-Carbomethoxy-2-thiouracil. Some workers [10] have suggested in pyrimidine n- π^* transition corresponds to out of plane transition while $\pi - \pi^*$ and n- σ^* transition to inplane transitions. They originate from A_{1g} → B_{2u} and A_{1g} → A_{1u} transition of benzene [11]. In accordance with these assignments n- π^* transitions around 335, 340, 330nm have been taken to represent out of plane transition while $\pi - \pi^*$ around (210,210,210nm) are Co-related to in plane transition in the present investigation.

EFFECT OF SOLVENTS ON ELECTRONIC TRANSITION

An increase in the solvent polarity does not effect either the position or the intensity of the B-band of benzene, but produces a hyperchromic effect (an increase in absorption intensity) for Pyridine and its homologous [5,6]. This effect is assigned to the hydrogen bonding through the lone pair of electrons of the nitrogen atom [5,6]. In 3C 1,2,3,4 THQ 1,4D molecule, hyperchromic effect is not observed with an increase in solvent polarity because of the presence of tautomerism existing between N-atom of the ring and Carboxylic group. So that the Sp² electron of N atom of the ring do not participate in hydrogen bonding with the solvent particles. This tautomeric behaviour is further find evidence by the infrared and Raman spectra of 3C 1,2,3,4 THQ 1,4D molecule, which confirms the presence of N-H stretching vibrational mode. An increase in solvent polarity also causes a slight effect on the position of the B-band.

In the present investigation B-band ($\pi - \pi^*$ transition band) shows a marked red shifts as the polarity of the solvents increases [5,6].

The R-band shows a blue shifts on increasing the polarity of the solvent [5,12]. The n- π^* transition (R-band) will be of higher energy i.e of lower wavelength (blue shift). According to Ram et al [11]. The blue shift with increasing polarity of solvent is the useful means of recognizing n- σ^* transition. In the present investigation the blue shift has been observed by n- π^* transition as the polarity of the Solvent increases

i.e ethanol-methanol water Table-1. The amount of blue shift has been used as a measure of the strength of the H-bonding.

The K-band (so called E₂ band) i.e the $\pi-\pi^*$ transition has shifted to the longer wavelength i.e red shifted (Lower energy) in a more polar solvent [5]. The polar excited state or the $\pi-\pi^*$ transition is stabilized by H-bonding in more polar solvent. Becker et al [12] has suggested the $\pi-\pi^*$ transition undergo red shifts (lower energy) as the polarity of the solvent increases. In view of the above discussion it is obvious (Fig-1) and (Table-1) that there is a marked bathochromic shifts (red) in $\pi-\pi^*$ transition with increasing polarity of the solvents (ethanol-methanol-water) in 3C,1,2,3,4 THQ 1,4D.

This lowers the distance between π and π^* levels with a subsequent lowering in the energy or raising the wavelengths of the transition shown in Figure-3.

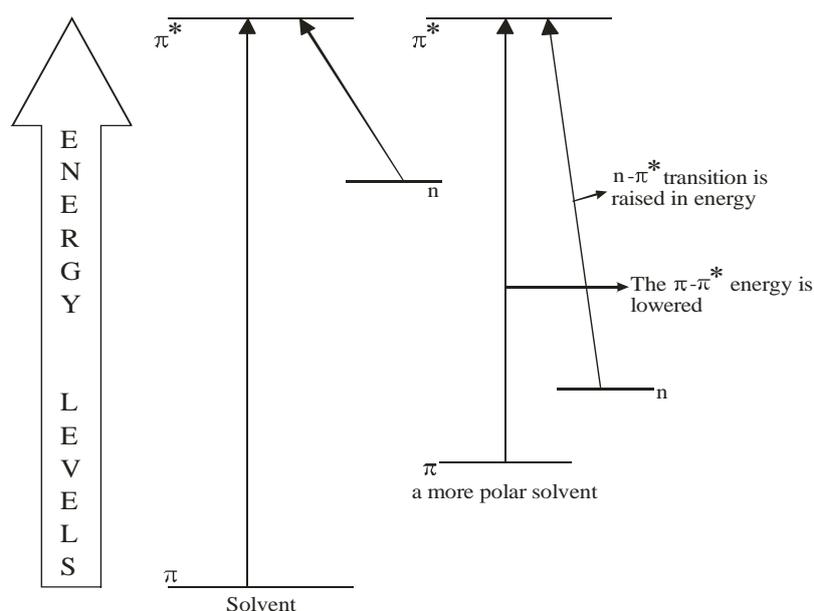


Fig 3. Solvent effects on n- π^* and $\pi-\pi^*$ transitions.

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