

## Electronic Absorption Spectra of 5,7-Dibromo-8-hydroxy Quinoline

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The present paper presents the electronic absorption spectra of 5,7-dibromo-8-hydroxy quinoline. The effect of solvents *viz.*, ethanol, methanol and water has also been studied and discussed on the electronic transitions of the said molecules. The spectra have been recorded in the region 1900-4000 Å. The transitions have been identified as  ${}^1A' \rightarrow {}^1A'$  under the Cs symmetry of the molecules studied, corresponding to  ${}^1B_{su} \rightarrow {}^1A_g$  transition.

**Key Words:** 5,7-Dibromo-8-hydroxy quinoline, Electronic spectra, Solvent effect.

### INTRODUCTION

The electronic absorption spectra of heteroaromatic two ring molecules especially the nitrogen heterocyclics with two fused six membered rings, form an interesting class of molecules are least studied. The electronic absorption spectra of quinoline and iso-quinoline have been reported by many workers<sup>1-3</sup>. Nitrogen heterocyclic compounds such as pyrimidines, pyridines, cytosines, uracils, quinolines and their derivatives are of great biological importance as they play an important role in the structure and properties of nucleic acids<sup>4-6</sup>. However, due to their great complexity and low symmetry, spectroscopic work appeared on these compounds<sup>7-9</sup>. The quinoline which have some substitution like OH, Br, gives more biological important molecules<sup>10,11</sup>. In contribution and as a part of our programme to study the spectroscopic aspects of aromatic molecules and in particular to study the effect of substitution on the parent molecule experimentally. Ayachit *et al.*<sup>12</sup> have found the evidence of presence of some more transitions other than  $n-\pi^*$  and  $\pi-\pi^*$  in the ultraviolet spectra of quinolines and their derivatives.

In the electronic spectra of quinolines three bands have been found between the region 200-400 nm. In addition to the  $n-\pi^*$  transitions. These bands are presumably  $\pi-\pi^*$  or  $n-\sigma^*$  transitions. As the electronic transi-

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tion are derived from that of benzene, therefore, the spectrum of each waves is simply related to the spectrum of the quinolines. The benzene serves as the absorbing chromophore for quinolines<sup>13</sup>.

In view of the above discussion, the present paper reports the electronic spectra of 5,7-dibromo-8-hydroxy quinoline in various polar solvents. The solvent effect on electronic transitions is also studied and explained.

### EXPERIMENTAL

Spec-pure grade samples of 5,7-dibromo-8-hydroxy quinoline (5,7,8-DBHQ) (Fig. 1) were obtained from M/s Aldrich Chemie, West Germany and used as supplied.

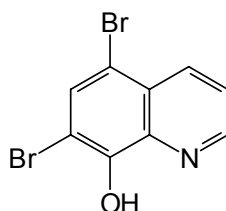


Fig. 1. Molecular structure of 5,7-dibromo-8-hydroxy quinoline

The electronic spectra of these compounds were recorded on Beckman spectrophotometer model M-35. All the solvents used were of spectroscopic grade. The concentration of all the solutions was kept to be constant ( $8 \times 10^{-3}$  g/L). The ultraviolet absorption spectra of the said compounds in vapour phase could not be recorded under the best experimental conditions because of high melting point of 5,7,8-DBHQ.

### RESULTS AND DISCUSSION

The analysis of electronic transitions of 5,7,8-DBHQ is given in Table-1.

TABLE-1  
SOLVENT EFFECT ON ELECTRONIC TRANSITIONS OF 5,7,8-DBHQ

Solvent	R.I.*	D.C.**	n- $\pi^*$	$\pi$ - $\pi^*$	n- $\sigma^*$
Ethanol	1.3773	25.0	330	240	200
Methanol	1.3362	32.0	310	242	206
Water	1.3380	80.5	318	236	200

\*R.I. = Refractive index; \*\*D.C. = Dielectric constant.

In quinoline base, the ultraviolet bands observed around 2400 Å which corresponds to  $A_1 \rightarrow B_1$  transitions are derived from  $A_{1g} \rightarrow B_{2u}$  transitions of benzene or lowering the symmetry of  $D_{6h}$  or  $C_{2v}$ . Singh *et al.*<sup>14</sup> have

assigned this band at 2200 Å in the ultraviolet spectra of 5-carbethoxy-2-thiouracil. Some workers<sup>15</sup> have suggested in pyrimidine bases  $n-\pi^*$  transitions corresponds to out-of-plane transitions while  $\pi-\pi^*$  and  $n-\sigma^*$  transitions to in plane transitions. The  $\pi-\pi^*$  and  $n-\sigma^*$  transitions originate from  $A_{1g} \rightarrow B_{2u}$  and  $A_{1g} \rightarrow A_{1u}$  transitions of benzene<sup>11</sup>. In accordance with these assignment then  $n-\pi^*$  transitions around (330, 310, 318 nm) have been taken to represent out of plane transitions while  $\pi-\pi^*$  and  $n-\sigma^*$  around (240, 242, 236 and 200, 206, 200 nm) respectively are co-related to in plane transitions in the present investigation.

The hypsochromic shift of  $n-\pi^*$  bands is observed on changing the solvents in increasing order of polarity, because the ground state is stabilized by the hydrogen bonding in the solvents and increase in transition energy. This energy is essential to break or weaken the hydrogen bond<sup>15,16</sup>. The hypsochromic shift with increasing order of polarity of the solvents is useful in recognizing the  $n-\pi^*$  transitions. In the present study the hypsochromic shift is observed in increasing order of the polarity of solvents (ethanol  $\rightarrow$  methanol  $\rightarrow$  water) for the molecules (Table-1). From Table-1 it is also clear that hypsochromic shift has been observed in  $n-\pi^*$  transitions of the compound with the increase of refractive index of the solvents which is similar to the trend reported in the literature<sup>11,17</sup>.

For a non polar solute undergoing a  $\pi-\pi^*$  and  $n-\sigma^*$  the shift of the band depends upon the polarity of the solvent which is due to the difference in polarization. Since the shifting is larger in polar solvents in comparison to non polar solvents, therefore the bathochromic shift will be observed. Since most of the molecules has bonding electrons, which are localized around the electronegative atom of a polar group. In excited state the localized non bonding electrons are delocalized around the less electronegative atom over the excited orbitals ( $\sigma^*$  or  $\pi^*$ ) extends which decreases the dipole moment in excited state. If the excited state has high dipole moment than ground state, it may be possible to have  $\pi-\pi^*$  or  $n-\sigma^*$  transitions<sup>18,19</sup>.

In view of the above discussion, it is obvious (Table-1) that there is a marked bathochromic shift in  $\pi-\pi^*$  or  $n-\sigma^*$  transitions with increasing polarity of the solvents (ethanol  $\rightarrow$  methanol  $\rightarrow$  water) in 5,7,8-DBHQ.

#### ACKNOWLEDGEMENT

The authors are grateful to Department of Chemistry, Punjab University, Chandigarh for providing the necessary facility for recording the ultraviolet absorption spectra.

## REFERENCES

1. M.A. Shashidhar, *Indian J. Pure Appl. Phys.*, **11**, 13 (1973).
2. M.A. Shashidhar, *Indian J. Pure Appl. Phys.*, **11**, 37 (1973).
3. M.A. Shashidhar, *Indian J. Pure Appl. Phys.*, **12**, 532 (1974).
4. G.T. Martin, *Biological Antagonism*, Blakiston, New York (1951).
5. B.S. Yadav, M.K. Singh, Seema and V. Singh, *Orient. J. Chem.*, **14**, 397 (1998).
6. B.S. Yadav, M.K. Yadav and V. Kumar, *Acta Botan. Indica*, **26**, 11 (1998).
7. R.K. Goel and C. Gupta, *J. Raman Spectrosc.*, **16**, 1 (1985).
8. B.S. Yadav, M.K. Singh, M. Singh and V. Singh, *Ultra Sci.*, **11**, 46 (1999).
9. H. Suzuki, *Electronic Absorption Spectra of Organic Molecules*, Chapman and Hall Ltd., London (1971).
10. B.S. Yadav, V. Singh and M.K. Yadav, *Indian J. Pure Appl. Phys.*, **35**, 305 (1997).
11. B.S. Yadav, Seema and V. Kumar, *Indian J. Pure Appl. Phys.*, **35**, 587 (1997).
12. H.A. Narasimha, K.S. Rao and M.A. Shashidhar, *Indian J. Phys.*, **58B**, 234 (1984).
13. B.S. Yadav, M.K. Yadav, V. Kumar and V. Singh, *Asian J. Chem.*, **9**, 372 (1997).
14. V. Singh, Seema, S. Chand and B.S. Yadav, *Orient. J. Chem.*, **12**, 295 (1996).
15. W. Hug and I. Tinoco, *J. Am. Soc.*, **95**, 2803 (1973).
16. R.S. Becker, A.B.F. Duncan, F.A. Masten, D.R. Scott and W. West, *Chemical Application of Spectroscopy*, John Wiley & Sons, New York (1968).
17. N. Mataga and T. Kobota, *Molecular Interactions and Electronic Spectra* Deckkar, New York (1970).
18. B.S. Yadav, *Orient. J. Chem.*, **6**, 108 (1990).
19. W. West, *Chemical Applications of Spectroscopy*, Interscience Publishing Inc., New York (1956).

(Received: 18 November 2006;

Accepted: 29 September 2007)

AJC-5916

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