Ultraviolet Absorption Spectra, Solvent Effect and Non-Linear Optical Properties of Tetrahydroxy-1,4-quinone Hydrate by Hartee-Fock and Density Functional Theory

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In present work, the ultraviolet absorption spectrum of tetrahydroxy-1,4-quinone hydrate (TH,1,4-QH) has been carried out experimentally (in water, methanol dimethyl sulfoxide, acetonitrile and chloroform) and theoretically in the range 3500-2300 cm^{-1} in the solution phase. Predicted electronic absorption spectra from time dependent density functional theory (TD-DFT) calculation have been analyzed and compared with the experimental UV-visible spectrum. The effects of hydroxy group substituent in benzoquinone ring have been analyzed. The electronic properties such as excitation energy, wavelength corresponding to absorption maxima (λ_{max}), oscillator strength (f), HOMO and LUMO energies are calculated by time-dependent density functional theory (TD-DFT) using HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) as basis sets. The electric dipole moment (μ), α (polarizability) and β (first hyperpolarizability) have been computed to evaluate the NLO (non-linear optical) response of the investigated compound by Hartree-Fock (HF) and density functional theory (DFT) with B3LYP basis sets. Mulliken atomic charges of the atoms are calculated by DFT (B3LYP). In addition natural bond orbital (NBO) analysis has been done using TD-DFT with B3LYP/6-311++G(d,p) basis sets.

Keywords: Tetrahydroxy-1,4-quinone hydrate, Ultraviolet spectrum, Density Functional Theory, NLO properties, Hartee-Fock.

INTRODUCTION

Electronic spectroscopy (UV) is concerned with electron transition between orbital of different energy, generally from the occupied orbital of highest energy to unoccupied orbital of lowest energy. The excitation is as a result of absorption of light, the quantum energy (E) of which is a function of frequency (ν). The excitation probability depends on the wave functions of both the excited and ground states of orbital concerned, however not all absorption of radiation by organic molecules result in electronic excitation. The rules about which a transition is allowed or forbidden, is a function of symmetry and multiplicity of the ground and excited state of the orbital concerned. The ultraviolet (electronics excitation) in a molecule is accompanied by change in rotational and vibrational quantum numbers; therefore absorption lines become a broad peak containing vibrational and rotational fine structures. However, the interaction of solute and solvent molecules blurred out the fine structures and a smooth curve is observed [1-4].

In extension of the earlier works on the ultraviolet absorption spectra of some substituted compounds of benzene [5-13], the present investigation is confined to the study of the UV absorption spectrum of tetrahydroxy-1,4-quinone hydrate (TH-

1,4-QH) (Fig. 1). There is no earlier report on the UV absorption spectrum and NBO of this molecule.
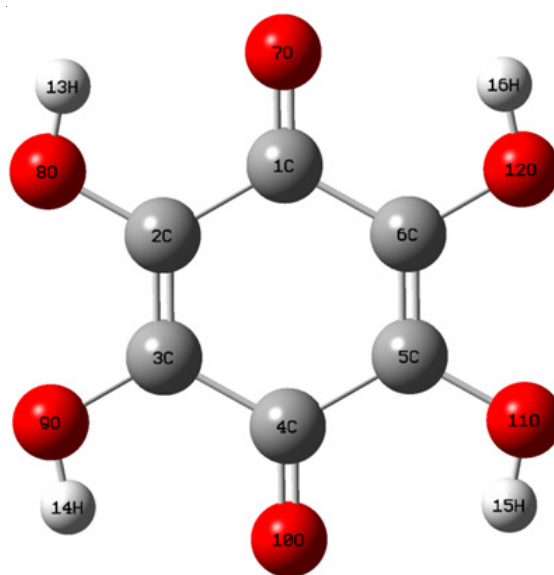

Fig. 1. Optimized geometric structure with atoms numbering of tetrahydroxy-1,4-quinone hydrate

As part of this investigation on spectroscopy, the detailed experimental studies on the electronic absorption spectra have been carried out. The object of present study is to investigate the of solvent's effect and substituent's on the absorption spectra of tetrahydroxy-1,4-quinone hydrate. The aim of present study is twofold namely:

i) To record the electronic absorption spectra for the substituted benzoquinone in different solvents and to study the effect of these solvents on the absorption spectra.

ii) To study the effect of substituent's on the absorption spectra.

EXPERIMENTAL

The compound tetrahydroxy-1,4-quinone hydrate (TH-1,4-QH) in the solid form was purchased from Sigma Aldrich Chemical Pvt. Ltd., Germany with a stated purity of greater than 99 % and was used as such without further purification. UV/visible spectra of TH-1,4-QH was recorded in solvents water, methanol, DMSO, acetonitrile and chloroform of different polarity (Fig. 2). The solvents were distilled several times to spectroquality grade, while the solute was used without further purification.
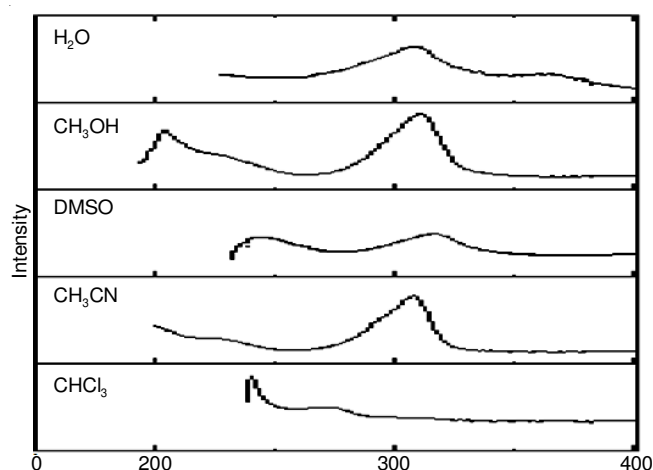

Fig. 2. UV-visible spectra of tetrahydroxy-1,4-quinone hydrate

Computational details: The computational work was done to determine the optimized geometry of TH-1,4-QH. The HF (Hartree Fock) and DFT (hybrid B3LYP: the Becke's three-parameter hybrid method with the Lee, Yang and Parr correlation functional) [14,15] method was chosen for compound TH-1,4-QH. The entire calculations were performed by using the Gaussian 09 program package on a personal computer [16]. The electronic absorption spectra for optimized molecule calculated with the time dependent density functional theory (TD-DFT) at HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) levels. The time-dependent HF and DFT (TD-HF and TD-DFT) proved to be a powerful and effective computational tool for the study of ground and excited state properties by comparison to the available experimental data. Hence, we used TD-B3LYP to obtain excitation energy, wavelengths (λ_{max}), oscillator strengths and compare with the experimental results of TH-1,4-QH. The HOMO and LUMO energies are calculated by using HF and DFT methods with the same basis sets. The non-

linear parameters (dipole moment, polarizability and first order hyperpolarizability), Mulliken atomic charges of the atoms are calculated by using HF and DFT methods with the same basis sets.

RESULTS AND DISCUSSION

UV-visible absorption spectra

Shift of n-π* and σ-σ* band of tetrahydroxy-1,4-quinone hydrate in different solvents: Kasha [17], Sponer and Rush [18] have shown that the n-π* system of benzoquinone appears at 245-280 nm and σ-σ* appears above than 280 nm in vapour phase. In present study, the spectra was studied in different solvents and in solid phase. The n-π* band has been observed at 268.99 and 265.06 nm in TH-1,4-QH with solvent chloroform and water respectively. It shows that band system is shifted towards shorter wavelength in TH-1,4-QH. The red shift observed at or above than 280 nm in TH-1,4-QH. The σ-σ* band has been observed at 310.98 nm, 307.90 nm and 316.52 nm in TH-1,4-QH with solvent methanol, acetonitrile and DMSO respectively.

Solvent effect: As suggested by Ram *et al.* [19] in benzoquinone the introduction of –O= group in place of –CH in benzene exhibit a blue shift in transition 2600 Å band (n-π*). In the present study the near ultraviolet spectra of the molecule TH-1,4-QH was observed in different solvents *viz.* water, methanol, DMSO, acetonitrile and chloroform as shown in Fig. 3. The bands as higher absorption are taken to be σ-σ* band. The band system corresponds to 1_{Alg}-1_{B2u} 2600 Å (n-π*) transition of benzene has been observed between 2650-2690 Å in TH-1,4-QH for different solvents. The shift of absorption band occurring upon a change from one solvent to another is due to the salvation energy of the solute in the ground and excited state and is equal to $\Delta v = v_{sol1} - v_{sol2}$. According to Finar [20], polar solvents and those which can form hydrogen bands tend to interact electrostatically with various chromophores which changes the charge distribution in the molecule and results in increased delocalization. For n-π* system both ground and excited states are stabilized and absorption maxima moves towards longer wavelength as the polarity of the solvent increases.
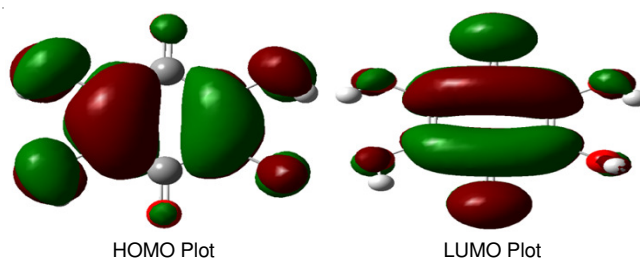
Fig. 3.   Atomic orbital HOMO and LUMO compositions of the frontier molecular orbital for tetrahydroxy-1,4-quinone hydrate

The n-π* transition shift towards shorter wavelength with the increase in the polarity of the solution because in this transition ground state is more stabilized than the excited state. In present study of TH-1,4-QH the n-π* system shift towards the shorter wavelength with the increase of the polarity of the solvent while going from DMSO to water (Table-1) with the

TABLE-1
EFFECT OF SOLVENTS ON n-π* AND π-π* TRANSITION IN TETRAHYDROXY-1,4-QUINONE HYDRATE

Solvent	Refractive index	λ_{max} for TH-1,4-QH
Water	1.3380	265.06
Methanol	1.3773	310.98
Chloroform	1.4458	268.99
Acetonitrile	1.3441	307.90
DMSO	1.4790	316.52

exception in case of methanol. The wavelength also shifts towards shorter wavelength in case of *n*-hexane *i.e.* non polar solvent. From these, it seems that ground state is more stabilized than excited state in both n-π* transitions.

In the spectra of monocyclic enzymes the absorption band due to transition of an electron from a lone pair orbital to a π orbital of the ring is shifted towards red region by *meta* directing group. Stephensen [21] and Goodmen & Harrall [22] have observed a blue shift in *ortho* halogenated pyridine and pointed out the substitution in *ortho* position exerted an influence through interaction with the non-bonding electron of the nitrogen. Therefore, as observed in present case the n-π* system is observed blue shifted to *meta* directing TH-1,4-QH. In TH-1,4-QH the blue shift from *n*-hexane to water is in the order of decreasing refractive index of the solvents (Table-2) which is in accordance with the work of Mataga and Kubota [23].

TABLE-2
ELECTRONIC ABSORPTION SPECTRA OF TETRAHYDROXY-1,4-QUINONE HYDRATE [ABSORPTION WAVELENGTH λ_{max} (nm), EXCITATION ENERGY (eV) AND OSCILLATOR STRENGTH (f)] USING TD-DFT WITH B3LYP/6-311++G(d,p) BASIS SETS

Solvents	B3LYP/6-311++G(d,p)*cis*			Experimental λ_{max}	Assignments
	λ_{max}	E	F		
Chloroform	289.73	4.2793	0.0038		σ-σ*
	286.16	4.3327	0.0323	268.99	σ-σ*
	274.05	4.5241	0.0081		n-π*
Methanol	294.33	4.2124	0.1246		σ-σ*
	282.36	4.3911	0.0149	310.98	σ-σ*
	273.78	4.5286	0.4407		n-π*
Water	294.47	4.2104	0.1283		σ-σ*
	282.25	4.3928	0.0160	265.06	σ-σ*
	273.89	4.5268	0.5003		n-π*
Acetonitrile	294.47	4.2104	0.1283		σ-σ*
	282.25	4.3928	0.0160	307.90	σ-σ*
	273.89	4.5268	0.5003		n-π*
DMSO	294.83	4.2052	0.1385		σ-σ*
	281.97	4.3970	0.0199	316.52	σ-σ*
	274.26	4.5206	0.6730		n-π*

On the basis of fully optimized ground-state structure, calculations have been performed to determine the low-lying excited states of TH-1,4-QH using B3LYP/6-311++G(d,p) basis sets. The calculated result involving the vertical excitation energies, oscillation strength (f) and wavelength (λ_{max}) are carried out as shown in Table-3 and compared with measured experimental wavelength listed in Table-2.

TH-1,4-QH the transitions for the transitions for B3LYP/6-311++G(d,p) basis set are observed at wavelengths at 274, 286 and 289 nm in chloroform, at 273,282 and 294 nm in

TABLE-3
CALCULATED ENERGY VALUES (eV) OF TETRAHYDROXY-1,4-QUINONE HYDRATE BY USING TD-DFT/B3LYP/6311++G(d,p)

Parameter	Values
E_{HOMO}	-0.3813
E_{LUMO}	-0.0117
E_{HOMO-1}	-0.4072
E_{LUMO-1}	-0.0433
ΔE	0.3696
∂E	0.3639
E_{Total} (Hartree)	-379.87

$\Delta E = E_{LUMO} - E_{HOMO}$, $\partial E = E_{LUMO+1} - E_{HOMO-1}$

methanol and at 273, 282 and 294 nm in water at 273, 282 and 294 in acetonitrile at 274, 281 and 294 in DMSO solvent. There are three values of wavelengths for each solvent. For each solvent the first wavelength corresponding to n→π* and another two corresponding to σ-σ* transitions. The results obtained in B3LYP are nearer to experimental results.

HOMO-LUMO energy: The HOMO (highest occupied molecular orbital) energy characterizes the ability of electron giving, the LUMO (least unoccupied molecular orbital) characterizes the ability of electron accepting and the gap between HOMO and LUMO characterizes the molecular chemical stability. The energy gap between the HOMOs and LUMOs is a critical parameter in determining molecular electrical transport properties because it is a measure of electron conductivity. Both HOMO and LUMO are the main orbitals that take part in chemical stability. The energy values of LUMO and HOMO and their energy gap determines the kinetic stability, chemical reactivity and, optical polarizability and chemical hardness-softness of a molecule [24]. The molecule has a large energy gap is known as hard and having a small energy gap is known as soft molecule. The hard molecule is not more polarizable than the soft ones because they need big energy to excitation [25,26]. The decrease in the energy of HOMO and LUMO explains the ICT (intra molecular charge transfer) interaction taking place within the molecule which is highly responsible for the activity of the molecule. The HOMO-LUMO energy separation has served as a simple measure of kinetic stability. A molecule with a small or no HOMO-LUMO gap is a chemically reactive. Pearson showed that the HOMO-LUMO gap represents the chemical hardness of the molecule [27]. Another parameter that is calculated is electrophilicity index which measures the energy lowering of a ligand due to maximal electron flow between donor and acceptor [28]. The energies of HOMO, LUMO, HOMO-1 (second highest occupied molecular orbital) and LUMO+1 (second least unoccupied molecular orbital) and corresponding energy gap in different solvents for TH-1,4-QH are calculated with the TD-DFT method and same basis sets and presented in Table-3.

The complete equations for calculating ionization potential, electron affinity, chemical potential, global hardness, global softness, electronegativity and electrophilicity index are as follows (Table-4):

Ionization potential (I) = $-E_{HOMO}$

Electron affinity (A) = $-E_{LUMO}$

Chemical potential (μ) = $(E_{LUMO} + E_{HOMO})/2$

Global hardness (η) = $(E_{LUMO} - E_{HOMO})/2$

Global softness (S) = 1/η

Electronegativity (σ) = − μ

Electrophilicity index (ω) = μ²/2η

These values will be same for the solvents ethanol, methanol and water for each basis set since the values of E_{HOMO} and E_{LUMO} are same in all the solvents as shown in Table-4.

TABLE-4
COMPUTED IONIZATION POTENTIAL (I), ELECTRON AFFINITY (A), CHEMICAL POTENTIAL (μ), GLOBAL HARDNESS (η), GLOBAL SOFTNESS (S) IN eV⁻¹, ELECTRONEGATIVITY (σ) AND ELECTRO-PHILICITY INDEX (ω) USING B3LYP/6-311++G(d,p) BASIS SETS

Parameters	B3LYP/6311++G(d,p) (eV)
E_{HOMO}	-0.3813
E_{LUMO}	-0.0117
Ionization potential (I)	0.3813
Electron affinity (A)	0.0117
Chemical potential (μ)	-0.1962
Global hardness (η)	0.1848
Global softness (S)	5.4100
Electronegativity (σ)	0.1962
Electrophilicity index (ω)	0.1041

Mulliken charges: Mulliken charges estimates partial atomic charges calculated from the Mulliken population analysis [29,30]. Here HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) basis sets used to calculate mulliken charges. The calculations are carried out by the methods of computational chemistry; particularly those based on the linear combination of atomic orbitals and are routinely used as variables in linear regression procedures. The mulliken charges of TH-1,4-QH is shown in Fig. 4. The figure shows positive and negative charges of atoms of TH-1,4-QH.
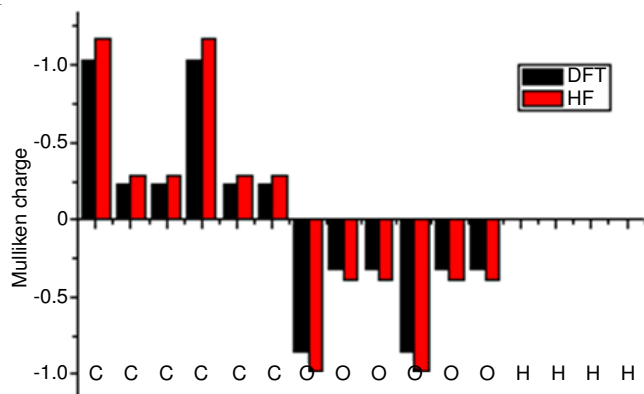

Fig. 4. Mulliken charges of TH-1,4-QH computed by HF/6-311++G(d,p) and B3LYP/6-31+G(d,p) basis sets [N-nitrogen, C-carbon, H-hydrogen]

Non-linear optical (NLO) properties: The non-linear optical (NLO) effects arise from the interactions of electromagnetic fields in various media to produce new fields altered in frequency, amplitude, phase or other propagation characteristics from the incident fields. Non-linear optical is at the forefront of present research because of its importance in providing the key functions of optical modulation, frequency shifting, optical switching, optical logic and optical memory for promising technologies in the areas such as signal processing, telecommunications and optical interconnections [30-33].

TABLE-5
MULLIKEN CHARGES OF TETRAHYDROXY-1,4-QUINONE HYDRATE COMPUTED BY HF/6-311++G(d,p) AND B3LYP/6-311+G(d,p) BASIS SETS

S. No.	Atom	DFT	HF
1	C	1.025978	1.174681
2	C	0.228656	0.292202
3	C	0.228656	0.292202
4	C	1.025978	1.174681
5	C	0.228656	0.292202
6	C	0.228656	0.292202
7	O	-0.853804	-0.987257
8	O	-0.314742	-0.385914
9	O	-0.314742	-0.385914
10	O	-0.853804	-0.987257
11	O	-0.314742	-0.385914
12	O	-0.314742	-0.385914
13	H	0.000000	0.000000
14	H	0.000000	0.000000
15	H	0.000000	0.000000
16	H	0.000000	0.000000

The dipole moment (μ), polarizability (α) and second-order polarizability or the first hyperpolarizability (β), are calculated using DFT with 6-31+G(d,p) and 6-311++G (d,p) basis sets on the basis of the finite-field approach. The complete equations for calculating the magnitude of total static dipole moment μ, the mean polarizability <α>, the anisotropy of the polarizability Δα and the mean first hyperpolarizability $β_{total}$, using the x, y, z components from Gaussian 09W output is as follows:

$$\text{Dipole moment} \quad \mu = \sqrt{\mu_x^2 + \mu_y^2 + \mu_z^2} \quad (1)$$

The mean polarizability and anisotropy of polarizability respectively are defined by

$$\langle \alpha \rangle = \frac{1}{3}\left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right) \quad (2)$$

$$\Delta\alpha = \frac{1}{\sqrt{2}}\left[\left(\alpha_{xx} - \alpha_{yy}\right)^2 + \left(\alpha_{yy} - \alpha_{zz}\right)^2 + \left(\alpha_{zz} - \alpha_{xx}\right)^2 + 6\left(\alpha_{xz}^2 + \alpha_{xy}^2 + \alpha_{yz}^2\right)\right]^{\frac{1}{2}} (3)$$

the mean first-order hyperpolarizability $β_{Total}$ is defined as:

$$\beta_{Total} = \left(\beta_x^2 + \beta_y^2 + \beta_z^2\right)^{\frac{1}{2}} \quad (4)$$

where $\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$, $\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yzz}$, $\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz}$

It has been already proved that the higher values of dipole moment, molecular polarizability and hyperpolarizability are important for more active NLO properties. The calculated value of dipole moment was found to be 0.7129 Debye using B3LYP/6-311++G(d,p) for tetrahydroxy-1,4-quinone hydrate. The highest value of dipole moment is observed for component $μ_x$ for TH-1,4-QH at all levels of theory. The calculated values of dipole moment with all components are shown in Table-6. The polarizabilities and first hyperpolarizability are reported in atomic units (a.u), the calculated values have been converted in to electrostatic units (esu) (α: 1 a.u =0.1482 × 10⁻²⁴ esu, β: 1 a.u = 8.6393 × 10⁻³³ esu) [26].

The mean polarizabilities (α) and anisotropy of polarizability (Δα) are also included in Table-6 (molecules are in the xy

TABLE-6
NON-LINEAR OPTICAL PARAMETERS (DIPOLE MOMENT, POLARIZABILITY AND FIRST ORDER HYPERPOLARIZA-BILITY) OF TETRAHYDROXY-1,4-QUINONE HYDRATE

Parameters	Values	Parameters	Values
Dipole moments (Debye)		Hyperpolarizability (a.u)	
μ_x	0.0015	β_{xxx}	0.0134
μ_y	-0.7104	β_{xxy}	-2.0508
μ_z	-0.0601	β_{xyy}	-0.0135
μ_{Total}	0.7129	β_{yyy}	-5.6205
α_{xx}	-78.5673	β_{xxz}	-0.1667
α_{xy}	-0.1892	β_{xyz}	0.0421
α_{yy}	-63.7181	β_{yyz}	-0.4983
α_{xz}	0.2964	β_{xzz}	0.0080
α_{yz}	0.4358	β_{yzz}	-0.5324
α_{zz}	-67.0579	β_{zzz}	-0.1276
Polarizability (a.u)		β_{Total}	8.242 (a.u)
α	-69.955 (a.u) = -10.3367 × 10^{-24} (esu)	β_{Total}	71.205 × 10^{-33} (esu)
$\Delta\alpha$	258.802 (a.u) = 38.354 × 10^{-24} (esu)		

plane). It is observed that the B3LYP/6-311++G(d,p) level of theory leads to higher polarizability in comparison to other method. The calculated values of polarizability is-10.367 × 10^{-24} esu using B3LYP/6-311++G(d,p). Additionally, the anisotropy of the polarizability (α) has been determined using *ab initio* and DFT methods. The calculated values is 38.354 × 10^{-24} esu at B3LYP level for TH-1,4-QH. The first static hyperpolarizability calculated values are presented in Table-6. The values of β_{total} is 71.205 × 10^{-33} esu at B3LYP/6-311++G(d,p). The large value of hyperpolarizability calculated by the HF and B3LYP methods show that the studied compound is a good NLO material. The theoretical calculation of hyperpolarizability components is very useful as this clearly indicates the direction of charge delocalization [34].

NBO analysis: The natural population analysis performed on the electronic structure of title compound clearly describes the distribution of electrons in various sub-shells of their atomic orbitals. The accumulation of charges on the individual atom and accumulation of electrons in the core, valance and Rydberg sub-shells of tetrahydroxy,1-4-quinone hydrate are presented in Table-7. The most electronegative atoms like O_8, O_9, O_{11}, O_{12}, each have charges -0.65277 and O_7, O_{10} both have the same charges-0.56287. The most electropositive atoms are H_{13}, H_{14}, H_{15}, H_{16}, with same charge 0.48987 and C_1, H_{46}, with same charge 0.45455. From the point of view of electrostatic, electropositive atoms have a tendency to accept an electron, whereas the electronegative atoms have a tendency to donate an electron. Further, natural population analysis showed that 88 electrons in the title compound are distributed on the sub-shells as follows:

Core: 23.99130 (99.9637 % of 24)
Valence: 63.77933 (99.6552 % of 64)
Rydberg: 0.22937 (0.2606 % of 88)

The occupancies and energies of lone pair molecular orbitals (LP) and anti-bonding (BD*) molecular orbitals of the Tetrahydroxy-1,4-quinone hydrate are predicted at B3LYP/6-311++G(d,p) level of theory and is presented in Table-8. The variations in occupancies and energies of the title molecule directly give the evidence for the delocalization of charge upon substitution and this leads to the variation of bond lengths.

TABLE-7
ACCUMULATION OF NATURAL CHARGE POPULATION OF ELECTRON IN CORE, VALENCE AND RYDBERG ORBITALS OF TETRAHYDROXY-1,4-QUINONE HYDRATE

Atom	Charge	Natural population			Total
		Core	Valence	Rydberg	
C_1	0.45455	1.99923	3.50769	0.03852	5.54545
C_2	0.21706	1.99857	3.75903	0.02535	5.78294
C_3	0.21706	1.99857	3.75903	0.02535	5.78294
C_4	0.45455	1.99923	3.50769	0.03852	5.54545
C_5	0.21706	1.99857	3.75903	0.02535	5.78294
C_6	0.21706	1.99857	3.75903	0.02535	5.78294
O_7	-0.56287	1.99979	6.54592	0.01716	8.56287
O_8	-0.65277	1.99977	6.64063	0.01237	8.65277
O_9	-0.65277	1.99977	6.64063	0.01237	8.65277
O_{10}	-0.56287	1.99979	6.54592	001716	8.56287
O_{11}	-0.65277	1.99977	6.64063	0.01237	8.65277
O_{12}	-0.65277	1.99977	6.64063	0.01237	8.65277
H_{13}	0.48987	0	0.50526	0.00487	0.51013
H_{14}	0.48987	0	0.50526	0.00487	0.51013
H_{15}	0.48987	0	0.50526	0.00487	0.51013
H_{16}	0.48987	0	0.50526	0.00487	0.51013

Core: 23.99141 (99.9642 % of 24)
Valence: 63.72687 (99.5732 % of 64)
Natural Minimal Basis: 87.71829 (99.6799 % of 88)
Natural Rydberg Basis: 0.28171 (0.3201 % of 88)

TABLE-8
SECOND ORDER PERTURBATION THEORY ANALYSIS OF FOCK MATRIX IN NBO BASIS OF TETRAHYDROXY-1,4-QUINONE HYDRATE

Donor NBO	Acceptor NBO	E(2)	E_j-E_i	F(i,j)
C_1-C_2	C_1-C_6	0.53	1.12	0.022
	C_1-O_7	0.83	1.25	0.029
	C_2-C_3	2.88	1.30	0.055
	C_3-O_9	4.98	1.07	0.065
	C_6-O_{12}	1.93	1.07	0.041
C_1-C_6	C_1-C_2	0.53	1.12	0.022
	C_1-O_7	0.83	1.25	0.029
	C_2-O_8	1.93	1.07	0.041
	C_5-C_6	2.88	1.30	0.055
	C_5-O_{11}	4.98	1.07	0.065
C_1-O_7	C_1-C_2	0.98	1.51	0.035
	C_1-C_6	0.98	1.51	0.035
	C_2-C_3	0.76	1.69	0.032
	C_5-C_6	0.76	1.69	0.032
	C_2-C_3	5.21	0.42	0.045
	C_5-C_6	5.21	0.42	0.046
C_2-C_3	C_1-C_2	1.92	1.19	0.043
	C_1-O_7	1.52	1.32	0.040
	C_2-O_8	1.59	1.14	0.038
	C_3-C_4	1.92	1.19	0.043
	C_3-O_9	1.59	1.14	0.038
	C_4-O_{10}	1.52	1.32	0.040
	O_8-H_{13}	1.38	1.17	0.036
	O_9-H_{14}	1.38	1.17	0.036
	C_1-O_7	21.34	0.28	0.070
	C_4-O_{10}	21.34	0.28	0.070
C_2-O_8	C_1-C_6	1.04	1.36	0.034
	C_2-C_3	1.56	1.54	0.044
	C_3-C_4	1.49	1.36	0.041
C_3-C_4	C_2-C_3	2.88	1.30	0.055
	C_2-O_8	4.98	1.07	0.065
	C_4-C_5	0.53	1.12	0.022
	C_4-O_{10}	0.83	1.25	0.029
	C_5-O_{11}	1.93	1.07	0.041

C_3-O_9	C_1-C_2	1.49	1.36	0.041
	C_2-C_3	1.56	1.54	0.044
	C_4-C_5	1.04	1.36	0.034
C_4-C_5	C_3-C_4	0.53	1.12	0.022
	C_3-O_9	1.93	1.07	0.041
	C_4-O_{10}	0.83	1.25	0.029
	C_5-C_6	2.88	1.30	0.055
	C_6-O_{12}	4.98	1.07	0.065
C_4-O_{10}	C_2-C_3	0.76	1.69	0.032
	C_3-C_4	0.98	1.51	0.035
	C_4-C_5	0.98	1.51	0.035
	C_2-C_3	5.21	0.42	0.045
	C_5-C_6	5.21	0.42	0.045
C_5-C_6	C_1-C_6	1.92	1.19	0.043
	C_1-O_7	1.52	1.32	0.040
	C_4-C_5	1.92	1.19	0.043
	C_4-O_{10}	1.52	1.32	0.040
	C_5-O_{11}	1.59	1.14	0.038
	C_6-O_{12}	1.59	1.14	0.038
	O_{11}-H_{15}	1.38	1.17	0.036
	O_{12}-H_{16}	1.38	1.17	0.036
	C_1-O_7	21.34	0.28	0.070
	C_4-O_{10}	21.34	0.28	0.070
C_5-O_{11}	C_1-C_6	1.49	1.36	0.041
	C_3-C_4	1.04	1.36	0.034
	C_5-C_6	1.56	1.54	0.044
C_6-O_{12}	C_1-C_2	1.04	1.36	0.034
	C_4-C_5	1.49	1.36	0.041
	C_5-C_6	1.56	1.54	0.044
O_8-H_{13}	C_1-C_2	0.82	1.16	0.028
	C_2-C_3	4.77	1.34	0.072
O_9-H_{14}	C_2-C_3	4.77	1.34	0.072
	C_3-C_4	0.82	1.16	0.028
O_{11}-H_{15}	C_4-C_5	0.82	1.16	0.028
	C_5-C_6	4.77	1.34	0.072
O_{12}-H_{16}	C_1-C_2	0.82	1.16	0.028
	C_5-C_6	4.77	1.34	0.072
LP(1)-O_7	C_1-C_2	1.08	1.15	0.032
	C_1-C_6	1.08	1.15	0.032
LP(2) –O_7	C_1-C_2	17.28	0.72	0.101
	C_1-C_6	17.28	0.72	0.101
	O_8-H_{13}	2.02	0.70	0.035
	O_{12}-H_{16}	2.02	0.70	0.035
LP(1) –O_8	C_1-C_2	5.77	1.03	0.070
LP(2) –O_8	C_2-C_3	33.66	0.34	0.099
LP (1)-O_9	C_3-C_4	5.77	1.03	0.070
LP (2)-O_9	C_2-C_3	33.66	0.34	0.099
LP (1)-O_{10}	C_3-C_4	1.08	1.15	0.032
	C_4-C_5	1.08	1.15	0.032
LP (2)-O_{10}	C_3-C_4	17.28	0.72	0.101
	C_4-C_5	17.28	0.72	0.101
	O_9-H_{14}	2.02	0.70	0.035
	O_{11}-H_{15}	2.02	0.70	0.035
LP (1)-O_{11}	C_4-C_5	5.77	1.03	0.070
LP (2)-O_{11}	C_5-C_6	33.66	0.34	0.099
LP (1)-O_{12}	C_1-C_6	5.77	1.03	0.070
LP (2)-O_{12}	C_5-C_6	33.66	0.34	0.099
C_1-O_7	C_2-C_3	57.15	0.03	0.074
	C_5-C_6	57.15	0.03	0.074
	C_2-C_3	57.15	0.03	0.074
	C_5-C_6	57.15	0.03	0.074

The interactions result in a loss of occupancy from the localized NBO (nuclear bond orbital) of the idealized Lewis structure into an empty Non-Lewis orbital. NBO analysis of some pharmaceutical compounds has been performed by many spectroscopists [10-12]. The loan pair-anti-bonding interaction can be quantitatively described by second-order perturbation interaction [13-16] energy E(2). For each donor (i) and acceptor (j), the stabilization energy E(2) associated with the delocalization i→j is estimated as:

$$E(2) = \Delta E_{ij} = q_i F(ij)^2 / \varepsilon_j - \varepsilon_i$$

where q_i is the donor orbital occupancy, ε_i and ε_j are the diagonal elements and F(i,j) is the off diagonal NBO Fock matrix element. The NBO analysis provides an efficient method for studying intermolecular and intramolecular bonding. It also provides a convenient basis for intermolecular charge transfer (ICT) or conjugative interactions in molecular system. Table-8 presents the second order perturbation energies (often called as stabilizations energies or interaction energies) of most interaction NBO of tetrahydroxy-1,4-quinone hydrate. The second order perturbation energies correspond to the hyper conjugative interactions of the title compound such as LP(2)O_8→C_2-C_3, LP(2)O_9→C_2-C_3 LP(2)O_{12}→C_5-C_6 and V that are considerably very large with 33.66 kJ mol^{-1}, respectively. These hyper conjugative interactions are most responsible ones for stability of title compound.

Electron contribution in *s*-type and *p*-type subshells: NBO analysis of title compound is performed to estimate the delocalization patterns of electron density (ED) from the principal occupied Lewis-type (bond or lone pair) orbitals to occupied non-Lewis (anti-bonding or Rydberg) orbitals. The list of occupancies and energies of most interacting NBOs along with their percentage of hybrid atomic orbitals is listed in Table-9.

TABLE-9 OCCUPANCIES AND ENERGIES OF ONE PAIR ORBITALS (LP) AND ANTI-BONDING (BD*) MOLECULAR ORBITALS OF TETRAHYDROXY-1,4-QUINONE HYDRATE					
Bond	Occupancy	Energy	Bond	Occupancy	Energy
C_1-C_2	1.97598	-0.72242	LP(1)-O_{10}	1.98140	-075877
C_1-C_6	1.97598	-0.72242	LP(2)-O_{10}	1.88206	-0.33020
C_1-O_7	1.99404	-1.11244	LP(1)-O_{11}	1.97521	-0.64175
C_1-O_7	1.95775	-0.42977	LP(2)-O_{11}	1.84249	-0.35268
C_2-C_3	1.97759	-0.79565	LP(1)-O_{12}	1.97521	-0.64175
C_2-C_3	1.78698	-0.32614	LP(2)-O_{12}	1.84249	-0.35268
C_2-O_8	1.99326	-0.96565	C_1-C_2	0.06639	0.39266
C_3-C_4	1.97598	-0.72242	C_1-C_6	0.06639	0.39266
C_3-O_9	1.99326	-0.96565	C_1-O_7	0.00867	0.52743
C_4-C_5	1.97598	-0.72242	C_1-O_7	0.25358	-0.04223
C_4-O_{10}	1.99404	-1.11244	C_2-C_3	0.02761	0.57700
C_4-O_{10}	1.95775	-0.42977	C_2-C_3	0.28762	-0.01009
C_5-C_6	1.97759	-0.79565	C_2-O_8	0.01754	0.34425
C_5-C_6	1.78698	-0.32614	C_3-C_4	0.06639	0.39266
C_5-O_{11}	1.99326	-0.96565	C_3-O_9	0.01754	0.34425
C_6-O_{12}	1.99326	-0.96565	C_4-C_5	0.06639	0.39266
O_8-H_{13}	1.98490	-0.76349	C_4-O_{10}	0.00867	0.52743
O_9-H_{14}	1.98490	-0.76349	C_4-O_{10}	0.25358	-0.04223
O_{11}-H_{15}	1.98490	-0.76349	C_5-C_6	0.02761	0.57700
O_{12}-H_{16}	1.98490	-0.76349	C_5-C_6	0.28762	-0.01009
LP(1)-O_7	1.98140	-0.75877	C_5-O_{11}	0.01754	0.34425
LP(2)-O_7	1.88206	-0.33020	C_6-O_{12}	0.01754	0.34425
LP(1)-O_8	1.97521	-0.64175	O_8-H_{13}	0.01718	0.37179
LP(2)-O_8	1.84249	-0.35268	O_9-H_{14}	0.01718	0.37179
LP(1)-O_9	1.97521	-0.64175	O_{11}-H_{15}	0.01718	0.37179
LP(2)-O_9	1.84249	-0.35268	O_{12}-H_{16}	0.01718	0.37179

The percentage of hybrid atomic orbitals of oxygen lone pair atom (O_7) and (O_{10}) shows that oxygen is partially contributed to both *s*-type and *p*-type subshells for LP(1), while oxygen is predominantly contributed to *p*-type subshell for LP(2). In contrast, all the anti-bonding orbitals of title compound shows that oxygen is partially contributed to both *s*-type and *p*-type subshell [35] as stated in Table-10.

TABLE-10
NATURAL ATOMIC ORBITAL OCCUPANCIES OF MOST INTERACTING (LONE PAIR AND ANTI-BONDING) NBO's OF TETRAHYDROXY-1,4-QUINONE HYDRATE

Bond	Hybridization	S (%)	P (%)
C_1-C_2	$0.7045sp^{1.86}+0.7097sp^{2.05}$	49.63	50.37
C_1-C_6	$0.7045sp^{1.86}+0.7097sp^{2.05}$	49.63	50.37
C_1-O_7	$0.5943sp^{2.32}+0.8042sp^{1.47}$	35.32	64.64
C_1-O_7	$0.5634sp^{1.0}+0.8262sp^{1.0}$	31.74	68.26
C_1-C_3	$0.7071sp^{1.50}+0.7071sp^{1.00}$	50.00	50.00
C_2-C_3	$0.7071sp^{1.00}+0.7071sp^{1.50}$	50.00	50.00
C_1-O_8	$0.5862sp^{2.70}+0.8102sp^{1.99}$	34.36	65.64
C_3-C_4	$0.7097sp^{2.05}+0.7045sp^{1.86}$	50.37	49.63
C_3-O_9	$0.5862sp^{2.70}+0.8102sp^{1.99}$	34.36	65.64
C_4-C_5	$0.7045sp^{1.86}+0.7097sp^{2.05}$	49.63	50.37
C_4-O_{10}	$0.5943sp^{2.32}+0.8042sp^{1.47}$	35.32	64.68
C_4-O_{10}	$0.5634sp^{1.00}+0.8262sp^{1.00}$	31.74	68.26
C_5-C_6	$0.7071sp^{1.50}+0.7071sp^{1.50}$	50.00	50.00
C_5-C_6	$0.7071sp^{1.00}+0.7071sp^{1.00}$	50.00	50.00
C_5-O_{11}	$0.5862sp^{2.70}+0.8102sp^{1.99}$	34.36	65.64
C_6-O_{12}	$0.5862sp^{2.70}+0.8102sp^{1.99}$	34.36	65.64
O_8-H_{13}	$0.8677sp^{3.75}+0.4972sp^{0.00}$	75.28	24.72
O_9-H_{14}	$0.8677sp^{3.75}+0.4972sp^{0.00}$	75.28	24.72
O_{11}-H_{15}	$0.8677sp^{3.75}+0.4972sp^{0.00}$	75.28	24.72
O_{12}-H_{16}	$0.8677sp^{3.75}+0.4972sp^{0.00}$	75.28	24.72
LP(1)-O_7	$Sp^{0.68}$		
LP(2)-O_7	$Sp^{1.00}$		
LP(1)-O_8	$Sp^{1.19}$		
LP(2)-O_8	$Sp^{1.00}$		
LP(1)-O_9	$Sp^{1.99}$		
LP(2)-O_9	$Sp^{1.00}$		
LP(1)-O_{10}	$Sp^{0.68}$		
LP(2)-O_{10}	$Sp^{1.00}$		
LP(1)-O_{11}	$Sp^{1.19}$		
LP(2)-O_{11}	$Sp^{1.00}$		
LP(1)-O_{12}	$Sp^{1.99}$		
LP(2)-O_{12}	$Sp^{1.00}$		
C_1-C_2	$0.7097sp^{1.86}-0.7045p^{2.05}$	50.37	49.63
C_1-C_6	$0.7097sp^{1.86}-0.7045p^{2.05}$	50.37	49.63
C_1-O_7	$0.8042sp^{2.32}-0.5943sp^{1.47}$	64.68	35.32
C_1-O_7	$0.8262sp^{1.00}-0.5634sp^{1.00}$	68.26	31.74
C_2-C_3	$0.7071sp^{1.50}0.7071sp^{1.50}$	50.00	50.00
C_2-C_3	$0.7071sp^{1.00}0.7071sp^{1.00}$	50.00	50.00
C_2-O_8	$0.8102sp^{2.70}-0.5862sp^{1.99}$	65.64	34.36
C_3-C_4	$0.7045sp^{2.05}-0.7097sp^{1.86}$	49.63	50.37
C_3-O_9	$0.8102sp^{2.70}-0.5862sp^{1.99}$	65.64	34.36
C_4-C_5	$0.7097sp^{1.86}-0.7045p^{2.05}$	50.37	49.63
C_4-O_{10}	$0.8042sp^{2.32}-0.5943sp^{1.47}$	64.68	35.32
C_4-O_{10}	$0.8262sp^{1.00}-0.5634sp^{1.00}$	68.26	31.74
C_5-C_6	$0.7071sp^{1.50}0.7071sp^{1.50}$	50.00	50.00
C_5-C_6	$0.7071sp^{1.00}0.7071sp^{1.00}$	50.00	50.00
C_5-O_{11}	$0.8102sp^{2.70}-0.5862sp^{1.99}$	65.64	34.36
C_6-O_{12}	$0.8102sp^{2.70}-0.5862sp^{1.99}$	65.64	34.36
O_8-H_{13}	$0.4972sp^{3.75}-0.8677sp^{0.00}$	24.72	75.28
O_9-H_{14}	$0.4972sp^{3.75}-0.8677sp^{0.00}$	24.72	75.28
O_{11}-H_{15}	$0.4972sp^{3.75}-0.8677sp^{0.00}$	24.72	75.28
O_{12}-H_{16}	$0.4972sp^{3.75}-0.8677sp^{0.00}$	24.72	75.28

Conclusion

In the present work, an attempt has been made on the experimental and theoretical UV-visible spectral studies, HOMO-LUMO energies, Mulliken charges and NLO properties of industrially important tetrahydroxy-1,4-quinone hydrate. Equilibrium geometries, electronic parameters and thermodynamic parameters of tetrahydroxy-1,4-quinone hydrate have been analyzed at HF and DFT/B3LYP using 6-311++G(d,p) basis set. The Time dependent-DFT calculations on the molecule provided deep insight into their electronic structures and properties. In addition, the calculated UV-visible results functions are all in good agreement with the experimental data. The lowering of HOMO-LUMO band gap supports bioactive property of the molecule. The predicted NLO properties show that the title compound is a good candidate as non-linear optical material. The calculated first hyperpolarizability is comparable with the reported values of similar derivatives and is an attractive object for future studies of non-linear optics.

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