

# UV absorption spectra, NLO properties and HOMO-LUMO analysis of 4-chloro-6,7-dimethoxyquinoline by Density Functional Theory

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**Abstract:** The present work deals with UV absorption spectra of 4-chloro-6,7-dimethoxyquinoline in methanol, ethanol and acetone. The computational UV spectra is obtained by density functional theory (DFT) using B3LYP/6-311G(d,p) basis set and absorption wavelength calculated are compared with experimental values. DFT calculations are used to calculate energy of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). The non-linear optical (NLO) properties like hyperpolarizability are calculated by DFT at B3LYP/6-311G(d,p) basis set.

**Keywords:** UV absorption spectra, DFT, HOMO, LUMO, NLO.

## I. INTRODUCTION

Quinoline and its derivatives has been a subject of study by researchers due to its importance in various applications. The derivatives of quinoline acts as antibacterial [1-3], antimalarial [4-8], antifilarial [9], anti-breast cancer [10] activities. UV spectral studies on quinoline derivatives have been done by various researchers [11-14]. K. Kumru et. al. [11] studied quonoline-7-carboxaldehyde by IR, Raman and UV spectral investigations. N. Prabavathi et. al. [13] used IR, Raman, UV, and NMR spectroscopic techniques to study hydroxyquinoline derivatives and used density functional theory to study non-linear optical properties and natural bond orbital analysis. Etem Kose et. al. [15] performed UV, NMR and vibrational studies on 2-chloro-3-methylquinoline using DFT.

The present work is an extension of earlier works on substituted quinolines. In this work, UV absorption spectra of 4-chloro-6,7-dimethoxyquinoline along with nonlinear optical (NLO) properties and highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are calculated and analysed by density functional theory (DFT).

## II. EXPERIMENTAL DETAILS

The molecule was purchased from Tokyo chemical industry and used as such. The figure of the molecule along with numbering is shown in Figure 1. UV spectra of 4-chloro-6,7-dimethoxyquinoline is recorded in solvents ethanol, methanol and acetone from 200 nm to 400 nm range as shown in Figure 2.

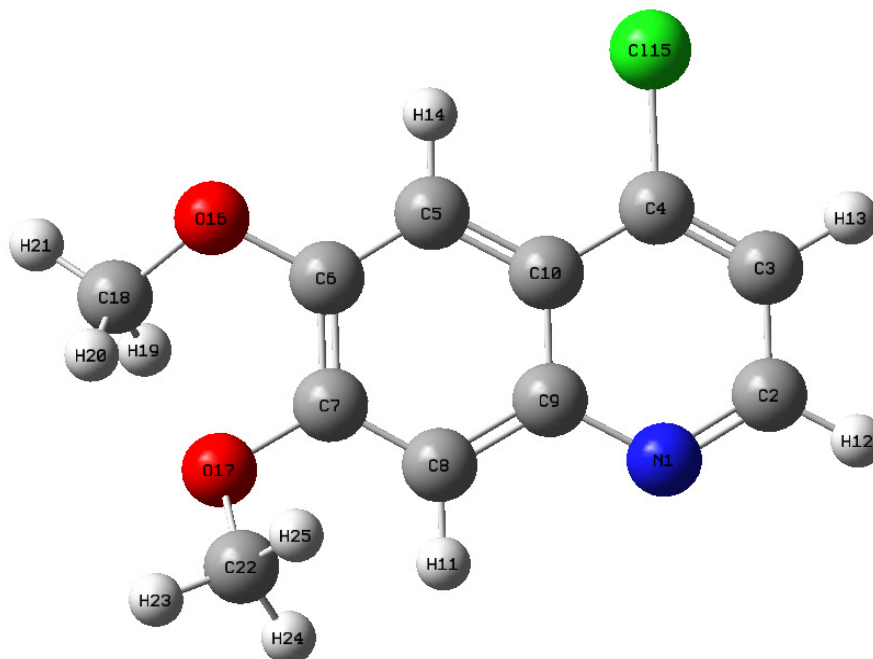


Figure 1. Optimized geometric structure of 4-chloro-6,7-dimethoxyquinoline with numbering of atoms.

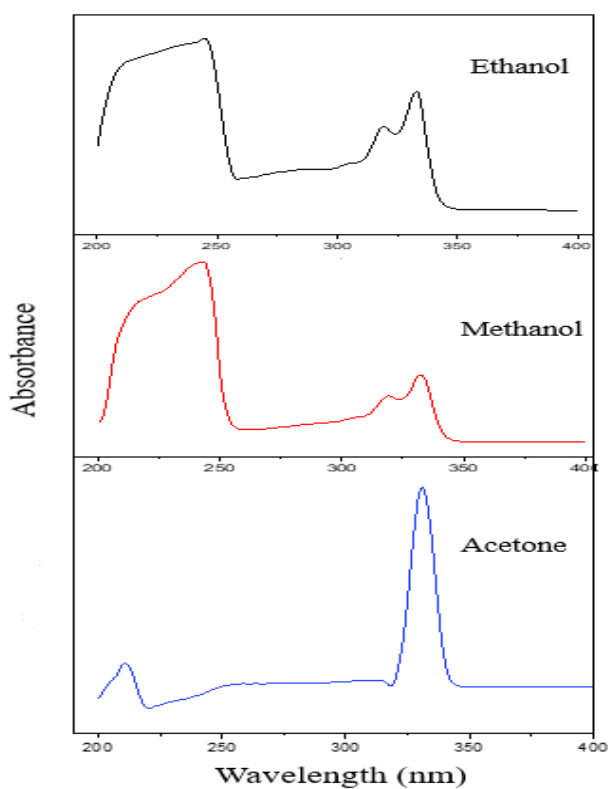


Figure 2. Experimental electronic absorption spectra of 4-chloro-6,7-dimethoxyquinoline in ethanol, methanol and acetone.

### III. COMPUTATIONAL DETAILS

The computational calculations are performed using Gaussian 09 program. The optimised structure of 4-chloro-6,7-dimethoxyquinoline is obtained with time dependent density functional theory (TD-DFT) using

B3LYP/6-311G(d,p) basis set, where B3LYP is Becke's three-parameter hybrid method with the Lee, Yang and Parr correlation functional [16, 17]. The optimised structure is used to obtain electronic absorption spectra of 4-chloro-6,7-dimethoxyquinoline in ethanol, methanol and acetone and then compared with experimental data. The calculations are used to calculate excitation energy, absorption wavelength ( $\lambda_{\max}$ ) and oscillator strength. The HOMO and LUMO energies and nonlinear optical (NLO) properties are also calculated at B3LYP/6-311G(d,p) basis set.

#### IV. RESULTS AND DISCUSSION

##### 4.1 UV absorption spectra

The observed UV absorption spectra of 4-chloro-6,7-dimethoxyquinoline is studied in ethanol, methanol and acetone solvents as shown in figure 2. The observed absorption wavelength along with DFT calculated parameters such as excitation energy, absorption wavelength ( $\lambda_{\max}$ ) and oscillator strength are shown in Table 1. The theoretically calculated  $\lambda_{\max}$  are same in all the solvents. The experimental absorption wavelengths in ethanol are observed at 333, 319 and 244 nm; in methanol are observed at 332, 319 and 243 nm and in acetone are observed at 331 and 211 nm. The transition  $\pi \rightarrow \pi^*$  is observed on smaller wavelength side and the transition  $n \rightarrow \pi^*$  is observed on larger wavelength side.

Table -1 Electronic absorption spectra of 4-chloro-6,7-dimethoxyquinoline [Absorption wavelength ( $\lambda_{\max}$  nm), Excitation Energy (eV) and Oscillator Strength (f)] using B3LYP/6-311G(d,p) basis set.

Solvents	$\lambda_{\max}$ (Experimental)	$\lambda_{\max}$ (Theoretical)	E	f	Assignments
Ethanol	333	324	3.82	0.1643	$n \rightarrow \pi^*$
	319	304	4.07	0.0082	$n \rightarrow \pi^*$
	244	302	4.09	0.0503	$\pi \rightarrow \pi^*$
Methanol	332	324	3.82	0.1610	$n \rightarrow \pi^*$
	319	304	4.08	0.0080	$n \rightarrow \pi^*$
	243	302	4.05	0.0481	$\pi \rightarrow \pi^*$
Acetone	331	324	3.82	0.1643	$n \rightarrow \pi^*$
	-	304	4.07	0.0072	$n \rightarrow \pi^*$
	211	302	4.10	0.0513	$\pi \rightarrow \pi^*$

##### 4.2 HOMO-LUMO energy

HOMO is highest occupied molecular orbital and thus HOMO energy characterises the ability of giving electron. LUMO is least unoccupied molecular orbital and thus it characterises the ability to take electrons from fully filled orbitals. The ease with which this transition takes place depends on band gap between HOMO and LUMO and tells the properties of the substance such as kinetic stability, chemical reactivity, chemical hardness-softness and optical polarizability which. The molecule is soft if energy gap is less and such a molecule is more polarizable. The molecule is hard if energy gap is large [14]. The HOMO energy ( $E_{\text{HOMO}}$ ) is -0.24 eV and LUMO energy ( $E_{\text{LUMO}}$ ) is -0.08 eV in all the three solvents. The band gap between HOMO and LUMO is 0.16 eV. The contours of the occupied and unoccupied molecular orbitals using B3LYP/6-311G(d,p) basis set is shown in Figure 3.

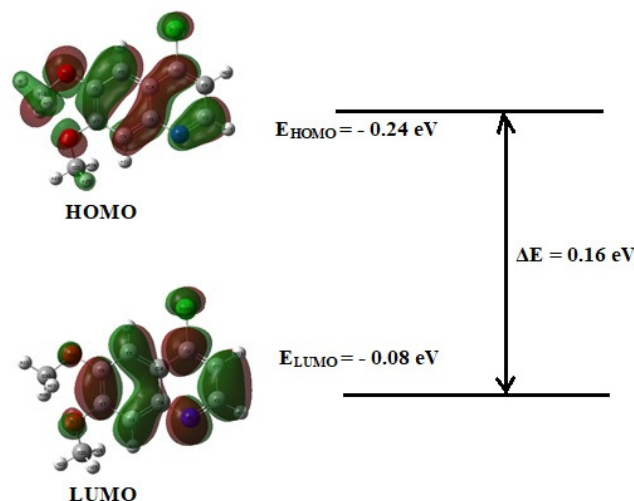


Figure 3. Computed HOMO-LUMO contours of 4-chloro-6,7-dimethoxyquinoline with energy gap at B3LYP/6-311G(d,p) basis set.

The computed Ionisation Potential, Electron Affinity, Chemical Potential, Global Hardness, Global Softness, Electronegativity and Electrophilicity Index of 4-chloro-6,7-dimethoxyquinoline using B3LYP/6-311G(d,p) basis set are given in Table 2 and calculated by following relations:

Ionisation Potential ( $I$ ) =  $-E_{\text{HOMO}}$ , Electron Affinity ( $A$ ) =  $-E_{\text{LUMO}}$ , Chemical Potential ( $\mu$ ) =  $(E_{\text{HOMO}} + E_{\text{LUMO}})/2$ , Global Hardness ( $\eta$ ) =  $(E_{\text{LUMO}} - E_{\text{HOMO}})/2$ , Global Softness ( $S$ ,  $\text{eV}^{-1}$ ) =  $1/\eta$ , Electronegativity( $\sigma$ ) =  $-\mu$  and Electrophilicity Index ( $\omega$ ) =  $\mu^2/2\eta$ .

Table -2 Computed Ionisation Potential ( $I$ ), Electron Affinity ( $A$ ), Chemical Potential ( $\mu$ ), Global Hardness ( $\eta$ ), Global Softness ( $S$ ,  $\text{eV}^{-1}$ ), Electronegativity( $\sigma$ ) and Electrophilicity Index ( $\omega$ ) of 4-chloro-6,7-dimethoxyquinoline using B3LYP/6-311G(d,p) basis set [Values are same for all the three solvents]

Parameters	Values in eV
$E_{\text{HOMO}}$	-0.24
$E_{\text{LUMO}}$	-0.08
Ionisation Potential ( $I$ )	0.24
Electron Affinity ( $A$ )	0.08
Chemical Potential ( $\mu$ )	-0.16
Global Hardness ( $\eta$ )	0.08
Global Softness ( $S$ )	$12.5 \text{ eV}^{-1}$
Electronegativity( $\sigma$ )	0.16
Electrophilicity Index ( $\omega$ )	0.16

4.3. Non-Linear optical properties

The first order hyperpolarizability  $\beta_{total}$ , dipole moment  $\mu$ , mean polarizability  $\langle\alpha\rangle$ , anisotropy of the polarizability  $\Delta\alpha$  are calculated using B3LYP/6-311G(d,p) basis set for 4-chloro-6,7-dimethoxyquinoline to examine any potential non-linear optical properties. The charge density and the energy of the system changes in the presence of external electric field F. The field dependent energy E(F) can then be described in terms of Taylor expansion in the components of uniform electric field F and relative to its field free energy E(0) (i, j and k run over cartesian components, i.e., x, y and z):

$$E(F) = E(0) - \sum_i \mu_i F_i - 1/2 \sum_i \sum_j \alpha_{ij} F_i F_j - 1/6 \sum_i \sum_j \sum_k \beta_{ijk} F_i F_j F_k + \dots$$

where  $F_i$  is the component of the field in the i direction,  $\mu_i, \alpha_{ij}$  and  $\beta_{ijk}$  are the components of dipole moment, polarizability and the first order hyperpolarizabilities, respectively. The 27 components of first order hyperpolarizability can be lowered to 10 components on account of Kleinman symmetry [18]. The total static dipole moment  $\mu$ , mean polarizability  $\langle\alpha\rangle$ , anisotropy of the polarizability  $\Delta\alpha$  and total first order hyperpolarizability  $\beta_{total}$  utilizing x, y, z components can be defined as:

$$\begin{aligned} \mu &= (\mu_x + \mu_y + \mu_z)^{1/2} \\ \langle\alpha\rangle &= (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3 \\ \Delta\alpha &= \{1/2 [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6(\alpha_{xz}^2 + \alpha_{xy}^2 + \alpha_{yz}^2)]\}^{1/2} \\ \beta_{total} &= [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{xxy} + \beta_{yzz})^2 + (\beta_{zzz} + \beta_{xxz} + \beta_{yyz})^2]^{1/2} \end{aligned}$$

The calculated polarizabilities  $\alpha$  and hyperpolarizabilities  $\beta$  in atomic mass units (a.u.) for 4-chloro-6,7-dimethoxyquinoline is shown in Table 3. The component  $\alpha_{yy}$  of polarizability has the maximum negative value while the component  $\alpha_{xy}$  has maximum positive value. The component  $\beta_{xxy}$  of hyperpolarizability has maximum value and the value of  $\beta_{total}$  is maximum in case of methanol which is more polar and minimum in acetone which is less polar among the three solvents.

Table-3 Non-linear Optical Parameters (Dipole moment, Polarizability and First Order Hyperpolarizability of 4-chloro-6,7-dimethoxyquinoline in B3LYP/6-311g(d,p) basis set.

Parameters	B3LYP/6-311g(d,p)		
	Dipole Moment (Debye)		
	Ethanol	Methanol	Acetone
$\mu_x$	1.57	1.57	1.57
$\mu_y$	2.06	2.06	2.05
$\mu_z$	0.05	0.05	0.05
$\mu_{total}$	2.59	2.59	2.58
Polarizability(a.u.)			
$\alpha_{xx}$	-74.76	-74.69	-74.82
$\alpha_{yy}$	-97.19	-97.19	-97.18
$\alpha_{zz}$	-96.53	-96.53	-96.54
$\alpha_{xy}$	3.50	3.51	3.49
$\alpha_{xz}$	-0.48	-0.48	-0.49
$\alpha_{yz}$	-2.47	-2.47	-2.47
$\langle\alpha\rangle$	-89.49	-89.47	-89.49
$\Delta\alpha$	23.33	23.40	23.27

Hyperpolarizability(a.u.)			
$\beta_{xxx}$	28.96	28.96	28.95
$\beta_{xxy}$	43.65	43.55	43.75
$\beta_{yyz}$	0.29	0.29	0.29
$\beta_{yyy}$	-12.36	-12.38	-12.33
$\beta_{xxx}$	-1.06	-1.06	-1.05
$\beta_{xyz}$	-8.69	-8.68	-8.71
$\beta_{zzz}$	-1.46	-1.46	-1.45
$\beta_{xzz}$	11.63	11.62	11.64
$\beta_{xyy}$	11.91	11.90	11.92
$\beta_{yzz}$	-4.11	-4.11	-4.10
$\beta_x$	52.50	52.52	39.82
$\beta_y$	27.19	27.05	27.32
$\beta_z$	-1.23	-2.23	-2.79
$\beta_{total}$	53.00	59.14	48.37

## V. CONCLUSION

In this work, the experimental and theoretical UV spectral study is done for 4-chloro-6,7-dimethoxyquinoline in methanol, ethanol and acetone. The calculated HOMO and LUMO energies are used to calculate ionization potential, electron affinity, chemical potential, global hardness, global softness, electronegativity and electrophilicity index. The total static dipole moment, mean polarizability, anisotropy of the polarizability and total first order hyperpolarizability are calculated. The parameters calculated can be used to access the molecule having non-linear property and potential applications in various fields.

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