# Comparative Structural and Vibrational Study of 8-Hydroxyquinoline and 8-Hydroxyquinoline Succinate Compounds: A DFT Study 

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#### Abstract

Quinoline based compounds efficiently form molecular complexes with various organic acids through hydrogen bonding. These compounds are classified as electron-deficient heterocyclic in nature and exhibit acceptor-donor properties with intramolecular charge transfer. 8-Hydroxyquinolinesuccinate is a $\pi$ donor-acceptor molecular compound in which 8-HQ acts as donor and succinic acid as electron acceptor. The present work deals with the interaction of title compounds using Density Functional Theory (DFT) implemented in Gaussian-09 software package. All geometry optimizations, the vibrational analysis, electronic transition study of $U V$ and NMR spectra of title compounds were interpreted with aid of normal coordinate analysis based on DFT/B3LYP using 6-311G basis set. Dihedral angles of 8-HQ varies between $0^{\circ}$ and 180 : This shows that the molecule of 8-HQ is practically planar. 8-HQSC crystal is stabilized by the hydrogen bonds N2-H13....O22 and O22-H12....O1 formed by the existence of complementary functional groups. The negative chemical shift values of -145.5869 ppm do exist for nitrogen atom in 8-HQ. Energy gap of 8-HQ is obtained theoretically by DFT method is 4.52 eV and from HOMO-LUMO diagram is 4.53 eV. From the Mulliken atomic charges confirms the extensive intermolecular charge transfer between adsorbate and adsorbent of the title compound during the interaction. The calculated results are found to be in good agreement with the previous investigations.


Keywords: 8-Hydroxyquinoline, 8-Hydroxyquinoline Succinate, Vibrational spectra, Density Functional Theory (DFT), HOMO, LUMO.

## I. INTRODUCTION

8-Hydroxyquinoline is a bicycle compound and has typical phenolic properties. It consists of carbocyclic ring and pyridine ring with hydroxyl group substituted at position-8. Due to the unique chemical properties of $8-\mathrm{HQ}$, these compound derivatives have application in agricultural and medical fields.
The compound shows a variety of applications ranging from pharmacological and pharmaceutical agents to electron carriers in organic light emitting diodes and fluorescent chemo sensors for metal ions. In medical field, its derivatives can be used as insecticides, antibacterial, fungicidal, neuroprotective, and anti-HIV agents [1]. Organic functionalized NLO materials attracted a great deal of attention due to its extensive applications in harmonic generation, amplitude, phase modulation, switching and other signal processing devices [2-4].
A possible reason for the significant increase in the effective nonlinear optical response observed in organic molecules is due to the existence of $\pi$-conjugation between the appropriate electron donor and acceptor groups, chirality and hydrogen bonding. Functional modification in electron-donor systems affects the optical and electrical properties of the quinolone derivatives. 8Hydroxyquinolinesuccinate is a $\pi$ donor-acceptor molecular compound in which $8-\mathrm{HQ}$ acts as donor and succinic acid as electron acceptor. Theoretical studies are valuable approaches to explore the mechanism of reactions in the molecules and their electronic structures levels in addition to electronic parameters that acquired by means of theoretical calculations employ the computational methods of quantum chemistry. The improvement in theoretical studies and applications have accomplish a point where predicted features of logical accuracy can be obtained from DFT (density functional theory) studies [5,6].
Geometry of the molecules in its ground state, as well as the nature of their molecular orbitals, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are involved in the properties of activity of molecules reaction. The object of the present paper is to carry out DFT calculations on 8 -Hydroxyquinoline and 8 -Hydroxyquinoline succinate and to determine a relationship between some quantum chemical parameters obtained from the structure of the compounds and experimental parameters of IR, Raman spectra, UV and NMR reported by the previous studies.

## II. DFT CALCULATIONS

Molecular geometries of the singlet ground state of compounds $8-\mathrm{HQ}$ and $8-\mathrm{HQSC}$ were fully optimized at B3LYP/6-311G level using Gaussian09 program. In geometry optimizations every bond length, bond angle and dihedral angle was permitted to relax, free of constraints. For each compound frequency calculations were carried out, verifying that the optimized structure obtained corresponded to energy minimum, thus only positive frequencies were expected. Frontier molecular orbitals were used to identify the adsorption centers of the inhibitor molecule. For the simplest transfer of electrons, adsorption should occur at the part of the molecule where the softness $(\sigma)$ has the highest value. Electronegativity, hardness and softness have conformed to be very useful quantities in quantum molecular description calculations [7]. Moreover, we have computed UV, Nuclear Magnetic Resonance (NMR), highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) energies in order to understand the properties of the molecules.

## III. RESULTS AND DISCUSSION

We have computed the structures of 8 -HQ and 8 -HQSC compounds using DFT calculations and quantities of the spectroscopic interest for the two compounds and compared the results with previous studies.

## A. Molecular Geometries

The optimized molecular structures of the $8-\mathrm{HQ}$ and $8-\mathrm{HQSC}$ with atomic labeling are shown in Fig. 1.


Fig. 1 optimized molecular structures of the 8-HQ and 8-HQSC with atomic labeling
The interatomic bond lengths and bond angles of 8-HQ and 8-HQSC derived from DFT study are listed in Table 1 and 2.8-HQ consists of two rings, one phenol and other pyridine type ring. The angle between the phenolic and pyridine ring is only $1.382^{\circ}$ [8]. The average C-C bond length in the rings is $1.456 \AA$ whereas the average C-N bond is $1.387 \AA$. The observed C-C bond length in the two rings vary from 1.349 to $1.540 \AA$. Nearly identical C-C bonds indicate the complete delocalization of $\pi$-electrons in the individual hetero atom rings. The obtained $\mathrm{C}-\mathrm{O}$ bond length is $1.43 \AA$. It is found that the $\mathrm{C}-\mathrm{C}$ bonds and hetero atom C-N bond are nearly the same as that found in experimental result. The average value of the bond angles in the two benzene rings is $120^{\circ}$. The deviation from this ideal value is quite significant. Dihedral angles are useful to identify the molecular conformation. Dihedral angles of $8-\mathrm{HQ}$ varies between $0^{\circ}$ and $180^{\circ}$. This shows that the molecule of $8-\mathrm{HQ}$ is practically planar. $8-\mathrm{HQSC}$ single crystal growth and its characterization were reported by R.Thirumurugan et.al (2014). The N -site of the 8 -HQ leads to the formation of cation and it is confirmed by the enhancement of the internal angle at N 2 ( $\mathrm{N} 2-\mathrm{C} 11-\mathrm{C} 10$ bond angle of 121.0427) compared with $122.12(2)^{\circ}$ observed in 8-HQSC single crystal study [9]. The deprotonation occurs due to the succinic acid molecule and it leads to an anion. The variations of the carboxyl bond distances C26-O21 and C26-O22 are $1.3013 \AA$ and $1.2584 \AA$ respectively. The dihedral angle between 8 -hydroxyquinolinium cation and succinate anion are $8.8499^{\circ}$ coincide with the already existing report. It indicates that they are essentially planar. 8 -HQSC crystal is stabilized by the hydrogen bonds $\mathrm{N} 2-\mathrm{H} 13 \ldots . \mathrm{O} 22$ and $\mathrm{O} 22-\mathrm{H} 12 \ldots \mathrm{O} 1$ formed by the existence of complementary functional groups.

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TABLE I
Optimized Geometrical Parameters ${ }^{\mathrm{b}}$ of 8-Hydroxyquinoline at b3lyp/6-311g level.

| Definition ${ }^{\text {a }}$ | 8-HQ | Definition ${ }^{\text {a }}$ | 8-HQ | Definition ${ }^{\text {a }}$ | 8-HQ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| r( 1,5 ) | 1.43 | A (3,6,9) | 119.9293 | $\mathrm{D}(7,3,6,9)$ | 180.0 |
| r $(1,18)$ | 0.96 | A $(3,6,12)$ | 120.0353 | $\mathrm{D}(7,3,6,12)$ | 0.0 |
| r $(2,4)$ | 1.4759 | A(9,6,12) | 120.0353 | $\mathrm{D}(4,3,7,10)$ | 0.0 |
| $\mathrm{r}(2,11)$ | 1.2993 | A $(3,7,10)$ | 118.812 | $\mathrm{D}(4,3,7,13)$ | 180.0 |
| r $(3,4)$ | 1.3555 | A $(3,7,13)$ | 120.594 | $\mathrm{D}(6,3,7,10)$ | 180.0 |
| r $(3,6)$ | 1.5396 | A(10,7,13) | 120.594 | $\mathrm{D}(6,3,7,13)$ | 0.0 |
| r(3,7) | 1.5344 | A $(5,8,9)$ | 120.0394 | $\mathrm{D}(2,4,5,1)$ | 0.0 |
| $\mathrm{r}(4,5)$ | 1.5403 | A $(5,8,14)$ | 119.9803 | $\mathrm{D}(2,4,5,8)$ | 180.0 |
| r(5,8) | 1.3556 | A $(9,8,14)$ | 119.9803 | $\mathrm{D}(3,4,5,1)$ | 180.0 |
| r(6,9) | 1.3549 | A(6,9,8) | 119.9704 | $\mathrm{D}(3,4,5,8)$ | 0.0 |
| $\mathrm{r}(6,12)$ | 1.07 | A(6,9,15) | 120.0148 | $\mathrm{D}(1,5,8,9)$ | 180.0 |
| r $(7,10)$ | 1.3494 | A $(8,9,15)$ | 120.0148 | $\mathrm{D}(1,5,8,14)$ | 0.0 |
| r $(7,13)$ | 1.07 | A(7,10,11) | 119.2979 | $\mathrm{D}(4,5,8,9)$ | 0.0 |
| r $(8,9)$ | 1.5401 | $\mathrm{A}(7,10,16)$ | 120.3511 | $\mathrm{D}(4,5,8,14)$ | 180.0 |
| $\mathrm{r}(8,14)$ | 1.07 | $\mathrm{A}(11,10,16)$ | 120.3511 | $\mathrm{D}(3,6,9,8)$ | 0.0 |
| r $(9,15)$ | 1.07 | $\mathrm{A}(2,11,10)$ | 120.4693 | $\mathrm{D}(3,6,9,15)$ | 180.0 |
| $\mathrm{r}(10,11)$ | 1.5399 | $\mathrm{A}(2,11,17)$ | 119.7653 | $\mathrm{D}(12,6,9,8)$ | 180.0 |
| $\mathrm{r}(10,16)$ | 1.07 | $\mathrm{A}(10,11,17)$ | 119.7653 | $\mathrm{D}(12,6,9,15)$ | 0.0 |
| r $(11,17)$ | 1.07 | $\mathrm{D}(18,1,5,4)$ | 180.0 | $\mathrm{D}(3,7,10,11)$ | 0.0 |
| A(5,1,18) | 109.4712 | $\mathrm{D}(18,1,5,8)$ | 0.0 | $\mathrm{D}(3,7,10,16)$ | 180.0 |
| A(4,2,11) | 121.4793 | $\mathrm{D}(11,2,4,3)$ | 0.0 | $\mathrm{D}(13,7,10,11)$ | 180.0 |
| A $(4,3,6)$ | 120.2281 | $\mathrm{D}(11,2,4,5)$ | 180.0 | D(13,7,10,16) | 0.0 |
| A(4,3,7) | 119.4712 | D (4,2,11,10) | 0.0 | D (5,8,9,6) | 0.0 |
| $\mathrm{A}(6,3,7)$ | 120.3008 | $\mathrm{D}(4,2,11,17)$ | 180.0 | $\mathrm{D}(5,8,9,15)$ | 180.0 |
| $\mathrm{A}(2,4,3)$ | 120.4703 | $\mathrm{D}(6,3,4,2)$ | 180.0 | D(14,8,9,6) | 180.0 |
| A(2,4,5) | 119.7557 | $\mathrm{D}(6,3,4,5)$ | 0.0 | D (14,8,9,15) | 0.0 |
| A(3,4,5) | 119.774 | $\mathrm{D}(7,3,4,2)$ | 0.0 | $\mathrm{D}(7,10,11,2)$ | 0.0 |
| A(1,5,4) | 119.9706 | $\mathrm{D}(7,3,4,5)$ | 180.0 | $\mathrm{D}(7,10,11,17)$ | 180.0 |
| A(1,5,8) | 119.9706 | $\mathrm{D}(4,3,6,9)$ | 0.0 | $\mathrm{D}(16,10,11,2)$ | 180.0 |
| A(4,5,8) | 120.0589 | $\mathrm{D}(4,3,6,12)$ | 180.0 | $\mathrm{D}(16,10,11,17)$ | 0.0 |

${ }^{\mathrm{a}}$ For atomic numbering scheme, see Fig. 1.
${ }^{\mathrm{b}}$ Bond lengths (r) in Angstrom, bond angles (A) and dihedral angles (D) in degree.

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Table II
Optimized Geometrical Parameters ${ }^{\text {b }}$ of 8-Hydroxyquinoline Succinate At B3lyp/6-311g Level

| Definition ${ }^{\text {a }}$ | 8-HQSC | Definition ${ }^{\text {a }}$ | 8-HQSC | Definition ${ }^{\text {a }}$ | 8-HQSC |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{R}(1,5)$ | 1.43 | $\mathrm{A}(6,9,17)$ | 120.0282 | $\mathrm{D}(6,3,7,10)$ | -179.9999 |
| $\mathrm{R}(1,12)$ | 0.96 | $\mathrm{A}(8,9,17)$ | 120.0282 | $\mathrm{D}(6,3,7,15)$ | 0.0001 |
| $\mathrm{R}(1,22)$ | 1.8825 | $\mathrm{A}(7,10,11)$ | 119.8521 | $\mathrm{D}(2,4,5,1)$ | 0.0 |
| $\mathrm{R}(2,4)$ | 1.3428 | $\mathrm{A}(7,10,18)$ | 120.0739 | $\mathrm{D}(2,4,5,8)$ | 180.0 |
| $\mathrm{R}(2,11)$ | 1.3461 | $\mathrm{A}(11,10,18)$ | 120.0739 | $\mathrm{D}(3,4,5,1)$ | -179.9999 |
| $\mathrm{R}(2,13)$ | 1.0 | $\mathrm{A}(2,11,10)$ | 121.0427 | $\mathrm{D}(3,4,5,8)$ | 0.0001 |
| $\mathrm{R}(3,4)$ | 1.3977 | $\mathrm{A}(2,11,19)$ | 119.4787 | $\mathrm{D}(1,5,8,9)$ | 179.9999 |
| $\mathrm{R}(3,6)$ | 1.4007 | $\mathrm{A}(10,11,19)$ | 119.4787 | $\mathrm{D}(1,5,8,16)$ | -0.0001 |
| $\mathrm{R}(3,7)$ | 1.393 | $\mathrm{A}(2,13,22)$ | 148.4574 | $\mathrm{D}(4,5,8,9)$ | -0.0001 |
| $\mathrm{R}(4,5)$ | 1.4016 | $\mathrm{A}(27,20,28)$ | 120.0 | $\mathrm{D}(4,5,8,16)$ | 179.9999 |
| $\mathrm{R}(5,8)$ | 1.4021 | A(1,22,13) | 70.0498 | $\mathrm{D}(3,6,9,8)$ | -0.0001 |
| $\mathrm{R}(6,9)$ | 1.4012 | $\mathrm{A}(1,22,26)$ | 123.381 | $\mathrm{D}(3,6,9,17)$ | 180.0 |
| $\mathrm{R}(6,14)$ | 1.07 | $\mathrm{A}(12,22,13)$ | 91.8638 | $\mathrm{D}(14,6,9,8)$ | -179.9999 |
| R(7,10) | 1.3966 | $\mathrm{A}(12,22,26)$ | 102.5442 | D(14,6,9,17) | 0.0002 |
| R(7,15) | 1.07 | A(13,22,26) | 165.2736 | D(3,7,10,11) | 0.0 |
| $\mathrm{R}(8,9)$ | 1.4019 | $\mathrm{A}(25,24,26)$ | 109.4712 | $\mathrm{D}(3,7,10,18)$ | 179.9998 |
| $\mathrm{R}(8,16)$ | 1.07 | $\mathrm{A}(25,24,29)$ | 109.4712 | $\mathrm{D}(15,7,10,11)$ | 180.0 |
| $\mathrm{R}(9,17)$ | 1.07 | $\mathrm{A}(25,24,30)$ | 109.4712 | $\mathrm{D}(15,7,10,18)$ | -0.0003 |
| $\mathrm{R}(10,11)$ | 1.3588 | A(26,24,29) | 109.4712 | D (5,8,9,6) | 0.0001 |
| $\mathrm{R}(10,18)$ | 1.07 | $\mathrm{A}(26,24,30)$ | 109.4712 | D(5,8,9,17) | -180.0 |
| $\mathrm{R}(11,19)$ | 1.07 | $\mathrm{A}(29,24,30)$ | 109.4712 | $\mathrm{D}(16,8,9,6)$ | -179.9999 |
| $\mathrm{R}(12,22)$ | 2.281 | $\mathrm{A}(24,25,27)$ | 109.4712 | $\mathrm{D}(16,8,9,17)$ | 0.0 |
| $\mathrm{R}(13,22)$ | 2.2785 | A(24,25,31) | 109.4712 | $\mathrm{D}(7,10,11,2)$ | -0.0001 |
| R(20,27) | 1.3013 | $\mathrm{A}(24,25,32)$ | 109.4712 | $\mathrm{D}(7,10,11,19)$ | 179.9999 |
| R $(20,28)$ | 0.96 | $\mathrm{A}(27,25,31)$ | 109.4712 | $\mathrm{D}(18,10,11,2)$ | -179.9999 |
| R(21,26) | 1.3013 | $\mathrm{A}(27,25,32)$ | 109.4712 | $\mathrm{D}(18,10,11,19)$ | 0.0001 |
| $\mathrm{R}(22,26)$ | 1.2584 | $\mathrm{A}(31,25,32)$ | 109.4712 | D(2,13,22,1) | -10.4696 |
| $\mathrm{R}(23,27)$ | 1.2584 | A(21,26,22) | 120.0 | D (2,13,22,12) | 0.5153 |
| $\mathrm{R}(24,25)$ | 1.54 | A(21,26,24) | 120.0 | $\mathrm{D}(2,13,22,26)$ | -167.6271 |
| $\mathrm{R}(24,26)$ | 1.54 | A(22,26,24) | 120.0 | D(28,20,27,23) | -179.9999 |
| $\mathrm{R}(24,29)$ | 1.07 | A(20,27,23) | 120.0 | D(28,20,27,25) | 0.0001 |
| $\mathrm{R}(24,30)$ | 1.07 | $\mathrm{A}(20,27,25)$ | 120.0 | $\mathrm{D}(1,22,26,21)$ | 8.8499 |
| $\mathrm{R}(25,27)$ | 1.54 | A(23,27,25) | 120.0 | $\mathrm{D}(1,22,26,24)$ | -171.1501 |
| $\mathrm{R}(25,31)$ | 1.07 | D(12,1,5,4) | -150.0 | D(12,22,26,21) | -4.9169 |
| $\mathrm{R}(25,32)$ | 1.07 | $\mathrm{D}(12,1,5,8)$ | 30.0 | D(12,22,26,24) | 175.0831 |
| $\mathrm{A}(5,1,12)$ | 109.4712 | $\mathrm{D}(22,1,5,4)$ | -7.9361 | D(13,22, 26, 21) | 162.9376 |
| $\mathrm{A}(5,1,22)$ | 141.3484 | D(22,1,5,8) | 172.0639 | D(13,22,26,24) | -17.0624 |
| $\mathrm{A}(4,2,11)$ | 121.1776 | $\mathrm{D}(5,1,22,13)$ | 8.773 | D(26,24,25,27) | 180.0 |
| $\mathrm{A}(4,2,13)$ | 119.4112 | $\mathrm{D}(5,1,22,26)$ | -178.0139 | D(26,24,25,31) | -60.0 |
| A(11,2,13) | 119.4112 | D(11,2,4,3) | -0.0003 | D(26,24,25,32) | 60.0 |
| $\mathrm{A}(4,3,6)$ | 120.3662 | $\mathrm{D}(11,2,4,5)$ | 179.9999 | D(29,24,25,27) | 60.0 |
| A(4,3,7) | 118.9875 | $\mathrm{D}(13,2,4,3)$ | 179.9998 | D(29,24,25,31) | 180.0 |
| A(6,3,7) | 120.6463 | $\mathrm{D}(13,2,4,5)$ | 0.0 | D (29,24,25,32) | -60.0 |
| $\mathrm{A}(2,4,3)$ | 120.194 | $\mathrm{D}(4,2,11,10)$ | 0.0003 | D(30,24,25,27) | -60.0 |
| $\mathrm{A}(2,4,5)$ | 119.9813 | $\mathrm{D}(4,2,11,19)$ | -179.9997 | D(30,24,25,31) | 60.0 |
| A(3,4,5) | 119.8247 | $\mathrm{D}(13,2,11,10)$ | -179.9998 | D(30,24,25,32) | 180.0 |
| A(1,5,4) | 119.9988 | D (13,2,11,19) | 0.0002 | D(25,24,26,21) | 150.0 |
| $\mathrm{A}(1,5,8)$ | 119.9988 | $\mathrm{D}(4,2,13,22)$ | 7.8278 | D(25,24,26,22) | -30.0 |
| $\mathrm{A}(4,5,8)$ | 120.0023 | D(11,2,13,22) | -172.1721 | D(29,24,26,21) | -90.0 |
| A $(3,6,9)$ | 119.8369 | D(6,3,4,2) | -179.9999 | $\mathrm{D}(29,24,26,22)$ | 90.0 |
| $\mathrm{A}(3,6,14)$ | 120.0816 | $\mathrm{D}(6,3,4,5)$ | -0.0001 | D(30,24,26,21) | 30.0 |
| $\mathrm{A}(9,6,14)$ | 120.0816 | $\mathrm{D}(7,3,4,2)$ | 0.0001 | $\mathrm{D}(30,24,26,22)$ | -150.0 |
| $\mathrm{A}(3,7,10)$ | 118.746 | $\mathrm{D}(7,3,4,5)$ | 179.9999 | D(24,25,27,20) | 30.0 |
| $\mathrm{A}(3,7,15)$ | 120.627 | $\mathrm{D}(4,3,6,9)$ | 0.0001 | D(24,25,27,23) | -150.0 |
| A(10,7,15) | 120.627 | $\mathrm{D}(4,3,6,14)$ | 179.9999 | $\mathrm{D}(31,25,27,20)$ | -90.0 |
| A(5,8,9) | 120.0263 | $\mathrm{D}(7,3,6,9)$ | -180.0 | D(31,25,27,23) | 90.0 |
| $\mathrm{A}(5,8,16)$ | 119.9868 | D(7,3,6,14) | -0.0002 | $\mathrm{D}(32,25,27,20)$ | 150.0 |
| $\mathrm{A}(9,8,16)$ | 119.9868 | D(4,3,7,10) | 0.0 | D(32,25,27,23) | -30.0 |
| A(6,9,8) | 119.9436 | D(4,3,7,15) | -180.0 |  |  |

${ }^{\text {a}}$ For atomic numbering scheme, see Fig. 1.
${ }^{\mathrm{b}}$ Bond lengths (r) in Angstrom, bond angles (A) and dihedral angles (D) in degree.

## B. Vibrational Spectra

The 8 -hydroxyquinoline has 18 atoms with 48 fundamental modes of vibration. These vibrations are divided into 33 in-plane and 15 out-of-plane vibrations. The detailed vibrational assignment of fundamental modes of frequencies of 8 - HQ reported by Krishnakumar et al. [10] and calculated frequency using B3LYP/6-311G method are reported in Table 3. IR and Raman spectra of $8-\mathrm{HQ}$ and $8-\mathrm{HQSC}$ are shown in Fig. 2 and 3. The accurate position of the OH bond is based on the strength of the hydrogen bond. In $8-\mathrm{HQ}, \mathrm{OH}-\mathrm{N}$ hydrogen bond absorption is found at $3688 \mathrm{~cm}^{-1}$. The OH group in-plane and out-of-plane modes are found at 1518 $\mathrm{cm}^{-1}(\delta \mathrm{OH})$ and $896 \mathrm{~cm}^{-1}(\gamma \mathrm{OH})$ respectively in agreement with the literature data [10,11]. In addition, a certain number of diatomic molecular fragments such as C 2 and CN provide useful indications for identification of organic materials [12,13] and also the mixing of several bands are possible in this region. $v \mathrm{C} 11 \mathrm{~N} 2$ and $v \mathrm{C} 9 \mathrm{~N} 1$ are appeared at $1354 \mathrm{~cm}^{-1}$ and $1306 \mathrm{~cm}^{-1}$ respectively. In the IR spectra of $8-\mathrm{HQ}$, the non-linearity of hydrogen bond have an impact over the carbonyl group frequency. The IR band is observed at $1231 \mathrm{~cm}^{-1}$ and assigned to vC 5 O 1 vibration. The frequencies at $591 \mathrm{~cm}^{-1}$ and $491 \mathrm{~cm}^{-1}$ are active due to $\delta \mathrm{C} 5 \mathrm{O}$ and $\gamma$ C5O respectively. Generally, The presence of skeletal modes of semi-unsaturated C-C bonds vibrations are appeared in the 1650 $1450 \mathrm{~cm}^{-1}$ frequency region [14]. Due to stretching modes, a change of dipole moment occurs in mono-substituted benzene. As a result of this, strong to medium intensity bands are expected for aromatic C-C modes. The medium intensity IR bands have been assigned to the ring stretching modes at $1657 \mathrm{~cm}^{-1}$ and $1551 \mathrm{~cm}^{-1}$. The rest of bands are observed at $1475,1441,1394,1294$ and $1251 \mathrm{~cm}^{-1}$. Table 3 shows that the results of observed and calculated IR and Raman frequencies yield good agreement.


Fig. 2 IR spectra of 8-HQ and 8-HQSC


Fig. 3 Raman spectra of $8-\mathrm{HQ}$ and $8-\mathrm{HQSC}$

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Table III
Detailed Assignment Of Fundamental Vibrations Of 8-Hydroxyquinoline

| No | Symmetry Species CS | Observed frequency <br> [Ref 10] |  | Calculated using B3LYP/6-311G method |  |  | Characterization of normal modes |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | Infrared | Raman | Frequency $\left(\mathrm{cm}^{-1}\right)$ | IR intensity | Raman activity |  |
| 1 | $\mathrm{A}^{\prime}$ | 3418 | -- | 3688 | 39.4493 | 174.2442 | OH Stretch |
| 2 | $\mathrm{A}^{\prime}$ | 3097 | -- | 3197 | 31.5145 | 307.2668 | C10H Stretch |
| 3 | $\mathrm{A}^{\prime}$ | 3084 | -- | 3192 | 36.7406 | 184.4129 | C9H Stretch |
| 4 | $\mathrm{A}^{\prime}$ | -- | 3066 | 3170 | 25.6162 | 143.3291 | C7H, C8H Stretch |
| 5 | $\mathrm{A}^{\prime}$ | 3048 | -- | 3167 | 10.3337 | 19.5749 | C11H, C10H Stretch |
| 6 | $\mathrm{A}^{\prime}$ | -- | 3019 | 3160 | 15.594 | 119.7586 | C5H Stretch |
| 7 | $\mathrm{A}^{\prime}$ | -- | 3003 | 3157 | 15.4611 | 91.6807 | C8H, C11H Stretch |
| 8 | $\mathrm{A}^{\prime}$ | -- | 1585 | 1657 | 10.6069 | 2.417 | C11C10, C11N2 Stretch |
| 9 | $\mathrm{A}^{\prime}$ | 1577 | -- | 1632 | 7.9544 | 10.349 | C9C8, C10C7 Stretch |
| 10 | $\mathrm{A}^{\prime}$ | 1508 | -- | 1595 | 54.174 | 38.5904 | C5C3, C11C10 Stretch |
| 11 | $\mathrm{A}^{\prime}$ | 1472 | 1475 | 1551 | 17.919 | 3.2791 | C5C9, C5C4 Stretch |
| 12 | $\mathrm{A}^{\prime}$ | 1454 | -- | 1518 | 4.028 | 6.1479 | OH In plane bending |
| 13 | $\mathrm{A}^{\prime}$ | 1434 | 1432 | 1475 | 24.5718 | 48.8213 | C10H In plane bending |
| 14 | $\mathrm{A}^{\prime}$ | 1410 | 1404 | 1441 | 2.4819 | 32.7303 | C11H In plane bending |
| 15 | $\mathrm{A}^{\prime}$ | 1381 | 1382 | 1394 | 43.874 | 116.1304 | C8C5 Stretch |
| 16 | $\mathrm{A}^{\prime}$ | 1286 | -- | 1354 | 57.3398 | 20.6337 | C7H In plane bending |
| 17 | $\mathrm{A}^{\prime}$ | 1273 | 1276 | 1306 | 5.8492 | 11.8936 | C9N1 Stretch |
| 18 | $\mathrm{A}^{\prime}$ | -- | 1229 | 1294 | 63.3758 | 3.1707 | C5C4, C7C3 Stretch |
| 19 | $\mathrm{A}^{\prime}$ | 1221 | -- | 1251 | 9.4239 | 3.2718 | C8H In plane bending |
| 20 | $\mathrm{A}^{\prime}$ | 1206 | -- | 1231 | 19.0607 | 3.1143 | C5O1, C4N2 Stretch |
| 21 | $\mathrm{A}^{\prime}$ | 1169 | -- | 1198 | 32.0379 | 1.1901 | C10H, C9H In plane bending |
| 22 | $\mathrm{A}^{\prime}$ | -- | 1161 | 1176 | 6.3397 | 5.1521 | C8H, C11H In plane bending |
| 23 | $\mathrm{A}^{\prime}$ | 1147 | 1141 | 1105 | 31.3946 | 16.7081 | C5H In plane bending |
| 24 | $\mathrm{A}^{\prime}$ | 1093 | 1100 | 1065 | 112.562 | 2.4727 | C11H, C8H In plane bending |
| 25 | $\mathrm{A}^{\prime}$ | 1059 | 1061 | 1054 | 11.922 | 7.2649 | C7H In plane bending |
| 26 | $\mathrm{A}^{\prime \prime}$ | 1034 | -- | 1021 | 0.776 | 0.4964 | C9H, C5H, C10H In plane bending |
| 27 | A" | 974 | -- | 997 | 0.4162 | 0.2262 | $\mathrm{C} 11 \mathrm{H}, \mathrm{C} 8 \mathrm{H}$ out of plane bending |
| 28 | $\mathrm{A}^{\prime \prime}$ | 958 | -- | 969 | 0.2897 | 1.3472 | C5H, C 10 H out of plane bending |
| 29 | $\mathrm{A}^{\prime}$ | -- | 951 | 897 | 11.6846 | 2.123 | $\mathrm{C} 9 \mathrm{H}, \mathrm{C} 7 \mathrm{H}$ out of plane bending |
| 30 | $\mathrm{A}^{\prime \prime}$ | 896 | 891 | 896 | 0.9874 | 0.8258 | OH out of plane bending |
| 31 | $\mathrm{A}^{\prime \prime}$ | 867 | 866 | 849 | 23.1273 | 0.5872 | $\mathrm{C} 10 \mathrm{H}, \mathrm{C} 11 \mathrm{H}$ out of plane bending |
| 32 | $\mathrm{A}^{\prime}$ | 818 | -- | 832 | 11.2632 | 0.9562 | In plane bending |
| 33 | $\mathrm{A}^{\prime \prime}$ | -- | 808 | 827 | 79.5941 | 0.5774 | C7H, C5H out of plane bending |
| 34 | $\mathrm{A}^{\prime \prime}$ | 781 | -- | 775 | 31.62 | 1.0173 | $\mathrm{C} 8 \mathrm{H}, \mathrm{C} 10 \mathrm{H}$ out of plane bending |
| 35 | $\mathrm{A}^{\prime}$ | 741 | -- | 711 | 7.8229 | 30.3592 | In plane bending |
| 36 | $\mathrm{A}^{\prime \prime}$ | 710 | 707 | 665 | 0.7412 | 0.3332 | Ring torsion out of plane |
| 37 | $\mathrm{A}^{\prime \prime}$ | 636 | -- | 603 | 0.6398 | 1.5936 | Ring torsion out of plane |
| 38 | $\mathrm{A}^{\prime}$ | 575 | 579 | 591 | 1.4922 | 10.9747 | C5O In plane bending |
| 39 | $\mathrm{A}^{\prime}$ | 545 | 548 | 551 | 7.1895 | 10.9747 | In plane bending |
| 40 | $\mathrm{A}^{\prime}$ | 493 | 496 | 497 | 0.2951 | 5.2661 | Ring torsion out of plane |
| 41 | $\mathrm{A}^{\prime \prime}$ | 465 | 464 | 491 | 0.0504 | 0.1473 | C5O out of plane bending |
| 42 | $\mathrm{A}^{\prime}$ | 440 | -- | 472 | 0.6737 | 6.1355 | C5O In plane bending |
| 43 | $\mathrm{A}^{\prime \prime}$ | 422 | 423 | 444 | 2.7541 | 2.5516 | In plane bending |
| 44 | $\mathrm{A}^{\prime \prime}$ | 355 | -- | 394 | 135.057 | 4.8773 | In plane bending |
| 45 | $\mathrm{A}^{\prime}$ | 266 | 268 | 284 | 10.2579 | 1.6713 | Butterfly, C 5 O out of plane bending |
| 46 | $\mathrm{A}^{\prime \prime}$ | 194 | 195 | 268 | 4.7871 | 0.9137 | Ring torsion out of plane |
| 47 | $\mathrm{A}^{\prime \prime}$ | 137 | -- | 180 | 9.7229 | 0.1523 | Ring torsion out of plane |
| 48 | A" | 98 | -- | 136 | 0.769 | 1.3099 | Ring torsion out of plane |

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The detailed frequencies of 8 -HQSC with their assignments using B3LYP/6-311G method are reported in Table 4. Absorption bands are appeared at $3671.19 \mathrm{~cm}^{-1}$ for O-H stretching vibration and the peaks at $3179 \mathrm{~cm}^{-1}$ to $3234 \mathrm{~cm}^{-1}$ for $\mathrm{C}-\mathrm{H}$ stretching. The C N stretching vibration is observed at $1685 \mathrm{~cm}^{-1}$. C-O-H plane bending vibration peak is assigned at $1476 \mathrm{~cm}^{-1}$. The peaks at 1265 , 1243 and $1109 \mathrm{~cm}^{-1}$ are found due to the absorption band for $\mathrm{C}-\mathrm{H}$ in plane bending. The band near $788 \mathrm{~cm}^{-1}$ represents the C-H out of plane bending. These bands give significant information about the type of aromatic substitution. The carbonyl anti symmetric stretching vibration band of COO- group is reported at $1550 \mathrm{~cm}^{-1}$. The ring C-C stretching vibration takes place in the region of $1685 \mathrm{~cm}^{-1}$ [15]. The band observed at $901 \mathrm{~cm}^{-1}$ is coincide with out of plane bending of C-O deformation reported by Dhanya et.al.[16] and Thirumurugan et. al.[9]. The ring breathing mode is assigned for frequencies vary from $1135 \mathrm{~cm}^{-1}$ to $1221 \mathrm{~cm}^{-1}$ which is in good agreement with the quinolone and isoquinoline. The vibrations $573 \mathrm{~cm}^{-1}, 588 \mathrm{~cm}^{-1}$ and $596 \mathrm{~cm}^{-1}$ are assigned to C-O in plane bending vibration which is similar to the quinoline vibrations [17]. The $\mathrm{C}-\mathrm{C}$ in plane and out of plane bending was observed at $1094 \mathrm{~cm}^{-1}$ and $811 \mathrm{~cm}^{-1}$. The ring stretching vibration of quinoline is appeared at $1388 \mathrm{~cm}^{-1}$ due to $\mathrm{CH}_{2}$ deformation. The in plane bending vibrations of quinoline was reported between 500 and $750 \mathrm{~cm}^{-1}$ [9]. 763, 726,712 , and $517 \mathrm{~cm}^{-1}$ are the observed vibrational frequencies and it represents the position of in plane bending vibrations of quinoline [18].

Table IV
Detailed Assignment Of Fundamental Vibrations Of 8-Hydroxyquinoline Succinate

| No | Symmetry <br> Species CS | Calculated using B3LYP/6-311G method |  |  | Characterization of normal modes |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | Frequency ( $\mathrm{cm}^{-}$ ${ }^{1}$ ) | IR intensity | Raman activity |  |
| 1 | A | 17.704 | 4.7703 | 2.1324 |  |
| 2 | A | 20.1561 | 0.0849 | 4.2526 |  |
| 3 | A | 43.3615 | 1.2506 | 2.1156 |  |
| 4 | A | 53.0698 | 1.5074 | 2.3815 |  |
| 5 | A | 60.2886 | 6.3626 | 0.6632 |  |
| 6 | A | 78.7225 | 4.4232 | 0.9685 |  |
| 7 | A | 98.4331 | 1.7687 | 0.9418 |  |
| 8 | A | 149.7372 | 14.0647 | 1.7833 | Ring torsion out of plane |
| 9 | A | 158.376 | 2.042 | 1.4286 |  |
| 10 | A | 168.6823 | 9.1345 | 1.2512 |  |
| 11 | A | 189.3775 | 0.4449 | 0.4868 | Ring torsion out of plane |
| 12 | A | 211.9531 | 17.2501 | 1.3824 |  |
| 13 | A | 261.482 | 1.2386 | 1.9407 | Ring torsion out of plane |
| 14 | A | 284.4859 | 0.4151 | 2.337 | Butterfly, C-O out of plane bending |
| 15 | A | 315.4841 | 124.4251 | 0.8878 |  |
| 16 | A | 419.5327 | 5.2182 | 5.2244 |  |
| 17 | A | 444.755 | 9.0316 | 3.0373 | In plane bending |
| 18 | A | 473.7569 | 71.8554 | 1.8973 | C-O In plane bending |
| 19 | A | 483.7636 | 27.8823 | 8.0535 |  |
| 20 | A | 489.0768 | 2.3909 | 0.5339 |  |
| 21 | A | 493.2749 | 59.1196 | 4.4129 | Ring torsion out of plane |
| 22 | A | 517.1057 | 17.804 | 2.9363 |  |
| 23 | A | 557.5937 | 0.9324 | 6.168 |  |
| 24 | A | 573.2466 | 8.77 | 3.3844 | C-O In plane bending |
| 25 | A | 588.9931 | 4.213 | 14.1451 | C-O In plane bending |
| 26 | A | 596.047 | 6.7392 | 2.5574 | C-O In plane bending |
| 27 | A | 618.7497 | 82.0213 | 0.493 |  |
| 28 | A | 648.4574 | 3.2074 | 0.184 |  |
| 29 | A | 670.6983 | 0.808 | 0.2296 | Ring torsion out of plane |
| 30 | A | 712.0108 | 28.5188 | 12.0959 | In plane ring bending |
| 31 | A | 726.3639 | 135.3893 | 30.7011 | In plane ring bending |
| 32 | A | 763.458 | 22.4179 | 0.8622 | In plane ring bending |
| 33 | A | 788.6721 | 6.0965 | 0.4678 | C-H out of plane bending |
| 34 | A | 811.1474 | 3.2219 | 0.6847 | C-C out of plane bending |
| 35 | A | 829.7912 | 4.6196 | 0.4663 | C-H In plane bending |
| 36 | A | 845.3951 | 78.4139 | 0.06 | C-H out of plane bending |
| 37 | A | 848.6118 | 68.1817 | 3.741 | C-H out of plane bending |

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| 38 | A | 901.049 | 44.5341 | 0.391 | C-O deformation |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 39 | A | 921.5914 | 1.8191 | 0.74 | OH out of plane |
| 40 | A | 931.972 | 4.2592 | 14.9542 | C-C Stretch |
| 41 | A | 982.1853 | 1.4416 | 0.5616 | C-H out of plane bending |
| 42 | A | 1012.1852 | 0.0239 | 0.7336 | C-H twisting |
| 43 | A | 1032.50 | 0.8316 | 0.3784 | C-H twisting |
| 44 | A | 1055.3228 | 2.883 | 1.2055 |  |
| 45 | A | 1061.79 | 0.2874 | 1.848 |  |
| 46 | A | 1064.718 | 5.5046 | 5.2345 |  |
| 47 | A | 1094.3708 | 2.2443 | 20.628 | $\mathrm{C}-\mathrm{C}$ in plane bending |
| 48 | A | 1109.5658 | 137.8005 | 19.6538 | C-H In plane bending |
| 49 | A | 1135.8563 | 62.4353 | 1.6332 | In plane bending ring |
| 50 | A | 1165.4514 | 35.669 | 2.2518 | In plane bending ring |
| 51 | A | 1186.2482 | 4.5663 | 6.451 | In plane bending ring |
| 52 | A | 1212.8627 | 256.9344 | 7.4529 | In plane bending ring |
| 53 | A | 1221.7421 | 1.8444 | 1.7833 | In plane bending ring |
| 54 | A | 1243.6844 | 128.5237 | 20.8728 | C-C Stretch; C-H in plane bending |
| 55 | A | 1259.9714 | 67.7117 | 3.2453 | C-C Stretch; $\mathrm{C}-\mathrm{H}$ in plane bending |
| 56 | A | 1261.1842 | 151.9825 | 1.6521 | C-H In plane bending |
| 57 | A | 1265.0347 | 93.747 | 6.1412 | C-H In plane bending |
| 58 | A | 1297.9659 | 253.547 | 3.031 | C-C Stretch |
| 59 | A | 1315.1723 | 5.4672 | 0.9914 | $\mathrm{CH}_{2}$ Wagging |
| 60 | A | 1342.1056 | 20.0742 | 13.3958 | $\mathrm{CH}_{2}$ Twisting |
| 61 | A | 1347.2734 | 19.1216 | 4.0157 | C-C Stretch |
| 62 | A | 1373.6268 | 80.3438 | 12.0537 | Asymmetry COO Stretching |
| 63 | A | 1388.1458 | 156.8427 | 8.1857 | Ring stretch |
| 64 | A | 1399.9736 | 73.0545 | 58.3957 | C-C Stretch |
| 65 | A | 1409.7217 | 73.2905 | 61.9312 | In plane bending |
| 66 | A | 1419.2441 | 542.7768 | 0.8832 | Wagging |
| 67 | A | 1476.6181 | 76.4168 | 13.015 | C-O-H plane bending |
| 68 | A | 1487.4443 | 78.0765 | 18.6307 | In plane bending ring |
| 69 | A | 1508.5421 | 0.738 | 16.2588 | $\mathrm{CH}_{2}$ symmetry stretch |
| 70 | A | 1520.6674 | 30.8446 | 9.3289 | In plane bending ring |
| 71 | A | 1524.4133 | 20.6308 | 1.199 | $\mathrm{CH}_{2}$ symmetry stretch |
| 72 | A | 1550.4135 | 121.8452 | 2.5442 | Anti-symmetry $\mathrm{COO}^{-}$group |
| 73 | A | 1612.6288 | 42.7094 | 36.8778 | C-C Stretch |
| 74 | A | 1631.0969 | 13.9091 | 56.5387 | C-C Stretch |
| 75 | A | 1638.6294 | 136.6119 | 9.6169 | C-C Stretch |
| 76 | A | 1685.2279 | 575.2508 | 3.9248 | C-C, C-N Stretch |
| 77 | A | 1759.0941 | 257.989 | 18.2197 | COO Stretch |
| 78 | A | 2157.0276 | 1235.975 | 106.9134 | COO Stretch; OH Stretch |
| 79 | A | 2369.0515 | 5683.2459 | 277.3536 | OH Stretch |
| 80 | A | 3017.2281 | 5.2265 | 150.2304 | $\mathrm{CH}_{2}$ rocking |
| 81 | A | 3027.6895 | 17.1555 | 39.0364 | $\mathrm{CH}_{2}$ Symmetrical Stretching |
| 82 | A | 3073.2668 | 19.3408 | 64.8093 | $\mathrm{CH}_{2}$ Symmetrical Stretching and rocking |
| 83 | A | 3141.1116 | 2.4908 | 26.9589 | $\mathrm{CH}_{2}$ Asymmetrical Stretching |
| 84 | A | 3179.1 | 3.8786 | 55.3858 | CH Stretch |
| 85 | A | 3184.2364 | 3.9848 | 85.8094 | CH Stretch |
| 86 | A | 3197.6576 | 20.2462 | 177.0382 | CH Stretch |
| 87 | A | 3217.8745 | 9.8881 | 60.2354 | CH Stretch |
| 88 | A | 3218.2467 | 0.594 | 236.2681 | CH Stretch |
| 89 | A | 3234.2359 | 1.1029 | 164.5032 | CH Stretch |
| 90 | A | 3671.1951 | 15.5036 | 68.4411 | OH Stretch |

## C. NMR spectral analysis

NMR chemical shifts calculations of 8-HQ have been carried out by using B3LYP/6-311G GIAO (Gauge Including Atomic Orbital) method. GIAO method is somewhat superior since it exhibits a faster convergence of the calculated properties upon extension of the basis set used [19]. GIAO method is one of the most common approaches for calculating isotropic nuclear magnetic shielding tensors [20]. The chemical shifts are used to identify the organic compounds and ionic species. It is helpful to recognize the accurate predictions of optimized molecular geometrics for the reliable calculations of magnetic properties [21]. The NMR spectrum of 8-HQ and $8-\mathrm{HQSC}$ is presented in Fig. 4.
In $8-\mathrm{HQ}$, the observed chemical shift of the carbon atoms was identified from 17.8577 ppm to 70.1716 ppm . The chemical shift value of hydrogen atoms was reported from 23.4832 ppm to 28.9341 ppm . The chemical shift of oxygen atom is 185.9363 ppm . The negative chemical shift values of -145.5869 ppm do exist for nitrogen atom. This is due to the strong shielding effect of the macrocyclic aromatic ring current on protons inside the macrocycle oppose the protons outside the macrocycle.
In the case of 8-HQSC, the observed chemical shift of the carbon atoms was identified from 0.0939 ppm to 154.041 ppm . The peak appeared in 154.041 ppm clearly indicates the presence of imine carbon. An imine is a functional group of $\mathrm{C}-\mathrm{N}$ double bond. The chemical shift value of hydrogen atoms was reported from 25.686 ppm to 31.802 ppm . The chemical shift of oxygen atom varies from -198.067 to 127.993 ppm . The chemical shift value nitrogen atom appears at 82.095 ppm . It is interesting to note that the NMR signals for $8-H Q S C$ which was found in the experimental spectrum showed its presence in the computed NMR spectrum.


Fig. 4 NMR spectrum of 8-HQ and 8-HQSC

## D. UV Spectral Analysis

Computation of UV spectra using B3LYP/6-311G is able to detect accurate absorption wavelengths at a relatively small computing time which is correspond to vertical electronic transitions computed on the ground state geometry. The UV-VIS spectrum of 8-HQ and 8-HQSC is shown in Fig. 5. The experimental and theoretical excitation energies, absorption wavelength and oscillator strength are noted in Table 5. These transitions are on the basis of major contribution of molecular orbitals. The orbitals contributions $\leq 10 \%$ are neglected [22]. Experimentally measured absorption wavelengths of $8-\mathrm{HQ}$ are good in agreement with the theoretical wavelengths $274,315,340$, and 408 nm . Energy gap of $8-\mathrm{HQ}$ is obtained theoretically by DFT method is 4.52 eV and from HOMOLUMO diagram is 4.53 eV .
Optical transmission range and the cutoff wavelength are very important factor for optical application. The energy gap of the 8HQSC corresponding to the cutoff wavelength $434.39 \mathrm{~nm}, 241.7 \mathrm{~nm}, 192.87 \mathrm{~nm}$ is $2.85 \mathrm{eV}, 5.13 \mathrm{eV}$ and 6.43 eV respectively. The group contributions to the molecular orbital and the density of state (DOS) are calculated using Gauss-sum 2.2 program [23]. The calculated TDOS diagram of $8-\mathrm{HQ}$ and $8-\mathrm{HQSC}$ is shown in Fig. 6. The DOS spectra were produced by convoluting the molecular orbital information with Gaussian cures of unit height [24].


Fig. 5 UV-VIS spectrum of 8-HQ and 8-HQSC

Table V
The Experimental and Theoretical Excitation Energies, Absorption Wavelength and Oscillator Strength.

| $\lambda \max (\mathrm{nm})$ | Band gap <br> $(\mathrm{eV})$ | Energy (cm- <br> 1) | f |
| :--- | :--- | :--- | :--- |
| 8-Hydroxyquinoline |  |  |  |
| 274.03 | 4.52 | 36492 | 0.0024 |
| 315.43 | 3.93 | 31701 | 0.0747 |
| 340.35 | 3.64 | 29381 | 0.0024 |
| 408.84 | 3.03 | 24458 | 0.0014 |
| 8-Hydroxyquinoline Succinate |  |  |  |
| 192.87 | 6.43 | 50830.26 | 0.0226 |
| 241.7 | 5.13 | 6297.554 | 0.0028 |
| 434.39 | 2.85 | 78269.6 | 0.0348 |




Fig. 6 The calculated TDOS diagram of 8-HQ and 8-HQSC

## E. Chemical Reactivity Studies

The highest occupied molecular orbitals and the lowest unoccupied molecular orbitals are the main orbital taking part in chemical reactions of the molecules called as Frontier molecular orbitals (FMOs) [25]. The HOMO behaves as an electron donor and LUMO acts an electron acceptor. The molecular orbital analysis provides a platform for understanding the phenomenon of charge transfer through optical molecular excitations [26]. The chemical hardness and reactivity of 8 -Hydroxyquinoline ( $8-\mathrm{HQ}$ ) and 8Hydroxyquinolinium succinate ( $8-\mathrm{HQSC}$ ) can be predicted from HOMO-LUMO energy gap. Calculated quantum molecular descriptors of 8-HQ and 8-HQSC compounds are presented in Table 6.
The HOMO and LUMO energies of 8 -Hydroxyquinoline are -6.08 eV and -1.55 eV respectively. The energy gap between the HOMO and LUMO shows the molecular chemical stability [27]. The energy gap of $8-\mathrm{HQ}$ is 4.53 eV . The ionization energy (I) and electron affinity (A) can be expressed through HOMO and LUMO orbital energies as $\mathrm{I}=-\mathrm{E}_{\text {номо }}=6.08 \mathrm{eV}$ and $\mathrm{A}=-\mathrm{E}_{\text {LUмо }}=1.55$ eV . The global hardness $(\eta)$ is predicted by the relation $\eta=(\mathrm{I}-\mathrm{A}) / 2=2.265 \mathrm{eV}$. The electron affinity can be used in combination with ionization energy to give electronic chemical potential $\mu=-\left(\mathrm{E}_{\text {номо }}+\mathrm{E}_{\mathrm{LUMO}}\right) / 2=3.815 \mathrm{eV}$. Considering the chemical hardness, if one molecule has large HOMO-LUMO gap, it is a hard molecule or small HOMO-LUMO gap it is a soft molecule. The global electrophilicity index $(\omega)$ is calculated in terms of chemical potential and the hardness as $\omega=-\left(\mu^{2} / 2 \eta\right)=-3.212 \mathrm{eV}$ and assess the lowering of energy due to maximal electron flow between donor and acceptor. The inverse of the hardness is expressed as the global softness $S=(1 / \eta)=0.441 . \Delta N_{\max }=-\mu / \eta=-1.68$ is the maximum amount of electronic charge that the electrophile system may accept.
In the $8-\mathrm{HQSC}$ compound, the HOMO and LUMO energies are -6.56 eV and -3.1 eV respectively. The energy gap of $8-\mathrm{HQSC}$ is 3.46 eV . The ionization energy ( I ) and electron affinity ( A ) of the $8-\mathrm{HQSC}$ is $\mathrm{I}=-\mathrm{E}_{\text {номо }}=6.56 \mathrm{eV}$ and $\mathrm{A}=-\mathrm{E}_{\mathrm{LU} \text { о }}=3.1 \mathrm{eV}$. The global hardness $(\eta)$ is $\eta=(\mathrm{I}-\mathrm{A}) / 2=1.73 \mathrm{eV}$. The electronic chemical potential is found to be $\mu=4.83 \mathrm{eV}$. The global electrophilicity index $(\omega)$ of 8 -HQSC is -6.74 eV . The global softness is calculated using the relation $\mathrm{S}=(1 / \eta)=0.578$. The maximum amount of electronic charge $\Delta \mathrm{N}_{\text {max }}$ is -2.79 .

Table VI
Calculated Quantum Molecular Descriptors Of 8-HQ and 8-HQSC Compounds

| S.No. | Parameters | Values |  |
| :---: | :---: | :---: | :---: |
|  |  | 8-HQ | 8-HQSC |
| 1 | Еномо $^{\text {( }}$. u ) | -6.08 | -6.56 |
| 2 | $\mathrm{E}_{\text {LUMO }}$ (a.u) | -1.55 | -3.1 |
| 3 | IA: Ionization energy $=-\mathrm{E}_{\text {Номо }}(\mathrm{eV})$ | 6.08 | 6.56 |
| 4 | EA: Electron affinity $=-\mathrm{E}_{\text {LUMO }}(\mathrm{eV})$ | 1.55 | 3.1 |
| 5 | $\mathrm{E}_{\mathrm{g}}$ : Energy gap $=\mathrm{E}_{\text {номо }}-\mathrm{E}_{\text {LUмо }}(\mathrm{eV})$ | 4.53 | 3.46 |
| 6 | $\eta$ : Hardness = Energy gap/2 (eV) | 2.265 | 1.73 |
| 7 | $\mu$ : Electronic chemical potential $=\left(\mathrm{E}_{\text {Номо }}+\mathrm{E}_{\mathrm{LUMO}}\right) / 2(\mathrm{eV})$ | 3.815 | 4.83 |
| 8 | $\omega$ : Electrophilicity index $=\mu^{2} / 2 \eta$ | -3.212 | -6.74 |
| 9 | S: softness $=(1 / \eta)$ | 0.441 | 0.578 |
| 10 | $\chi$ : Electro negativity $=-\mu$ | -3.815 | -4.83 |
| 11 | $\Delta \mathrm{N}_{\max }=-\mu / \eta$ | 1.68 | -2.79 |

## F. Mulliken Atomic Charges

The binding capacity and the molecular conformation are greatly depending on the electric charges of the atoms [28-30]. The bar diagram of Mulliken charge distribution is shown in Fig. 7. In the case of $8-\mathrm{HQ}$, the atom O 1 and N 2 presents a strong electronegativity. All hydrogen atoms have a net positive charge. In particular, the hydrogen atom H 18 has large net positive charge. In the 8 -HQSC, Totally 13 carbon atoms are present. Among these atoms, six atoms have positive charge value and seven have negative charge value. The atoms C3 $(-0.135)$ and $\mathrm{C} 10(-0.263)$ enforce a small positive charge on $\mathrm{C} 7(0.004)$. All the hydrogen atoms present less positive charge except H 13 which confirms the electron movement through the nitrogen atom to the quinoline ring. The atom N 2 shows the largest electronegativity and the atom C27 shows the largest electro positivity. Negative charge is observed for oxygen atoms and highest negative value of oxygen $(-0.628)$ is observed in quinoline ring. Thus analysis of Mulliken atomic charges reveals the extensive intermolecular charge transfer in the molecule.


Fig. 7 The bar diagram of Mulliken charge distribution

## IV. CONCLUSIONS

The optimized stable molecular structure of $8-\mathrm{HQ}$ and $8-\mathrm{HQSC}$ were calculated using B3LYP/6-311G basis set. Nearly identical CC bonds indicate the complete delocalization of $\pi$-electrons in the individual hetero atom rings. The dihedral angle between 8hydroxyquinolinium cation and succinate anion are $8.8499^{\circ}$ coincide with the already existing report. It indicates that they are essentially planar. $8-\mathrm{HQSC}$ crystal is stabilized by the hydrogen bonds $\mathrm{N} 2-\mathrm{H} 13 \ldots . \mathrm{O} 22$ and $\mathrm{O} 22-\mathrm{H} 12 \ldots . \mathrm{O} 1$ formed by the existence of complementary functional groups. The results of observed and calculated IR and Raman frequencies yield good agreement. The negative chemical shift values of -145.5869 ppm do exist for nitrogen atom in $8-\mathrm{HQ}$. This is due to the strong shielding effect of the macrocyclic aromatic ring current on protons inside the macrocycle oppose the protons outside the macrocycle. In the case of 8HQSC, the peak appeared in 154.041 ppm clearly indicates the presence of imine carbon. An imine is a functional group of C-N double bond. Energy gap of 8-HQ is obtained theoretically by DFT method is 4.52 eV and from HOMO-LUMO diagram is 4.53 eV . The energy gap of the 8 -HQSC corresponding to the cutoff wavelength $434.39 \mathrm{~nm}, 241.7 \mathrm{~nm}, 192.87 \mathrm{~nm}$ is $2.85 \mathrm{eV}, 5.13 \mathrm{eV}$ and 6.43 eV respectively. All the hydrogen atoms in 8-HQSC present less positive charge except H 13 which confirms the electron movement through the nitrogen atom to the quinoline ring.

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